Process Intensification in the Demulsification of Water-in-Crude Oil Emulsions via Crossflow Microfiltration through a Hydrophilic PolyHIPE Polymer (PHP)

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Declaration

This thesis is submitted in fulfilment of the requirements for the degree of Doctor of Philosophy at Newcastle University, United Kingdom. I hereby declare that all studies and work described within this thesis are my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which has been submitted for a degree or any other qualification at the above or any other University or Institute, except where due acknowledgement has been made in the text. All work was carried out at the School of Chemical Engineering and Advanced Materials (CEAM) under the supervision of Professor G. Akay between March 2007 and October 2012.

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Abstract

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A. M. Shakorfow

In petroleum industry, highly stable water-in-oil (w/o) emulsions are formed during extraction process and these emulsions are stabilized by the indigenous surface active species in the oil. The recovery of crude oil through emulsion breakdown and subsequent separation (demulsification) should be carried out at source in order to avoid costly pumping and cooling of emulsion which enhances emulsion stability. Although conventional methods available for emulsion breakdown using demulsifiers and electric field separation, in the case of viscous crude oils with large amounts of indigenous surfactants, such methods are not satisfactory to achieve on-site oil-water separation. Therefore, such emulsions may have to be chemically treated.

It was previously shown that when hydrophilic micro-porous polymers, known as PolyHIPE Polymers (PHPs) were added to the emulsion, it caused emulsion to separate as a result of selective removal of surfactants. This separation process was further enhanced in the presence of electric field. This current study focuses on cross-flow microfiltration of w/o emulsions through a sulphonated hydrophilic microporous polymeric material in the absence or presence of electric field. However, sulphonated PHPs used in the experiments do not have an active membrane layer with pores at micron- or nano- scale. The thickness of the separation layer is ca. 4 mm and pore size is in 10 micrometer range. We used either 50 or 70 vol. % oil phase in the w/o emulsions. Effect of: pore size, crossflow velocity and electric field strength on permeate flux rate decay and separation efficiency of emulsions which are stable for more than 70 days otherwise was investigated. It was found that the permeate flux rate decayed rapidly with crossflow filtration time before the flux reached steady state. The application of electric field enhanced the permeate flux rate. Under steady state conditions, permeate flux rate was not significantly affected by the PHP pore size.

Permeate from the crossflow filtration was collected in glass cylinders and allowed to separate under gravity as a function of time. It was found that the demulsification time was affected primarily by the applied electric field, emulsion water content, crossflow velocity and PHP pore size. Demulsification rate increased with increasing electric field and water fraction of emulsion and with decreasing pore size of PHP. Demulsification was achieved within 6-7 hr. The results were interpreted in terms of 'confinement phenomenon' in which it was postulated that the PHP filtration media selectively retained the surface active agents and; thus, causing the demulsification of the emulsions. The surface active agents were deposited within the pores of the separation media and; thus, causing flux decay. Although the deposits of surface active agents could break-up due to permeate flow through the separation media, they could not be re-distributed at the oil-water interface to re-stabilize the emulsion. However, some water can be trapped within the oil as oil-in-water-in-oil multiple emulsion which would be more resistant to demulsification.

Publications

Akay, G., Pekdemir, T., Shakorfow, A. M. and Vickers, J. (2012) 'Intensified demulsification and separation of thermal oxide reprocessing interfacial crud (THORP-IFC) simulants'', *Green Process Synthesis.*, 1, pp. 109-127. .

Akay, G., Allinson, J. M., Bennett, B., Larter, S. a. and Shakorfow, A. M. (in preparation) 'Process intensification in the demulsification of highly stable water-in-crude oil emulsions. ', *AIChE Journal.*

Science is organized knowledge. Wisdom is organized life.

Immanuel Kent

1724-1804

Preface

Back in March 2007, I have commenced my studies for the degree of Doctor of Philosophy (Ph D) in the School of Chemical Engineering and Advanced Materials (CEAM), at Newcastle University under the supervision of Professor G. Akay. For the completion of this study, 3-3.5 years were required. Now, it is October 2012. During this period, extensive research and experimental work have been carried out. Initially, I thought that these tasks are easy, clear and straight forward to achieve; nevertheless, I can say that they are typically in reality are unfortunately not. In fact, they are dodgy, expensive, time consuming and tedious; *it is always more*. Frustration may perhaps have always been there. Therefore, personally speaking; I think that these tasks require patience, understating, flexibility and keenness to have them running through so the ‘ball can get rolling’. Against these requirements, I guess rush was the worst obstacle. In fact, one should have patience and be inspired since, according to Rohn, E. J.: ‘the worst days of those who enjoy what they do, are better than the best days of those who don’t’.

This study has aimed to investigate the feasibility of microfiltering (breakdown) of water-in-crude oil emulsion through a bespoke hydrophilic polymeric membrane. High internal phase emulsion was used to prepare this polymeric membrane. The study has also aimed to investigate the possibility of enhancement of demulsification efficiency in the presence of an electrical field at different intensities. The study was based on a model water-in-crude oil emulsion(s). It is hoped that the results obtained from this work can provide information that can benefit the oil industry, although it may still require further consideration from both technical and economical viewpoints.

Acknowledgements

First of all, my humble thanks are expressed to Allah almighty for the strength, inspiration, guidance and encouragement through out this lengthy and difficult journey. In fact, many experiences and knowledge have been gained.

It is doubtful that someone makes it to the end of their theses without a great deal of help and support along the way. I, the author of this thesis, have been certainly no exception. First of those I should thank is my academic supervisor, Prof. G. Akay. I would like to thank and appreciate him for his supervision, invaluable encouragement, critics and comments on my work through out the experimental work period, authentic interest and important contributions to this thesis. Although in this work the road may have been circuitous, he; however, has been a great mentor and advisor through his guidance, positive attitude and patience. It has been a great privilege and an honour for me to work with such an inspirational and expert inventor who has been credited with several EU and US patents in different disciplines so far.

My deepest sincere thanks are also extended to the Higher Education Ministry, Tripoli-Libya for providing this chance for me to acquire knowledge and expertise. I also acknowledge them for their financial support while pursuing my Ph D studies, in a hope that this might contribute to Libya's long term vision. In fact, since 17th.02.11 in a strong and probably an unprecedented conflict at least in the modern history, brave, honourable and liberal Libyans have been going towards a democratic destination in which a newer, better and civilian state is built. However, this has been inevitably through a bloody, revolutionary and honorary route fighting against a typical-42-years-tyrant. Brave rebels across Libya are really thanked for this and this work is also dedicated to all of them including martyrs.

Newcastle University is also thanked for facilitating office space, various laboratory equipment and providing the opportunity to 'exploit' its highly talented technicians team at the mechanical workshop in the School of Chemical Engineering and Advanced Materials (CEAM) for technical assistance including: James Banks, Simon Daley, Iain Ditchburn, Brian Grover, Stewart Latimer and Iain Strong. Names have not been listed in terms of help and advice offered, but only alphabetically. I also wish to thank all the staff in the School of CEAM for their help. The author of this thesis wishes also to thank Pauline Carrick for her generous technical assistance relating to scanning electron microscopy at the Advanced Chemical and Materials Analysis (ACMA) Centre in Herschel building, Newcastle University. For the transmissional electron microscopy thanks are also submitted to Tracey Davey and Kathryn White at the Electron Microscopy Research Services, Medical School, Newcastle University.

Whilst working in the laboratory, I have really benefited from working within a multi-national students community and post-doc. associates, whom provided friendships, pleasant working environment, intellectual assistance, constructive criticism and fruitful direct/indirect discussions especially where chemistry was involved. Within such a community I think, I have been constantly learning and broadening my horizons. I indeed would like to convey words of thanks and acknowledgement to all of them.

I would also like to express my sincere gratitude to my family members who have always been the source of love, encouragement and support. To my mother, whom in times when it seemed impossible has made me go ahead with the Ph D via her words and supplications, to the soul of my father, to my son Anas, to my other nearly two and half years son Ayhm whom since he was born I have not physically seen as of yet and also to my five sisters. In fact, without their love, patience and support completion of this thesis would never have been possible. I am really indebted for all of them. Finally, I am very thankful to any one, supportive friends in particular, who have wished me the success.

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Nomenclature

- Abbreviations:

AC	Alternative current.
BP	British petroleum.
C	Cell of filtration.
CFV	Crossflow velocity.
CIP	Cleaning-in-place.
CMC	Critical micelle concentration.
COP	Cleaning-out-off-place.
DAF	Dissolved air flotation.
DC	Direct current.
DSM	Dutch state mines.
DVB	Divinylbenzene.
EC1	Electrode one (polymer).
EC2	Electrode two (foil).
ESEM	Environmental scanning electron microscope.
E1	Water-in-oil emulsion with 30 % vol. water.
E2	Water-in-oil emulsion with 50 % vol. water.
F	Feed tank.
HIPE	High internal phase emulsion.
HIPRE	High internal phase ratio emulsions.
HLB	Hydrophile-Lipophile balance.
HMW	High molecular weight.
LMW	Low molecular weight.
NSO	Nitrogen, sulphur and oxygen.
O/w	Oil-in-water.
O/w/o	Oil-in-water-in-oil.
PHP	PolyHIPE polymer.
PI	Process intensification.
P1/P2	Pressure manometers.
SAA	Surface area analysis.
SARA	Saturates-aromatics-resins-asphaltenes.
SDR	Spinning disc reactor.
T	Terminal.
TEM	Transmissional electron microscope.
TMP	Transmembrane pressure.
V1/V2	Valves.
W/o	Water-in-oil.
W/o/w	Water-in-oil-in-water.

- Symbols:

- Roman Symbols:

Symbol	Definition	Dimensions
A	Filter/membrane surface area.	m^2
A_M	Cross-sectional area occupied by each adsorbate molecule (A_M = 0.162 m^2 for nitrogen).	m^2
A_p	Cross-sectional area of the pipe.	m^2
C_F	Concentration of the solute in the feed stream.	mole/ m^3
C_P	Concentration of the solute in the permeate stream.	mole/ m^3
C_R	Concentration of the solute in the retentate stream.	mole/ m^3
D_d	Emulsion droplet diameter.	µm
DE	Demulsification efficiency, %.	-
D_p	Membrane pore diameter.	µm
E	Electrical field strength	V/cm
EI	Emulsion with 30 vol. % of water (dispersed phase) content.	-
EII	Emulsion with 50 vol. % of water (dispersed phase) content.	-
F	Attractive force between droplets.	N
G	Conductivity.	µS/cm
I	Current.	A
J	Permeate flux rate.	L/m^2 hr
N_A	Avogadro's number.	$6.02214129(27)\times10^{23}$ mol^{-1}
P	Pressure.	bar
P_M	Pressure of the dose manifold.	bar
P_{M1}	Initial manifold pressure.	bar
P_{M2}	Final manifold pressure.	bar
P_0	Saturation pressure.	bar
P_S	Sample pressure.	bar
P_{Sn}	Sample pressure.	bar
Q_F	Volumetric flow rate of feed stream.	volume/time
Q_P	Volumetric flow rate of permeate stream.	volume/time
Q_R	Volumetric flow rate of retentate stream.	volume/time
$Q, Q_1, Q_2, Q_3,\ldots, Q_n$	Volumetric flow rates.	volume/time
r	Droplet radius.	cm
R	Membrane solute rejection, %.	-
R_{ef}	External and reversible resistance due to concentration polarization on the membrane	-

	surface.	
R_d	Deposit resistance.	-
R_m	Membrane resistance.	-
S	Total volume of permeate sample.	m^3
T_M	Temperature of the dose manifold.	K
u	Terminal droplet velocity.	m/sec
V	Filtrate volume.	m^3
$Vads_n$	Volume adsorbed.	m^3
Vd_n	Volume dosed.	m^3
Vd_{n-1}	Volume dosed from previous data point.	m^3
V_M	Volume of the dose manifold.	m^3
V_m	Volume of monolayer.	m^3
V_1, V_2	Crossflow velocity.	m/sec
W	Volume of water in the permeate sample.	m^3

- Greek Symbols:

Symbol	Definition	Dimensions
ρ_1, ρ_2	External fluid and droplet density, respectively.	kg/m^3
μ	Bulk viscosity.	cP
τ	Sampling duration.	hr

- Constants:

Constant	Definition	Dimensions
C	Constant related to the enthalpy of adsorption.	-
g	Gravitational constant.	9.8 m/sec^2
R	Gas Constant.	8.3144621 J/mol K

If we begin with certainties, we shall end in doubts;
but if we begin with doubts, and are patient in
them, we shall end in certainties.

Francis Bacon
(1561-1626)

Chapter One

General Introduction

Chapter One

General Introduction

> And when all is said, he that publishes a book runs a very great hazard, since nothing can be more impossible than to compose one that may secure the approbation of every reader.
>
> Miguel de Cervantes Saavedra.
> (1547-1616)

1.1 Background

In petroleum industry, natural emulsion formation is a common phenomenon. Indigenous crude components with surface-active properties upon oil-water contact have been quoted to be responsible for the formation of highly stable emulsions. Although, most of this water in contact with crude can readily be removed; nevertheless, a considerable amount remains as emulsified droplets dispersed throughout it creating an emulsion (Moran and Czarnecki, 2007a). Such components include: asphaltenes, resins, waxes, acids and solids. Since concentrations of these components in different crudes may be different, one can expect that the stability level of the resultant emulsion can be accordingly different. The stability level of an emulsion can be days or even years. Such emulsions should not be underestimated as large amount (almost two thirds) of extracted petroleum exists in an emulsion form (Elsharkawy et al., 2005). In addition to stability-related problems due to the presence of these components in a crude, asphaltenes in particular adversely have an effect on the value of crude oil and obstruct production, transportation due to high viscosities and refining due to their metal content at high temperatures in particular.

There are several occasions where oil and water become in contact during oil exploitation, production and processing while which water/oil droplets become dispersed through the oil/water as small droplets, respectively. Down in a reservoir, crude oil and water are naturally accompanied (formation water). Besides, in enhanced oil recovery (EOR) processes water is also injected into depleted reservoirs in order to help force the crude oil out of a reservoir (produced water). Other refinery units may also comprise water injection. This binary system (oil and water) along its journey through choke vales, pipes and pumps undergoes further agitation through which emulsification is further promoted. Moreover, large amount of crude oil spills into seas and oceans during crude tankers accidents can also be a source of such emulsions.

1.2 Problem Statement

Emulsions are undesirable because in the first instance they have the impact of increasing the crude viscosity resulting in crude transportation problems. In fact, this entails additional operational and capital costs. Furthermore, they lead to production losses and may provoke corrosion of pipes, equipment and pumps, etc. Efficient demulsification of these emulsions is; therefore, an important and of great significance element for oil producers to avoid such emulsion-based problems. One vital requirement to attain sound demulsification efficiency is understanding how these emulsions are stabilized through studying nature, properties and behaviour of their indigenous emulsifiers.

So far, conventional methods that have been employed to break down such emulsions have included chemical and/or electrical and thermal methods. Although these methods have been successful in the demulsification task; however, they still have been a major challenge to the petroleum industry world-wide. They generally demonstrate limited efficiencies and inevitably may multiply the problem as they are associated with problems of side products in case of chemical processes as a result of chemicals use and possibility of crude degradability under the influence of excessive temperature elevation in thermal methods. Obviously, chemical methods rely on introducing chemical(s) to the emulsion investigated by which the interface between oil and water is restructured leading to emulsion breakdown; that’s to an extent dependable on emulsion stability extent and the efficiency of the employed commercial demulsifier. However, removal of these chemicals from the emulsion system is required which entails additional units and cost. In order to meet the growing crude oil demand along with good specifications, it becomes more and more essential to develop better techniques to efficiently deal with such crude oil-based emulsions.

1.3 Process Intensification (PI)

Such limitations can be overcome or at least minimized through the implementation of process intensification (PI) strategy. In fact, due to some financial and resources concerns, technical problems in the current technologies and other related environmental problems, PI has been a necessity. Historically, the term PI was used in the mid- 1960s and early 1970s. It was mainly used in Eastern Europe publications in the field of metallurgical processing referring to improved processing. It took until 1983, when a paper on the application of centrifugal fields (HiGee) in distillation processes published by Colin Ramshaw of the ICI, New Science Group, London, UK, for the PI to be first used in the field of chemical engineering. He described PI as 'devising an exceedingly compact plant which reduces both the main plant item and installation's costs'. PI until the early 1990s, was mainly studied in Britain mainly in the areas of: use of centrifugal forces, compact heat transfer, intensive mixing and combined technologies. Then, it has found increased attention worldwide; in Holland, France, Germany, China and also in the United States. Commercialization of PI by several companies was also introduced. It was applied in the methyl acetate process of Eastman Chemical, the hydrogen peroxide distillation system of Sulzer and the hypochlorous acid process of Dow Chemical. By the end of the 20th century and beginning of the 21st, PI, due to reduced costs, number of process steps, emissions and waste, and risks of chemicals processed and low energy consumption, has been involved in wider academic and industrial applications (Stankiewicz and Drinkenburg, 2004).

PI is characterized by four words: smaller, cheaper, safer and slicker (Stankiewicz and Drinkenburg, 2004). Unlike traditional processes, through PI not only chemical reactions rates, fluid dynamics and heat/mass transfer rates are optimized, but also capital and operating costs, number and size of the required facilities/units, power consumption and generated waste are reduced by several orders of magnitude. Essentially important, with no compromise in the process output. For instance, sky-scraping distillation columns of DSM (Dutch state mines) are replaced by a compact, clean and tidy indoor plant, see Fig. (1.1). PI offers several benefits including reduced costs, increased process safety and reduced time to market. Reduced costs are due to reduced costs of: land, raw materials, piping, utilities and waste processing, etc. (Stankiewicz and Drinkenburg, 2004). PI also increases the process safety. Unlike add-on safety where safety devices such as interlocks, etc. are used with a finite failure probability, PI offers an increased process safety. As the inventory of hazardous material(s) or energy in an intensified process is reduced, failure to control that hazardous material(s) or energy can accordingly be reduced (Ehrfeld, 2004; Hendershot, 2004). Also, by PI time required to deliver a product to market can be shortened, e.g. fine chemicals and pharmaceutical sectors. In Figs. (1.2-3), main benefits from PI are shown. To this end, PI can be considered as an indispensable route if in the first instance; consumption of both energy and raw materials is to be minimized with a great opportunity to discover novel materials, production units as well as control procedures and equally important protecting the environment.

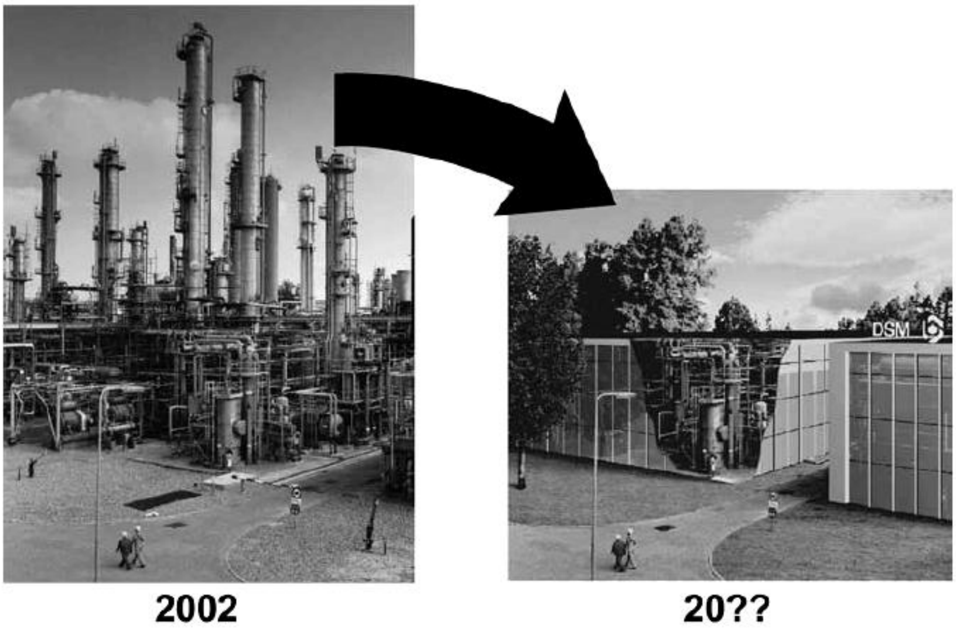


Fig. (1.1): DSM’s vision of process intensification (Stankiewicz and Drinkenburg, 2004)

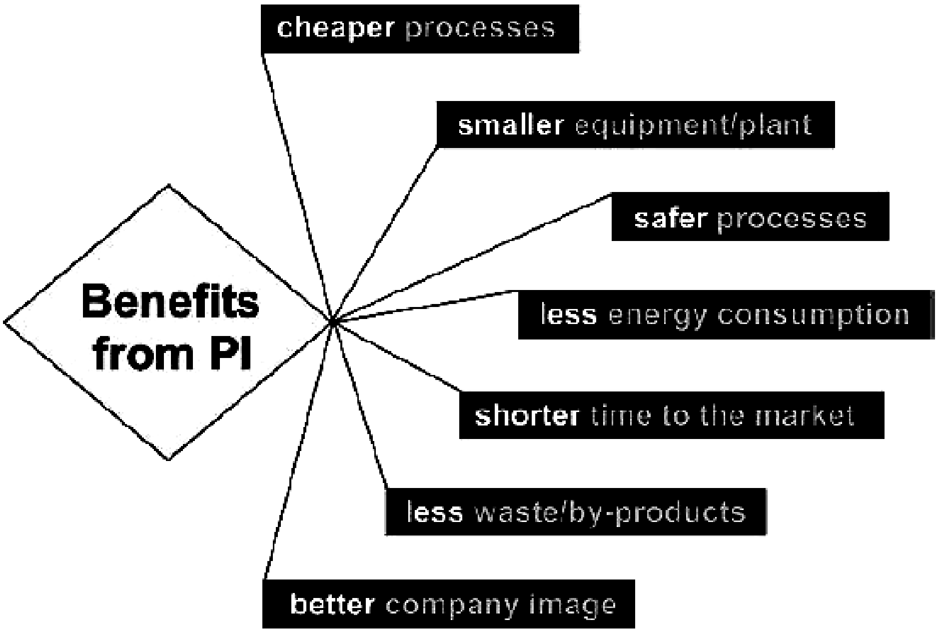


Fig. (1.2): Main benefits from process intensification (Stankiewicz and Drinkenburg, 2004)

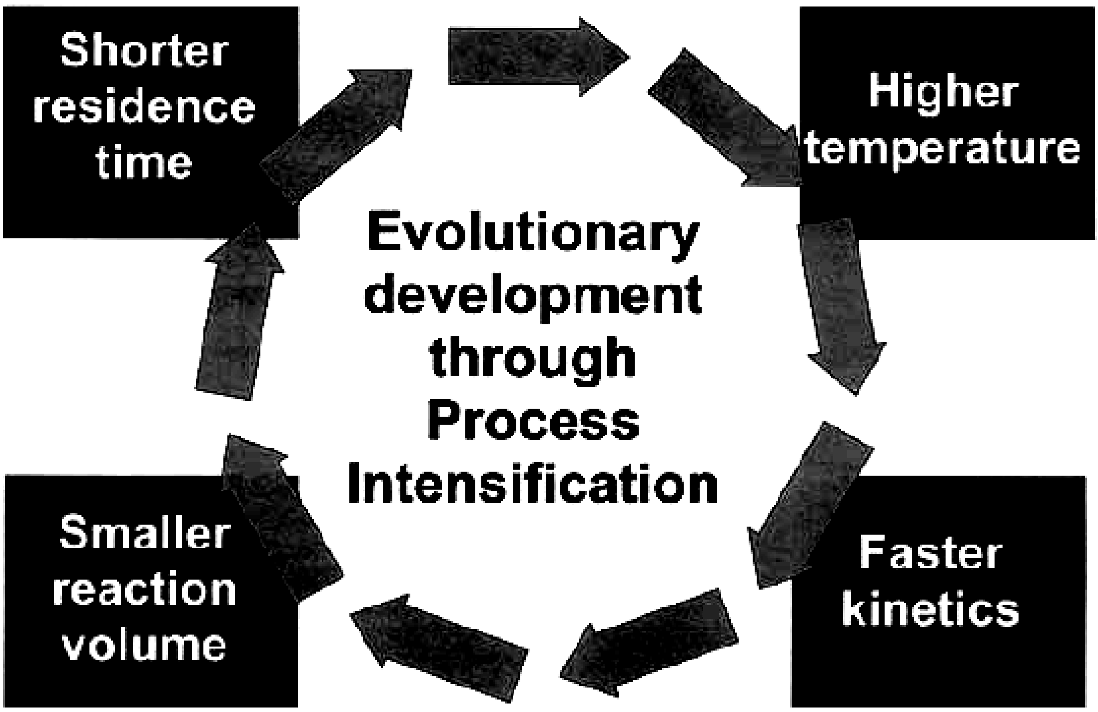


Fig. (1.3): Evolutionary development through process intensification (Ehrfeld, 2004).

PI is usually delivered through a synergic effect of at least two effects and/or field forces. The toolbox that's process-intensifying equipment (hardware) and process intensifying methods (software) for PI is schematically shown in Fig. (1.4). Successful implementations of PI technique have been involved in: compact heat exchangers, spinning disk reactors (SDR), utilization of in-line devices such as rotor-stator mixers, etc. Some examples of processes in which PI is applied have included: nitration reactions, polymerization, tubular/jet reactors, heat exchangers, distillation, combined unit operations (reactive distillation), extraction and innovative energy sources (laser light, ultraviolet light, microwaves and ultrasonic energy), etc. (Hendershot, 2004). Key factors of these processes are: increased surface area per unit volume, increased heat and mass transfer coefficients following formation of thin unstable liquid films and increased mixing rates by several orders of magnitude in comparison to the conventional processes; respectively. Another route to achieve PI is through the application of different fields such as acoustic, electrostatic, magnetic, centrifugal, solar and/or microwave radiation (Akay et al., 2005; Zanfir and Gavriilidis, 2001; Mason and Cordemans, 1996).

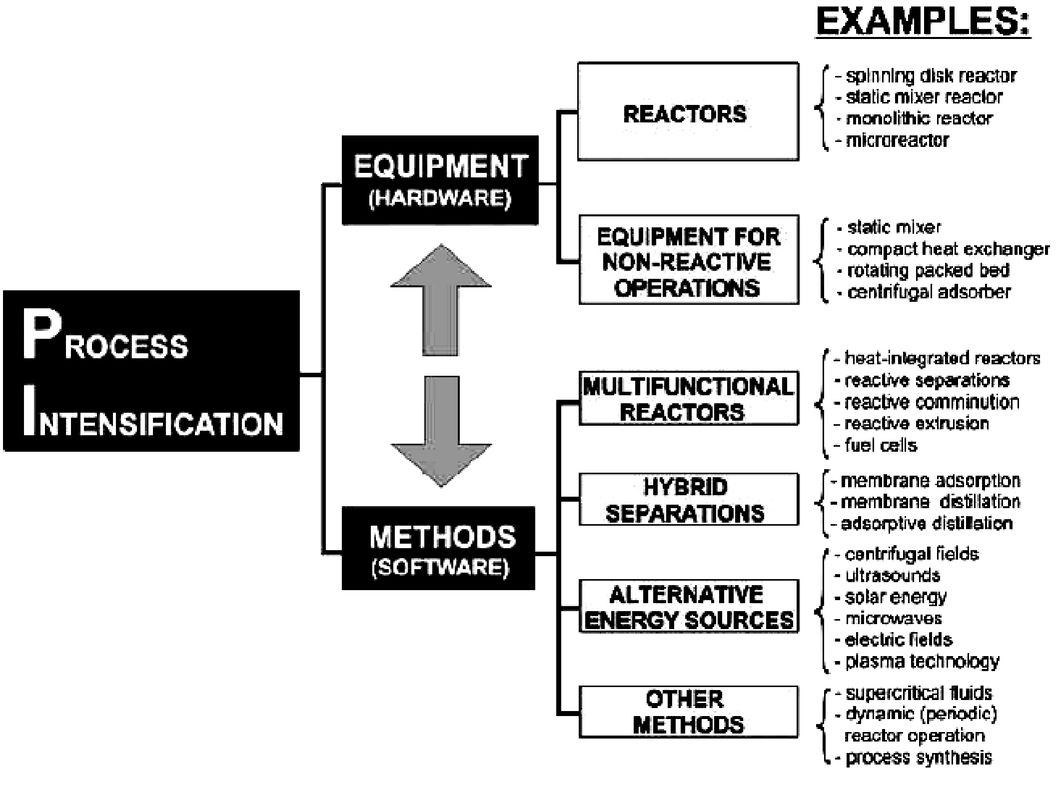


Fig. (1.4): Process intensification toolbox (Stankiewicz and Drinkenburg, 2004)

1.4 Thesis Hypothesis, Aims and Objectives

The hypothesis of this research is that a bespoke hydrophilic polymer prepared through high internal phase emulsion and traditionally known as PHP would be capable to breakdown a model w/o emulsion.

The main aim of this work is to investigate the feasibility of microfiltration (breakdown) of water-in-crude oil emulsion through a bespoke hydrophilic polymeric membrane, prepared in-house in Newcastle University laboratory. The study is also extended to investigate the possibility of enhancement of demulsification efficiency via PI approach; that's crossflow microfiltration in the presence of an electrical field at different intensities. With such intensified approach important economical, operational and environmental advantages can be offered. The required equipment can be made compact, portable, robust and efficient, by which it is; therefore, possible to conduct the demulsification task as close to the source of crude production as possible in which the space for operation and maintenance is usually confined, e.g. offshore sites. This is also crucially important to utilize the chemistry of the extracted crude at both high pressure and temperature before it is pumped to the oil platform where its temperature may fall rapidly due which separation of oil from water may become a more difficult process. In addition, significant crude transportation costs over considerable distances through undersea pipelines from wellheads to onshore refineries can also be reduced. Further, according to the literature, employing electrical fields in filtration processes offers the potential of reduced pumping costs since lower crossflow velocities in such processes can deliver what higher velocities can deliver but in the absence of an electrical field (Tarleton, 1992). In both configurations, effect of parameters such as water content of emulsions, feed cross flow velocity (CFV) and membrane properties on both membrane flux rate and demulsification efficiency is investigated. In order to conduct the experiments required to achieve this aim, the following objectives were set:

- Preparation and Characterization of Model w/o Emulsions: W/o emulsions will be prepared. The oil phase (continuous phase) is a crude oil, provided by BP-Amoco, whereas the aqueous phase (dispersed phase) is model sea water containing 0.6 g/l $CaCl2$, 5 g/l $MgCl2$ and 28.1 g/l NaCl. Emulsions will be made out with two different water contents, namely 30 and 50 vol. % in an effort to imitate emulsions that are usually found in oil industry. Having prepared these emulsions, they will be characterized by measuring their conductivities and their stability level by bottle tests.

- Preparation and Modification of Several PHP Membranes: Several batches of PHP membranes will be prepared using high internal phase emulsion (HIPE) polymerization route. In order to produce membranes with different pore size ratings, time of mixing throughout polymerization will be different. Chemistry of the prepared membranes will be modified by means of sulphonation. In terms of characterization of these membranes, surface area analysis (SAA) and environmental scanning electron microscope (ESEM) will be employed.

- Investigation of the Main Factors that Influence Microfiltration and Demulsification of w/o Emulsions: Effect of influent emulsion water content, filtration duration, feed crossflow velocity (CFV), electric field and membrane pore size on the permeate flux rate will be studied. This will then be followed by an investigation of the effect of these filtration variables on demulsification efficiency.

1.5 Thesis Overview

This thesis covers the work undertaken over the last five and half years. The thesis has been organized into seven chapters. It first provides a survey of the relevant literature in the fields of emulsions, demulsification techniques and emulsion microfiltration processes. Chapter two represents a summary of emulsion principles and stability issues as explained in the literature. These include the emulsion systems, origin of crude emulsions, issues of stability of such emulsions and problems arisen from them. Also, multiple emulsions, crude oil and its characteristics are briefly examined. Finally, this Chapter represents emulsion instabilities processes such as sedimentation (creaming), flocculation, coalescence, Ostwald ripening and emulsion phase inversion. Chapter three gives the state-of-the-art review on demulsification methods of water-in-oil emulsions. It describes the mechanisms involved in chemical, thermal and electrical demulsification procedures of water-in-oil emulsion.

In Chapter four, principles and mechanisms of microfiltration and electro-microfiltration and those involved in crossflow microfiltration (with and without electrical field) are discussed. In Chapter five, the experimental procedure details and equipment description, chemicals used to prepare the PHP polymer and the emulsion and the analytical methods involved in this work are all described. Chapter six contains results and discussion for crossflow microfiltration of water-in-oil emulsions. Results and discussion for crossflow microfiltration of water-in-oil emulsions in the presence of electrical fields of different strengths are also discussed in this Chapter. Conclusions based on these results are highlighted in Chapter seven along with the outstanding issues that require further investigation and evaluation.

A synopsis plan showing the layout of this thesis is illustrated in Fig. (1.5)

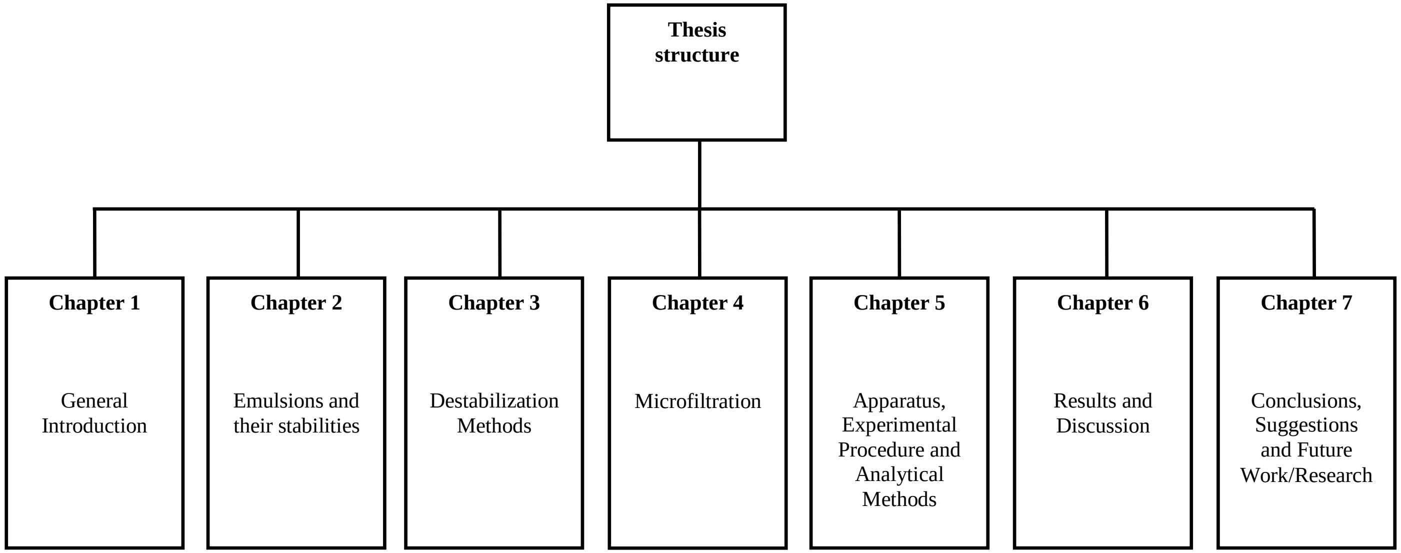


Fig. (1.5): Thesis structure showing areas of study according to Chapter.

Chapter Two

Literature Review

Emulsions and Their Stabilities/Instabilities

Chapter Two
Literature Review
Emulsions and Their Stabilities/Instabilities

> We can be absolutely certain only about things
> we do not understand.
>
> Eric Hoffer
> (1902-1983)

2. 1 Introduction

Problematic emulsions are ubiquitously found in oil industry (Sullivan et al., 2007; Havre and Sjöblom, 2003; Sjöblom et al., 2003; Eow and Ghadiri, 2002a; Angle, 2001; Yang et al., 2001; Sams and Zaouk, 2000; Sams and Zaouk, 1999). These emulsions are encountered in as early stages as the exploitation stage down through the different refining and processing stages (Mohebali et al., 2012). In this literature review, an overview of the existing knowledge and researchers findings on the chemistry of emulsion formation is provided. It is intended to spotlight and summarize what is available in the relevant literature about the emulsion formation process. Among the examined studies, there has not been a general agreement on what the cause(s) or factor(s) which may lead to or influence emulsion formation and stabilization. It seems that the topic is somewhat associated with some uncertainty in which there has been no general notion that can be precisely used to identify which crude component(s) are responsible for emulsion formation or describe an universal mechanism that explains the role played by these component(s) whether individually or collectively.

Within the scope of this review basic principles of water-in-oil emulsions, origin and the problems associated with emulsion formation highlighting the necessity for emulsion demulsification and subsequent separation, multiple emulsions and crude oil and its general characteristics have been briefly addressed. This was then followed by an extensive review of some research studies concerned with emulsion stability. This section was structured with a great deal of attention to study asphaltenes and resins as they were, according to several studies, undoubtedly considered as the most important crude components behind the formation of tremendously stable emulsions.

In fact, knowledge of crude components structure properties, their association tendencies, accommodation at water-oil interface, solubilities and sensitivity towards changes in ambient pressure and/or temperature, is necessary (Ekott and Akpabio, 2010). Next, a brief discussion was given to highlight the contribution of other indigenous and non-indigenous crude oil components towards emulsion formation and stabilization. Although it may seem, to some extent, digressive to include in this literature review, emulsifying agents other than the crude components with surfactant properties such as asphaltenes and resins. In fact, based on the identified literature; however, it was felt that it is difficult to disregard the interaction between asphaltenes/resins and other emulsifying agents such as waxes, acids and solids and the resultant role towards emulsion stability. This was inferred from some studies concluding that emulsion stability is influenced not only by asphaltenes and resins, but also by a synergic interaction between other stabilizers. Therefore, in an effort to obtain a better understanding as possible, it was decided to disclose some basic information about the other emulsifying agents than asphaltenes and resins. At the tail of the review, emulsion instabilities including sedimentation, flocculation, coalescence, Ostwald ripening and emulsion phase inversion are also discussed.

2.2 Emulsion Systems

An emulsion can be defined as a system of at least two immiscible liquids one of which is mono/poly-dispersed in the other. For instance, if water is dispersed in oil, the resultant emulsion is called water-in-oil emulsion (w/o) with droplet diameter in the range of 10-100 microns (Johansen et al., 1989); on the other hand, when oil is dispersed in water; this produces oil-in-water emulsion (o/w). Hereafter, throughout this thesis w/o is used to refer to water-in-oil emulsions and o/w is used to refer to oil-in-water emulsions. The dispersed phase is also sometimes referred to as the internal phase; the other phase (continuous) is referred to as the external phase (Holmberg et al., 2002; Kokal, 2002; Becher, 2001; Pal, 1994; Schramm 1992). According to their droplet size, emulsions are classified into three broad groups: micro-emulsions (10-100 nm) in the form of small aggregates, mini (nano, ultrafine or submicron) emulsions (20-1000 nm) in the form of relatively large droplets and macro-emulsions (0.5-100 µm) (Jafari et al., 2008; Solans et al., 2005; Angle, 2001; Becher, 2001). As a rule of thumb, the smaller the average size of the dispersed phase droplets, the more stable the emulsion is. Interfacial tension, nature of emulsifying agents, presence of solids, shear and bulk properties of both oil and water influence the droplet size distribution of the resultant emulsion (Kokal, 2002). Generally, these emulsions apart from micro-emulsions are thermodynamically unstable (Drelich et al., 2010; Ekott and Akpabio, 2010; Fredrick et al., 2010; Gutiérrez et al., 2008; Jafari et al., 2008; Samanta and Basak, 2008; Lif and Holmberg, 2006; Solans et al., 2005; Ichikawa and Nakajima, 2004; Bouchama et al., 2003; Buist and Lewis, 2002; Holmberg et al., 2002; Kokal, 2002; Angle, 2001; Becher, 2001; Kilpatrick and Spiecker, 2001; Liggieri et al., 2001; Bibette et al., 1999; Márquez et al., 1996; Kellay et al., 1994; Schramm 1992; Aveyard et al., 1990; Isaacs et al., 1990; Kenneth J, 1988); however, they are kinetically are for months or years due to the presence of surface active compounds with their surfactant properties (Márquez et al., 1996; Schramm 1992; Aveyard et al., 1990). A stable emulsion is the one that its structure does not change with time, nor does it depend on how it was prepared and is characterized by small water droplets and a low conductivity (de Morais Coutinho et al., 2009; Gutiérrez et al., 2008; Jafari et al., 2008; Othman et al., 2008; Samanta and Basak, 2008; Chen and Tao, 2005; Clausse et al., 2005; Ichikawa et al., 2004; Sjöblom et al., 2003; Robins et al., 2002; Lagaly et al., 1999; Mason, 1999; Fingas, 1995; Davis, 1994; Israelachvili, 1994; Pal, 1994; Schramm 1992; Arirachakaran et al., 1989; Thomas and Ali, 1989). The stability of an emulsion can be affected by density difference of its phases, viscosity of the oil phase, interfacial viscosity, water droplet size, surfactant concentration, interfacial tension, film compressibility, electrolyte concentration in the water phase and also by the operating conditions (Isaacs et al., 1990). Indeed, although in food industries; for instance, high emulsion stability for long periods of time is usually sought, in crude oil processes; however, a great deal of efforts is devoted to destabilize these undesirable highly stable emulsions, mostly, through a difficult, complex and costly task (Drelich et al., 2010; Fredrick et al., 2010; Sullivan and Kilpatrick, 2002; Liggieri et al., 2001). Fig. (2.1) illustrates these two emulsions (Kilpatrick and Spiecker, 2001).

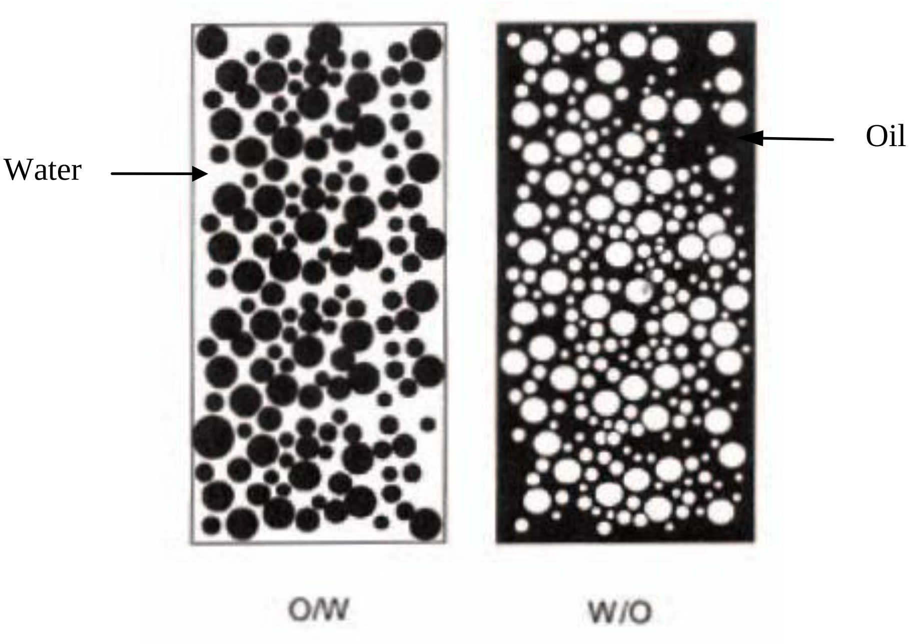
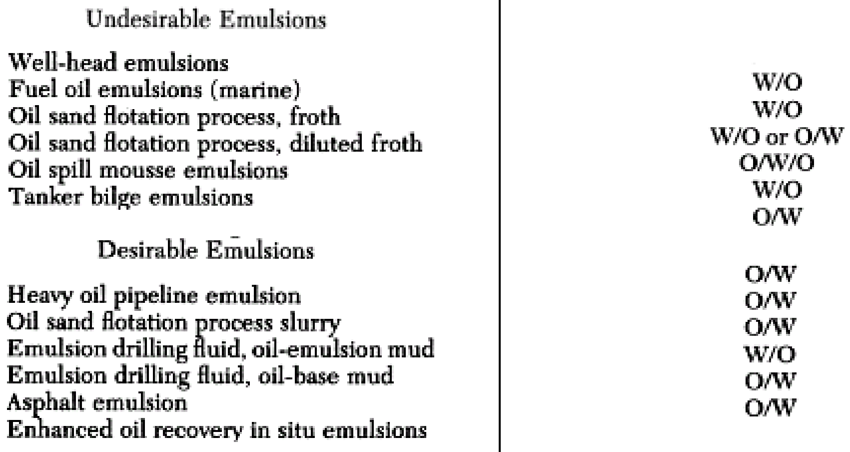


Fig. (2.1): Schematic drawing of emulsion types. Reproduced from (Kilpatrick and Spiecker, 2001).

Basically in the oil industry, emulsions are either w/o which usually refers to oil field emulsions (regular emulsions) or o/w (reverse emulsions), with the latter type accounts for less than 5 % of the resultant emulsions (Ekott and Akpabio, 2010; Fredrick et al., 2010; Fingas and Fieldhouse, 2009; Nour et al., 2007a; Elsharkawy et al., 2005; Noïk et al., 2005; Pena et al., 2005; Xia et al., 2004; Bouchama et al., 2003; Fingas and Fieldhouse, 2003; Kokal, 2002; Angle, 2001; Becher, 2001; Dalmazzone and Clausse, 2001; Kilpatrick and Spiecker, 2001; Ali and Alqam, 2000; Ahmed et al., 1999; Tirmizi et al., 1996; Fingas, 1995; Pal, 1994; Tambe and Sharma, 1993; Schramm 1992; Eley et al., 1988a). The role by which emulsion type is determined is known as Bancroft’s rule, which was known in the second decade of the twentieth century. This rule states that an emulsion continuous phase would be the phase that the surfactant is preferentially soluble in. Therefore, a surfactant with a solubility tendency into water phase will favour the formation of o/w emulsions; likewise, a surfactant that’s soluble into oil phase prefers the formation of w/o emulsions (Ekott and Akpabio, 2010; Langevin et al., 2004; Holmberg et al., 2002; Angle, 2001;

Becher, 2001; Akay, 1998). This rule had been in use until 1949 when Griffin introduced the concept of hydrophile- lipophile balance (HLB) number (Holmberg et al., 2002; Boyd et al., 1972). HLB is a quantitative measure of Bancroft's rule; it is an important variable in determining the type of the resultant emulsion based on surfactant molecular composition and structure. The maximum value of HLB number is 20; low values of this number (1-10) relate to hydrophobic surfactants that are oil soluble, whereas higher values up to 20 correspond to hydrophilic surfactants by which o/w emulsions are formed (Othman et al., 2008; Binks, 2002; Buist and Lewis, 2002; Holmberg et al., 2002; Vander Kloet et al., 2002; Pal, 1997; Davis, 1994). Although HLB has been used to characterize the nature of the resultant emulsion, it; however, does not take into account the nature of the oil phase and the additives in the aqueous phase, the effect of temperature and the interactions between the aqueous phase and the hydrophilic groups of the emulsifiers and between the oil phase and the lipophilic groups (Boyd et al., 1972). Furthermore, volumes of emulsion phases can also dictate the resultant emulsion since a phase with a very small volume will usually be the dispersed phase (Ekott and Akpabio, 2010; Othman et al., 2008; Schramm 1992). In Table (2.1), some examples of petroleum emulsions are given.

Table(2.1): Examples of emulsions in the petroleum industry (Schramm 1992).



Occurrence	Usual type
Undesirable Emulsions	
Well-head emulsions	W/O
Fuel oil emulsions (marine)	W/O
Oil sand flotation process, froth	W/O or O/W
Oil sand flotation process, diluted froth	O/W/O
Oil spill mousse emulsions	W/O
Tanker bilge emulsions	O/W
Desirable Emulsions	
Heavy oil pipeline emulsion	O/W
Oil sand flotation process slurry	O/W
Emulsion drilling fluid, oil-emulsion mud	O/W
Emulsion drilling fluid, oil-base mud	W/O
Asphalt emulsion	O/W
Enhanced oil recovery in situ emulsions	O/W

In real applications in petroleum industry, there are different routes where these emulsions may be formed. O/w emulsions may be formed when it is necessary to reduce a heavy crude's viscosity; that's usually between 1000 cP to at least 100000 cP at 25 C (Ahmed et al., 1999; Eley et al., 1988a), for transportation purposes. Although it is feasible to achieve this either by heating (by steam/water injection) or addition of low viscosity meanwhile cheap hydrocarbon diluents, these techniques are either costly/inconvenient or inapplicable; respectively (Abdurahman et al., 2012; Shigemoto et al., 2007; Angle, 2001; Ahmed et al., 1999; Zaki, 1997; Pal, 1994). Alternatively, in order to turn a heavy crude pipelineable by reducing its tremendously high viscosity down to 200 cP (Ahmed et al., 1999), water injection is usually practised. As a result o/w emulsion is deliberately made (Langevin et al., 2004; Kilpatrick and Spiecker, 2001; Ahmed et al., 1999; Zaki, 1997; Pal, 1994; Schramm 1992; Arirachakaran et al., 1989; Plegue et al., 1986). It is also found in massive amounts in emits of metal finishing industries, most different food industries and also from refineries (Fredrick et al., 2010; Mohammadi et al., 2005a; Gomez and Lin, 2004; Holmberg et al., 2002; Tirmizi et al., 1996). Further details on these emulsions including the methods used to break them are beyond the scope of this review; hence, they will not be further discussed; however, they are studied in a series of different publications, some of which are: (Qiu et al., 2009); (Gutiérrez et al., 2008); (Lobo et al., 2006); (Hu et al., 2002); (Faibish and Cohen, 2001); (Park et al., 2001); (Ahmed et al., 1999); (Kong and Li, 1999); (Srijaroonrat et al., 1999); (Zaki, 1997); (Daiminger et al., 1995); (Marc, 1995); (Lipp et al., 1988), etc. The first emulsion type (w/o); the main focus of this work, is mostly encountered in the oil industry as a result of high solubility of indigenous crude surfactant molecules in oil rather than in the water phase (Langevin et al., 2004). These emulsions are unfortunately encountered throughout crude oil exploitation, processing and transportation. This widespread and occurrence of w/o emulsions have made emulsion-based systems an important subject of investigation as demonstrated in the literature.

2.3 Formation of Water-in-Oil Emulsions

Water-free-crude is rarely produced (Maia Filho et al., 2012; Noïk et al., 2005; Kokal, 2002). Depending on the oil reservoir condition, between 10-50 % of produced crudes is water (Aveyard et al., 1990). In fact, in crude oil industry, there have been several processes which promote emulsion formation. The crude oil in a virgin reservoir is naturally accompanied with gas and water ‘formation water’(Mohebali et al., 2012); this seems to be a reservoir-wide property. This water contains large amounts of divalent cations such as calcium, magnesium, barium and strontium

(Dudásová et al., 2008). The amount of this water is constantly expected to rise from both onshore and offshore fields where the production environment is more challenging, risky and more expensive; at higher rates in the latter case as the reservoir depletes as shown in Fig. (2.2) (Alinezhad et al., 2010; Ekott and Akpabio, 2010; Dudásová et al., 2009; Fakhru'l-Razi et al., 2009; Nour et al., 2007a/b; Sullivan et al., 2007; Elsharkawy et al., 2005; Ezzati et al., 2005; Pena et al., 2005; Sjöblom et al., 2003; Sullivan and Kilpatrick, 2002; Angle, 2001; Kilpatrick and Spiecker, 2001; Goldszal and Bourrel, 2000; Sams and Zaouk, 2000; Sams and Zaouk, 1999; Pal, 1994; Bhattacharyya, 1992; Schramm 1992; Isaacs et al., 1990). In addition to that, water is also injected into depleted reservoirs; for enhancing oil recovery (EOR), in order to help force the crude oil out of the reservoir (Mohebali et al., 2012). As a result, some of this water ‘produced water’ is coproduced with oil as free water and some of it may be in the emulsion form (water ubiquitously dispersed through oil) due to turbulence and pressure drop in valves at the wellhead (Maia Filho et al., 2012; Ekott and Akpabio, 2010; Dudásová et al., 2009; Dudásová et al., 2008; Nour et al., 2007a; Moran and Czarnecki, 2007a; Sullivan et al., 2007; Elsharkawy et al., 2005; Pena et al., 2005; Sjöblom et al., 2003; Kokal, 2002; Sullivan and Kilpatrick, 2002; Angle, 2001; Kilpatrick and Spiecker, 2001; Sjöblom et al., 2001; Cumming et al., 2000; Holdich et al., 1998; Pal, 1994; Mohammed et al., 1993; Thomas and Ali, 1989; Eley et al., 1988b; Taylor, 1988; Thompson et al., 1985). Dissolved organic compounds (hydrocarbons), dissolved minerals and suspended solids, chemical additives from production line and heavy metals are the main constituents of this artificial water (Dudásová et al., 2009; Dudásová et al., 2008). Free water may settle out quite easily and quickly; however, that water in the emulsion form *does* require treatment technique(s) to be resolved (Kokal, 2002).

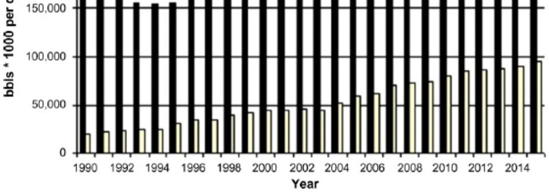


Fig. (2.2): Global onshore/offshore water production. (Fakhru'l-Razi et al., 2009).

Also, in order to desalt crude oils, to prevent refinery catalysts fouling and overhead distillation corrosion, wash water; in the preliminary refinery treatment, is deliberately brought into contact with oil where some interactions may take place between the crude oil hydrophilic materials and water, as a result water becomes emulsified through oil. Moreover, in heavy oil production fields where hot water is used to extract the bitumen, stable emulsions are also created (Sullivan et al., 2007; El Gamal et al., 2005; Sullivan and Kilpatrick, 2002; Angle, 2001; Sams and Zaouk, 2000; Sams and Zaouk, 1999; McLean and Kilpatrick, 1997a; Schramm 1992). Emulsions are also created as the crude oil with its water (formation/injected water) content is passed through choke valves and pumps due to the turbulent flow pattern which develops some eddies by which a mixing effect is imposed; hence an emulsion is formed (Alinezhad et al., 2010; Verruto et al., 2009; Less et al., 2008; Nour et al., 2007a; Pena et al., 2005; Sjöblom et al., 2003; Angle, 2001; Janssen et al., 2001; Márquez et al., 1996; Sjöblom et al., 1992a; Bhattacharyya, 1992; Schramm 1992; Aveyard et al., 1990; Isaacs et al., 1990; Taylor, 1988). A schematic diagram of petroleum production and refining processes in which emulsions are encountered is given in Fig. (2.3). Besides, large amount of crude oil spills, which known as chocolate mousse or mousse, into seas and oceans during crude tankers accidents is also a source of w/o emulsions with agitation required for emulsification is facilitated by wind (Buist and Lewis, 2002; Angle, 2001). Catastrophic oil rig explosion in the Gulf of Mexico resulting in months of oil leakage into the Atlantic ocean without a hope to manage it until several months have elapsed has also been a source for such emulsions. It is worth mentioning that these emulsions sooner or later will separate into water and oil phases, unless there are some surface active compounds that can stabilize them hampering the settlement process (Kenneth J, 1988).

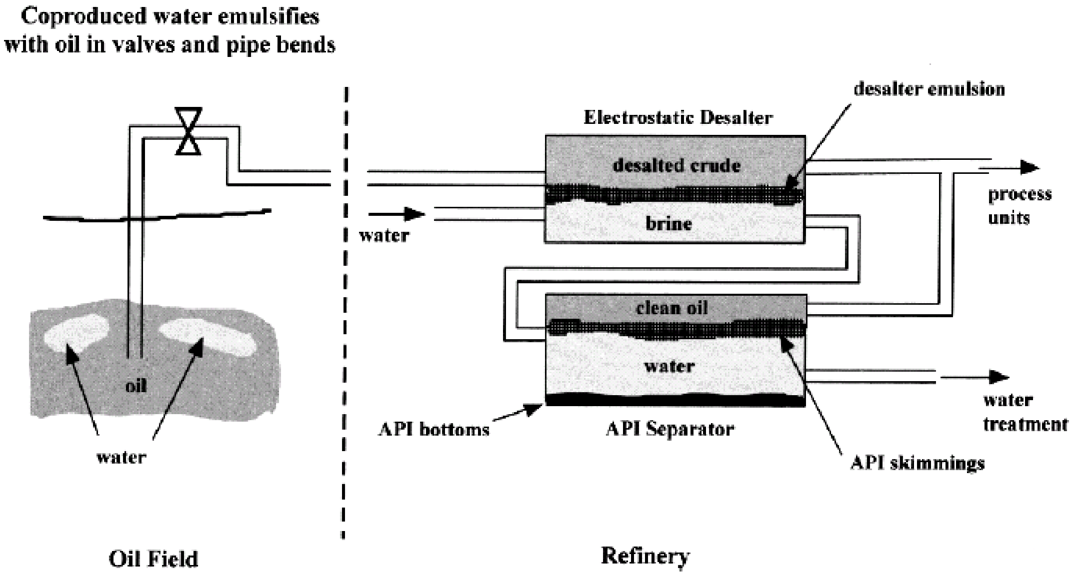


Fig. (2.3): A schematic diagram of petroleum production and refining processes in which emulsions are encountered (Sullivan and Kilpatrick, 2002).

Upon emulsion formation, the properties of the starting oil change to some extent (Fingas and Fieldhouse, 2004; Fingas, 1995). In studies by El Gamal and co-workers and Fingas (El Gamal et al., 2005; Fingas, 1995), it was shown that w/o emulsion density is slightly increased as the crude’s asphaltene amount increases. It was also demonstrated that an increase in the asphaltene content leads to a decrease in the emulsion’s kinematic viscosity. Also, Fingas, Fingas and Fieldhouse (2003), (2004) and (2009) (Fingas and Fieldhouse, 2009; Fingas and Fieldhouse, 2003; Fingas, 1995) stated that the viscosity of stable emulsions; where the asphaltene content is expected to be high, increases by 1000 fold and 500 fold; respectively, creating a heavy semi-solid material and that the density only increases by nearly 25 % which means an increase in the kinematic viscosity. An emulsion viscosity is a function of viscosities of both oil and water, volume fraction of water dispersed, droplet size distribution, temperature, shear rate and amount of solids present (Kokal, 2002). The acidity of w/o emulsions was linearly correlated with the asphaltene content of the emulsion. Clays were reported to increase the emulsion density and kinematic viscosity.

2.4 Issues of Stability of Water-in-Oil Emulsions

It was reported by Lee (Lee, 1999) that stable w/o emulsions, ‘in which the water persists for 5 days or longer’ or for years (Bibette et al., 1999; Mason, 1999) are highly viscous, with high water content of 50-90 % or 60-80 % somewhere else (Fingas and Fieldhouse, 2003), small water droplets (1-10 µm), low conductivity (Fingas, 1995; Pal, 1994; Schramm 1992) and more dense than the original oil. The stability of an emulsion is largely dependent on the stability of the interface layer between oil and water phases (Alinezhad et al., 2010; Sztukowski and Yarranton, 2005; Kim, 1999; Kim and Wasan, 1996; Taylor, 1988). Size of emulsified phase droplets (water in case of w/o emulsion), viscosity of the continuous phase (oil in case of w/o emulsion), difference in density of the two liquids and volume percentage of water cut are also some other important factors that may influence the stability of an emulsion (Othman et al., 2008; Buist and Lewis, 2002; Sams and Zaouk, 2000; Sams and Zaouk, 1999). Un-stable emulsions; however, are characterized by bigger droplet size and; therefore, coalesce sooner (El Gamal et al., 2005).

In a study by Kumar and others (Kumar et al., 2001) the mechanism by which w/o emulsions are stabilized was explained. It was claimed that although in a w/o emulsion water droplets are ubiquitously dispersed in the crude oil and; therefore, will be surrounded by a film of layers consist of surface active components of the crude oil such as asphaltene and resins. However, these droplets (water droplet) due to multiple body interactions will still endeavour to approach each other. On the other hand; however, some repulsive forces between water droplets are induced by the oily film around water droplet. These forces hinder water droplets from approaching each other; therefore, can neither flocculate nor coalescence (stable emulsion) (Schramm 1992).

High emulsifying agents concentrations hinder water droplet coalescence resulting in stable emulsions (El Gamal et al., 2005). Traditionally, surfactants such as asphaltenes and resins, oil soluble organic acids and other finely divided substances such as iron, zinc and aluminium sulphates, calcium carbonate, silica and iron sulphide of which they are less soluble, wettable or dispersible in the water phase than in oil phase, have been cited as the responsible components for crude oil emulsions through the formation of a film around the surface of the dispersed droplets. These emulsifying agents with their ability to diffuse from the bulk phase or from within the interface can reduce the interfacial tension between oil and water leading to broadening the interfacial layer meanwhile impeding droplet coalescence i.e., promoting emulsion stability (Maia Filho et al., 2012; Yarranton et al., 2007a; Pena et al., 2005; Pekdemir et al., 2003; Holmberg et al., 2002; Kokal, 2002; Vander Kloet et al., 2002; Akay, 1998; Davis, 1994; Pal, 1994; Nordli Børve et al., 1992; Schramm 1992; Thomas and Ali, 1989; Ogino and Umetsu, 1978). A description of the interface matrix has been given by Angle (2001) showing that crude components are assembled around water droplets with their hydrophilic heads in the water phase and their hydrophobic tails oriented toward the oil phase as depicted in Fig. (2.4).

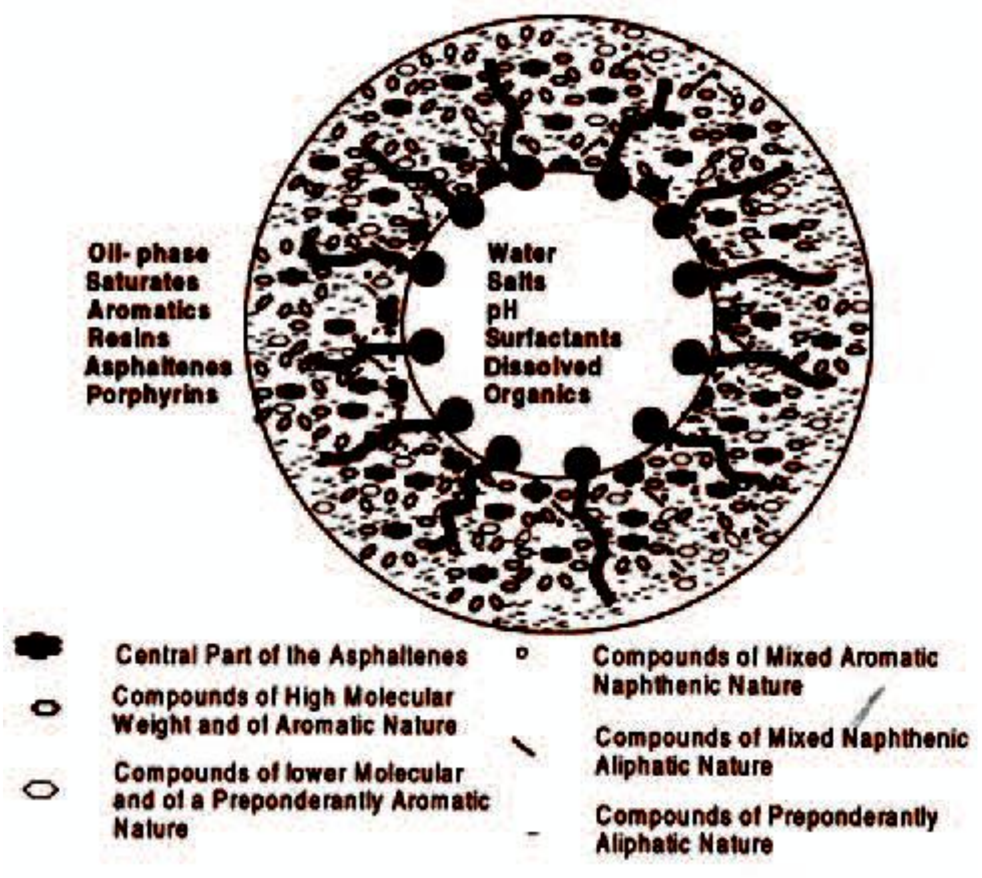


Fig. (2.4): Schematic of droplet of w/o emulsion with petroleum fractions arranged in the interfacial layer of skin around the droplet at early stage of formation. From (Angle, 2001).

Higher resins to asphaltenes concentration ratios keep more of the asphaltenes aggregate dissolved in the oil phase; thereby, minimize the amount of asphaltene aggregates (less stable emulsion). Also, a reduction in the pressure but above the bubble point results in a reduced asphaltene solubility, but further reduction in the pressure below the bubble point results in increased asphaltene solubility (Carnahan et al., 2007; Ali and Alqam, 2000). In addition, Ali and Alqam (2000) have also reported that asphaltenes contribute to the stability of w/o emulsions through the formation of a viscous interfacial film at the interface between oil and water. This film is built up through the adsorption of asphaltenes on the finely divided solids, due to the hydrophobicity of these solids, which are naturally present in a crude such as iron and calcium carbonate, etc. Therefore, a change in the wettability and other characteristics of these solids occurs allowing further adsorption and; thus, re-structuring. However, due to the complexity of chemical nature of crude oils as well as differences in each crude characteristics, it is difficult to generate an universal mechanism that describes the dispersion behaviour through the physico-chemical properties at the oil-water interface (Ali and Alqam, 2000).

Furthermore, clay particles and the organic-clay particulates in the sea are like surfactants, i.e. have hydrophilic and hydrophobic parts and; therefore, will choose the interface between oil and water to reside at (Buist and Lewis, 2002; Holmberg et al., 2002; Kokal, 2002). As a result, some interactions occur between the asphaltene particles (hydrophobic) and the hydrophobic-hydrophilic clay particles; thus, a highly hydrophobic asphaltene-based matrix is produced which further stabilizes the emulsion (Menon and Wasan, 1988). Also, according to Lee (Lee, 1999) crude indigenous surfactants such as metallic salts, organic acids and bases and organometallics and particles such as waxes and asphaltenes and water phase particles such as particulates and sediments play an important role in stabilizing an emulsion by somehow residing them selves at the oil-water interface, see Fig. (2.5) below. Moreover, at high concentrations of these particles and surfactants stable emulsions are formed in which water droplet coalescence is prevented.

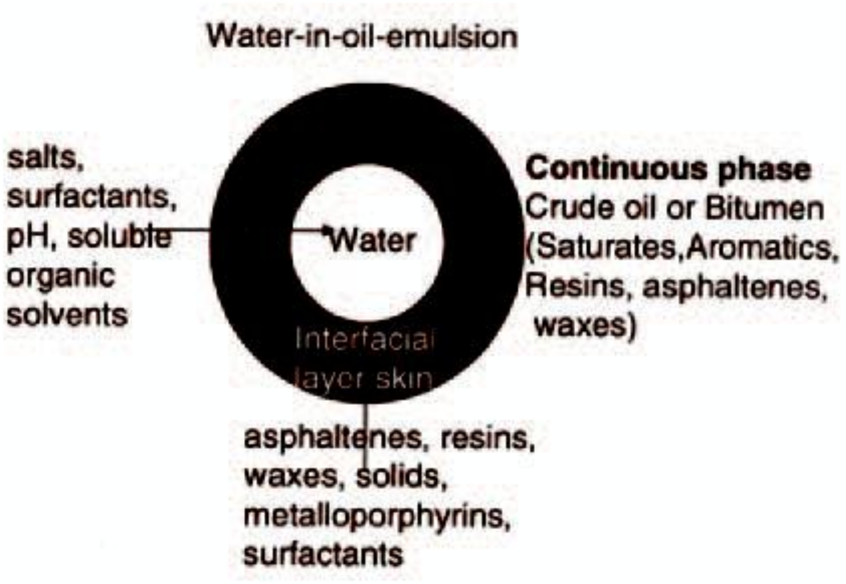


Fig. (2.5): Schematic of components of crude oils and bitumen to be considered in an emulsion droplet and the interfacial layer (Angle, 2001)

Ali and Alqam (2000) stated that there are two grades of emulsions stability, namely, stable (tight) emulsions and un-stable (loose) emulsions; physical and chemical properties of each type are distinctive (Khadim and Sarbar, 1999). The former grade refers to an emulsion that's difficult to break (when it does, it requires hours, days, weeks, months or even years) whereas in the latter one an emulsion is easily broken in a matter of few minutes (Elsharkawy et al., 2005; Kokal, 2002). This to a large extent depends on the properties and amount of both oil and water phases, agitation severity (energy input) and on the nature and concentration of emulsifying agents that indigenously exist in the crude. In subsequent studies by Fingas and Fieldhouse (Fingas and Fieldhouse, 2004; Fingas and Fieldhouse, 2003) based on the lifetime of the emulsion and its visual appearance, elasticity and differences in viscosity, the stability was categorized into four classes, namely, stable, unstable and mesostable emulsions and entrained water. The last one is a black colour emulsion with water content of less than 10 % entrained by viscous oil. Stable emulsions are reddish to brown in colour and contain 80 % water and can exist for several weeks with higher viscosity at least three times than the original oil viscosity. This viscosity increase is attributed to the asphaltenes and resins ability to align at the interface creating strong visco-elastic films. In unstable emulsions water and oil separate out in a matter of few hours with water content lower than 50 %. Their final viscosity is less than 20 times greater than the original oil viscosity. The emulsion's colour is the same as the starting oil's colour which can be black or brown. Mesostable emulsions are red, black or brown in colour. They, due to their aromatic and aliphatic/paraffinic of little asphaltene content, may produce emulsions with low stability and a tendency to destabilize, but their high viscosity renders them stable for a period of time. Upon decomposition, they produce layers of oil and stable emulsions (Sztukowski and Yarranton, 2005; Fingas and Fieldhouse, 2004).

In addition, due to the acidic nature of the active compounds at the oil-water interface, pH was also reported to have an effect on the film stability and; therefore, on the emulsion stability. Increasing the pH was found to be associated with ionization of the polar functional groups in both asphaltene and resin molecules. Due to this ionization, high surface charge densities are developed resulting in changing (destroying) the mechanical film properties through some internal repulsive interactions which ultimately may help reduce the emulsion stability (McLean and Kilpatrick, 1997a). Temperature was also found to have an influence on emulsion stability. Increasing the emulsion temperature leads to a decrease in the oil phase viscosity and to an increase in the collision rate between aqueous phase droplets which ultimately means reduced system stability (Kokal, 2002; Thompson et al., 1985).

The stability of this layer can; however, be influenced by some processes which lead to weakening it. Such processes may include dispersed phase drops flocculation and coalescence. For the flocculation to take place, surface forces such as repulsion forces and adhesion energies are important. Fairly, low repulsion forces and fairly high adhesion character lead to drops flocculation. Once drops approach each other (flocculation), the film around the dispersed droplets which is made from the continuous phase undergoes thinning and eventually ruptures, this latter process is referred to as coalescence. However, the complexity of such a process further complexes with increased amounts of asphaltenes along with solid particles in the form of thick, irregular and large aggregate films around water droplet. This in turn promotes the emulsion stability (Langevin et al., 2004). In the following sections, the focus will be devoted to discuss in detail the functionality of these compounds in stabilizing w/o emulsions based on a number of review articles among the available literature.

2.5 Problems of Crude Oil Emulsions

There are a number of reasons as to why w/o emulsions should be thoroughly studied. There are many operational and commercial indications reveal that emulsions are problematic, undesirable and require attention. Among these are the production of off-specifications crude oil, production losses, tripping of separation equipment in gas-oil separation units, corrosion of pipes, equipment and pumps through contaminants such as chloride, catalyst poisoning, organics deposition in processing equipment, increased demulsifier(s) usage, increased oil viscosity and the additional transportation pipeline infrastructure, which may also entail additional capital and operational costs, required to accommodate the volume increment resulted from water existence and to produce a crude oil that's in accordance with the specifications (Alinezhad et al., 2010; Ekott and Akpabio, 2010; Dudásová et al., 2009; Verruto et al., 2009; Less et al., 2008; Nour et al., 2007a; Moran and Czarnecki, 2007; Sullivan et al., 2007; Elektorowicz et al., 2006; El Gamal et al., 2005; Elsharkawy et al., 2005; Noïk et al., 2005; Pena et al., 2005; Pekdemir et al., 2003; Eow and Ghadiri, 2002a; Kim et al., 2002; Kokal, 2002; Sullivan and Kilpatrick, 2002; Angle, 2001; Kilpatrick and Spiecker, 2001; Yang et al., 2001; Sams and Zaouk, 2000; Khadim and Sarbar, 1999; Sams and Zaouk, 1999; Førdedal et al., 1996; Mohammed et al., 1993; Urdahl et al., 1993; Sjöblom et al., 1992a; Bhattacharyya, 1992; Schramm 1992; Aveyard et al., 1990; Isaacs et al., 1990; Thompson et al., 1985). Therefore, breaking these emulsions is of great importance and practicality for crude oil producers.

2.6 Multiple Emulsions

In addition to the binary w/o and o/w emulsions, multiple, double, complex or emulsified emulsions are also encountered. There are two kinds of these emulsions; one kind is water-in-oil-in-water emulsion (w/o/w) (Kilpatrick and Spiecker, 2001) and the other is oil-in-water-in-oil emulsion (o/w/o) as shown in Fig. (2.6) (Lindenstruth and Muller, 2004; Holmberg et al., 2002; Kokal, 2002; Bibette et al., 1999; Davis, 1994) with a bigger droplet size compared to the simple parent emulsion droplets. A droplet in a multiple emulsion can be only one big internal droplets, some small internal droplets or great number of internal droplets (Pal, 2008). Type of internal, intermediate and continuous phases is crucial in determining the resultant emulsion. Volume fraction, water to oil ratio or oil to water ratio and water or oil droplet size are important parameters in the preparation of (w/o/w) or (o/w/o); emulsions; respectively (Balinov and Soderman, 2001).

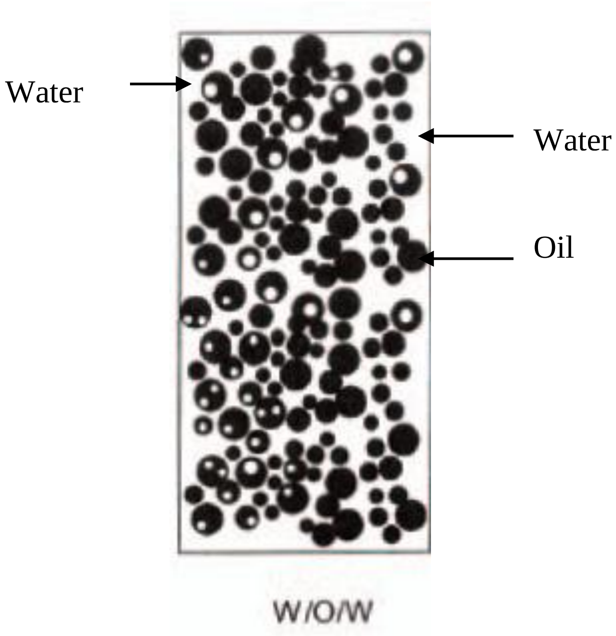


Fig. (2.6): Schematic drawing of w/o/w emulsion. Taken from (Kilpatrick and Spiecker, 2001)

These emulsions can be formed spontaneously or artificially. Spontaneous formation is achieved through the inversion of a simple emulsion i.e. w/o to o/w or vice versa during which an intermediate phase is formed which represents the multiple emulsion phase (Dalmazzone and Clausse, 2001). Artificial formation of these emulsions, so as to trap some substances and control their release in food, drug, cosmetic and food industries, is facilitated by dispersing an existing simple emulsion into its dispersed phase (Balinov and Soderman, 2001; Dalmazzone and Clausse, 2001; Bibette et al., 1999). In case of (w/o/w) emulsions, oil globules which contain water droplets are dispersed in water phase (Dalmazzone and Clausse, 2001; Muguet et al., 2001). Whereas in (o/w/o) emulsions, the emulsion is created through the dispersion of water globules, where the oil droplets are contained, in oil (Dalmazzone and Clausse, 2001). Two surfactants of different solubility character with respect to

HLB number are commonly employed to prepare these multiple emulsions (Binks, 2002; Pays et al., 2002; Bibette et al., 1999). In terms of the stability, double emulsions are unstable and eventually turn to simple ordinary emulsions; however, with lower w/o ratios, the stability is promoted where the multiple droplet breakdown is delayed (Bibette et al., 1999; Csoka and Eros, 1997). It is again outside the scope of this survey to discuss these multiple emulsions in detail; therefore, these are only briefly highlighted.

2.7 Crude Oil and its Characterization

A crude oil is a mixture of organic and inorganic compounds. Carbon and hydrogen constitute the organic portion; inorganic compounds (heteroatoms) include nitrogen, oxygen and sulphur. In terms of composition, carbon and hydrogen are the major constituents of a crude due to their large presence ranging between (83-87 %) and (10-14 %), respectively (Sjöblom et al., 2003; Angle, 2001). Inorganic compounds; however, represent a trivial amount of the elemental composition with sulphur is the most predominant compound among them. Metals in the form of porphyrins are also found which contribute towards increased polarity of the crude. Among these metals are vanadium, nickel and iron (Sjöblom et al., 2003; Angle, 2001). Although carbon content of most crudes may be relatively invariable; hydrogen and heteroatoms contents are; however, different from a crude to another. This difference is considered to be a significant route for crudes differences from a well to another. Indeed, even crudes from two different adjacent wells can be different in composition (Ekott and Akpabio, 2010; Angle, 2001). This largely depends on the nature of the biomass sediment, temperature and pressure in the underground environment, the migration process and the method of crude extraction. To this end, it is expected; therefore, physical, chemical and surface properties of the resultant emulsion are to be different with respect to the crude source (Angle, 2001).

As a sequence of crude composition complexity, characterization by individual molecular types is unachievable (Sjöblom et al., 2003). Therefore, crudes are traditionally characterized by fractionation into four fractions through boiling-point, solubility and polarity differences among these fractions. These fractions include saturates (alkanes/paraffins/aliphatics), aromatics (rings), resins and asphaltenes (SARA) (Sjöblom et al., 2003; Wang and Buckley, 2003; Angle, 2001;

Vazquez and Mansoori, 2000; Bobra, 1991). Fig. (2.7) below gives a schematic representation of petroleum demonstrating its native components interaction (Angle, 2001). According to SARA analysis, the first fraction (saturates or aliphatics) embodies the non-polar part of a crude with a trend of increased aromaticity, polarity and molecular weight with the transition from a fraction to another towards the asphaltenes fraction (Sjöblom et al., 2003; Aske et al., 2002; Bobra, 1991). A typical schematic of SARA analysis is illustrated in Fig. (2.8). Reviewing such components along with their physical and chemical properties is a huge topic and may further widen the scope of this study. Therefore, only resins and asphaltenes will be addressed in the subsequent parts throughout this Chapter due to their significant contribution towards emulsion stability perhaps due to their polar character. Wax, some acids, clays are also briefly highlighted revealing their interaction with asphaltenes and resins which has the consequence of emulsion stability promotion.

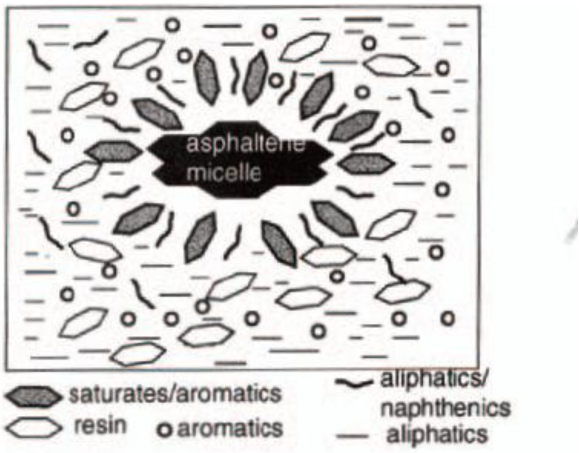


Fig. (2.7): Schematic of petroleums. Taken from (Angle, 2001).

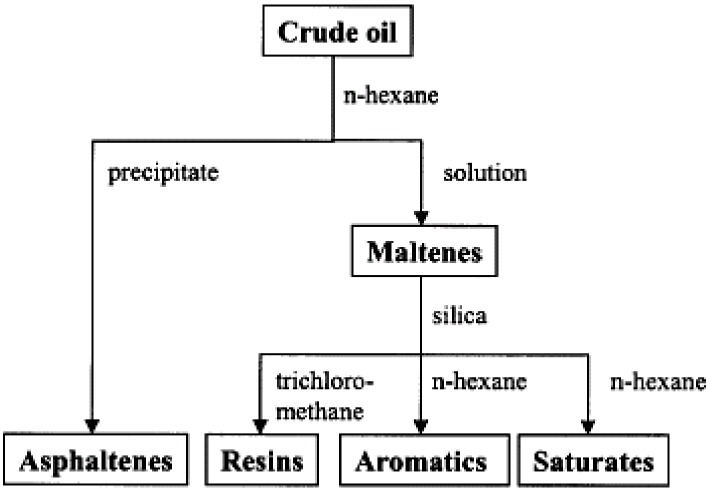


Fig. (2.8): SARA-separation scheme (Sjöblom et al., 2003)

2.8 Stability of Water-in-Oil Emulsions

2.8.1 Introduction

Crude oil emulsions are inevitably formed during oil recovery (wellhead emulsion/oil sands production), processing (refinery slop emulsion) and transportation (Sztukowski and Yarranton, 2005). Unfortunately, the viscosity of an emulsion is higher than that of the oil phase or the aqueous phase leaving behind a fluid that's difficult to transport and/or process (Pena et al., 2005; Schramm 1992; Eley et al., 1988b). Also, although these emulsions are thermodynamically unstable they exhibit a good resistance to coalescence. Crude emulsions stability studies have routinely been with the interest to study the characteristic properties, interactions and solubility of asphaltenes and resins due to their ability to create mechanically very stable interfacial films at the interface between oil and water (Fingas and Fieldhouse, 2009; Nour et al., 2007a; Yang et al., 2007; Yarranton et al., 2007a/b; Fingas and Fieldhouse, 2004; Aske et al., 2002; Sullivan and Kilpatrick, 2002; Angle, 2001; Eow et al., 2001; Li et al., 2001; Liggieri et al., 2001; Goldszal and Bourrel, 2000; Sams and Zaouk, 2000; Andersen and Speight, 1999a; Sams and Zaouk, 1999; Schorling et al., 1999; Ese et al., 1998; Friberg et al., 1998; Førdedal et al., 1996; Márquez et al., 1996; Fingas, 1995; Kim et al., 1995; Bhattacharyya, 1992; Nordli Børve et al., 1992; Schramm 1992; Aveyard et al., 1990).

Kokal classified these films with respect to their mobility into two categories; rigid/solid and mobile/liquid films. Rigid films are characterized with high interfacial viscosities whereas mobile ones are characterized with low interfacial viscosities. Occurrence of rigid films is due to the presence of crude oil emulsifiers; however, mobile films are formed when a demulsifier has been added to an emulsion (Kokal, 2002). On the other hand, there has also been another approach suggesting that wax, clay and some acids also play a role with asphaltenes and resins in stabilizing emulsions (Coutinho et al., 2010; de Morais Coutinho et al., 2009; Fingas and Fieldhouse, 2009; Less et al., 2008; Fortuny et al., 2007; Moran and Czarnecki, 2007b; Elektorowicz et al., 2006; El Gamal et al., 2005; Elsharkawy et al., 2005; Noïk et al., 2005; Pena et al., 2005; Alboudwarej et al., 2003; Havre and Sjöblom, 2003; Sjöblom et al., 2003; Ekholm et al., 2002; Kokal, 2002; Eow et al., 2001; Kilpatrick and Spiecker, 2001; Li et al., 2001; Sjöblom et al., 2001; Yang et al., 2001; Khadim and Sarbar, 1999; Lee, 1999; Pal, 1994; Schramm 1992; Bobra, 1991; Aveyard et al., 1990; Isaacs et al., 1990; Johansen et al., 1989). They, in association with asphaltenes and/or resins, hinder droplets growth and; therefore, coalescence by their ability to adsorb at the oil-water interface through the formation of rigid films around water droplets (Alinezhad et al., 2010; Verruto et al., 2009; Nordgard et al., 2008; Fortuny et al., 2007; Elektorowicz et al., 2006; Langevin et al., 2004; Kilpatrick and Spiecker, 2001; Førdedal et al., 1996; Fingas, 1995; Bobra, 1991; Johansen et al., 1989). El Gamal and co-workers (El Gamal et al., 2005) pointed out that the stability of the resultant emulsions is directly related to the concentration of these crude oil compounds. With this in mind, several investigators have stated that asphaltene alone irrespective of the presence of other emulsifiers can stabilize emulsions (Verruto et al., 2009; Dudásová et al., 2008; Yarranton et al., 2007a/b; Elsharkawy et al., 2005; Fingas and Fieldhouse, 2004; Havre and Sjöblom, 2003; Sjöblom et al., 2003; Buist and Lewis, 2002; Vander Kloet et al., 2002; Sjöblom et al., 2001; Yang et al., 2001; Lee, 1999; Eley et al., 1988a). This observation has also been emphasized by Langevin and his colleagues (Langevin et al., 2004) in which they found that asphaltenes presence is essential for these other emulsifiers to be able to stabilize emulsions.

In fact, although the significance of the everlasting stability of this elastic, physically strong, viscous and rigid film surrounding water droplets ,acting like an artificial skin, is well established; nevertheless, there has been a lack of a rudimentary methodology that precisely interprets the stability of w/o emulsions. By far, this ambiguousness is attributed to a poor understanding of complex crude oil composition, lack of knowledge of molecular weights of asphlatenes and their distribution along with their flocculation mechanisms, properties of the film layer as well as the chemistry of the surfactants in the crude (Sun et al., 2010; Nordgard et al., 2008; Sullivan et al., 2007; Yarranton et al., 2007a/b; Langevin et al., 2004; Andersen and Speight, 1999a; McLean and Kilpatrick, 1997a). In fact, while some studies have cited some crude oil indigenous non-hydrocarbon components, namely, asphaltenes and resins, due to their active surface properties i.e. they have a tendency towards the oil-water interface, as the culprit components for w/o emulsions formation (Ekott and Akpabio, 2010; Xia et al., 2004; Khadim and Sarbar, 1999; Schorling et al., 1999; Ese et al., 1998; Førdedal et al., 1996; Rønningsen et al., 1995). Other studies; however, have concluded that waxes, acids and non-indigenous inorganic fine solids are also of great importance in the formation of w/o emulsions (Xia et al., 2004; Lee, 1999; Márquez et al., 1996; Nordli Børve et al., 1992). However, in recent studies by (Sjöblom et al., 2003; Auflem et al., 2001; Dalmazzone and Clausse, 2001) it was emphasized that none of these single components is individually capable of stabilizing w/o emulsions. Instead, it was suggested that the interaction between these components within the crude is the driving force for emulsion stabilization. It is; therefore, evident that the presence of these ‘native’ and ‘foreigner’ crude oil emulsions emulsifiers is with immense problematic impact on the oil industry through refinery problems through emulsion stabilization. Emulsion stability level is proportional with crude content of these emulsifiers and their interactions; higher content of these compounds; of-course, grants the emulsion a higher stability extent. Indeed, understanding the properties and behaviour of these indigenous emulsifiers is crucial in understanding the mechanism by which an emulsion is formed. The preceding discussion gives a summary of the contribution of these natural crude oil stabilizers towards w/o emulsions stability.

2.8.2 Indigenous and Non-indigenous Stabilizers of Water-in-Oil Emulsions

2.8.2.1 Asphaltenes and Resins as Water-in-Oil Emulsions Stabilizers

2.8.2.1.1 Chemistry of Asphaltenes and Resins:

Perusal of the relevant literature in petroleum industry reveals the responsibility of both asphaltenes and resins, which are irrespective of the crude type and/or location always present in crude oils with different amounts, in creating crude oil emulsions. This responsibility may have arisen from the fact that, these indigenous crude oil components, due to their surface activities, have been considered the main cause(s) of these emulsions. They have an affinity towards the interface between oil and water at which a firm film is; therefore, created hindering water droplets coalescence leaving behind emulsions with different levels of stability. To this end, it is necessary to understand the characteristics of emulsion systems including the nature, role and behaviour of the interfacial layer so as to understand the grounds behind emulsion stability. In order to understand this, a thorough understanding of the complex behaviour and physical and chemical properties of asphaltenes and resins is required. In fact, their structural properties, surface-activity and state of aggregation *do* influence the rigidity and; therefore, the stability of this layer. In addition to asphaltenes and resins there are also other crude components including waxes, acids and solids which can interact with asphaltenes and resins, have been reported to have a significant contribution in emulsion formation and stabilization. In the following sections; therefore, the first two indigenous crude oil components, i.e., asphaltenes and resins will be comprehensively discussed whereas the rest of previously mentioned other crude components will be briefly touched upon.

The term asphaltenes was first used by Boussingault in 1837 in France to describe the constituents of some bitumen (asphalts). Asphaltenes are extremely polar, complex and high molecular weight polynuclear molecules with the core is condensed poly-aromatic condensed rings and aliphatic chains as peripherals (Maia Filho et al., 2012; Alinezhad et al., 2010; Sun et al., 2010; Verruto et al., 2009; Dudásová et al., 2008; Nour et al., 2007b; Nour et al., 2007a; Sullivan et al., 2007; Yasar et al., 2007; Elektorowicz et al., 2006; Alboudwarej et al., 2003; Havre and Sjöblom, 2003; Sjöblom et al., 2003; Buist and Lewis, 2002; Sullivan and Kilpatrick, 2002; Angle, 2001; Yang et al., 2001; Fingas, 1995; Eley et al., 1988b). Their ring structure, in contrast; for instance, to benzene or naphthalene of which they are monocyclic or dicyclic respectively, is largely pericyclic (Badre et al., 2006). Several studies have also identified carboxylic acids, carbonyl groups and phenols as other functional groups that *do* exist among an asphaltene molecule structure (El Gamal et al., 2005; Langevin et al., 2004). The asphaltene intermolecular interactions are greatly influenced by the aromatic and aliphatic groups attached to their structure (Islas-Flores et al., 2006).

Asphaltenes are non-hydrocarbons due to their content of polar heteroatom groups in addition to carbon and hydrogen such as nitrogen, sulphur and oxygen, (NSO functionality) and trivial amounts of metals including iron which its ions (Fe^{3+}) were found crucial in the asphaltene polarity (Havre and Sjöblom, 2003; Sjöblom et al., 2003; Buist and Lewis, 2002; Yang et al., 2001; Nalwaya et al., 1999), nickel and vanadium as work conducted by Ball and co-workers (Ball et al., 1960) showed a substantial reduction in the metal content of the crude oil following deasphaltening process (Dudásová et al., 2008; Nordgard et al., 2008; Yasar et al., 2007; Nalwaya et al., 1999; Taylor, 1998; Yen et al., 1961). X-ray absorption near-edge structure (XANES) spectroscopy studies by Mitra-Kirtley and others (Mitra-Kirtley et al., 1993) revealed that nitrogen exists in the aromatic form with the main type is pyrroles, pyridines, pyridones and aromatic amines, respectively. Sulphur is the dominant heteroatom with concentrations of up to 10 wt %, in some crudes (Waldo et al., 1991).

Operationally, asphaltenes are described by a solubility classification, as the component of crude oil that is insoluble in an excess of a light low-boiling liquid hydrocarbon (n-alkanes) such as n-pentane, C_5 or n- heptane, C_7 ; however, it is soluble in aromatic solvents such as toluene, benzene or xylene at room temperature (Verruto et al., 2009; Dudásová et al., 2008; Nordgard et al., 2008; Carnahan et al., 2007; Nour et al., 2007a; Sullivan et al., 2007; Yasar et al., 2007; Badre et al., 2006; Oh et al., 2004; Havre and Sjöblom, 2003; Sjöblom et al., 2003; Wang and Buckley, 2003; Kilpatrick and Spiecker, 2001; Yang et al., 2001; Andersen and Speight, 1999a/b; Førdedal et al., 1996; Kim et al., 1996; Rogel, 1995). They possess H/C ratios roughly between 1.14-1.29 and it is to a large extent dependent on the crude source (Spiecker et al., 2003; Førdedal et al., 1996). Asphaltenes from stable emulsions have higher carbon and lower hydrogen contents than those from less stable emulsions (Khadim and Sarbar, 1999). Although asphaltenes due to their physical properties, complex chemistry and uncertainty cannot be studied by gas chromatography, gas chromatography-mass spectrometry or liquid chromatography as the case with hydrocarbons (Buist and Lewis, 2002; Yang et al., 2001; Behar et al., 1984). There have been some NMR and X-ray studies, based on analyses of nitrogen, oxygen and sulphur and the other aforementioned functional groups of carboxylic acids, carbonyls and phenols, have endeavoured to approximate the asphaltene structure. Figs. (2.9-10) illustrate some various chemical asphaltene structures; in these structures complexity of asphaltene molecule, high molecular weight and NSO compounds can be seen (Nordgard et al., 2008; Kilpatrick and Spiecker, 2001; Speight, 1999).

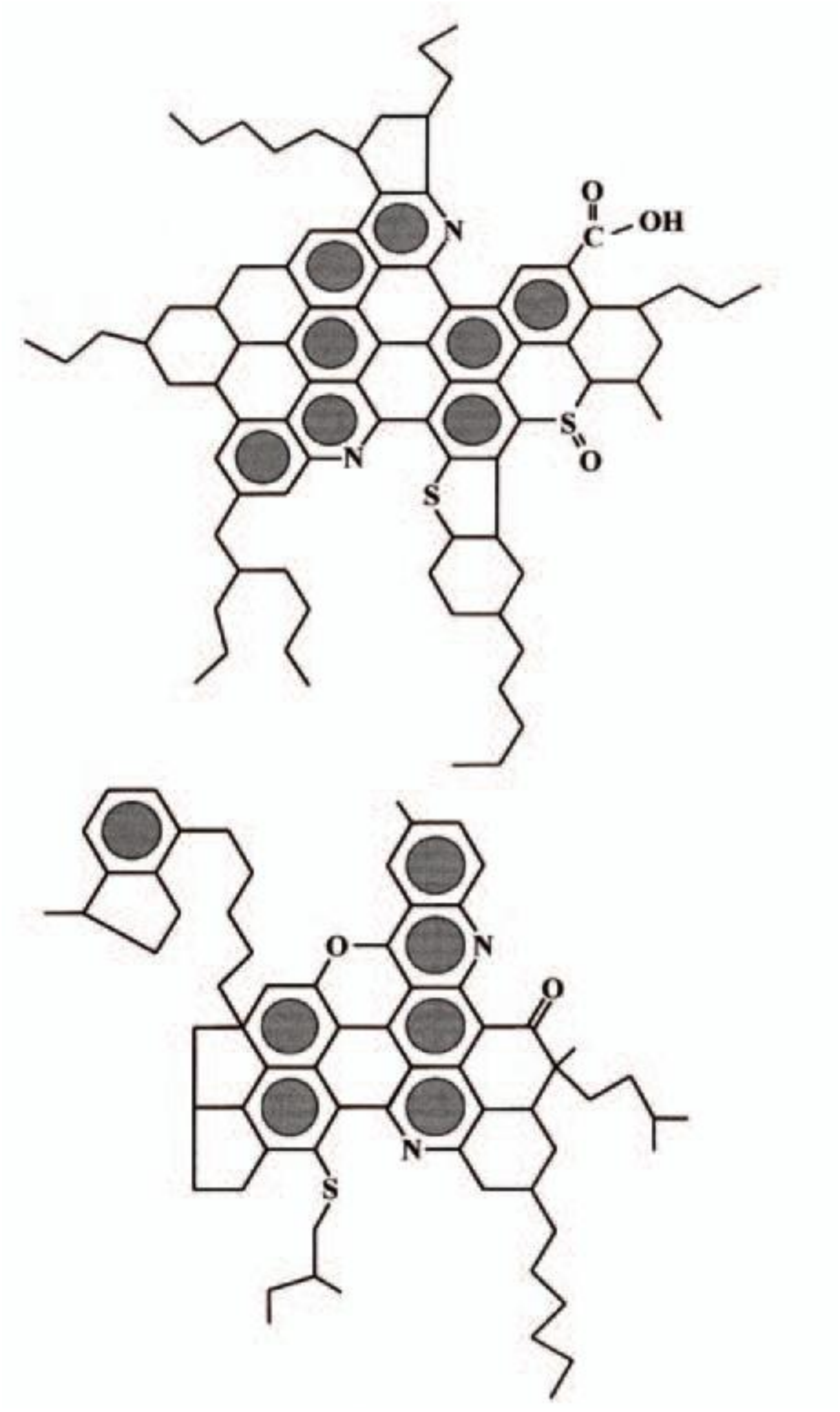
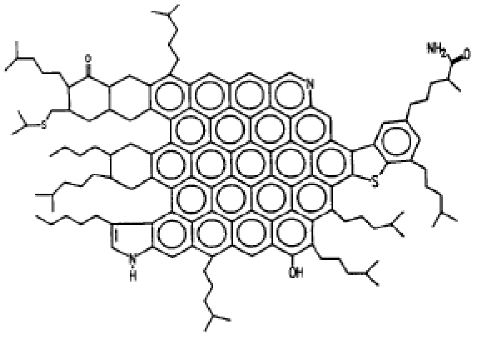
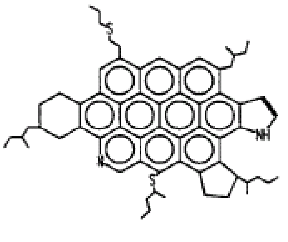


Fig. (2.9): Hypothetical structure of a petroleum asphaltene (Kilpatrick and Spiecker, 2001).

In another two separate studies by Rogel (Rogel, 1995) and Langevin and co-workers (Langevin et al., 2004) on Venezuelan crude oils, average molecules of asphaltene fractions were depicted as in Fig. (2.10) below:



ASPHALTENE A



ASPHALTENE B

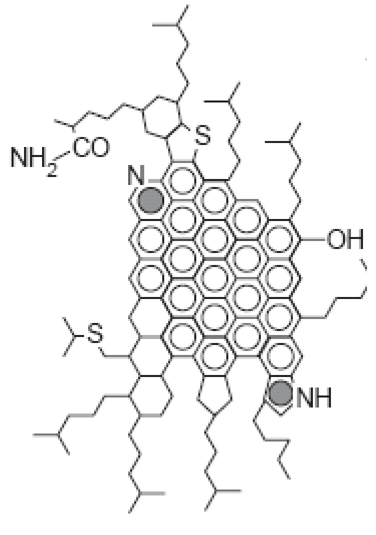


Fig. (2.10): Average molecules of asphaltene fractions (Langevin et al., 2004; Rogel, 1995).

Asphaltenes have a wide range of molecular weight between 1000 and 2000,000 g/mole. The accuracy of the measured molecular weight varies with the employed measurement method and is highly affected, in some methods, by the measurement conditions such as solvent molecular properties and measurement temperature (Rogel, 1995). Among the methods implemented to determine the asphaltenes molecular weight have been: ultracentrifuge, electron microscope, solution viscometery and cryoscopic methods, time resolved fluorescence depolarization spectroscopy and vapour pressure osmometry, etc. with the latter method being the most widely used one (Speight, 1999).

With regards to resins, they in spite of the major role they play in stabilizing w/o emulsions through asphaltene-resin interactions due to their interfacial activity, have not received considerable attention as asphaltenes (Islas-Flores et al., 2006; Schorling et al., 1999; Kim et al., 1996). High polarity and molecular weight are features differentiate resins from saturates and aromatics. Resins are described as naphthenic aromatic hydrocarbons with long alkyl chains and aliphatic substitutions and small aromatic rings (Nour et al., 2007a; Islas-Flores et al., 2006; Sullivan and Kilpatrick, 2002; Schorling et al., 1999). A hypothetical resin structure is illustrated in Fig. (2.11). Among their structure are polar heteroatom groups such as N, S and O and non-polar paraffinic groups (Boukir et al., 2001). Also, resins are characterized by higher H/C ratios than asphaltenes between 1.2-1.7, they; however, are reported to have a lower molecular weight than asphaltenes < 1000 g/mole (Aske et al., 2002; Buist and Lewis, 2002). Resins from stable emulsions have higher carbon and lower hydrogen contents than those from less stable emulsions (Khadim and Sarbar, 1999). Resins polarity, aliphaticity, aromaticity and dipole momentum are characteristics stimulate them to interact with asphaltenes through hydrogen bonding (Islas-Flores et al., 2006; Oh et al., 2004; Kilpatrick and Spiecker, 2001). This fraction (resins) of crude oil is procedurally defined with respect to the fractionation procedure used in which they are defined as the crude oil fraction soluble in light alkanes such as pentane C_5 and heptane C_7, but insoluble in liquid propane C_3 (Islas-Flores et al., 2006; Havre and Sjöblom, 2003; Kokal, 2002; Kim et al., 1996).

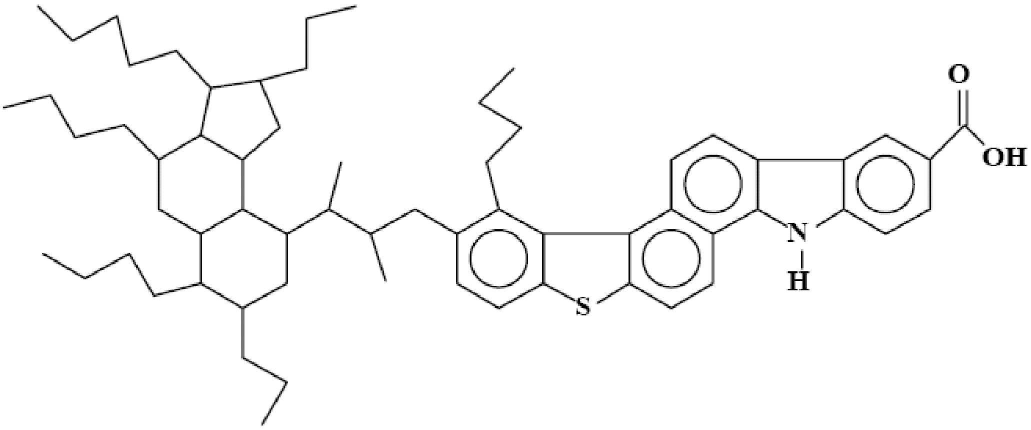


Fig. (2.11): Hypothetical structure of a petroleum resin (Spiecker, 2001).

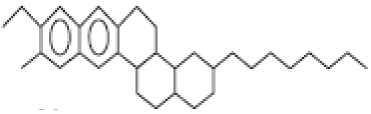


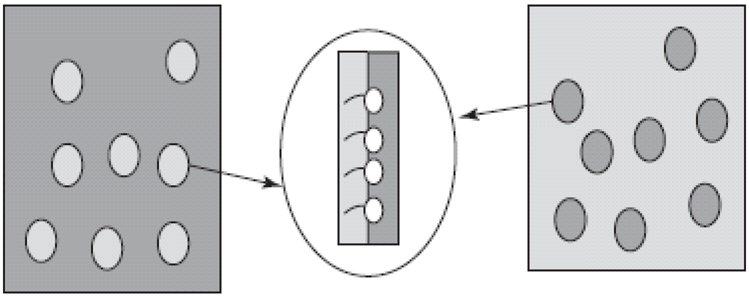
Fig. (2.12): Resin molecular structure (Langevin et al., 2004).

2.8.2.1.2 Asphaltenes and Resins as Water-in-Oil Emulsions Stabilizers

The crude oil in a virgin reservoir is naturally accompanied with water ‘formation water’ and gas. In addition to that, water is also injected into depleted reservoirs in order to help force the crude oil out of the reservoir. As a result, water is coproduced with oil in the emulsion form due to turbulence and pressure drop in the valves at the wellhead (Thompson et al., 1985) as well as a result of some interactions that take place between the crude oil hydrophilic materials and water (McLean and Kilpatrick, 1997a). Crude emulsions stability studies have routinely been with the interest to study the characteristic properties, interactions and solubility of asphaltenes and resins due to their ability to create mechanically very stable interfacial films at the interface between oil and water (Nour et al., 2007a/b; Yang et al., 2007; Sjöblom et al., 2003; Kokal, 2002; Angle, 2001; Auflem et al., 2001; Eow et al., 2001; Schorling et al., 1999; Ese et al., 1998; Mohammed et al., 1993).

However, although the importance of these compounds (asphaltenes and resins) in the oil industry is well established, it seems that identifying the asphaltene’s nature is still a matter of controversy. Among the identified literature there have been two viewpoints regarding the asphaltenes existence in a crude oil (Carnahan et al., 2007; Leontaritis and Ali Mansoori, 1988); one perspective states that asphaltenes are solid particles dispersed microcolloidally through the crude oil by means of resins molecules (Carnahan et al., 2007; Badre et al., 2006; El Gamal et al., 2005; Oh et al., 2004; Xia et al., 2004; Sjöblom et al., 2003; Aske, 2002; Sjöblom et al., 2001; Ali and Alqam, 2000; Lee, 1999; Schorling et al., 1999; Speight, 1999; Ese et al., 1998; McLean and Kilpatrick, 1997a; Kim et al., 1996; Acevedo et al., 1995; Sheu et al., 1995; Tadros, 1994; Bobra et al., 1992; Leontaritis and Ali Mansoori, 1988). However, there is also another scenario in which asphaltenes were diagnosed as molecules in liquid phase (Carnahan et al., 2007; McLean and Kilpatrick, 1997a; Leontaritis and Ali Mansoori, 1988). The latter hypothesis; however, seems not to be generally agreed on in the research community (Leontaritis and Ali Mansoori, 1988). In the following paragraphs, the structure, properties, solubility of asphaltenes and resins and their tendency to accumulate at the interface between oil and water are elucidated.

Alboudwarej et al. (2003) investigated the behaviour of asphaltene self-association in model emulsions-water systems. They found that asphaltenes adsorb as a monolayer micelles of different shapes such as cylinders, disks or spheres (Mousavi-Dehghani et al., 2004; Oh et al., 2004; Sjöblom et al., 2003; Yang et al., 2001), at the oil-water interface, owing to their amphiphilic nature and surface activity, contributing to the stabilization of the emulsion (Sullivan et al., 2007; Kokal, 2002). The hydrophilic (polar) part of an asphaltene molecule sits at the water side whereas the other part (hydrophobic) assembles at the oil side (Langevin et al., 2004). Sjoblom and co-workers (Sjöblom et al., 2003) performed some interfacial tension measurements between distilled water and a crude oil. Such measurements provide an imperative information regarding the properties of an emulsion including shear properties, mechanisms and kinetics of film formation, surfactant adsorption, film rupture and emulsion bulk viscosity (Ekott and Akpabio, 2010). They found that resins have the greatest tendency to reside at the interface. Resins were able to reduce the crude's interfacial tension by 50 % whereas asphaltenes reduced it by less than 20 %. The interface is then stretched due to the presence of asphaltenes and resins molecules, this is schematically shown by Langevin et al. (2004) as shown in Fig. (2.13) below. As a result, an interfacial gradient is generated; this in turn opposes the stretching and acts to restore the interface original state. Due to stretching and its opposition force the interface becomes elastic-like (Gibbs-Marangoni effect). Also, studies of adsorption kinetics of asphaltenes at toluene/acid solution interface, by Sheu and others (Sheu et al., 1995), have pointed out that the interfacial tension is diminished upon asphaltene adsorption at the interface between asphaltene and toluene/acid. The asphaltene critical micelle concentration (CMC) was not with an influence on the experiments since the results were in the same trend at both below and above the CMC.



a- b-

Fig. (2.13): Schematic representation of emulsion interface structures. a- o/w emulsion; b- w/o emulsion (Langevin et al., 2004).

Acevedo and co-workers (Acevedo et al., 1995) proposed that the formation of multilayers of asphaltenes at the oil-water interface is attributed to the asphaltenes chemical potential and total free energy. Emulsions stabilized by surfactant layers such as asphaltenes and resins are similar in their behaviour to hard sphere dispersions (Tadros, 1994). In a study investigating film forming properties of asphaltenes and resins, by Ese and others (Ese et al., 1998), it was found that asphaltene film is rigid and packs closer at the water surface. Also, it was stated that, based on molecular weight studies, asphaltenes form molecular aggregates as shown in Fig. (2.14) below. In these aggregates, asphaltene molecules are arranged in a sandwich-like network. It is not surprising that this network may be further solidified in the presence of other emulsion solid stabilizers such as wax and clay particles (Auflem et al., 2001). The size of these aggregates increases as the solvent aliphaticity and bulk concentration of asphaltene increase. Resins; however, were reported to be compressible, more polar than asphaltenes with a higher degree of sensitivity to oxidation and with a faster speed to reach and cover the interface layer but with a lower ability to contribute to the emulsion stability (Ekott and Akpabio, 2010; Fingas and Fieldhouse, 2004; Aske et al., 2002; Auflem et al., 2001; Eow et al., 2001; Li et al., 2001; Sjöblom et al., 2001; Førdedal et al., 1996).

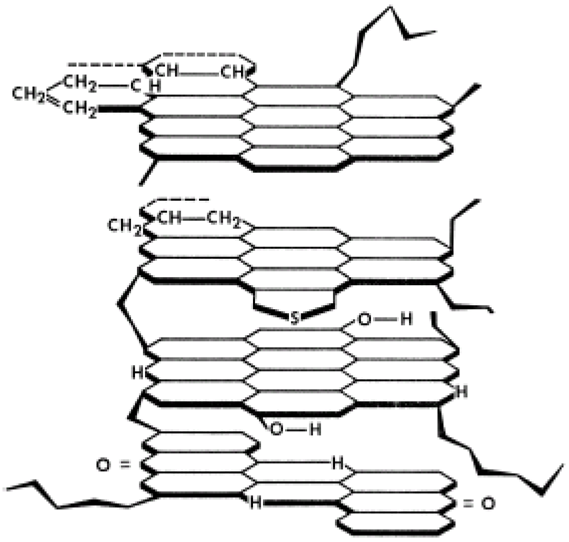


Fig.(2.14): Asphaltene micelle (Speight, 1999)

Sjoblom et al. (2001) strongly emphasized the interaction between asphaltenes and resins which is to a large extent thought to be a significant contributor towards asphaltenes aggregation and; therefore, towards the stability of w/o emulsions. Traditionally, this asphaltene-resin interaction is explained through the development of a steric repulsive layer structured with a core of asphaltene particles surrounded by an assembly of resins polar heads (Yarranton et al., 2007a; Carnahan et al., 2007; Sullivan et al., 2007; Yang et al., 2007; Wang and Buckley, 2003; Buist and Lewis, 2002; Kokal, 2002; Sjöblom et al., 2001; Andersen and Speight, 1999a; Kaminski et al., 1999; Nalwaya et al., 1999; Førdedal et al., 1996; Márquez et al., 1996; Mohammed et al., 1993). It is well known that, since 1940, resins are adsorbed on the surfaces or within the structure of asphaltenes particles forming micelles as shown in Fig.(2.15) (Andersen and Speight, 1999a; Speight, 1999). They, due to their surface-active properties, gather at the oil-water interface and construct an elastic film around water droplets ‘acting as a bag encapsulating water droplets’; thus, water droplets unity is obstructed meanwhile emulsion stability is established (Li et al., 2001; Mason, 1999; Mohammed et al., 1993). In a stability study by Xia et al. (2004) on Daqing crude oils in China, different emulsions with different asphaltene and resin contents were prepared. Results suggest that asphaltenes and resins stabilize w/o emulsions through the formation of mechanical films through adsorption. It was also reported that the state of dispersion of asphaltene and resin is important for the rigidity of the formed films which in turn further complexes the stability of the emulsion.

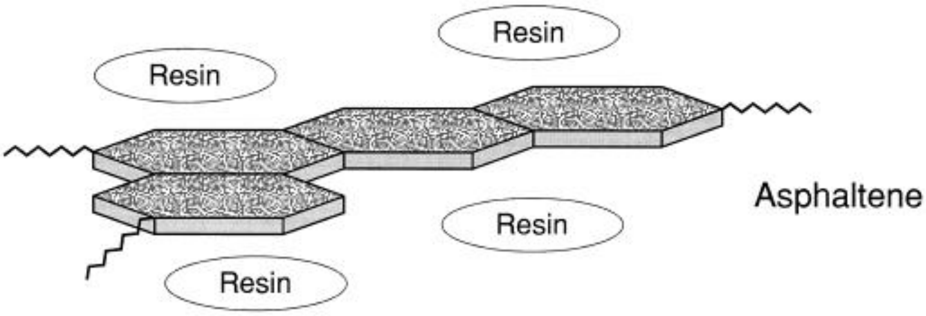


Fig.(2.15): Asphaltene-resin micelle (Speight, 1999)

Studies by (Andersen and Speight, 1999a; Speight, 1999; McLean and Kilpatrick, 1997a/b) directly linked the stability of an emulsion to its asphaltenes solubility state which is mainly governed by the resins/ambient crude medium-asphaltenes interaction. Experimental evidence suggests that there is a relationship between reins to asphaltenes ratios and the resultant crude emulsion (Carnahan et al., 2007). Crudes with higher resins to asphaltenes ratios tend to produce loose (unstable) emulsions (Speight, 1999). This is believed due to the fact that higher resins concentrations lead to an increase in the asphaltene solubility in the oil phase and; therefore, to a decrease in the interaction between asphaltenes and water droplets. In fact, this mechanism further highlights the importance of asphaltenes in stabilizing emulsions (Ali and Alqam, 2000). Asphaltenes and resins interact with each other through the adsorption of resins on the surfaces of asphaltenes as shown in Fig. (2.16). This layer of resins is less surface-active since the resin molecule is exposed to some internal forces due to electron cloud quenching and; thus, tends to weaken the surface-active character of the asphaltenes through the interaction with each other and with the surrounding crude medium. Following this interaction a resin-solvated asphaltene aggregate is formed (Yang et al., 2001; McLean and Kilpatrick, 1997a) as depicted schematically in Fig. (2.16) below.

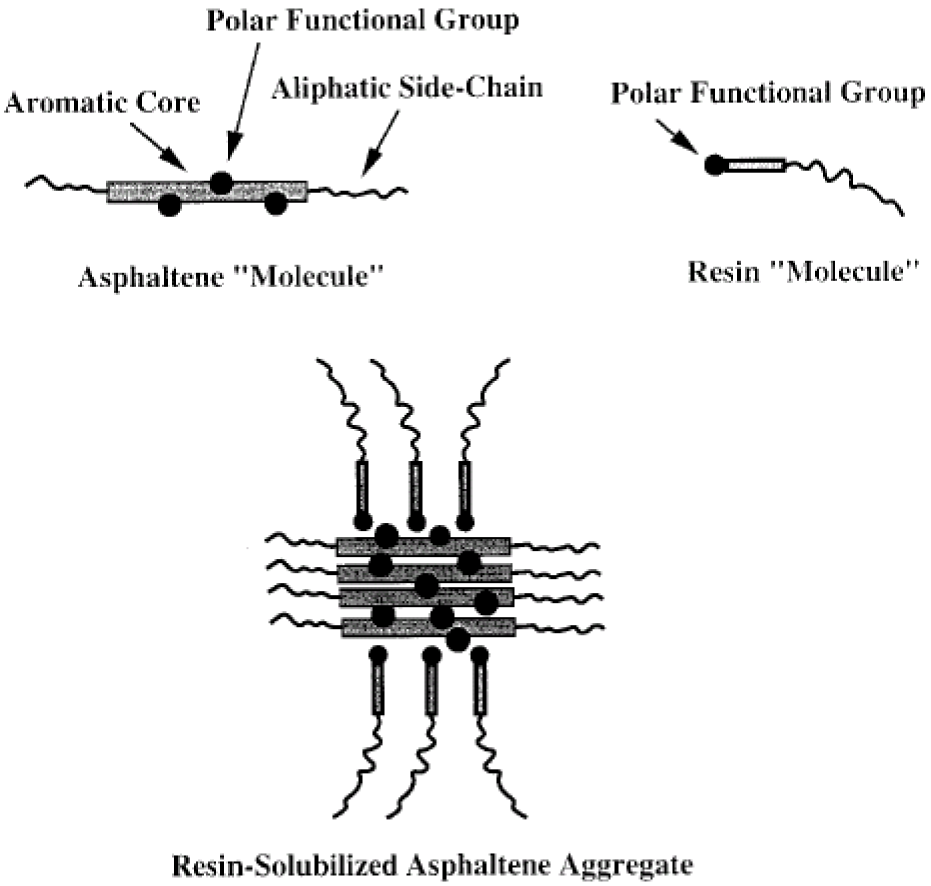


Fig. (2.16): Schematic of the proposed mechanism of asphaltenes-resins interaction (McLean and Kilpatrick, 1997a).

However, partial resin-solvated asphaltene is also possible in case the resin-asphaltene aggregate is able to reduce its free energy by shedding the adsorbed resins from one side of its surface, this is shown in Fig. (2.17). This in turn will re-facilitate the aggregate with surface activity (i.e. resides at the interface again). This asphaltene solubility scenario; however, does not take place in the distillate part of the crude oil or residual oil in the absence of resins.

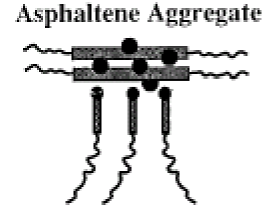


Fig. (2.17): Partial resin-solvated asphaltene (McLean and Kilpatrick, 1997b).

This shift from non-soluble asphaltenes to soluble asphaltenes was found to lessen the capability of asphaltenes to stabilize emulsions in comparison with colloidally non-soluble dispersed asphaltenes. On this basis, the lower the asphaltenes to resins ratio is, the lower the emulsion stability will be since asphaltenes have become less surface-active. The resins contribution to achieve this task (asphaltene solvating) is reported by creating an environment that's more 'like' the nature of the condensed and polyaromatic asphaltene molecules through increased aromaticity (McLean and Kilpatrick, 1997a). The effect of alkane and aromatic composition on the strength of asphaltene solvency was examined by Bobra and co-workers (Bobra et al., 1992). They concluded that heavier alkanes and aromatics demonstrated lower asphaltenes solubility; thereby, more asphaltene precipitation which accounts for stronger emulsion stability.

There are conditions; however, when resins may desorb from the asphaltenes resulting in an increase in the asphaltenes aggregate size which ultimately may lead to a difficult and irreversible asphaltene precipitation (Aske, 2002; Kaminski et al., 1999). Asphaltenes precipitation is a subject of interest in the oil industry and a great deal of efforts is exerted to predict its onset and amount (Mansoori, 1997). It has been repeatedly reported in a number of investigations that asphaltene deposition during the crude oil production, transportation and processing is a significant issue (Carnahan et al., 2007; Elsharkawy et al., 2005; Oh et al., 2004; Rejon et al., 2004; Vazquez and Mansoori, 2000; Nalwaya et al., 1999; Bobra, 1991; Leontaritis and Ali Mansoori, 1988). Pore spaces blockage and permeability drop; hence, production drop are all possible symptoms of asphaltene deposition downhole in a reservoir (Carnahan et al., 2007; Elsharkawy et al., 2005; Rejon et al., 2004; Sjöblom et al., 2003; Angle, 2001; Nalwaya et al., 1999; Kokal et al., 1995). Asphaltene precipitation can also be a source of several stability-based problems even after oil exploitation making emulsion separation a more difficult task (Elsharkawy et al., 2005; Oh et al., 2004; Rejon et al., 2004; Buist and Lewis, 2002; Sams and Zaouk, 2000; Khadim and Sarbar, 1999; Sams and Zaouk, 1999).

Different models have been developed to explain the nature of asphaltenes deposition due to asphaltene-oil interaction during crude processing (Speight, 1999).

In these models, it was hypothesized that asphaltenes are considered as solid particles suspended colloidally in the crude oil stabilized by resin molecules adsorbed on their surface (Sjöblom et al., 2003; Speight, 1999; Leontaritis and Ali Mansoori, 1988). One model is the continuous thermodynamic model in which asphaltenes are regarded as molecules dissolved in the oil phase. It utilizes the theory of heterogeneous polymer solutions to predict the onset point and amount of organic deposits from crudes. In this model, the chemical composition of the crude has an influence on the extent of dispersion of high molecular weight asphaltenes. This model predicts that solid-asphaltene formation and then precipitation is reversible and influenced by thermodynamic conditions of pressure, temperature and crude composition (Sjöblom et al., 2003; Kaminski et al., 1999; Speight, 1999; Leontaritis and Ali Mansoori, 1988). The other model is the steric colloidal model which is also able to predict the onset of organic deposition. The third model is the fractal aggregation model which combines both the continuous thermodynamic model and the steric colloidal model. This model postulates that asphaltenes associate together by means of π-π interactions between aromatic sheets. This assumption; however, was criticized by Speight as being not completely valid on the ground that resin-asphaltene interactions may prevail over asphaltene-asphaltene (π-π) interactions (Speight, 1999).

Asphaltene precipitation is governed by a mechanism that can be described as complicated and that not generally agreed on owing to the complexity of asphaltene's nature (Khadim and Sarbar, 1999; Speight, 1999). It is undesirable phenomenon as it can be associated with formation blockage, decreased reservoir yield and tubing plugging; thus, increased cost (Kokal, 2002; Rogel, 1995; Leontaritis, 1989). This in turn, has led to a number of investigations to identify the main factors that may lead to asphaltene precipitation (Rogel et al., 1999; Leontaritis, 1989). Among these, are studies by Rejon and co-workers and Wilhelms and Larter (Rejon et al., 2004; Wilhelms and Larter, 1994b) in which they concluded that the main controlling factors on asphaltene solubility in petroleum are flow regime, electro-kinetics effects, pressure, temperature, oil composition and the chemistry of asphaltenes in response to mixing with other oils/solvents, with the first factor being the most important and the last one is the less important.

Also, Speight (Speight, 1999) highlighted the impact of temperature and/or pressure on asphaltene precipitation stating that temperature and/or pressure reduction results in asphaltenes precipitation. In addition to that, due to the natural flow through the formation or during oil transportation, asphaltene particles can be deposited under the influence of the potential field generated through the oil stream by means of flow. This field is caused by the charge the asphaltenes particles carry as a result of polarization effect through the species that constitute the asphaltenes molecules. Little amount of aromatic compounds in a crude can also be a cause of asphaltene precipitation (Sams and Zaouk, 2000; Sams and Zaouk, 1999; Fingas, 1995).

Commingling crudes of different compositions is also another factor that influences asphaltene precipitation. Characterization work of some samples of natural gas from Ring Border Montney formation collected from a number of operating units by Catalan and others (Catalan et al., 1998) revealed that asphaltene, in addition to other precipitants, deposition was the most significant precipitant. Asphaltene deposition was found to be caused by mixing together two crudes of different compositions.

The finding by Wilhelms and Larter (Wilhelms and Larter, 1994a) is in line with work conducted by Branco and co-workers (Branco et al., 2001) to model the mechanism of asphaltene precipitation via statistical mechanics of polydisperse polymer solutions combined with kinetic theory of aggregation to predict the onset and amount of asphaltene precipitation. Their model was tested against variations in oil pressure, temperature and composition in which they found that there is a good consistency between the predicted and experimental data reflecting the accuracy of the model. Fingas and Fieldhouse (2009) and McLean and Kilpatrick (1997a) stated that w/o emulsions are stabilized by asphaltenes only when the latter are near or above their initial precipitation point. At this condition, asphaltene particles are finely divided and are with greater tendency to reside at the oil-water interface through increased surface-activity than sufficiently solvated or molecularly dispersed asphaltenes (Eley et al., 1988a).

It should be noted that asphaltenes amount in a crude seems not to be necessarily related to the formation of w/o emulsions (Lee, 1999). For instance, although a crude with 1.6 % asphaltenes concentration was found to form a very tight emulsion, another crude with 1.03 %; however, did not form a stable emulsion. Another example was given by Leontaritis and Ali Mansoori (Leontaritis and Ali Mansoori, 1988) that crudes with asphaltenes concentration between 0.4 to 9.8 % were susceptible to deposition, on the contrary; however, heavier crude with 17.2 % asphaltene content demonstrated no asphaltenes deposition. Therefore, it can be concluded that asphaltenes composition but not the concentration what contributes to asphaltenes capability to form stable emulsions (Lee, 1999).

Another factor that was reported to have an influence on the asphaltene solvency is the hydrogen bonding between asphaltene-asphaltene molecules and resin molecules through their functional groups (Nordgard et al., 2008; Islas-Flores et al., 2006; Fingas and Fieldhouse, 2004; Yang et al., 2001; Khadim and Sarbar, 1999). This system works well in case an asphaltene fraction contains a high concentration of C = O groups and that the resin fraction is in excess of carboxylic acid or other proton-donating polar functional groups. According to this last recipe (higher concentrations of functional groups on both asphaltenes and resins) strong asphaltene-resin interactions are possible by which the ability of asphaltenes to shed their resins layer, to become surface-active again, is minimal (McLean and Kilpatrick, 1997a).

Contrary to the approach that asphaltenes are solid particles is work conducted by Wilhelms and Larter (1994a) in which they stated that asphaltenes are not found as colloids solubilized by the resin fraction. They instead, based on various organic geochemical techniques, suggested that steric stabilization through n-alkyl groups is the driving force to keep the asphaltenes molecules (asphaltene precursor entities, APE) in solution. These APEs form a polymer solution in a maltene solvent and are with a diverse band of alkylated compounds. They, as a result of pressure, volume, temperature and compositional changes in the crude oil may undergo aggregation with the possibility to create lyophilic micelles (Carnahan et al., 2007; Zhu et al., 2003; Auflem et al., 2001; Andersen and Speight, 1999a).

In addition, due to the acidic nature of the active compounds at the oil-water interface, pH was also reported to have an effect on the film stability and; therefore, on the emulsion stability. Increasing the pH was found to be associated with ionization of the polar functional groups in both asphaltene and resin molecules. Due to this ionization high surface charge densities are developed resulting in changing (destroying) the mechanical film properties through some internal repulsive interactions which ultimately may help reduce the emulsion stability (McLean and Kilpatrick, 1997a).

2.8.2.2 Waxes as Water-in-Oil Emulsions Stabilizers

Waxes are high molecular weight alkanes and include normal, branched, iso- and cyclo- paraffins (Ali and Alqam, 2000; Lee, 1999). According to Thompson and co-workers (Thompson et al., 1985) wax crystallites in the North sea crudes are found in a diverse size range from sub-micrometer to micrometer (50µm) particles depending on crude type and temperature. There are two types of wax found in the oils, namely, macrocrystalline wax and microcrystalline (amorphous) wax (Ali and Alqam, 2000; Elsharkawy et al., 2000; Misra et al., 1995). In the first type, crystals are needle-shaped crystals and it includes normal or straight-chain paraffin (*n*-alkanes) hydrocarbons of 20-50 carbon atoms. Whereas microcrystalline wax contains isoparafins or cycloalkanes and naphthenes hydrocarbons of 30-60 carbon atoms. Macrocrystalline wax contributes to problems in production and transportation; tank bottom sludges are mainly attributed to microcrystalline wax (Angle, 2001; Misra et al., 1995).

In the oil industry during transportation and processing, temperature drop; below the oil’s cloud point, is a common practice at which wax particles are prone to precipitate through solubility reduction (Abdurahman et al., 2012; Kokal, 2002; Angle, 2001; Menon and Wasan, 1988). Crudes with high cloud point generally tend to form less stable and tight emulsions than those formed from emulsions with lower cloud point (Kokal, 2002). These wax precipitates can shift the crude oil flow pattern from Newtonian to non-Newtonian. Hence, the crude oil viscosity, pressure drop, due to clogging of production lines and vessels and; therefore, the cost of pumping are increased meanwhile tubing efficiency is reduced (Abdurahman et al., 2012; Angle, 2001; Kilpatrick and Spiecker, 2001; Elsharkawy et al., 2000; Vazquez and Mansoori, 2000). Due to the problematic existence of wax throughout a crude oil, several measurement methods have been implemented to determine the wax appearance temperature (WAT) such as differential scanning calorimetry, polarized microscopy and low-resolution NMR (Elsharkawy et al., 2000).

According to Li and co-workers; Lee; Fingas and Sjoblom and co-workers (Li et al., 2001; Lee, 1999; Fingas, 1995; Sjöblom et al., 1992a) some compounds in the crude oil such as waxes, asphaltenes and resins play a key role in stabilizing w/o emulsions. In fact, waxes in the presence of asphaltenes or resins were found to be able to produce stable emulsions, but were not able in the absence of asphaltenes or resins (Buist and Lewis, 2002; Kokal, 2002; Angle, 2001). This is justified by the extreme hydrophobic nature of waxes; however, this nature is altered when waxes interact with asphaltenes making them able to influence the interface and; therefore, stabilize the emulsion (Angle, 2001; Bobra et al., 1992). On the contrary, asphaltenes alone have the capability of producing a stable emulsion and so the resins but the most stable emulsion can be produced if resins are combined with asphaltenes and/or waxes (Sullivan et al., 2007; El Gamal et al., 2005; Elsharkawy et al., 2005; Angle, 2001; Lee, 1999; Førdedal et al., 1996). It should be noted that in order for all these wax particles to be effective emulsifying agents they should be in the form of finely divided sub-micrometer particles (Bobra et al., 1992) and have higher solubility in the oil phase than that in the aqueous phase (Lee, 1999).

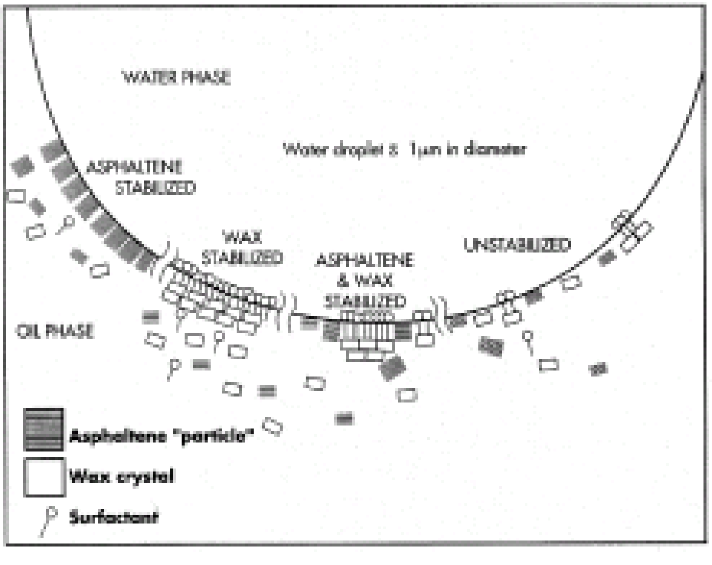
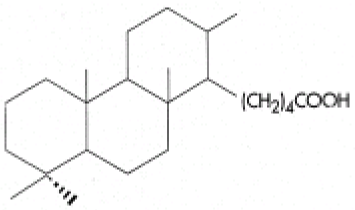


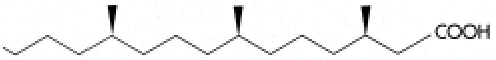
Fig. (2.18): Schematic diagram showing a water droplet in a w/o emulsion stabilized by asphaltenes particles, surfactants and waxes (Lee, 1999).

2.8.2.3 Acids as Water-in-Oil Emulsions Stabilizers

According to Lee (Lee, 1999) in addition to asphaltenes and resins there are also other compounds in the crude oil with surfactant properties and can stabilize w/o emulsions, among these are carboxylic acids and porphyrins. Carboxylic acids have the general formula RCOOH, where R represents a cycloaliphatic structure (Havre and Sjöblom, 2003). In a crude oil, they include straight and branched fatty acids and saturated cyclic naphthenic acids which are included among the resins fraction and can produce dispersions with different sizes and structures with concentration of up to 3 % in some crudes. The structure of these carboxylic acids is shown schematically in Fig. (2.19). These acids are identified to exist in a polydispersed state of size and structure (Sjöblom et al., 2003).



Naphthenic Acid



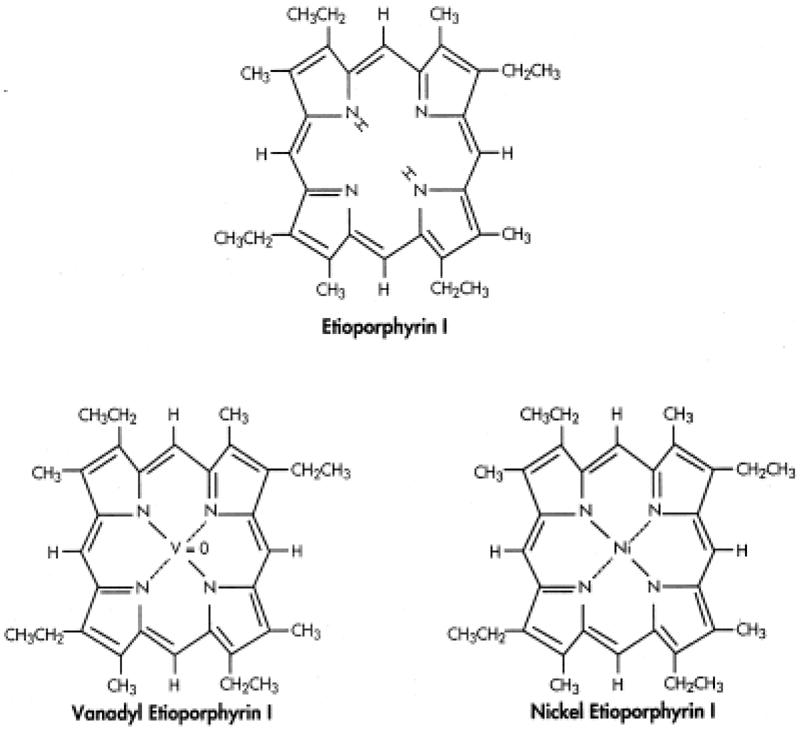
Fatty Acid

Fig. (2.19): Carboxylic acids found in crude oil (Langevin et al., 2004; Lee, 1999).

Meredith and co-workers (Meredith et al., 2000) stated that carboxylic acids are produced during in-reservoir biodegradation of petroleum hydrocarbons. The content of these acids in a heavy crude, from a fresh well, is much higher than in a paraffinic crude (Sjöblom et al., 2003). The composition of these carboxylic acids depends on the crude oil source and distillate fraction; however, they in general encompass C_{10}-C_{50} compounds of polycyclic fused saturated and unsaturated hydrocarbon rings with a carboxyl group attached to a ring with a short side chain. Another source for these acids that may help stabilize w/o emulsions is the photo-oxidation products (Fingas, 1995). Photo oxidation takes place once the crude oil, aromatic fractions in particular, is exposed to sunlight. In such oxidation reactions, polar products with surfactant properties (Fingas, 1995) such as carboxylic sulphonated acids are produced (Fingas, 1995).

Carboxylic acids are thought to play a direct or indirect role, through the interactions with other crude oil constituents, in the stability of crude oil emulsions (Havre, 2002). They, in addition to their corrosive nature, have a tendency to accumulate at the oil-water interface due to their surface activity in the form of particles reducing the interfacial tension and; therefore, stabilize w/o emulsions (Othman et al., 2008; Havre and Sjöblom, 2003; Sjöblom et al., 2003; Ekholm et al., 2002). These acids are natural surfactants with the carboxylic group being hydrophilic and carbon moiety being hydrophobic and have the ability to gather together at the oil-water interface. On this basis; with the presence of this hydrophilic acidic group, acids are more prone to be solubilized in water, producing micelles of these molecules aggregates, than in other crude oil constituents. It is also suggested that the acidic content of crude oil is associated with density increase, due to living micro-organisms due to biodegradation and paraffins content decrease (Rousseau et al., 2001). A micelle is structured with the hydrophobic part positioned at the micelle centre and the hydrophilic part pointing towards the water phase. Therefore, droplets coalescence is hindered through this micelle formation (Havre, 2002).

In addition, there are also crude oil porphyrins which are expected to stabilize w/o emulsions (Fingas, 1995). These porphyrins contain four indole nuclei and/or some metals including nickel or vanadium within their structure (Kaminski et al., 1999). Examples of these porphyrins are shown in Figs. (2.20-21). Vanadium porphyrins are more polar (more hydrophilic) than nickel porphyrins and; therefore, nickel porphyrins are more able to stabilize emulsions than non-metal porphyrins and vanadium porphyrins; respectively. These porphyrins are thought to locate at the oil-water interface and; therefore, contribute to the film formation which acts as a barrier for water droplets coalescence (Lee, 1999).


Etioporphyrin I

Vanadyl Etioporphyrin I

Nickel Etioporphyrin I

Fig. (2.20): Porphyrins from crude oil tested as emulsifying agents in the formation of w/o emulsions (Lee, 1999).

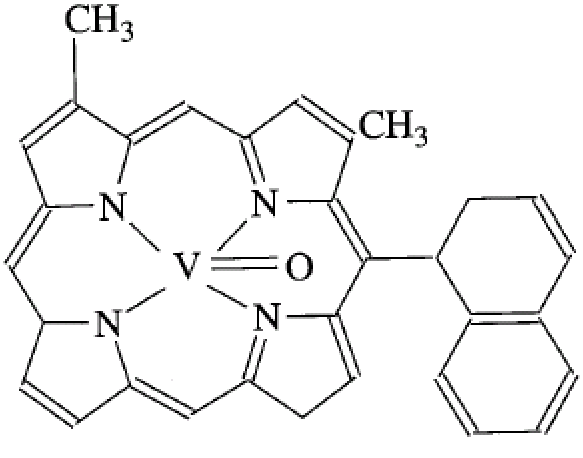


Fig. (2.21): Porphyrin structure (Kaminski et al., 1999).

2.8.2.4 Solids as Water-in-Oil Emulsions Stabilizers

Clay particles (inorganic fine solids) such as calcite and clay minerals such as Al, Ca, Na, Fe and Mg orient at the oil-water interface due to their possession of hydrophobic and hydrophilic parts, this orientation is envisaged help stabilize w/o emulsions (El Gamal et al., 2005; Sams and Zaouk, 2000; Sams and Zaouk, 1999;

Tambe et al., 1995; Tambe and Sharma, 1994; Tambe and Sharma, 1993) with the resultant emulsion called 'Pickering emulsion' (Langevin et al., 2004; Binks, 2002). Ali and Alqam (2000) have reported that asphaltenes contribute to the stability of w/o emulsions through the formation of a viscous interfacial film at the interface between oil and water as shown in Fig. (2.22). This film is built up through the irreversible adsorption of asphaltenes on the surfaces of finely divided solids, due to the hydrophobicity of these solids, which are naturally present in a crude which are as mentioned above such as iron and calcium carbonate, clay, etc. (Dudásová et al., 2009; Dudásová et al., 2008; Binks, 2002; Sams and Zaouk, 2000; Lee, 1999; Tambe and Sharma, 1994; Tambe and Sharma, 1993; Menon and Wasan, 1988). This in turn increases the ability of asphaltenes to stabilize w/o emulsions through increased hydrophobicity (Lee, 1999). Therefore, a change in the wettability of these solids occurs allowing further adsorption and; thus, re-structuring.

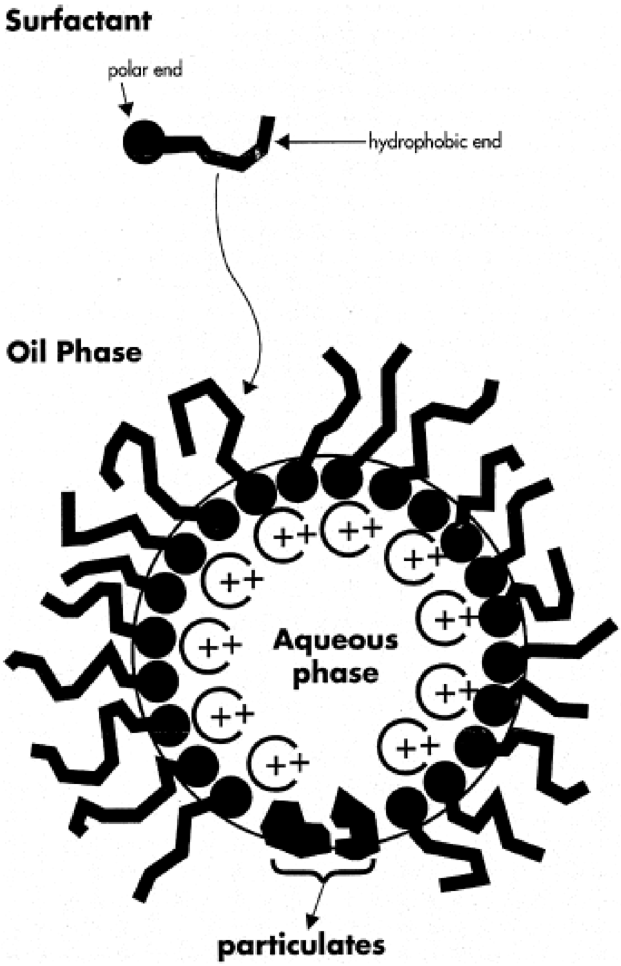


Fig. (2.22): W/o emulsions. Water droplet in oil showing stabilization by surfactants and particles (Lee, 1999).

Particles are originally oil wet (hydrophobic), probably due to the exposure to the crude, and; therefore, will remain in the oil phase. However, following adsorption of polar molecules such as asphaltenes and resins on their surfaces (Dudásová et al., 2008; Elsharkawy et al., 2005; Sullivan and Kilpatrick, 2002; Khadim and Sarbar, 1999; Kokal et al., 1995) which leads to the creation of a partially solvated particle, their wettability will shift from completely oil wet to an intermediate wettability particles (i.e. affinity to the water phase in addition to their original affinity towards the oil phase). Due to this change in their wettability, particles will also reside at the interface where both oil and water are present; thereby, stabilizing the emulsion (Dudásová et al., 2008; El Gamal et al., 2005; Tambe and Sharma, 1993). If these solids are also charged, they may further enhance the stability of the emulsion through electrostatic repulsion (Tambe and Sharma, 1993). Fig. (2.23), illustrates adsorption of asphaltenes/resins aggregates to a solid particle. Hence, with increased particles ,at the interface, it is accordingly expected that particle size is decreased which results in an increase in their surface area which in turn leads to an increase in the rate of the adsorption of surface-active materials (asphaltenes and resins, etc.) on their surfaces. In fact, trivial solid concentrations of less than 0.2 g/l were reported to be an adequate amount to generate tight stable emulsions (Ali and Alqam, 2000). These particles are reported to effectively contribute toward emulsion stabilization when a particle volume is so small compared to the emulsion's droplet volume and that the particle has a large contact angle at the three-phase interfaces (oil/water/solid) (Elektorowicz et al., 2006; Langevin et al., 2004; Kokal, 2002; Sullivan and Kilpatrick, 2002; Tambe and Sharma, 1993; Bobra, 1991; Thompson et al., 1985). These particles form a mono densely packed layer at the oil-water interface which inhibits the coalescence of emulsion droplets (Tambe and Sharma, 1995; Tambe and Sharma, 1994).

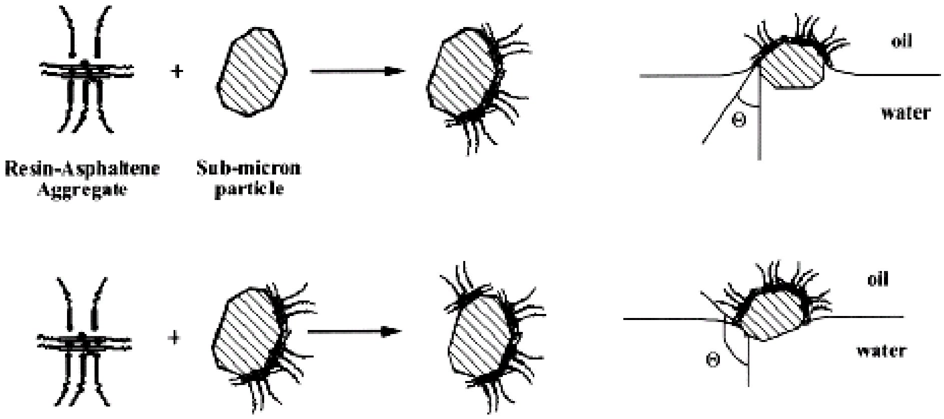


Fig. (2.23): Adsorption of asphaltenes/resins aggregates to a solid particle (Sullivan and Kilpatrick, 2002).

2.9 Emulsion Instabilities

Although crude oil emulsions might be extremely stable for long periods of time as discussed throughout Sec. 2.8, on the other hand; however, there exist emulsions which may thermodynamically, on standing, demonstrate instability behaviour, i.e. droplets are prone to combine together (emulsion physical degradation), perhaps due to their content(s) ‘seeds of its own destruction’, which may undergo a reduction in the interfacial energy (Badre et al., 2006). Several processes can occur in emulsion systems by which an emulsion is destroyed or altered, including creaming (sedimentation), flocculation, coalescence, Ostwald ripening and phase inversion (Becher, 2001; Li et al., 2001; Bibette et al., 1999; Smet et al., 1997; Tadros, 1994; Schramm 1992). These phenomena may occur concomitantly or consecutively making understanding and modelling of emulsion breakdown a rather difficult assignment (Drelich et al., 2010; Fredrick et al., 2010; Angle, 2001; Becher, 2001). These processes are shortly discussed in the following paragraphs.

2.9.1 Sedimentation (Creaming)

Sedimentation is the opposite of creaming; it refers to the formation of a droplet concentration gradient within the emulsion (Robins, 2000). This phenomenon is attributed to the density difference between emulsion constituents of oil phase and the aqueous phase (gravity effects) (Fredrick et al., 2010; Angle, 2001; Becher, 2001;

Schramm 1992). On this basis, oil droplets will aggregate to form a creaming layer sitting on top of water phase (settling). In this sense, it can be said that creaming induces droplets coalescence process as a result of droplet proximity. This reversible process, as original emulsion appearance can be brought back by a kind of homogenization (Drelich et al., 2010; Holmberg et al., 2002; Becher, 2001), is dependent on emulsion viscosity as high viscosity may hinder its rate. Elucidation of physical mechanisms involved in creaming process is given in a study by Robins (Robins, 2000). Monitoring this phenomenon has traditionally been through visual observation or ultrasound methods (Drelich et al., 2010; Langevin et al., 2004; Sjöblom et al., 2003; Holmberg et al., 2002; Robins et al., 2002; Robins, 2000; Lagaly et al., 1999; Sjöblom et al., 1992a; Schramm 1992). The creaming process is governed by Stoke's law, which states that:

$$u = 2\, r^2(\rho_2 - \rho_1)g / 9\mu$$

Where u is the terminal droplet velocity, r droplet radius, ρ_1 and ρ_2 external fluid and droplet density; respectively, g the gravitational constant and μ is the bulk viscosity. According to this law, if droplets are with lower density than that of the external phase, e.g. o/w emulsion; then the term $(\rho_2-\rho_1)$ will be negative which results in negative sedimentation (creaming) (Fredrick et al., 2010; Holmberg et al., 2002; Sullivan and Kilpatrick, 2002; Becher, 2001). Faster creaming or sedimentation will occur as a result of larger density difference $(\rho_2-\rho_1)$ and larger droplets diameters (r).

2.9.2 Flocculation

Flocculation, aggregation or coagulation is frequently used interchangeably. Due to flocculation the distance between emulsion droplets is largely reduced in a Brownian motion pattern under the influence of net attraction between the droplets. Interaction forces may include Van der Waals attraction as well as hydrodynamic effects which caused by motion of the liquid itself (Fredrick et al., 2010). However, due to this reversible process emulsion droplets undergo no change in their identity nor change in the total surface area (Drelich et al., 2010; Holmberg et al., 2002; Kokal, 2002; Becher, 2001; Sjöblom et al., 2001; Robins, 2000; Kim, 1999; Sjöblom et al., 1992a; Schramm 1992).

2.9.3 Coalescence

As the term dictates, emulsion droplets, in comparison to flocculation lose their identity, approach each other following losing the film, which as it has been demonstrated earlier within the scope of this study mainly constituted from surface-active species that naturally present within the crude, which surrounds them to form larger droplets with reduced total surface area. Ultimately, this leads to phase separation, which under normal conditions by no means can be reversible. High emulsion viscosity may slow down the rate of this process (Fredrick et al., 2010; Othman et al., 2008; Holmberg et al., 2002; Kokal, 2002; Angle, 2001; Becher, 2001; Sjöblom et al., 2001; Bibette et al., 1999; Kim, 1999; Lagaly et al., 1999; Sjöblom et al., 1992a; Schramm 1992).

2.9.4 Ostwald Ripening

Another irreversible phenomenon that may take place against emulsion stability is Ostwald ripening which seems first used by Liesegang in 1911 (Becher, 2001). According to Ostwald ripening, molecules of the dispersed phase diffuse through the continuous phase to form larger droplets while reducing their number on the expense of smaller ones. This mechanism in comparison to coalescence does not involve film rupture (Langevin et al., 2004; Holmberg et al., 2002; Bibette et al., 1999; Smet et al., 1997; Sjöblom et al., 1992a). On the one hand, Ostwald ripening in w/o emulsions may be due differences in water chemical potential due to capillary phenomena (Drelich et al., 2010). On the other hand, in o/w emulsions Ostwald ripening is attributed to the solubility of oil droplets in the aqueous phase and to differences in Laplace pressure (Fredrick et al., 2010; Holmberg et al., 2002). In either cases; however, Ostwald ripening can be negligible in case of highly immiscible liquids in which diffusion of dispersed phase droplets may not be favoured (Mason, 1999; Smet et al., 1997). Presence of salts in an emulsion slows down Ostwald ripening by decreasing the miscibility of the organic and aqueous phases. This accordingly results in an increased emulsion stability (Haibach et al., 2006; Sergienko et al., 2002). A schematic representation of these various phenomena is illustrated in Fig. (2.24).

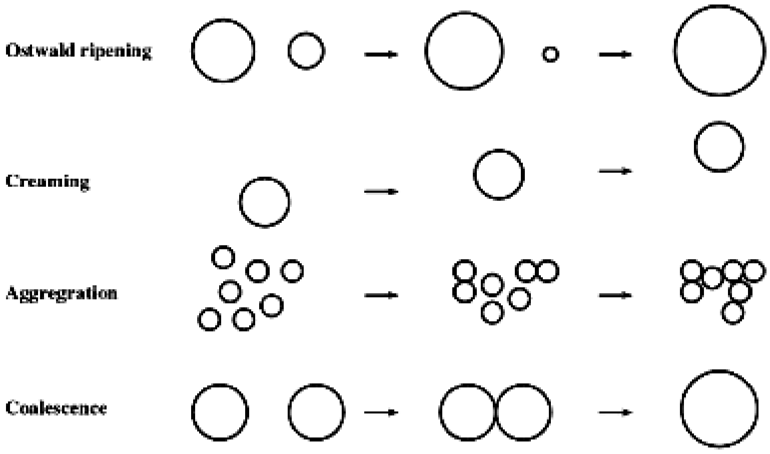


Fig. (2.24): Schematic presentation of potential instability mechanisms in w/o emulsions. Modified from (Fredrick et al., 2010).

2.9.5 Emulsion Phase Inversion

In addition to creaming (sedimentation), flocculation, coalescence and Ostwald ripening, there are also some conditions where phase inversion may take place; that’s a w/o emulsion turns to an o/w emulsion, or vice versa (Bouchama et al., 2003; Becher, 2001; Akay, 1998; Tadros, 1994; Schramm 1992; Arirachakaran et al., 1989). Such conditions may include changes in: the ambient temperature, the emulsion water-to-oil ratio, relative viscosities of emulsion phases, surfactant composition and/or its affinity for the two phases, concentration and its HLB balance, flow conditions and also the application of mechanical shear can also induce phase inversion. Phase inversion may be associated with the formation of multiple emulsions. Furthermore, once an emulsion has been inverted, its dispersed droplets are usually much smaller than those of the original emulsion with a very narrow droplet size distribution. Therefore, it is envisaged that an inverted emulsion will possess a higher level of stability compared to that of the parent emulsion. Another explanation of this stability difference could be attributed to the reduced free energy of the inverted emulsion compared to that of the original one (Akay, 1998; Schramm 1992). Fig. (2.25) illustrates a mechanism of phase inversion of o/w emulsion proposed by Schulman and Cockbain in 1940 (Becher, 2001).

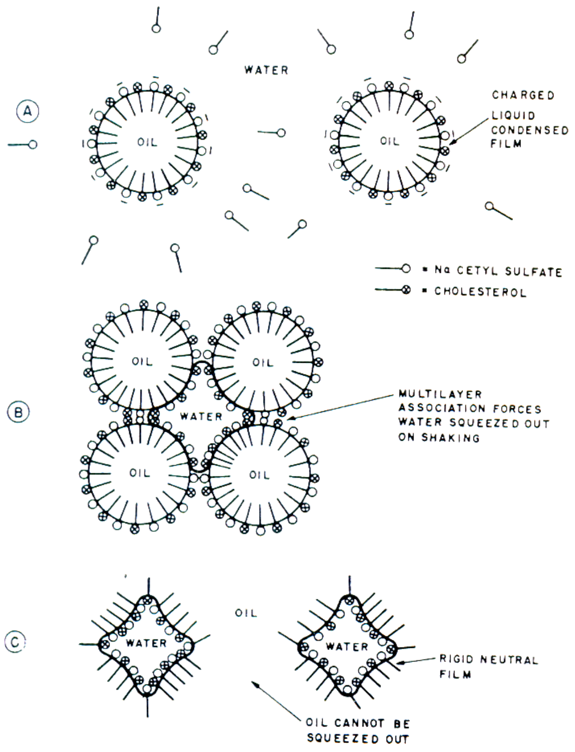


Fig. (2.25). Mechanism of phase inversion of an o/w emulsion (Becher, 2001).

2.10 Summary

In this Chapter, emulsion basics, emulsion formation routes, problems associated with their formation and factors which promote their stability have been examined. An emulsion is a collection of two or more immiscible liquids such as oil and water; one liquid is dispersed in the other. Crude oil emulsions can be in the form of binary emulsions such as w/o, o/w or multiple emulsions such as w/o/w or o/w/o. In the oil industry throughout exploitation, refinery and processing stages, although formation of both w/o and/or o/w emulsions is problematic it is unfortunately inevitable. Existence of formation water (natural water) with crude oil down in a reservoir and injection of artificial water (produced water) to enhance reservoir pressure; remove crude oil salts during crude processing to avoid catalyst poisoning and to extract bitumen in heavy oil production are means of emulsion formation. Flow through valves and pipes serves the energy input which has the effect of emulsifying water into oil, or vice versa. Based on the literature, what this investigation proves is that existence of these emulsions may give rise to a variety of problems. These broadly represent processing difficulties, increased infrastructure and increased cost.

Generally, these emulsions possess high level of stability against coalescence. Indeed, crude oil heavy polar materials meanwhile surface active (surfactants) are decisive with regards to the stability of these emulsions; without them emulsion breakdown though might be a lengthy task, it can be spontaneous. Asphaltenes, resins, waxes, acids and solids are among these surfactants. Asphaltenes and resins are believed to play a pivotal role in emulsion stabilization; other crude compounds on their own do not. In fact, different studies have concluded that stable emulsions are created mainly due to the presence of surfactants such as asphaltenes and resins; however, other emulsifying agents within the crude rely on the interaction with the asphaltenes and resins to be able to stabilize an emulsion. A summary of the rule played by these compounds is given below.

- Asphaltenes may be found in solid particles dispersed microcolloidally through the crude oil by means of resins molecules or as molecules in liquid phase. They have been found to be responsible to create stable emulsions through the formation of very stable interfacial films between oil and water. Asphaltenes at the interface have been found in different forms such as micelles, through self-association, of different shapes (cylinders, disks, spheres) or as monolayer as a result of their amphiphilic nature and their surface activity. They also can be found in multilayers due to their chemical potential and total free energy. Furthermore, they exist in molecular aggregates in a sandwich-like network. The rigidity of this network may further increase in the presence of wax and clay particles.

- Asphaltene-resin interaction is another major source of concern in terms of emulsion stability through the development of a steric repulsive layer in which asphaltene particles are contained in a resin assembly. Again, surface properties render this asphaltene-resin assembly capable of migrating and residing at the interface between oil and water, creating elastic films around water droplets (w/o emulsion).

- In addition, asphaltene solubility largely influences emulsion stability. Asphaltene solubility is influenced by crude characteristics such as resins or ambient crude medium-asphaltenes interaction. Unstable emulsions are produced with high resins to asphaltenes ratios since higher resins concentrations lead to an increase in asphaltene solubility; thereby, to a decrease in asphaltene-water interaction (reduced stability). Asphaltene solubility is also a function of alkane and aromatic composition within the crude. Heavier alkanes and aromatics provide an environment in which asphaltene is less soluble, i.e., more asphaltene deposits (increased stability).
- Asphaltenes precipitation is mainly due to mixing crudes of different compositions, temperature and/or pressure reduction and hydrogen bonding between asphaltene-asphaltene molecules and resins molecules. Indeed, asphaltene deposition is a difficult issue to deal with once it has happened as it is highly likely to be irreversible. It also should be noted that asphaltenes are more prone to stabilize emulsions when asphaltenes are near or above their initial precipitation point. Asphaltene deposition is undesirable phenomenon as it is associated with pore spaces blockages, permeability drop, tubing plugging, production drop and stability promotion; this all, of-course, entails additional cost(s).
- Asphaltenes interaction with waxes found in the crude can further promote emulsion stability. They, due to their hydrophobic character in collaboration with asphaltenes and/or resins can assemble at the interface giving a kind of strength to it. In addition to that, wax particles as a result of temperature drop can create precipitates by which the crude viscosity is dramatically increased.
- Carboxylic acids, which are found in high quantities in heavy crudes in comparison to light crudes, are thought to be generated during in-reservoir biodegradation and photo oxidation products when aromatic fraction in a crude is subjected to sunlight. These polar acids with their surfactant properties through interactions with other crude oil compounds have a tendency to accumulate at the oil-water interface in the form of particles giving rise to emulsion stability. This is also the case with crude porphyrins with their variable metal content.
- Finally, due to their amphiphilic nature clay particles and clay minerals can also head towards the interface between oil and water. As a result, they

provide surfaces for asphaltenes irreversible adsorption which can further promote the pickering emulsion stability.

- On the other hand, Phenomena like: creaming/sedimentation, flocculation, coalescence, Ostwald ripening and/or emulsion phase inversion may work against emulsion stability resulting in emulsion physical degradation whether individually or collectively. Also, due to some conditions phase inversion may be favoured resulting in an emulsion with finer droplets by which its stability is further promoted.

It is; therefore, of crucial importance to understand the contribution these compounds may have in terms of emulsion stabilization, so as to develop preventive measures for asphaltenes deposition and other asphaltenes-related problems, and; thus, be able to characterize crude oils and, ultimately, facilitate optimum emulsion destabilization, to completely separate water from the crude in a reasonable time scale prior to transportation and refining stages.

Chapter Three

Literature Review

Destabilization Methods

Chapter Three

Literature Review

Destabilization Methods

> *....we are suffering from a plethora of surmise, conjecture and hypothesis.*
> *The difficulty is to detach the framework of fact-of absolute*
> *undeniable fact-from the embellishments of theorists and reporters.*
> *Then, having established ourselves upon this sound basis,*
> *it is our duty to see what inference may be drawn*
> *and what are the special points upon which the whole mystery turns.*
>
> *Sir Arthur Conan Doyle*
> *Silver Blaze in Memoirs of Sherlock Holmes*
> *(1859-1930)*

3.1 Introduction

Emulsion formation is an inevitable phenomenon in crude oil industry due to multiple water and oil contact during oil processing (Nour et al., 2007b). In the previous parts of this study it was clearly elucidated that existence of surface-active compounds has an enormous problematic influence on the oil industry throughout production and refinery stages through emulsion stabilization. Emulsion stability level is proportional with crude content of these emulsifiers and their interactions; higher content of these compounds; of-course, grants the emulsion a higher stability extent. Therefore, in order to meet pipeline and exportation specifications; demulsifying of these emulsions (i.e. reversible flocculation/coagulation followed by irreversible coalescence of the dispersed phase droplets and eventually creating two distinctive layers of oil phase on top and water/aqueous phase at the bottom (Othman et al., 2008; Chen and He, 2003; Kokal, 2002; Liggieri et al., 2001; Wanli et al., 2000; Kim, 1999; Kenneth J, 1988) is an important but has been a difficult process in petroleum industry (Less et al., 2008; Nour et al., 2007b; Fortuny et al., 2007; Pena et al., 2005; Eow and Ghadiri, 2002a; Kim and Wasan, 1996; Márquez et al., 1996; Taylor, 1996; Tirmizi et al., 1996; Tambe and Sharma, 1993) as otherwise severe processing problems will arise. These generally include pipes and equipment corrosion, catalyst poisoning and difficulties in transportation.

In order meanwhile to effectively and economically demulsify w/o emulsions, it is crucial to understand how they have been stabilized. This, as shown in the previous Chapter, requires knowledge of asphaltenes and resins properties and interactions as they have been considered as the main emulsion stabilizers. Other aforementioned stabilizers are also of considerable importance due to their strong tendency to interact with asphaltenes and/or resins.

Although, Kenneth J back in 1988 (Kenneth J, 1988) concluded that not much work was reported about demulsification of emulsions for reasons that the basic work was already done and that no more work to be done, most of the work was commercially conducted; thus, cannot be published unless patented and also due to a difficulty of the area of emulsions. Currently, there has been progress; chemical, thermal and electrical demulsification works are underway. Chemical treatment through the use of chemical demulsifiers (surface active agents) have been the main methods used to separate these problematic emulsions, heating/ microwave demulsification and electro- demulsification have also been in use. Combination of these two techniques, in order to enhance demulsification efficiency, was also reported (Ekott and Akpabio, 2010; Less et al., 2008; Othman et al., 2008; Nour et al., 2007b; Nour et al., 2007a; Fortuny et al., 2007; Sullivan et al., 2007; Pena et al., 2005; Pangu and Feke, 2004; Eow and Ghadiri, 2002a; Buist and Lewis, 2002; Kokal, 2002; Angle, 2001; Eow et al., 2001; Sams and Zaouk, 2000; Førdedal et al., 1996; Kim et al., 1995; Mohammed et al., 1993; Tarleton and Wakeman, 1990). Microfiltration has also been used to breakdown w/o emulsions. It is worth observing that there has been no universal method that can be applied for all emulsions, i.e., methods are very application/crude specific, with the trial and error principle has been the basis to decide on the applied method for a given emulsion (Ortiz et al., 2010; Sun et al., 2010; Kang et al., 2006; Xia et al., 2004; Vander Kloet et al., 2002). This is simply due the diversity of crude oils as well as brines and; hence, resultant emulsions (Kokal, 2002).

This Chapter shall try to give a summary of these techniques, apart from microfiltration, demonstrating their theoretical aspects and practical applications highlighting the mechanism(s) by which these methods proceed in the demulsification task. Microfiltration of emulsions is the topic of this thesis and will be separately discussed in detail in the next Chapter.

3.2 Chemical Demulsification Methods

Various chemicals (chemical cocktails) which are of different surface-active characteristics have been widely implemented to destabilize w/o emulsions such as acids, bases, fatty acids and their derivatives, alcohols, amines, acetone, copolymers of ethylene oxide, polyoxyethylene, polypropylene or polyester and propylene oxide, etc. and some other commercial demulsifiers (Nour et al., 2007b; Noïk et al., 2005; Pena et al., 2005; Zhang et al., 2005; Sjöblom et al., 2001; Goldszal and Bourrel, 2000; Márquez et al., 1996; Urdahl et al., 1993; Aveyard et al., 1990; Menon and Wasan, 1988). Owing to their surface active character, demulsifier molecules consist of hydrophilic and hydrophobic groups. At an interface, hydrophilic groups will orient toward the polar phase (water) while hydrophobic groups will choose the oleic phase to orient toward (Zhang et al., 2005). For further information on the various employed chemical demulsifiers a rather comprehensive list is available (Angle, 2001).

Demulsifiers according to their molecular weight are classified into two grades; these are low molecular weight (LMW) demulsifiers, typically below 3000 Da, and high molecular weight (HMW) demulsifiers, usually above 10,000 Da. The latter demulsifiers due to their higher molecular weight diffuse slower than the former ones (Pena et al., 2005). For petroleum emulsions (w/o) the latter type is mostly used in comparison to the former one. In addition to high molecular weight, these demulsifiers should be highly branched and with a great affinity towards water droplets (Ekott and Akpabio, 2010). Generally, demulsifiers of the first class are some types of oil-soluble surfactants such as pure paraffinic hydrocarbons, aromatic hydrocarbons, alcohols and diols and they function through increasing the interfacial activity (suppression of the interfacial tension) and changing the wettability of surface active components, respectively. HMW demulsifiers represent polyelectrolytes and various types of oil-soluble polymers and macromolecules like block copolymers. These demulsifiers influence the interfacial film via their ability to penetrate through this film modifying the rheological properties inducing film drainage which has the sequence of droplet coalescence and subsequently phase separation (Pena et al., 2005; Sjöblom et al., 2001; Tambe et al., 1995).

Prior to the addition of a demulsifier to an emulsion, surface active components maintain a high interfacial tension within the interfacial film (Schramm 1992) and a low interfacial tension elsewhere away from the film within the emulsion. This set-up is reversed once a demulsifier has been added, owing to its strong surface-active properties, and that binding forces between water and oil droplets are reduced and the film is drained, i.e. the emulsion becomes unstable and; therefore, water droplets are flocculated and then coalesced (Ekott and Akpabio, 2010; Daniel-David et al., 2005; Zhang et al., 2005). Therefore, it can be inferred that the main contribution of a chemical demulsifier to reduce the stability of an emulsion (speed up droplet coalescence) is its ability to improve film drainage by suppressing the tension gradient (Gibbs-Marangoni effect) (Nour et al., 2007b; Pangu and Feke, 2004; Xu et al., 2004; Kim and Wasan, 1996; Kim et al., 1995; Urdahl et al., 1993). Interfacial tension measurements have been widely used to relate the adsorption of a demulsifier at the oil/water interface so that demulsifier/interface based-interactions (demulsifier functionality) can be studied (Yang et al., 2001; Wanli et al., 2000).

The structure of the demulsifier, its ability to distribute throughout the bulk of emulsion, speed of agitation, its partitioning character between the phases at the interface, ambient temperature, stability of the emulsion and pH and salinity of the water phase are all factors influence the demulsifier’s performance (Ekott and Akpabio, 2010; Khadim and Sarbar, 1999; Kim, 1999; Mohammed et al., 1994a). Concentration of the demulsifier is also an important factor as it was suggested that too high demulsifier concentration, that’s too higher than critical micelle concentration (CMC), weakens the demulsifier action through asphaltene solubilization. In fact, demulsifier(s) should be carefully dosed. Too little demulsifier will not be beneficial in term of emulsion breakdown, too much demulsifier(s); on the other hand, may further complicate the emulsion stability (Kokal, 2002; Aveyard et al., 1990). Too high demulsifier(s) concentration(s) may result in increased emulsion stability, perhaps as a result of a new stabilizing film around emulsion droplets by the demulsifier(s) (Pena et al., 2005). Experimental evidence shows that the rate of demulsification was increased with surfactant concentration until a threshold of surfactant aggregation is reached at which lower demulsification rates were obtained or the rate of demulsification became independent on the demulsifier concentration (Mohammed et al., 1994a; Mohammed et al., 1993).

In addition, there are some properties a good chemical demulsifier should possess. A good demulsifier in the first instance should be a poor emulsifier with a high molecular weight and amphiphile character with a tendency to thoroughly mix through the emulsion to speed up water-oil separation (Buist and Lewis, 2002; Angle, 2001; Márquez et al., 1996; Mohammed et al., 1994a; Menon and Wasan, 1988). Also, equal partitioning between both phases at the interface (water and oil) is considered as an important factor for swift demulsifier adsorption at the interface to reduce interfacial tension gradient and; therefore, it increases the demulsifier's performance (Ekott and Akpabio, 2010; Daniel-David et al., 2005; Buist and Lewis, 2002; Angle, 2001; Sjöblom et al., 2001; Sams and Zaouk, 2000; Kim and Wasan, 1996; Márquez et al., 1996). Its interfacial tension has to be notably lower than that of the indigenous surfactants of the crude so that demulsifier molecules can absorb at the interface so as to displace emulsifier molecules (Buist and Lewis, 2002; Vander Kloet et al., 2002; Angle, 2001; Sjöblom et al., 2001; Márquez et al., 1996; Isaacs et al., 1990). Furthermore, a successful demulsifier should have a high diffusivity and activity through the interfacial film so that it functions to reduce interfacial film elasticity and dynamic film tension (Ekott and Akpabio, 2010; Daniel-David et al., 2005; Kokal, 2002; Angle, 2001; Sjöblom et al., 2001; Kim, 1999; Sjöblom et al., 1992b).

Upon the successfulness of demulsifier(s) to demulsify an emulsion, there are two different water resolution profiles. One is the immediate water resolution profile which occurs when the demulsifier is not mixed with a carrier solvent prior to its addition to the emulsion. The second one is the inductive water resolution profile (not instantaneous) which was demonstrated as a result of mixing the demulsifier with carrier solvent before its usage as a demulsifier. It was stated that the mechanism by which a demulsifier disturbs oil/water interface is dependent on the nature of the demulsifier it self, as demulsifiers of alcoholic character act by altering the rigidity of the interfacial layer through diffusion/partitioning process, whereas aminic demulsifiers were reported to increase the hydrophilicity of the interfacial layer through the attachment to the functional groups of the compounds at the interface layer (Mohammed et al., 1994a).

Mohammed et al. (1994a) investigated the demulsification of w/o emulsions by using different non-ionic demulsifiers of different HLB numbers as shown in Fig. (3.1). At a glance, this investigation demonstrated that higher separation efficiency is obtained as the demulsifier concentration increases. Using Unidem120 demulsifier at low concentrations gave a very little separation. Hence, in practical applications this demulsifier is used at lower concentrations but with the assistance of heat and electrical treatment to help resolve the emulsion. However, higher demulsifier concentrations led to demulsification profiles with higher separation efficiencies until a plateau in demulsification efficiency is reached against concentration increment. In addition, the water resolved from this test was murky in its appearance.

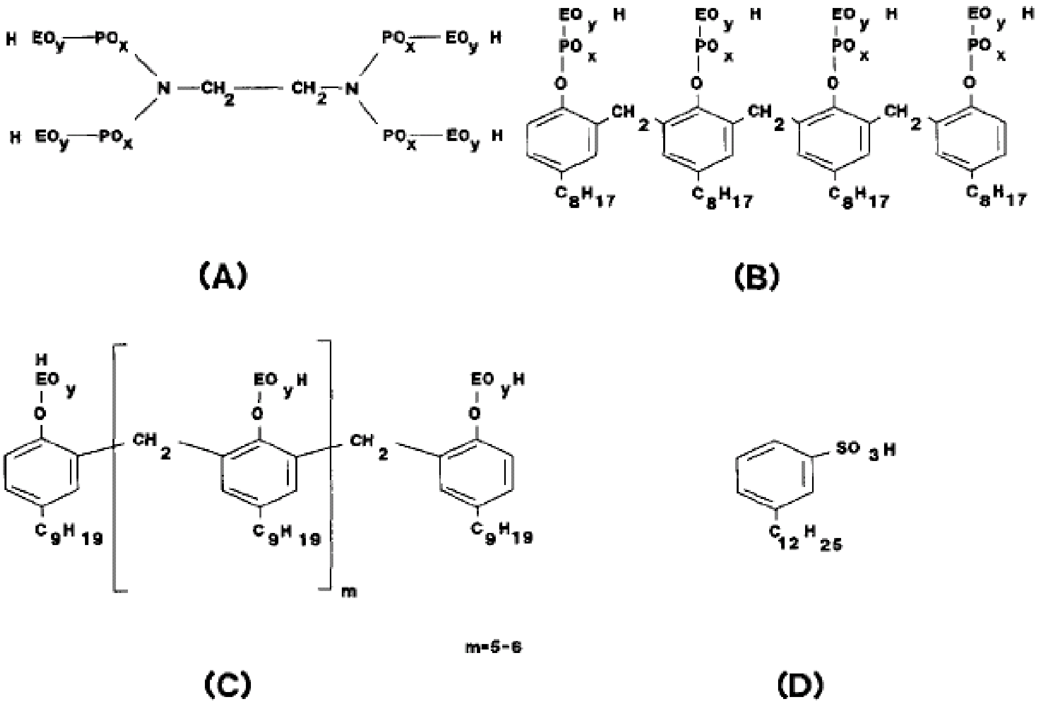


Fig. (3.1): The structure of the demulsifiers used (Mohammed et al., 1994a).

Adding T1301 (which displaces the asphaltene from the interface layer), T1302 (which partitions to the water phase due to its high ethylene oxide, EO number), T701 (which partitions to the oil phase due to its low solubility in water due to its small EO number) and T803 (which partitions to the water phase due to its high

EO number) to the emulsion increased the percentage of water being resolved. However, with overdosing, the separation efficiency collapsed to a plateau value even at higher concentrations. Different pattern was attained when BJ18 (which lacks enough wetting agent to drag the asphaltic film into the oil) or T150l (which displaces the asphaltene from the interface layer) were used, with higher deterioration to zero water separation. Nevertheless, Adding IL2 (wetting agent) which wets waxes and neutralizes basic groups found in the interfacial film increasing its hydrophilicity, DI12 and DW12 demonstrated increased separation efficiency with their concentrations without any drop with increased concentrations. In all these tests, water quality was good.

In summary, the variety of the employed demulsifiers apart from IL2 and BJ18 has shown ability to demulsify w/o emulsions by a similar mechanism. They head towards the interface and displace the asphaltic layer around water droplets and reduce the viscosity of the interfacial film (Li et al., 2001; Sjöblom et al., 2001; Taylor, 1988). Water droplets then flocculate and coalesce where larger water droplets are formed. IL2; however, was used to disturb the interface layer to provide places for the other demulsifiers at the interface, whereas BJ18 acted as a film inhibitor.

Sun and others (Sun et al., 2010) examined the influence of branch-chain (AE-121) and straight-chain (SP-169) demulsifiers on the interfacial properties of an oil-water interface that possesses surface active fractions from crude oil. They concluded that crude surfactants can be replaced by a chemical demulsifier through its tendency to adsorb at the interface owing to its structure of hydrophilic and hydrophobic (libophilic) ends. In this study, demulsifier adsorption and its capability to substitute the film making components were evidenced by the enlargement of interface film that took place upon the addition of a demulsifier. At the interface, demulsifier molecules in their vacancies can accommodate molecules of surface active components. This can be imagined as a new layer that consists of a mixture of demulsifier and surface active molecules, with mixed interfacial properties of both the emulsifier and demulsifier molecules.

The surfactant accommodation is dependent on the size of the surface active molecules; large molecules will find it difficult to enter the demulsifier vacancies, smaller ones would not as demonstrated in Fig. (3.2). If the surfactant molecules are smaller than the demulsifier vacancies, they can get through the demulsifier vacancies. In this case, the properties of the interface are; therefore, a mix-adsorption layer. If they are fairly larger than the demulsifier vacancies they; therefore, cannot enter the demulsifier vacancies and accordingly the interface layer properties are just of that of the demulsifier. In addition to the size of surface active molecules, the demulsifier structure is also important for the surfactant molecules not to be trapped in between the demulsifier vacancies at the interface and that the interface film is only composed of the demulsifier molecules (unstable interface).

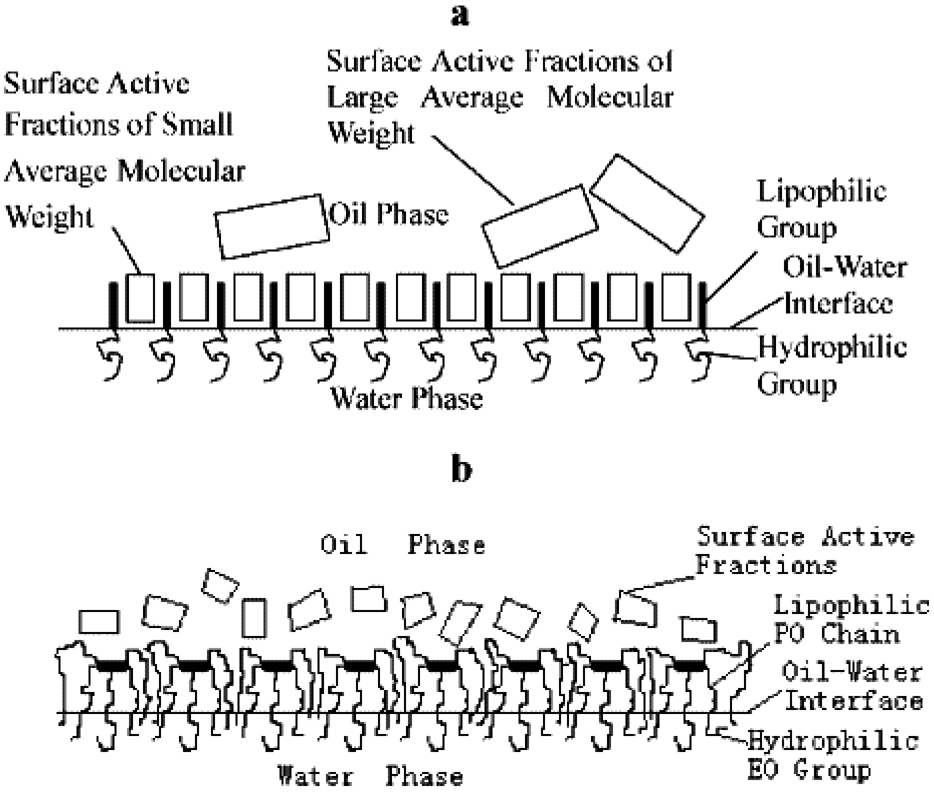


Fig. (3.2): Schematic diagram for mix-adsorption of demulsifier and surface active fraction molecules. (a) Straight-chain (SP-169) ;(b) Branch-chain (AE-121) (Sun et al., 2010).

In fact, in this study it has been demonstrated that the structure of the demulsifier plays an important role in the demulsification performance. A branched demulsifier, in comparison to a straight chain demulsifier, demonstrated a higher ability in replacing the surfactant molecules at the oil-water interface, i.e. more effective demulsification, irrespective of the surfactant molecules sizes examined.

This result was also supported by Zhang and co-workers in their work to demulsify w/o emulsions from Shengli Oilfield in China through the use of amphiphilic denderimer copolymers (Zhang et al., 2005). The other demulsifier; that's with straight chain structure showed a partial replacement of surfactant molecules from the interface; larger molecules were replaced and could not re-enter the demulsifier vacancies due to their sizes, whereas smaller ones were not replaced. Such a higher ability of branched demulsifiers over straight demulsifiers to replace crude surface active molecules is attributed to the small vacancies due to congested structure of the former type.

There is also another more recent study by Kang and co-workers (Kang et al., 2006) concerned with the interfacial properties between oil and water in the presence of a demulsifier which offers support to this mechanism. This study aimed to investigate the effect of four different demulsifiers (water/oil soluble) concentrations on film strength, film thinning, emulsion dewatering rate, interfacial tension and interfacial viscosity in a synthetic w/o emulsion. They concluded that high demulsifier concentrations result in more demulsifier adsorbed at the interface film. This in turn leads to film strength reduction and; therefore, accelerates film thinning which eventually leads to film rupture. The mechanism by which this process can be explained is that upon demulsifier adsorption at the interface, it partially replaces the emulsifiers leading to weakening the interfacial film (Goldszal and Bourrel, 2000; Kim, 1999; Mohammed et al., 1994b). Dewatering rate is also increased with increasing demulsifier concentration. However, increasing the demulsifier concentration has an opposite effect on both interfacial tension and interfacial viscosity. Indeed, this interfacial tension and interfacial viscosity reduction, as a result of increased demulsifier concentration is a key factor to improve the demulsification efficiency and dewatering rate (Buist and Lewis, 2002; Kim et al., 1995). It was also found that water-soluble demulsifiers such as polyoxyethylene and polyoxyethylene polymers have a higher ability in this regard than oil-soluble demulsifiers such as phenol-formaldehyde resin polyoxyethylene and polyoxyethylene.

3.3 Thermal Demulsification Methods

The application of heat to an emulsion results in a reduction in the mechanical strength of the interfacial film after which droplet coalescence is likely (Angle, 2001; Taylor, 1988). Both conventional and microwave heating have been extensively implemented to demulsify w/o emulsions. Microwave irradiation technique is considered advantageous over the conventional heating procedures which are labourious and time-consuming (Coutinho et al., 2010; Lemos et al., 2010; Fortuny et al., 2007; Xia et al., 2004). With microwave heating, the heating can be selective, the equipment can be miniaturized, electrical power consumption cost and environmental pollution can be reduced (Coutinho et al., 2010). Historically, first successful patent applications in demulsifying w/o emulsions by means of microwave heating were registered by Klaila in 1983 and Wolf in 1986. Microwave irradiation offers a clean, chemicals-free, inexpensive and convenient method of heating leading to the acceleration of the demulsification task. Microwave heating offers faster heat transfer rates as the energy is delivered to the targeted object directly through molecular interaction with the electromagnetic field in volumetric heating effects. Also, with microwave radiation uniform heating throughout the object volume is possible. It is recognized that the key for microwave heating, which is facilitated by dipole rotation and ionic conduction, is material-wave interactions which lead to thermal effects and selective absorption of microwave energy by polar molecules within the crude (Coutinho et al., 2010; Nour et al., 2010; Samanta and Basak, 2008; Fortuny et al., 2007; Fang and Lai, 1995). In case of crude oil emulsions in particular, microwaves interact with water molecules, dissolved salts and polar crude compounds such as asphaltenes and resins, leading to phase separation (Lemos et al., 2010). Water content of an emulsion and its salinity influence the microwave demulsification efficiency. The higher the water content, the larger the heating effect would be. Nevertheless, increased salinity level of water content results in a reduced microwave demulsification efficiency (Coutinho et al., 2010). Although microwave irradiation has been a successful process to demulsify w/o emulsions, the literature on this topic has been scarce.

Xia and his colleagues (Xia et al., 2004) employed microwave radiation to demulsify an emulsion stabilized by asphaltenes or resins. W/o model emulsions were prepared by dispersing distilled water in jet kerosene in the presence of different amounts of asphaltenes or resins as emulsifiers. They investigated the possibility of demulsifying the resultant emulsions (at low asphaltenes and resins concentrations; lowest of concentrations ranges examined) by means of microwave radiation. The successfulness of this technique for both emulsions stabilized by asphaltenes or resins was demonstrated via 100 % of water separation in a matter of hundred of seconds. In another study, Nour et al. (2010) used microwave heating instead of conventional heating to demulsify w/o emulsions. Having applied microwave heating to a w/o emulsion, results show that this technique is powerful to demulsify w/o emulsions. Microwave irradiation as a consequence of temperature elevation reduces emulsion viscosity and due to the expansion of the dispersed phase due to increased internal pressure of water droplets reduces the thickness of the interfacial surfactant(s) film and also reduces emulsion stability as a result of breaking hydrogen bonds between surfactant and water molecules (Nour et al., 2010; Eow and Ghadiri, 2002a; Angle, 2001; Bolster and Little, 1980).

Due to temperature increase, emulsion viscosity is decreased (decreased fluid flow resistance) and; therefore, water droplets settling velocity and collision rates, due to increased thermal energy of the droplets, will increase (Stoke’s law) (Coutinho et al., 2010; Ekott and Akpabio, 2010; Nour et al., 2010; Eow and Ghadiri, 2002a; Kim et al., 2002; Kokal, 2002; Angle, 2001; Johansen et al., 1989; Menon and Wasan, 1988; Bolster and Little, 1980). These new conditions (high temperature and low viscosity) lead to faster coagulation producing droplets of larger size which ultimately leads to phase separation with improved rate of film drainage (Angle, 2001). In addition, increasing an emulsion’s temperature results also in an increased density difference between oil and water phases as the density of the oil phase is reduced at a rate that’s faster than that of the aqueous phase. This; therefore, leads to increased frequency of droplets collision as well as increased settling velocity (Ekott and Akpabio, 2010; Angle, 2001). Solubility of surfactants in both oil and aqueous phases of an emulsion can be increased at higher temperatures (Larson et al., 1994). Furthermore, when heat and chemical methods are employed synergically to demulsify an emulsion, the former augments the performance of the latter (Angle, 2001). Microwave heating performance, to a large extent, depends on dielectric properties of emulsion components, emulsion viscosity, density and composition (water content), size and distribution of the dispersed phase within the emulsion, salinity level, pH of the aqueous phase, temperature level and frequency of microwave radiation (Coutinho et al., 2010; Fortuny et al., 2007). Effects of such variables were investigated in a patent by Coutinho and co-workers (Coutinho et al., 2010).

Also, Rajakovic and Skala (Rajakovic and Skala, 2006) obtained very good results of separating w/o emulsions via coupling freeze/thaw with microwave irradiation method. Freeze/thaw demulsification method has been found to be so successful to remove water from w/o (oily sludges) emulsions with 90 % water removal containing some organic materials. Freezing is used to expel surfactant molecules from ice lattice whereas thawing is to create surfactant micelles. In their work, they used microwave radiation to induce the freeze/thaw demulsification efficiency. The benefit of employing heat in freeze/thaw demulsification experiments is to selectively utilize the adsorption of radiation energy by surfactant molecules; therefore, these molecules become energized, leading to superheating at which reaction rates are increased. Also, heat is applied in order to reduce the viscosity of oil (continuous) phase and to help rupture the outer oily film around water droplets so that water droplets can coalesce together. In addition, Chen and He (Chen and He, 2003) used freeze/thaw process to demulsify w/o emulsions. Out of their work, it is concluded that demulsification is dependent on initial water content, freezing temperature and duration and thawing rate and temperature.

3.4 Electrical Demulsification Method

Although various chemical and thermal demulsification methods of w/o emulsions, as demonstrated in previous sections, have been to a large extent successful processes, in addition to the high cost of these demulsifiers, emulsion contamination irrespective of the chemical demulsifier used seems inevitable which entails further processing and cost (Luo et al., 2009; Hu and Scott, 2008; Hu and Scott, 2007; Nour et al., 2007a; Ezzati et al., 2005; Ichikawa and Nakajima, 2004; Pangu and Feke, 2004; Eow and Ghadiri, 2002a; Dezhi et al., 1999; Tirmizi et al., 1996; Larson et al., 1994). With regards to thermal methods, loss of crude oil light components which determine the crude price is likely (Alinezhad et al., 2010; Kim et al., 2002; Kokal, 2002; Sams and Zaouk, 2000). Also, due to temperature increase while heating the crude, separation efficiency may decline due to the formation of air bubbles which can absorb the surfactants found within the crude (Alinezhad et al., 2010; Eow and Ghadiri, 2002a; Kim et al., 2002; Sams and Zaouk, 2000; Dezhi et al., 1999). Furthermore, if thermal treatment is integrated with chemical methods in particular in case of heat-sensitive demulsifiers, heat may deactivate the performance of the demulsifier (Angle, 2001). Finally, heating a crude may also lead to increased propensity towards scale deposition and an increased risk of corrosion in treating vessels (Kokal, 2002).

Therefore, a physical method featured with simplicity of operation, efficiency and affordability and equally important with no chemical waste or moving parts, would clearly be advantageous. A candidate that may possess these features is electrical demulsification. In the petroleum industry during different processing units, electrical destabilization is widely used to break w/o emulsions that may develop throughout crude production and refining as reported in Chapter 2 in Sec. 2.3 of this review. It is a physical process and can be used alone or in conjunction with both chemical and/or thermal demulsification methods in an attempt to augment the performance of these methods (Lu et al., 1997; Taylor, 1988). Emulsion coalescence can be accelerated when gravity coalescence is coupled with an electrical field (Sjöblom et al., 2003; Larson et al., 1994). Using electrokinetic phenomenon in the oil industry application to disrupt w/o emulsions is advantageous due to simplicity and possibility of attaining good separation efficiencies at low power consumption levels. This; therefore, has inspired several researchers to further investigate this technique in dealing with w/o emulsions.

Electrical demulsification of w/o emulsions goes back in time to 1911 by Cottrell in the USA (Eow and Ghadiri, 2002a; Taylor, 1996; Chen et al., 1994). In electrical destabilization techniques different currents are applied; of these, are AC and DC fields; continuous or pulsed (Alinezhad et al., 2010; Luo et al., 2009; Eow and Ghadiri, 2002a/b; Kim et al., 2002; Wakeman and Williams, 2002; Sams and Zaouk, 2000; Taylor, 1996; Chen et al., 1994; Bowen and Sabuni, 1991; Hano et al., 1988; Zhong et al., 1987). AC field is the oldest and the commonest used current to demulsify crude emulsions (Eow et al., 2001; Taylor, 1996) and may be more economical than pulsed electric fields. The latter one; however, in particular in the case of emulsions with high water contents, is characterized with higher droplet coalescence efficiency (Luo et al., 2009; Taylor, 1996; Chen et al., 1994). When a DC current is applied throughout an emulsion, which mainly used in the treatment of low water content emulsions (Eow et al., 2001; Taylor, 1996), droplets coalescence is improved via electrophoretic motion of droplets. In AC fields; however, droplets coalescence is improved through the motion in the bulk field; therefore, this type of electrical fields is more suitable for continuous demulsification processes (Kim et al., 2002).

Depending on the placement of the electrodes in the demulsification cell, there are two types of fields may develop. These are uniform and non-uniform electric fields. When both electrodes are positioned in the emulsion, a uniform electrical field is created between these electrodes. Non-uniform electric field is resulted when only one electrode is contained within the emulsion whereas the other one is in an electrolyte solution. With this configuration, short circuiting due to development of water droplets chains is overcome. Electrode insulation with thin coatings of materials that are non-water wetting (hydrophobic) can also serve this purpose in the former setup (uniform field) (Eow and Ghadiri, 2002a; Eow et al., 2001; Chen et al., 1994; Larson et al., 1994).

Spontaneous but slow coalescence of droplets of an emulsion is well known to occur according to three consecutive steps. First, droplets approach each other with their surrounding film, which as stated before mainly composed of asphaltenes and resins, etc.; this process is called flocculation. This step is then followed by film thinning and drainage during which the thickness of interfacial film is reduced. Capillary and disjoining pressures affect the film thinning rate; according to Marangoni effect, film thinning rate is delayed in the presence of surfactants. At high shear rates, rate of film thinning is inversely proportional to the square of droplet diameter (Alinezhad et al., 2010; Kim et al., 2002; Márquez et al., 1996). Finally, further film thickness reduction; that’s to a critical thickness, by disturbance effects, leads to film rupture which eventually results in internal phase droplet-droplet coalescence. The coalescence phenomenon is accompanied with an increase of droplets size, meanwhile a reduced number of droplets (Less et al., 2008; Othman et al., 2008; Elektorowicz et al., 2006; Aske et al., 2002; Kim et al., 2002; Sullivan and Kilpatrick, 2002; Eow et al., 2001; Wanli et al., 2000; Lu et al., 1997; Chen et al., 1994; Isaacs et al., 1990).

Applying an electrical field across a flowing or a stationary emulsion to attain an appropriate droplets size, with which phase separation is possible, is evidently known to enhance the demulsification rate through some interactions between water droplets, small ones in particular, and the applied field (Less et al., 2008; Othman et al., 2008; Eow and Ghadiri, 2002a; Eow et al., 2001). This interaction leads to droplet charging and agglomeration which subsequently lead to droplet-droplet coalescence (Akay and Wakeman, 1996; Taylor, 1996). Generally, emulsion resolution by an electrical field has been irreversible; however, low electric fields (that's not high enough to induce droplet coalescence) have only been found to result in a linear chain-like configuration; these chains are prone to disappear upon switching off the applied field (Sjöblom et al., 2003; Eow et al., 2001; Førdedal et al., 1996). The success of high enough fields to achieve irreversible demulsification is credited to their ability to permanently rupture the protective film around water droplets, leading to irreversible droplets coalescence (Sjöblom et al., 2003; Førdedal et al., 1996). Electrical fields increase the internal droplets collision (motion energy) due to the oscillation of these droplets under the electric field. Water droplets attraction force is proportional to the square of the applied current as shown in the equation below (Larson et al., 1994; Taylor, 1988). Therefore, large groups of droplets flock, but with their surfactant film around them are formed. By this droplet-droplet proximity, the influence of electricity becomes further pronounced (Kim et al., 2002). This film is then stripped by the tearing force of the electric field, which also results in charging and agglomeration of water droplets, so that water droplets contained within this film have nothing halt them to prevent them combining with each other (coalescence) (Othman et al., 2008; Elektorowicz et al., 2006; Kim et al., 2002; Lu et al., 1997; Chen et al., 1994; Taylor, 1988).

$$F \, \alpha \, E^{2} r^{6} d^{-4}$$

Where F is the attractive force between droplets, E the electric field strength (V/cm), r the droplet radius and d the droplet separation (Larson et al., 1994).

These larger droplets will then settle down into the water phase under the influence of both gravity and electric forces (Kim et al., 2002; Hano et al., 1988). Behaviour of droplets of an emulsion under the influence of an electrical field is depicted in Fig. (3.3). According to this figure, water droplets are initially dispersed everywhere through the emulsion; Fig. (3.3- a). Following application of an electrical field, water, droplets due the effect of increased conductivity by water ions, become polarized as shown in Fig. (3.3- b). Further increase of the field makes water droplets line up between the two electrodes (chain formation), see Fig. (3.3- c) (Aske et al., 2002). Similar observations were also made by Sullivan et al. (2007), Havre and Sjöblom (2003) and (1994).

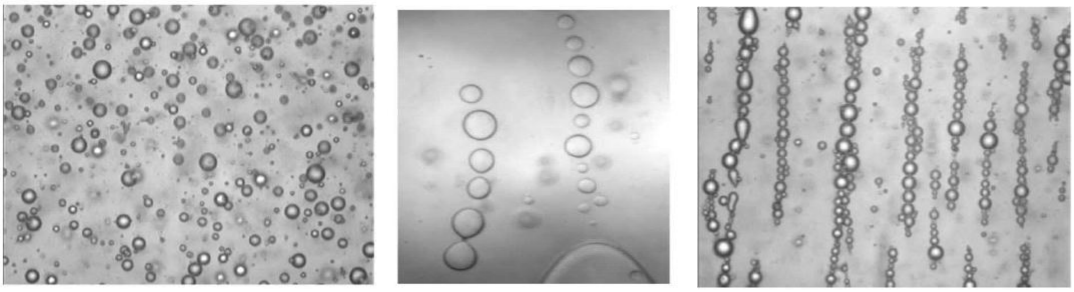

(a) (b) (c)

Fig. (3.3): Emulsion behaviour under the influence of an electrical field (Aske et al., 2002).

Several mechanisms have been put forward to explain the principal effect(s) that may develop during electrocoalescence. Among these are: chain formation of droplets, formation of intermolecular bonds, electrophoresis, dielectrophoresis, dipole coalescence, random collision and electrofining (Ekott and Akpabio, 2010; Eow et al., 2001; Taylor, 1996). A synopsis of these mechanisms along with the most prevailing factors which are with influential effect on separation efficiency is given by Eow and co-workers (Eow et al., 2001) as shown in Fig. (3.4). Chain formation occurs due to potential differences, with both AC/DC currents, among emulsion droplets due to their induced charges. Chains of droplets are then created as a result of individual droplets movement. It is worthwhile noting that these chains do not necessarily start/finish at an electrode nor touch neither electrode, also they are arranged in such a way that they are aligned in line with the field intensity direction. Droplet-droplet coalescence through chain formation depends on oil phase viscosity, dispersed phase fraction and intensity of the applied electric field (Sullivan et al., 2007; Eow et al., 2001).

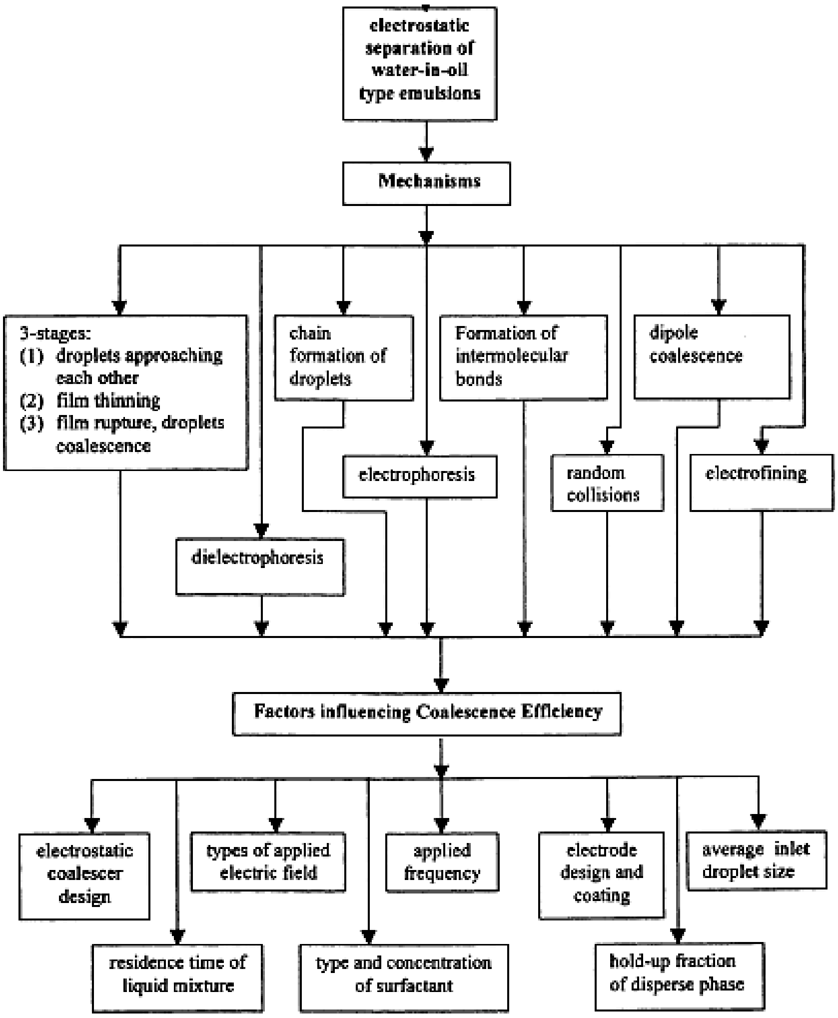


Fig. (3.4): Mechanisms and factors influencing the coalescence efficiency of electrostatic separation of w/o emulsions. Reproduced from (Eow et al., 2001).

Electrophoresis is concerned with applying an electrical field through a stationary fluid in which a charged particle is encouraged to move through it; particle-neighboured fluid is also susceptible to move. This process is based on charge separation between the particle surface and the fluid that’s immediately adjacent to it. Applying a non-uniform electric field results in the movement of water droplets in w/o emulsion towards the direction of field strength under the influence of polarization; this is known as dielectrophoresis. Practically, dielectrophoresis is less significant in terms of droplets coalescence than electrophoresis since a droplet velocity due to the first phenomenon is somewhat low in comparison to that resulting from electrophoresis. However, dielectrophoresis becomes crucial in case of moderately charged droplets when; for instance, insulated electrodes are used. In dipole coalescence, Brownian motion, sedimentation, flocculation or electrophoresis are required to bring emulsion droplets together. Electrofining involves electrophoresis, dipole coalescence, collision of drops of different charges meanwhile flowing in opposite directions and also collision of drops of different sizes moving in the same direction as the direction of the applied DC current (Alinezhad et al., 2010; Eow and Ghadiri, 2002a; Eow et al., 2001; Førdedal et al., 1996; Taylor, 1996; Chen et al., 1994; Larson et al., 1994).

Electrical demulsification kinetics can be influenced by some factors including: dielectric properties of both dispersed and continuous phase, volume fraction of the dispersed phase along with its droplets size distribution, temperature, emulsion viscosity and density, conductivity, electrode geometry, intensity of the applied electric field and its type (AC/DC), etc. (Sjöblom et al., 2003; Eow et al., 2001). Generally, separation efficiency is increased with voltage intensity (Alinezhad et al., 2010; Luo et al., 2009; Sullivan et al., 2007; Eow et al., 2001; Wang et al., 1994; Hirato et al., 1991). However, this was shown not always necessarily to be the case as shown by Eow and Ghadiri (2002b) and Kim et al. (2002). In the systems they examined, although separation efficiency increased as the strength of the applied field increased it decreased when the applied field passed a certain value by which droplet deformation and break-up took place; consequently, separation efficiency was decreased. Furthermore, emulsions with higher water volume fractions give higher separation efficiencies under the effect of electric field due to increased polarization effects (Alinezhad et al., 2010; Sams and Zaouk, 2000; Schramm 1992). To this end, it is expected that in crude oil emulsions with a high content of oil; that are less conductive than water, the separation efficiency may be reduced (Becher, 2001; Eow et al., 2001; Sams and Zaouk, 2000; Schramm 1992). Hano et al. (1988), in their investigation of kinetics of demulsification of w/o emulsions in an AC electric field, concluded that the viscosity of an emulsion has an important effect on electrostatic demulsification. With decreased emulsion viscosity, the rate of demulsification increases. Also, coalescence and water droplets settling increase as water droplet size is increased.

Furthermore, Taylor (Taylor, 1988) in his investigations into the electrical and coalescence behaviour of water in three different crude oils emulsions (Kuwait, Ninian and Romashkino crudes) in high voltage gradients noticed that electrical destabilization of w/o emulsions is largely dependent upon the nature of the resultant interfacial film between oil and water. Emulsions based on crudes that contain incompressible interfacial films tend to form chains of water droplets through the emulsion. In these emulsions, as water droplet-droplet coalescence was limited, emulsion conductivity was increased. However, in emulsions that possess surfactants at the interfacial film, rapid water droplets coalescence with low emulsion conductivity was demonstrated with no chain formation. This was ascribed to enhanced interfacial film mobility as a result of surfactants presence. A synopsis of these two mechanisms is given in Fig. (3.5). A similar conclusion was put forward by Chen and his colleagues (Chen et al., 1994), in terms of the influence of nature of the interfacial film on the coalescence mechanism, when they investigated emulsion resolution by the application of an electric field.

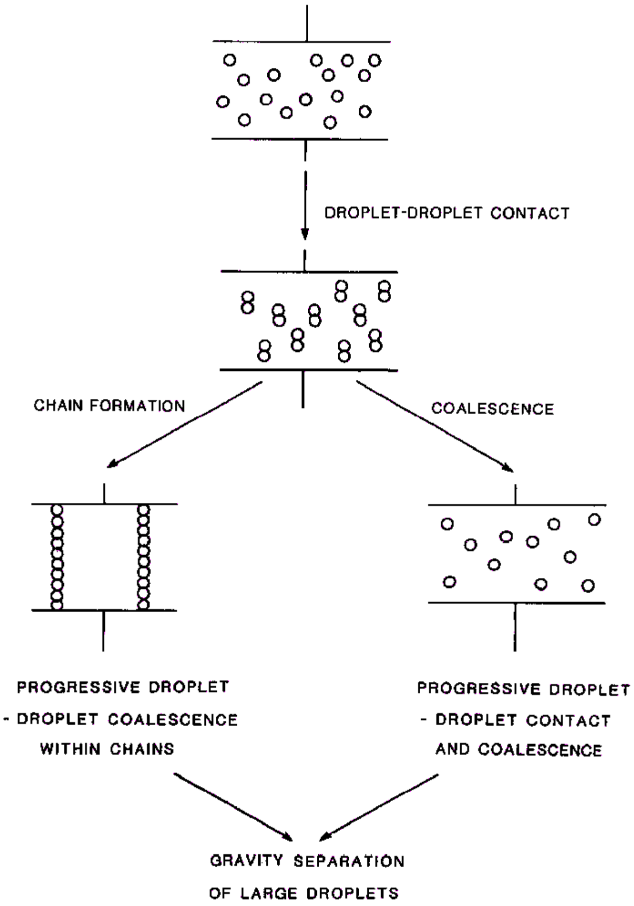


Fig. (3.5): Schematic representation of the stages of electrical coalescence process of an emulsion (Taylor, 1988).

In another study by Eow and Ghadiri (2002b) two novel compact electrocoalescer- separators to separate aqueous drops dispersed in flowing viscous oil were developed. One separator was based on coupling gravity forces with electrical potential, whereas in the other separator, centrifugal force was coupled with electrical forces. Successful separation results were obtained by using either separator, particularly when an optimum electrical field was applied. Optimum field is somewhere between a too low field value and a too high field value. Fields at values beyond this optimum field gave reversed results of decreased separation efficiencies due to water droplet deformation and break-up (smaller droplets).

3.5 Overview of Current Methods of Demulsification

It seems that currently implemented treatment techniques to demulsify w/o emulsions, mainly due to their high stability, have not been efficient enough to effectively and entirely deal with this problem (Lemos et al., 2010). Chemical treatment requires addition of chemicals (contamination) which in turn brings more complication to the emulsion system as it is required to remove these chemicals, at an additional cost, prior to the next downstream processes (Mohebali et al., 2012). Another obstacle with chemical methods is that for highly viscous w/o emulsions (which is usually the case), it might be difficult to mix the required chemical(s) with the emulsion (Fang and Lai, 1995).

Although thermal demulsification has been useful in the demulsification procedures, since, following heating up an emulsion its oil phase viscosity will accordingly be reduced; therefore, its fluidity will increase and more droplet collision takes place. By increasing the emulsion temperature, solubility of surfactants in both oil and aqueous phases of an emulsion can be increased (Larson et al., 1994). Also at elevated temperatures, difference in density of the phases, resulting in the heavier fluid (water) settles down and that the lighter fluid (oil) raises up to build the top layer, is increased (Eow and Ghadiri, 2002a; Sams and Zaouk, 2000; Mohammed et al., 1994a). In addition, due to elevated temperatures within a crude wax precipitation is reduced which, accordingly, can help mitigate emulsion stability (Sams and Zaouk, 2000). Also, demulsification by freeze/thaw method is safe, no chemicals are required; hence, no additional treatment is entailed, convenient and effective with demulsification efficiencies up to 90 % (Rajakovic and Skala, 2006). Thermal demulsification methods are; however, energy-intensive processes, heating a crude oil can promote loss of light components which dictate crude price. Also, due to temperature increase while heating the crude, separation efficiency declines due to the formation of air bubbles, which can adsorb the surfactants found within the crude. Furthermore, if thermal treatment is integrated with chemical methods, in particular in case of heat-sensitive demulsifiers, heat may deactivate the performance of that demulsifier (Angle, 2001).

Electrical and acoustic fields in membrane applications were reported to help enhance demulsification rates through electro-kinetic effects and high internal forces, respectively (Tarleton and Wakeman, 1990). However, most of electrococoalescer equipment currently in use are huge and bulky (Ekott and Akpabio, 2010). In addition, the need to use extremely high voltages to attain droplet coalescence may limit the use of this method (Ezzati et al., 2005; Tirmizi et al., 1996). Also, this method is considered ineffective to demulsify emulsions with high water contents (Dezhi et al., 1999). Likewise, electrical resolution of crude oil emulsions with low water contents can be ineffective due to low conductivity (Ekott and Akpabio, 2010). Another problem with this method particularly in offshore fields, where space is usually restricted, is that it is usually coupled with chemical methods to speed up the demulsification task (Daniel-David et al., 2005) for which additional hardware would be required.

Chapter Four

Literature Review

Microfiltration

Chapter Four
Literature Review
Microfiltration

> The art of our necessities is strange,
> that can make vile things precious.
> William Shakespeare
>
> (1564-1616)

4.1 Introduction

Bearing in mind the chemical, thermal and electrical processes for demulsification of w/o emulsions with their limitations as discussed previously, membrane technology, in comparison, is an inexpensive pressure-driven process. It can be operated continuously and is characterized by flexibility and simplicity of use and high separation efficiencies, which may not be easily achieved by other techniques. Meanwhile low operating cost and low energy consumption particularly when run at low pressures. Most importantly, chemical contamination, additional safety concerns and possibility of crude degradation encountered in chemical, electrical and thermal demulsifications; respectively, can all be eliminated (Salahi et al., 2010; de Morais Coutinho et al., 2009; Hu and Scott, 2008; Kukizaki and Goto, 2008; Mohammadi et al., 2005a; Ezzati et al., 2005; Mohammadi et al., 2004; Kocherginsky et al., 2003; Hu et al., 2002; Srijaroonrat et al., 1999; Ohya et al., 1998; Mueller et al., 1997; Scott, 1996; Tirmizi et al., 1996; Belfort et al., 1994; Fell et al., 1990).

In this Chapter, the intention is to first review general membrane separation processes from the varieties of processes available, historical aspects and mechanistic points of view. Next, characterization of microfiltration performance, mechanism of flux declination along with some various strategies being implemented to avoid/reduce membrane fouling and membrane cleaning are discussed. The effect of different operating conditions on membrane performance is also summarized. Towards the end of the Chapter, application of microfiltration in the separation of w/o emulsions is examined.

4.2 Introduction to Membrane Filtration Process

4.2.1 Definition of Crossflow Filtration

In crossflow filtration, the stream to be filtered (feed) is forced to flow in a parallel mode to the filtration media surface (Al-Malack and Anderson, 1997; Wakeman and Akay, 1997; Schulz and Ripperger, 1989; Wakeman and Tarleton, 1986). While some of this stream with molecules/particles smaller than membrane pores, due to pressure drop across the membrane (pressure-driven process), will penetrate through the filter as permeate/filtrate. Filtrate flow and feed flow are perpendicular to each other. Meanwhile, molecules/particles that are larger than membrane pore size will be retained; this is termed retentate (concentrate) which is usually recycled for further filtration. A typical crossflow filtration unit is schematically represented in Fig. (4.1).

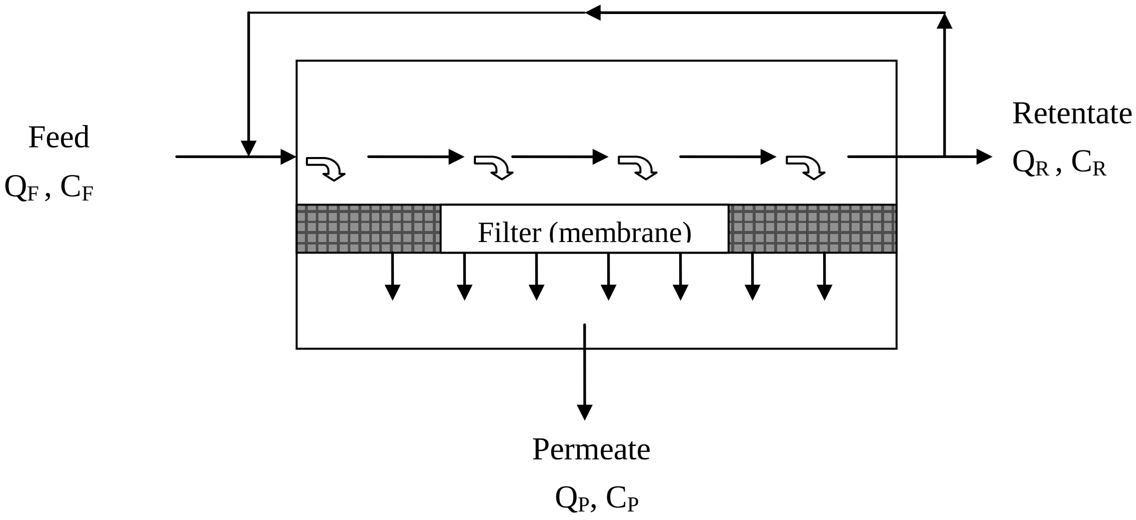


Fig. (4.1): Schematic representation of a typical crossflow filtration unit.

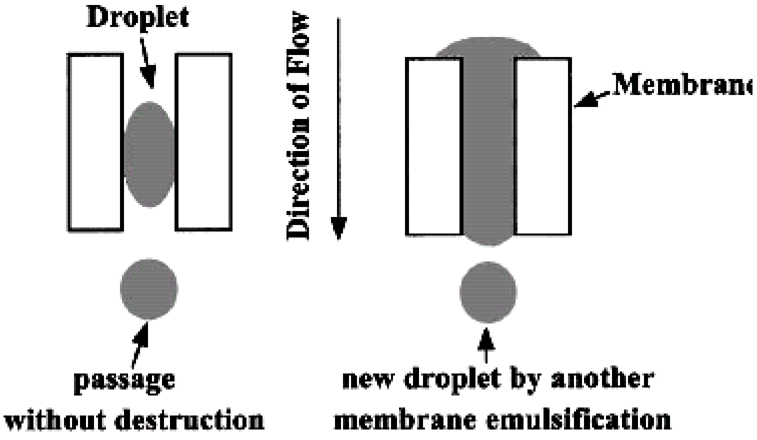
A simple material balance, gives:

$$Q_F = Q_R + Q_P$$

$$Q_F * C_F = Q_R * C_R + Q_P * C_P$$

Where Q_F, Q_R and Q_P are feed, retentate and permeate volumetric flow rates, respectively. C_F, C_R and C_P are the corresponding concentrations.

Fundamentally, emulsions microfiltration and other colloidal suspensions microfiltration are similar. However, from the operational point of view they are more different than they are alike. In the former process large emulsion dispersed droplets, in particular when compared to small ones are inevitably susceptible to deformation ‘flattening in the zone of contact’ (Ivanov and Kralchevsky, 1997), see Fig. (4.2) below, under the influence of high process pressure, coalescence and phase inversion (Chakrabarty et al., 2008; Kukizaki and Goto, 2008; Kocherginsky et al., 2003; Robins et al., 2002; Angle, 2001; Park et al., 2001; Cumming et al., 2000; Scott et al., 2000; Sun et al., 1998; Wakeman and Akay, 1997; Koltuniewicz et al., 1995; Schramm 1992). Droplets deformability largely depends on emulsion droplets-membrane interactions, emulsion concentration and surfactants concentration, transmembrane pressure (TMP) with respect to membrane pore size, size distribution and surface properties of droplets through the emulsion and the extent of imposed shear during filtration process (Saiki et al., 2007; Robins et al., 2002; Matsumoto et al., 1999; Srijaroonrat et al., 1999; Xu et al., 1999; Nazzal and Wiesner, 1996; Lipp et al., 1988).

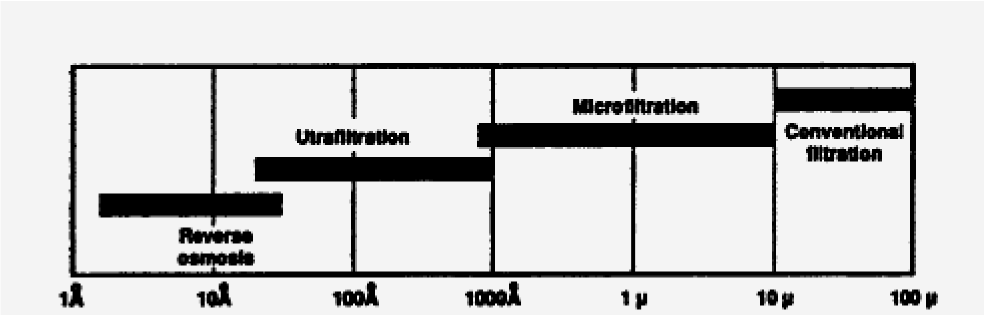


a- **b-**

Fig. (4.2): Droplet deformation mechanism. In a- emulsion droplet size is much smaller than emulsion droplet size in b. Modified from (Park et al., 2001).

4.2.2 Varieties of Some Pressure-Driven Membrane Crossflow Processes

Currently, membrane-based processes are well established technology and cover a wide range of applications including gas separation, water desalination, the food industry as well as the oil industry (Kong and Li, 1999). Among membrane processes there have been various modes of operation including microfiltration, reverse osmosis, nanofiltratio/ ultrafiltration. Although the driving force for such processes is the pressure difference that results from higher pressure above the porous membrane than that below the membrane, the extent of this difference; however, is different in each process (Lonsdale, 1982). Another common feature of these processes is that the separation is facilitated by size exclusion phenomenon and/or chemical interaction with the membrane matrix (de Morais Coutinho et al., 2009; Tansel et al., 2000; Elmaleh et al., 1998). The principle ranges of membrane pore size used in each technique are shown in Fig. (4.3).



Membrane pore diameter

Fig. (4.3): Classification of the different pressure-driven membrane separation processes according to average membrane pore diameter (Wakeman and Akay, 1997; Noble and Stern, 1995; Lonsdale, 1982).

A summary of the main membrane pressure driven processes is given below highlighting some important features in each process. There are also some other processes in which membranes are also used but governed by other driving forces including dialysis, electro-dialysis and pervaporation, etc. (Noble and Stern, 1995; Strathmann, 1985). Due to their irrelevance to this study, these processes; however, will not be considered any further. Crossflow membrane processes can be conducted by various configurations. These encompass: microfiltration, ultrafiltration, hyperfiltration and nanofiltration. Membrane pore size and operational pressure are distinctive for each process.

4.2.2.1 Microfiltration (MF)

Microfiltration is one of the oldest pressure-driven membrane processes (Belfort et al., 1994). In microfiltration, the pressure drop across microfilters is relatively low < 2 bar, with separation principle is the sieving mechanism. The pore sizes of microfiltration membranes vary between 0.1-10 µm (Saxena et al., 2009). This range renders microfiltration membranes appropriate for separating suspensions and emulsions. Both organic (polymeric i.e. hydrophilic/polymeric) and inorganic (ceramic, metallic or glass) membranes are used in microfiltration membranes. Generally, the latter membranes are featured with high chemical and thermal resistances and very narrow pore size distribution. In microfiltration membranes, the pores exist over the total membrane thickness, accordingly, membrane resistance is determined by the whole membrane thickness.

4.2.2.2 Ultrafiltration (UF)

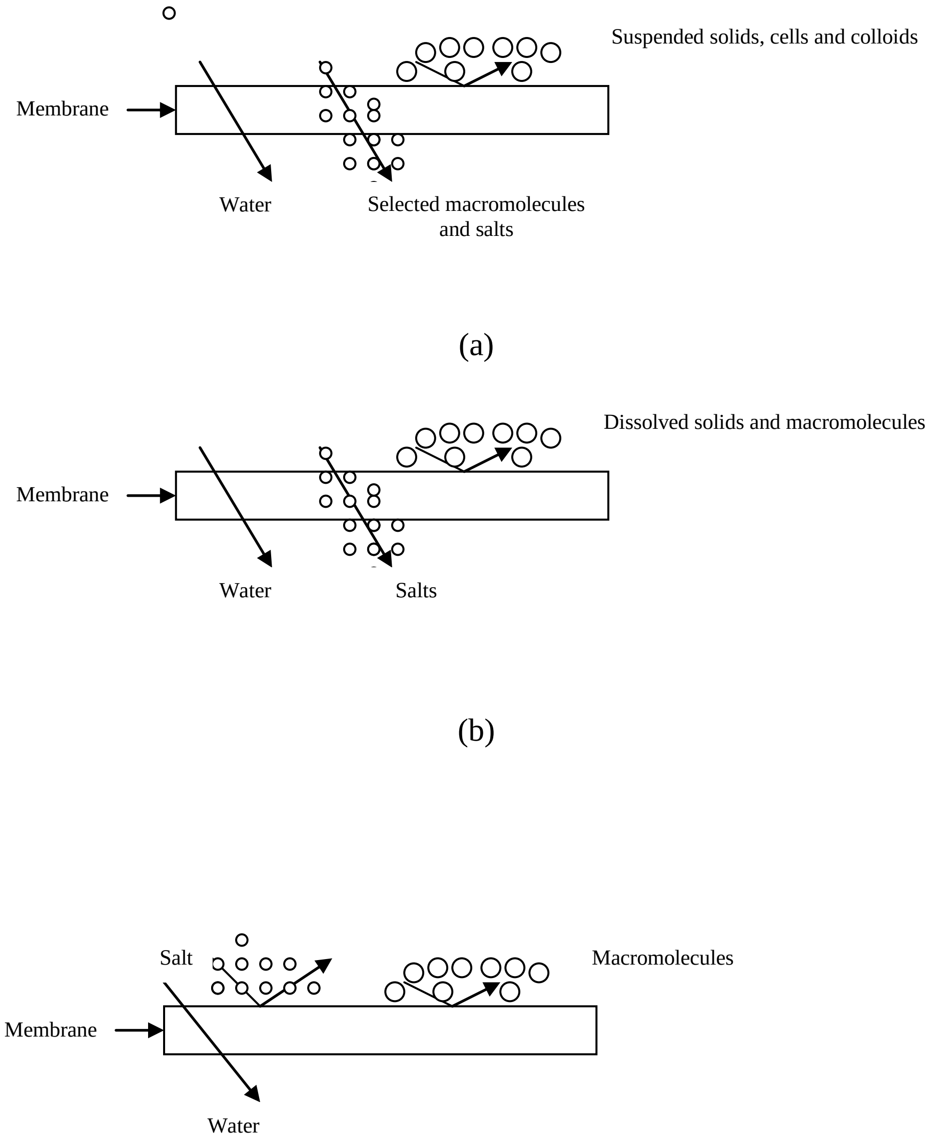
In ultrafiltration processes, the operational pressures range between 1-10 bar, with the separation principle again the sieving mechanism. The pore sizes of ultrafiltration membranes vary between 1-100 nm (Saxena et al., 2009). Ultrafiltration is used over a wide range of applications including food, dairy, textile and pharmaceutical industries (Scott and Hughes, 1996). Both organic (polymeric) and inorganic (ceramic) membranes have been used for ultrafiltration membranes. In ultrafiltration membranes, generally the pores are within the top porous-layer, membrane resistance is; therefore, determined only by this layer (asymmetric membrane). The former process (microfiltration) may be better than this process (ultrafiltration) in terms of higher permeate fluxes as well as higher strength of membranes used in microfiltration applications. On the other hand; however, in microfiltration it is possible for macromolecules or finer particles to pass into the permeate stream (Wakeman and Tarleton, 1987).

4.2.2.3 Hyperfiltration (HF)/Reverse Osmosis (RO)

In hyperfiltration, the operational pressure is somewhat high 15-80 bar or higher (Scott and Hughes, 1996), with solution-diffusion the mechanism of separation. Membranes used in this process possess pore sizes smaller than those present in micro/ultrafiltration processes. Hyperfiltration technique is mainly used for desalination of seawater, production of ultrapure water for electronic industry and for concentration of milk in dairy industry (Scott and Hughes, 1996). Asymmetric (integral and composite) membranes are used in this process. In integral asymmetric membranes, both top layer and sub-layer are made of the same material. Cellulose-based membranes are used in this process for their high permeability towards water in combination with a very low solubility towards the salt. Aromatic polyamides membranes are also used but their water flux is somewhat lower. In composite asymmetric membranes, the top layer and sub-layer are made of different polymeric materials. It is worthwhile mentioning that, typical flux rates with a clean membrane in a microfiltration process is much higher than that obtained from an ultrafiltration and reverse osmosis processes (Hu and Scott, 2008). In Table (4.1) and Fig. (4.4), performance of these three processes is summarized and depicted, respectively.

Table (4.1): Principle method of particle retention with respect to membrane process.

Membrane process	Principle method of particle retention	As shown in Fig.
Microfiltration	Suspended solids, cells and colloids.	(4.4-a)
Ultrafiltration	Dissolved solid and macromolecules	(4.4-b)
Hyperfiltration	macromolecules	(4.4-c)



(a)

(b)

(c)

Fig. (4.4): Separation using different membranes: a- microfiltration membrane, b- ultrafiltration membrane and c- hyperfiltration membrane (Scott, 1996).

4.2.3 Historical Perspective of Microfiltration

In 1855, Frick made a membrane by dipping a test tube in a collodion solution. Production of membranes with different pore size was reported by Bechhold in 1906. Later, Zsigmondy and Bachmann in 1918 were able to produce small quantities of ‘parchment-like’ microfiltration membranes with various pore sizes. An U.S. patent in 1922 was awarded to Zsigmondy for his work involving exposing a thin coating of a nitrocellulose solution to humid air. Five years later, the first commercial membrane production by Sartorius saw the light (Noble and Stern, 1995). Since then, no major commercial advances took place until World War II had come to an end (Noble and Stern, 1995; Belfort et al., 1994; Lonsdale, 1982).

A revolutionary invention was made by Gertrude Mueller at the Hygiene Institute in Germany which led to large-scale commercialization of microfilters. In this discovery, it was proposed that the micro flora from a large volume of water could be deposited intact on a small disk of microfiltration membrane. By culturing the membrane and counting the colonies, rapid and accurate determinations of the safety of drinking water could be made. Indeed, this invention at that time was a particular breakthrough (Noble and Stern, 1995).

Soon after, Alexander Goetz and co-workers from the U.S. Joint Intelligence Objectives Agency in their post-war assessment of German science and technology, scrutinized microfiltration technology. Their work was then further developed by Lovell Chemical Company in 1950. Through late 1950 to early 1954, intensive work was underway in an effort to widen microfiltration membrane synthesis from laboratory-based production to semi-commercial production. Later, Lovell Chemical Company sold the technology to Millipore Corporation which until now still a company that goes from strength to strength with regards to membrane fabrication (Noble and Stern, 1995; Lonsdale, 1982). Since then, membrane technology has received increased attention, which in turn has led to continuous developments.

4.2.4 Varieties of Membrane Modules, Materials and Structures

According to the application, different membrane designs such as flat sheet, spiral wound, tubular, capillary and hollow fibers as well as different materials have been in use (de Morais Coutinho et al., 2009; Fell et al., 1990; Tarleton and Wakeman, 1988; Wakeman and Tarleton, 1986). These materials include organic (porous) and inorganic (ceramic, glass and metallic) membranes. For an effective filtration, a membrane material should be chemically resistant to both feed and cleaning agent(s) in a range of operational conditions, mechanically and thermally stable along with high permeability and selectivity and with a stable operation (Merry, 1996; Scott and Hughes, 1996). Organic membranes can be synthesized from a variety of hydrophobic and hydrophilic polymeric materials of different molecular weight cut-off of 20000- 50000 such as: polypropylene, polyethylene, poly (vinylidene-fluoride), polycarbonate, poly (ether-imide), polyetherimide, polysulfone, acrylic zirconia, borosilicate glass, stainless steel, aluminum, silver and nickel (de Morais Coutinho et al., 2009; Saxena et al., 2009; Kong and Li, 1999; Belfort et al., 1994; Gekas and Hallström, 1990; Hsieh et al., 1988; Mulder, 1951). Due to their excellent chemical, mechanical and thermal resistance, chemical inertness to a wide range of feed conditions (high temperatures and concentrations) as well as very narrow pore size distribution, inorganic membranes have seen more applications compared to organic ones (Chen et al., 2009; Del Colle et al., 2007; Lobo et al., 2006; Mohammadi et al., 2005a; Mohammadi et al., 2004; Nicolaisen, 2002; Faibish and Cohen, 2001; Srijaroonrat et al., 1999; Xu et al., 1999; Gekas and Hallström, 1990; Hsieh et al., 1988). In spite of these advantages they are; however, associated with high cost; perhaps due to expensive raw materials used in their preparation, low membrane surface area/volume ratio and sophisticated manufacturing procedures. As a result, organic membranes which are relatively cheap, highly selective and easy to manufacture are still used (Chen et al., 2009; Qiu et al., 2009; Gekas and Hallström, 1990).

These membranes can be symmetric (uniform) or asymmetric (non-uniform) (Scott and Hughes, 1996). The former type can be porous or non-porous with membrane thickness varies between 10 to 200 µm. The permeation rate of these membranes is determined by the total membrane thickness, i.e., the thicker the membrane is, the lower the membrane permeate rate is. These membranes are usually used in microfiltration processes (Strathmann, 1985; Mulder, 1951). Asymmetric membranes can be either porous or composite and made of a very thin dense top layer with a thickness of < 0.5 µm; this layer controls the transport rate. Underneath this layer there is a porous sub-layer or multiple layers with a thickness range between 50-200 µm which serves no other purpose than to support the top layer as well as to add a strength to the membrane body (Xu et al., 1999). Since permeate flow rate is inversely proportional to the actual membrane thickness, asymmetric membranes are featured with higher permeation rates than symmetric membranes of a comparable thickness (Mulder, 1951). An organic polymer, in the acronym form referred to as ‘PHP’ as will be defined later, is a subdivision of these organic membranes and has been utilized throughout this study and; therefore, will be further discussed within the next section.

4.2.5 Overview on PolyHIPE Polymer (PHP)

Polymer is derived from the Greek, *poly* means many and *meros* means parts (Katz, 1998). Among the polymerization techniques is emulsion polymerization. Back in the 1970s, a high internal phase emulsion (HIPE) polymerization process of the continuous organic phase to produce microcellular, polymeric foam was described by Lissant and Mayhan (Menner et al., 2006; Hoisington et al., 1997). PolyHIPE polymers (PHPs) were then first patented by Barby and Haq of Unilever in 1985 (Zhang and Cooper, 2005; Benson, 2003; Deleuze et al., 2002; Hoisington et al., 1997). HIPEs are emulsions in which the internal (aqueous) phase that comprises water and a polymerization initiator such as potassium persulphate/peroxide, represents at least 74 vol. % of the emulsion volume. The continuous (organic) phase consists of monomers such as styrene or acrylates, crosslinking components such as divinylbenzene (DVB) and a surfactant to stabilize the emulsion such as sorbitan monooleate (Span80) (Ergenekon et al., 2011; Livshin and Silverstein, 2008; Haibach et al., 2006; Menner et al., 2006; Cameron, 2005; Krajnc et al., 2005; Zhang and Cooper, 2005; Deleuze et al., 2002; Sergienko et al., 2002; Tai et al., 2001; Hoisington et al., 1997; Bhumgara, 1995; Aronson and Petko, 1993; Hainey et al., 1991). In polymerization, a crosslinker is used in an effort to enhance the physical/structural stability of the produced polymer by tying together its backbones and also to prevent them not to separate to the larger intermolecular distances favoured for side-chain crystallization (Livshin and Silverstein, 2008). Alternatively, other monomers such as methacrylate, isobornyl acrylate, butyl acrylate, 4-vinylbenzyl chloride, 4-nitrophenyl acrylate, 2-ethylhexyl acrylate and 2,4,6-trichlorophenyl acrylate have also been in use (Haibach et al., 2006; Menner et al., 2006; Cameron, 2005).

Preparation of PHPs has been described in a number of studies. While depending on the features of the desired PHP, procedures of synthesis of different PHPs through a polymerization route may vary as demonstrated in the literature reviewed (Haibach et al., 2006; Menner et al., 2006; Barbetta et al., 2005; Bokhari et al., 2005; Cameron, 2005; Krajnc et al., 2005; Akay et al., 2004; Brown et al., 1999; Sotiropoulos et al., 1998; Hoisington et al., 1997; Walsh et al., 1996; Bhumgara, 1995; Hainey et al., 1991). However, it appears that in all cases the polymerization process principle remains the same and follows a two-stage process but with various compositions in accord to the application. In the first stage, an emulsion is created from an oil phase that contains a monomer mixture of styrene linked with DVB, and a dispersed phase which is made up from distilled water, a polymerization initiator such as potassium persulphate and a surfactant like Span80. This emulsion is afterwards rapidly stirred for a preset period of time depending on the desired PHP pore size. The longer the mixing time, the smaller the pore size of the PHP would be. A schematic representation of polymerization process is illustrated in Fig. (4.5). In addition, with respect to final production application, a third stage that involves product post-functionalization may also be required. Produced solid PHP can be of the closed/open-cell type and the internal aqueous phase is trapped within the cellular structure but can be readily and quickly removed (Hainey et al., 1991). PolyHIPEs are also known as aphrons, biliquid foams, hydrocarbon gels, gel emulsions and high internal phase ratio emulsions (HIPRE) (Aronson and Petko, 1993).

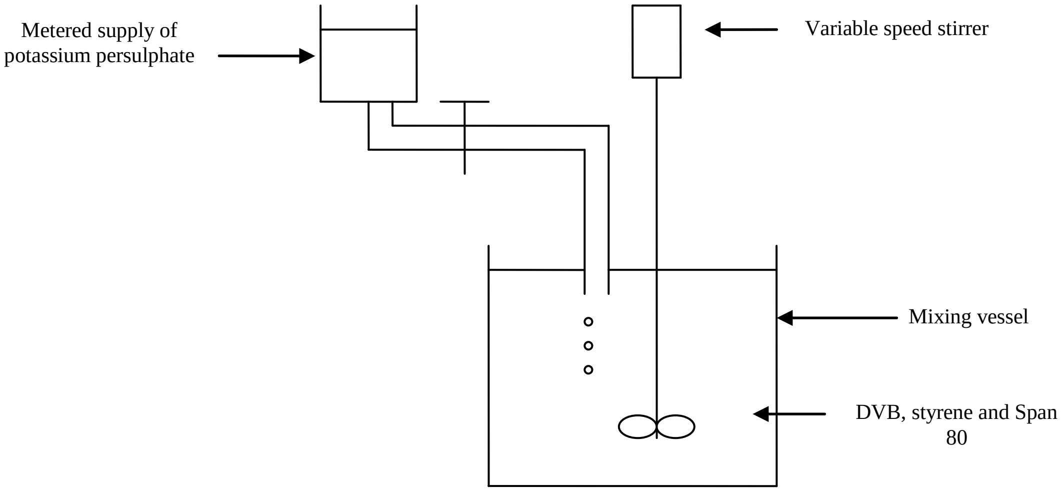


Fig. (4.5): Illustration of PHP production process.

Following polymerization, drying of the obtained PHPs is necessary so as to remove any residual water (Hoisington et al., 1997). In addition to that; depending on the application of the produced PHPs, further processing, e.g. sulphonation at different levels may also be required to modify their surface characteristics (hydrophobicity/hydrophilicty) (Al-Malack and Anderson, 1997). Once synthesized, a styrene-DVB PHP is with a hydrophobic character and it; therefore, prefers to absorb oil-based liquids. In order to modify this character, PHPs which comprise hydrocarbon residues (Haq, 1985) are sulphonated so as to become a hydrophilic (acidic) material instead (Shen et al., 2003; Smitha et al., 2003; Wakeman et al., 1998; Bhumgara, 1995). Sulphonated PHPs can possess higher conductivity, thermal stability, water absorption capability, biocompatibility, ion exchange capacity and swelling. Besides, in filtration applications, they can produce an improved permeate flux rates as a result of improved solute rejection/reduced solute-membrane adhesion through their modified surface chemistry (Howarter and Youngblood, 2009; Ochoa et al., 2003; Smitha et al., 2003; Faibish and Cohen, 2001; Srijaroonrat et al., 1999; Xu et al., 1999; Wakeman et al., 1998; Parvatiyar, 1996; Gatenholm et al., 1988; Anderson et al., 1987). To this end; therefore, the applicability of these hydrophilic PHPs is widened to be good candidates for numerous applications including chemical and wastewater treatment processes and fuel cell applications for their low methanol permeability and ion-conductive structure (Ergenekon et al., 2011; Naim et al., 2004; Shen et al., 2003; Cornelissen et al., 1998).

Sulphonation is a substitution reaction in which a ~SO_3H group is attached to a molecule of an organic compound via a chemical bond to a carbon or, rarely, to a nitrogen atom, of that organic compound. By far with respect to the application, sulphonating agents such as H_2SO_4, SO_3 and its complexes like acyl and alkyl sulphates and chlorosulphonic acid are the most extensively employed ones. Others such as fluorosulphonic acid, sulphur dioxide, sulphites and acid sulphites, sulphuryl chloride alkyl sulphates, oleum and N-pyridinium sulphonic acid, etc. are rarely used (Ergenekon et al., 2011; Gopichandran et al., 2003; Kučera and Jančář, 1998; Foster, 1997; Regas, 1984; Turbak, 1962; Gilbert and Jones, 1960; Roth, 1957). Sulphonation reaction schemes of aromatic systems with sulphur trioxide and sulphonic cation are shown in Fig. (4.6 a-b); respectively, and a general mechanism for the reaction is given in Fig. (4.7). Reaction conditions for sulphonation are usually set in accord to the desired final PHP. In the choice of these conditions, the following factors are taken into account: a- sulphonation level that's the number of ~SO_3H group entering into the aromatic ring, b- type of formed isomers and c- yield of sulphonic acid. There are some parameters that to an extent determine the overall efficiency of a sulphonation reaction. An important factor is temperature (Barona et al., 2007). According to the literature, successful sulphonation reactions over a wide range of temperatures from -20 to 300 C have been reported (Kučera and Jančář, 1998). Inner surface area, physical and chemical properties of the polymer to be sulphonated, concentration and purity of sulphonating agent, contact time with the sulphonating agent and intensity of agitation are also decisive factors with regard to sulphonation efficiency (Ergenekon et al., 2011; Barona et al., 2007; Roth, 1957). The chemical structure of a sulphonated crosslinked PHP is shown in Fig. (4.8).

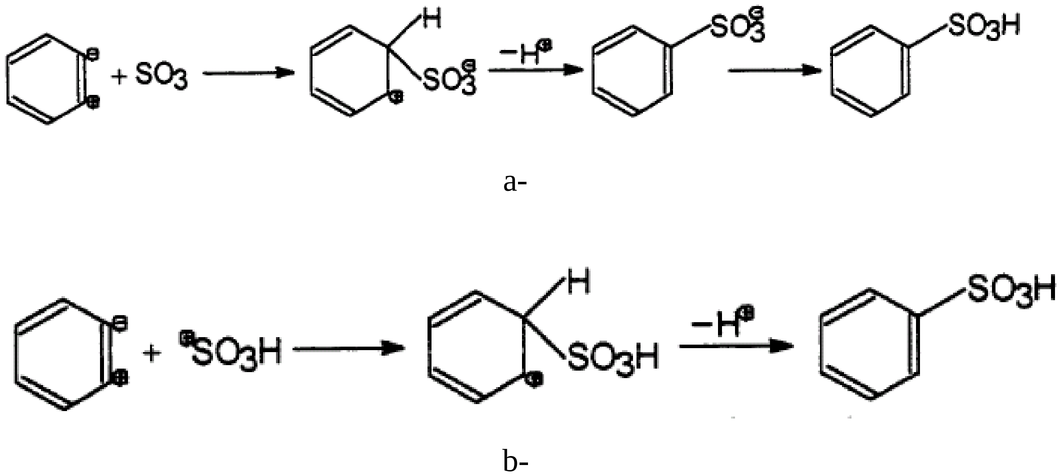


Fig.(4.6): Sulphonation of aromatic systems with; a-sulphur trioxide and b-sulphonic cation (Kučera and Jančář, 1998).

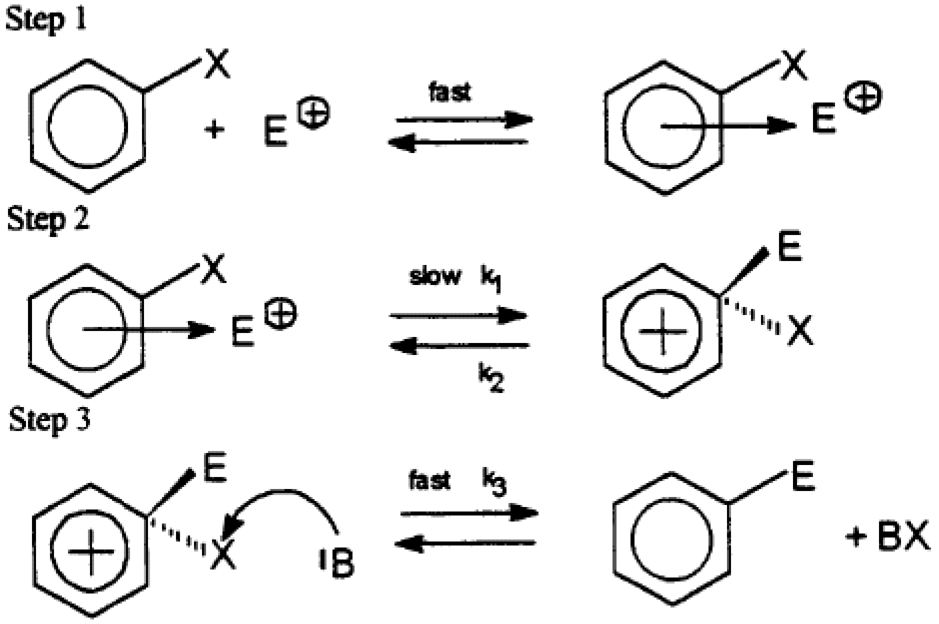


Fig. (4.7): General mechanism of the sulphonation reaction: Step 1: Formation of the π-complex, Step 2: Formation of the arenium ions (δ-complex), Step 3: Termination of the sulphonation by the release of X^+ (Kučera and Jančář, 1998).

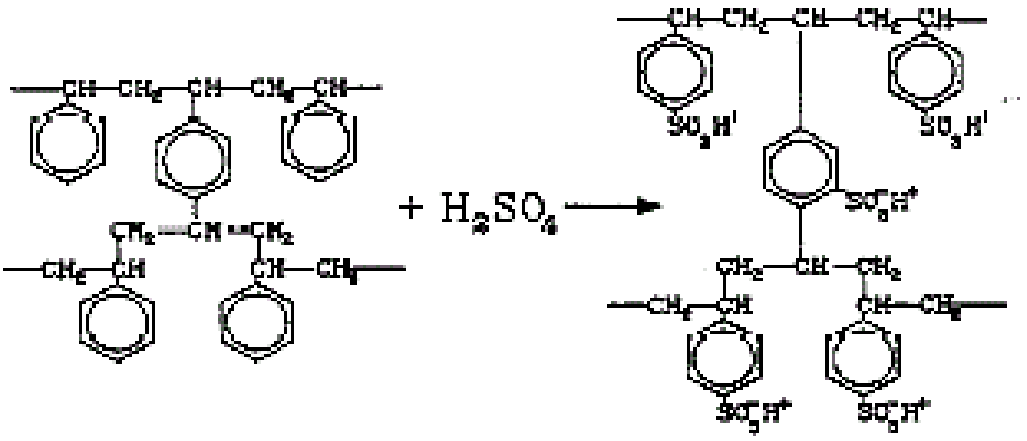


Fig. (127): Chemical structure of a sulphonated crosslinked PHP (Wakeman et al., 1998).

Sulphonation of polymers can be carried out as a homogenous or heterogeneous reaction (Kučera and Jančář, 1998) in a batch or a continuous process (Foster, 1997). The first homogenous sulphonation reaction was carried out using SO_3H /SO_3Cl as a sulphonating agent in a chloroform solution at -20 C (Kučera and Jančář, 1998). Details of different homogenous sulphonation processes are well described in the literature (Lin et al., 2004; Huang et al., 2001; Hanying et al., 1999; Feng et al., 1998; Kahraman et al., 1998; Weiss et al., 1991; Bagrodia et al., 1987; Bailly et al., 1987; Lundberg and Thaler, 1983; Thaler, 1983; Turbak, 1962). In heterogeneous sulphonation, as the name implies, the compound and sulphonating agent exist in different phases. Since in this sulphonation method there is no solvent problems nor it is necessary to separate out the sulphonated product from the reaction mixture, this method is considered advantageous over the homogenous one (Kučera and Jančář, 1998). There have been several studies in the literature disclosing sulphonation attempts based on this method (Toro et al., 2008; Hamza et al., 1997; Akovali and Ozkan, 1986; Regas, 1984). The degree of sulphonation can be expressed as the percentage of available benzene rings within the polymer structure that attain SO_3H groups. Due to polymer internal stresses as a result of polymer swelling and subsequently inability of the sulphonating agent to effectively penetrate through the material/polymer to be sulphonated (Akay et al., 2005), complete (100 %)

sulphonation is impossible (Wakeman et al., 1998). Also, Wakeman et al. (1998) concluded that temperature has an effect on the degree of sulphonation attained. It was found that the higher the temperature, the higher the degree of sulphonation and the shorter the required time to attain that degree of sulphonation.

Although, current sulphonation techniques might be powerful and; therefore, have found a wide range of applications; however, they reportedly suffer from some drawbacks. Among these are:

- Production of hazardous waste; that's the spent acid (dilute sulphuric acid) which requires a special disposal procedure; otherwise, it can be dangerous (Akay et al., 2005; Gopichandran et al., 2003);
- Promotion of side reactions, particularly at elevated temperatures (Gopichandran et al., 2003; Roth, 1957);
- Though sulphonation is a very rapid reaction; nevertheless, it is highly exothermic and *does* require some sort of cooling to avoid occurrence of side reaction(s) (Gopichandran et al., 2003);
- Necessity for precise control and difficulty to scale up (Gopichandran et al., 2003; Roth, 1957);
- Use of excessive amounts of sulphonating agents, perhaps due to low solubility of product in the reaction environment (Ergenekon et al., 2011; Gopichandran et al., 2003); and
- A long processing time is required (Ergenekon et al., 2011).

These light weight PHPs are produced with open cellular microstructures with a very high degree of porosity (of up to 97 %) and interconnectivity and homogenous morphology, low bulk density less than 0.15 g/m^3 (Sergienko et al., 2002) and good mechanical/thermal properties (Livshin and Silverstein, 2008; Haibach et al., 2006; Menner et al., 2006; Krajnc et al., 2005; Benson, 2003; Hoisington et al., 1997; Bhumgara, 1995). In fact, these polymers are characterized with accessibility of their pores, controllability of the pore and interconnected structures (pore sizes of 0.5-5000 µm have been reported), flexibility of production and chemical modification of their walls (Akay et al., 2005). Internal morphology of a PHP polymer can be revealed by an environmental scanning electron microscopy (ESEM). Within its internal network, PHP polymer pores, which in reference to the preparation conditions usually have a size of (5-100) μm (Haibach et al., 2006; Zhang and Cooper, 2005; Sergienko et al., 2002) connected via pore throats, are shown in Fig. (4.9) and an average surface area of 5 m^2 /g is reported (Haibach et al., 2006; Hainey et al., 1991). According to Williams et al. (1990), the concentration of polymerization initiator (e.g. potassium persulphate) in the aqueous phase has an adverse effect on the pore size of the resultant polymer. Likewise, this is also the case with a PHP pore size and the concentration of crosslinker (DVB) used, i.e., the lower the concentration of DVB is, the bigger the pores would be (Benson, 2003).

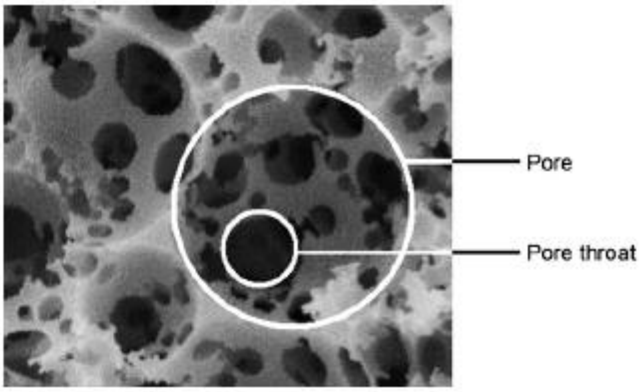


Fig. (4.9): Definition of pore and pore throat (Menner et al., 2006).

Due to their unique properties pointed out above, these post-functionalized (sulphonated) PHPs have found numerous applications in quite diverse ranges. Some of these are: filtration media (Haibach et al., 2006; Akay et al., 2005; Krajnc et al., 2005; Zhang and Cooper, 2005; Kučera and Jančář, 1998; Akay et al., 1995; Bhumgara, 1995; Hainey et al., 1991), support for heterogenic catalytic reactions (Haibach et al., 2006; Zhang and Cooper, 2005), tissue engineering applications (Ergenekon et al., 2011; Burke et al., 2010; Haibach et al., 2006; Menner et al., 2006; Akay et al., 2005; Barbetta et al., 2005; Zhang and Cooper, 2005; Busby et al., 2002; Busby et al., 2001; Hoisington et al., 1997), ion exchange module systems (Ergenekon et al., 2011; Menner et al., 2006; Naim et al., 2004; Benson, 2003; Kučera and Jančář, 1998; Wakeman et al., 1998; Hoisington et al., 1997), monolithic polymer supports for catalysis applications (Menner et al., 2006; Sergienko et al., 2002), removal of arsenic from contaminated water sources (Katsoyiannis and Zouboulis, 2002), production of nickel electrodeposits (Brown et al., 1999; Sotiropoulos et al., 1998), cleaning materials (Hoisington et al., 1997), medical applications, e.g., absorbent for body fluids (Hoisington et al., 1997; Hainey et al., 1991; Haq, 1985) and to enhance osteoblast growth and differentiation in vitro (Bokhari et al., 2005) and help growth of human stem cell-derived neurons (Hayman et al., 2005; Hainey et al., 1991), immobilization of pseudomonas syringe for the degradation of phenol (Erhan et al., 2004) and they also have even been used in the aerospace industry as well (Hoisington et al., 1997), etc.

4.2.6 Mechanism of Microfiltration

Generally, during microfiltration there are two scenarios encountered; surface filtration (sieving) and depth filtration. This is largely influenced by particle size/membrane pore size ratios. Surface filtration is usually used in crossflow filtration whereas depth filtration is used in dead-end filtration mode (Matsumoto et al., 1999) At larger ratios compared to unity, membrane pores, particularly those membranes with uniform pore size distribution, are not able to permit particles to pass through i.e. high permeate quality. Accordingly, particles will accumulate on the membrane surface (surface filtration) creating a filter cake layer. This is known as sieving mechanism in which smaller particles can easily go through the membrane pore, comparatively larger particles will block the membrane pore and other particles will stick to the membrane surface as shown in Fig. (4.10) (Kosvintsev et al., 2004; Starov et al., 2002; Filippov et al., 1994). On the other hand, in depth filtration, membranes with broad pore size distribution and larger than particle size can, accommodate these particles into their pore structure (Matsumoto et al., 1999). In real applications; however, the filtration behaviour cannot be described distinctively as surface filtration nor depth filtration, as both mechanisms may exist.

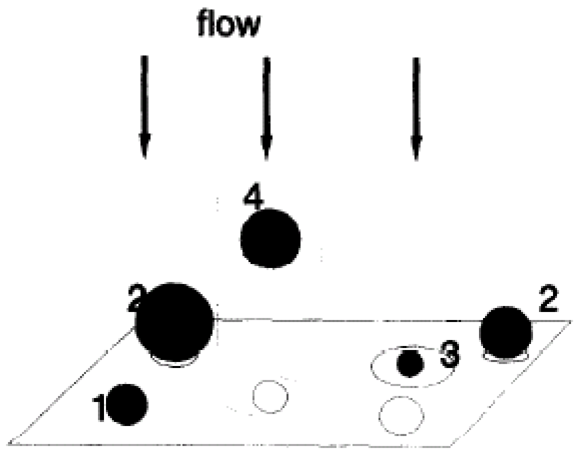


Fig. (4.10): Sieving mechanism. Reproduced from Filippov et al. (1994)

4.2.7 Conventional Filtration vs. Crossflow Filtration

Traditionally, filtration processes were conducted by supplying the feed stream in a normal mode against the filtration media; that's perpendicular to the membrane surface (Dead-end filtration) (de Morais Coutinho et al., 2009; Kosvintsev et al., 2004; Starov et al., 2002; Al-Malack and Anderson, 1997; Wakeman and Akay, 1997; Scott, 1996; Belfort et al., 1994). Due to pressure drop between the two sides of the filter, separation takes place which is also dependent on filter thickness, pore size and feed particles size. Larger particles than filter pores are retained which with time result in gel/cake layer formation; that's continuously growing as the filtration proceeds, and filter fouling. Gel/cake layer and membrane fouling result in a continuous catastrophic deterioration in filter performance as the filtration process proceeds (de Morais Coutinho et al., 2009; Song, 1998). A schematic representation of a standard dead-end filtration process is shown in Fig. (4.11).

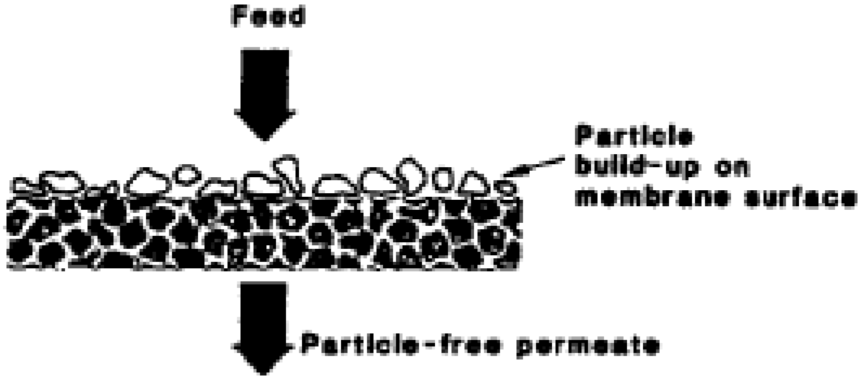


Fig. (4.11): Dead-end Filtration (Noble and Stern, 1995).

However, in crossflow filtration, as the name suggests, the feed stream flows parallel to the filter as shown in Fig. (4.12). Larger particles will be caught by the filter, but instead of complete accumulation on the filter surface, some of them will be continuously forced to flow away from the filter surface under the influence of crossflow; this in turn maintains a steady state operation over a prolonged period of operation time (de Morais Coutinho et al., 2009; Hu and Scott, 2008; Fradin and Field, 1999; Elmaleh et al., 1998; Song, 1998; Al-Malack and Anderson, 1997; Wakeman and Akay, 1997; Scott, 1996; Akay and Wakeman, 1994a; Belfort et al., 1994; Tarleton and Wakeman, 1988; Wakeman and Tarleton, 1987).

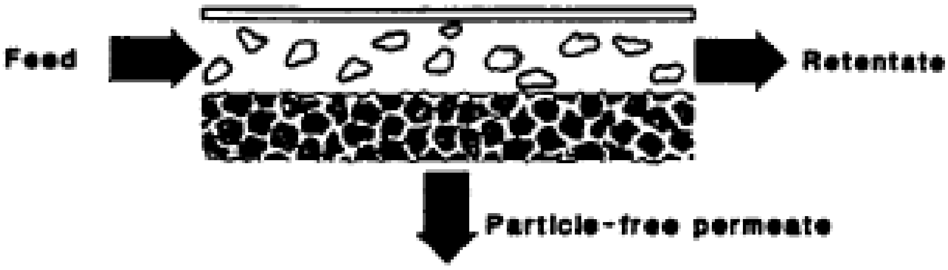
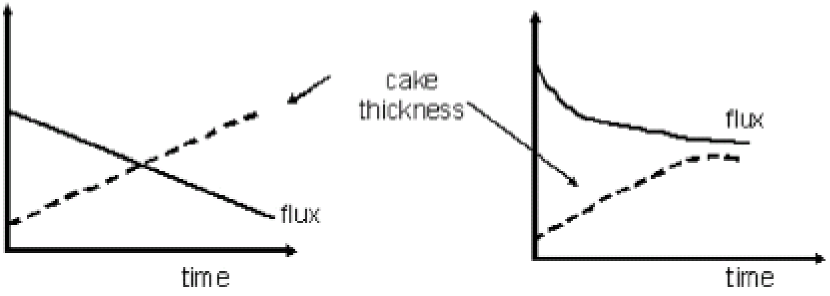


Fig. (4.12): Crossflow filtration (Noble and Stern, 1995).

There are some features that make crossflow microfiltration processes advantageous over conventional ones. In crossflow microfiltration, with respect to its underlying principle of tangential flow which inhibits the growth of gel/cake layer through shear forces in case of dispersion/suspension filtration; respectively, it is possible to control permeate flux decline with time (steady-state operation), refer to

Fig. (4.13) (de Morais Coutinho et al., 2009; Wakeman and Akay, 1997; Akay and Wakeman, 1996; Scott, 1996; Scott and Hughes, 1996; Tarleton and Wakeman, 1993; Roy et al., 1989). To this end, it is feasible to produce higher permeate fluxes compared to those obtained from conventional filtration processes (i.e. no crossflow) in which the gel/cake layer is continuously growing (Al-Malack, 2003; Fradin and Field, 1999; Belfort et al., 1994; Romero and Davis, 1988; Wakeman and Tarleton, 1987; Baker et al., 1985). In addition, in terms of product quality, effluent quality deterioration is present in conventional filters, whereas permeate quality in crossflow microfiltration is constant and reliable, irrespective of solute concentrations. It was also claimed that a pre-treatment is required for a conventional filter to be capable of producing an effluent that’s comparable with a permeate quality obtained from a crossflow microfiltration process in which no pre-treatment is necessary in doing so. Compactness and capital cost reduction are also achieved with crossflow microfilters implementation (Al-Malack, 2003).



a- b-

Fig. (4.13): Membrane flux and cake growth rate variation with time: a- conventional (perpendicular) filtration; b- crossflow (tangential) filtration. Modified from (de Morais Coutinho et al., 2009).

4.3 Characterization of Microfiltration Membrane Performance

4.3.1 Transient Filtration

‘Permeation rate or flux is the volumetric (mass or molar) flow rate of fluid passing through the membrane per unit area of membrane per unit time’ (Scott and Hughes, 1996). Permeate flux rate *(J)* according to Darcy’s law, introduced by Henry Darcy in 1856, is usually used to characterize microfiltration of viscous incompressible flows through a porous media (Waeger et al., 2010; de Morais Coutinho et al., 2009; Kukizaki and Goto, 2008; Belkacem et al., 2007; Hu and Scott, 2007; Li et al., 2006a; Lobo et al., 2006; Mohammadi et al., 2005b; Mohammadi et al., 2004; Mohammadi et al., 2003; Tay et al., 2003; Waniek et al., 2002; Tansel et al., 2000; Akay et al., 1998; Choo and Lee, 1998; Nassehi, 1998; Mueller et al., 1997; Elmaleh and Ghaffor, 1996; Nazzal and Wiesner, 1996; López et al., 1995; Juang and Jiang, 1994; Scott et al., 1994; Blanpain et al., 1993; Scott et al., 1992; Baker et al., 1985; Hubbert, 1956). In this formula, filter/membrane permeate is related to the driving force (pressure drop), flow resistance and viscosity of the filtered medium. As it will be indicated in the equation below, permeate flux is proportional with pressure drop but inversely with the summation of external resistance due to concentration polarization, membrane and deposits resistances. In addition, membrane permeation may also be directly influenced by the dynamics of the stream being processed i.e. too viscous systems will, to a large extent, obstruct membrane permeation. In case of both emulsion viscosity and membrane resistances are constant throughout the filtration process; TMP is proportional to membrane flux.

$$J = \text{driving force} / (\text{viscosity})(\text{total resistance})$$
$$J = P/\mu\ (R_{ef} + R_m + R_d) = 1/A\ dV/dt$$

Where P is the driving pressure (pressure drop across the membrane), μ the dynamic viscosity, R_{ef} the external and reversible resistance due to concentration polarization on the membrane surface, R_m the membrane resistance, R_d the deposit resistance, A filter/membrane surface area and V is the filtrate volume.

4.3.2 Particle/Droplet Retention by the Membrane

In addition to permeate flux, particles/droplets of solute rejection R by the membrane body is also another important feature in crossflow microfiltration processes; the latter highly influences the former. In fact, under steady state conditions, the permeate flux decreases as the rejection increases (Akay and Wakeman, 1994a; Wakeman and Akay, 1994). This to a large extent determines the efficiency of the membrane separation process. The rejection of a filtration process *R* is defined as:

$$R\,(\%) = (C_F - C_P)/\,C_F * 100$$
$$= (1 - C_P/\,C_F)/* 100$$

Where C_F and C_P as were shown in Sec. 4.2.1, are the concentration of the solute in the feed stream and permeate, respectively. According to this formula, for a given membrane, too low solute concentrations in the permeate side in comparison to those of the feed stream result in complete rejection ca. 100 %. Also, solute droplet/particle size and membrane pore size are important parameters in membrane rejection tendency, as membranes with smaller pores than particle size can demonstrate total rejection (Chen et al., 2009; de Morais Coutinho et al., 2009; Qiu et al., 2009; Chakrabarty et al., 2008; Barona et al., 2007; Li et al., 2006a; Lobo et al., 2006; Mohammadi et al., 2003; Shen et al., 2003; Herath et al., 2000; Xu et al., 1999; Akay et al., 1998; Ohya et al., 1998; Field, 1996; Scott, 1996; Yildiz et al., 1996; Karakulski et al., 1995; Akay and Wakeman, 1994b; Akay and Wakeman, 1994a; Juang and Jiang, 1994; Fell et al., 1990)

4.4 Mechanism of the Permeate Flux Decline

Membrane fouling is a source of concern in membrane technology (Huang et al., 2012; Waeger et al., 2010; Field, 1996). It mainly results from building up of some components of the stream to be filtered on the membrane surface or within the membrane pores (Huang et al., 2012; de Morais Coutinho et al., 2009; Fakhru'l-Razi et al., 2009; Mohammadi et al., 2004; Matsumoto et al., 1999; Cornelissen et al., 1998; Akay and Wakeman, 1994a; Scott et al., 1994). It is; therefore, obvious that streams with higher fouling material(s) concentration(s) may further multiply the flux decline problem (Palacios et al., 2002). There are two types of fouling; these are external and internal fouling. External fouling (cake formation/concentration polarization) is often reversible and it is thought to take place in the initial stages of filtration (Howarter and Youngblood, 2009; Mohammadi et al., 2003; Vernhet et al., 2003; Field et al., 1994; Bowen and Sabuni, 1991; Gekas and Hallström, 1990). It occurs in cases where membrane pores are smaller than the solute molecules in the feed solution; thus, solute molecules cannot pass through the membrane and will gather at the membrane surface leading to the formation of a gel-like layer that seals the membrane pores (de Morais Coutinho et al., 2009; Vincent Vela et al., 2009; Ohya et al., 1998; Belfort et al., 1994; Tarleton and Wakeman, 1993; Wakeman and Tarleton, 1987). Internal fouling (membrane fouling); however, is most of the time irreversible and is the main type of fouling in microfiltration processes (Howarter and Youngblood, 2009; Wenten, 1995; Bowen and Sabuni, 1991). This type of fouling occurs when membrane pores are larger than the solute molecules. The latter will easily enter the membrane pore resulting in deposition and adsorption of solute molecules on membrane pore walls leading to fouling that can be described as irreversible (de Morais Coutinho et al., 2009; Vincent Vela et al., 2009; Mohammadi et al., 2003; Vernhet et al., 2003; Tansel et al., 2000; Ohya et al., 1998; Field et al., 1994; Tarleton and Wakeman, 1993). If the membrane pores and solute molecules are similar in size, partial pore blocking is the outcome (de Morais Coutinho et al., 2009; Vincent Vela et al., 2009; Tansel et al., 2000; Ohya et al., 1998; Tarleton and Wakeman, 1993).

Both of these mechanisms can lead to membrane flux decline. External fouling creates an additional layer of resistance to permeate flow, while internal fouling increases the membrane resistance by reducing the effective size of the membrane pores (Mohammadi et al., 2003; Nicolaisen, 2002; Wakeman and Williams, 2002; Belfort et al., 1994; Le et al., 1984). Although membrane fouling is, to an extent, found in all membranes, the mechanism by which it occurs is largely dependent on the system under scrutiny including: emulsion droplet size, operating parameters and the type of membrane used (Salahi et al., 2010; Cornel and Krause, 2008; Vernhet et al., 2003; Cumming et al., 2000; Mueller et al., 1997; Trägårdh, 1989). These phenomena of concentration polarization, gel layer formation, adsorption of contaminants within the membrane pores and pore blockage are all shown in Fig. (4.14). Ultimately as a result of membrane fouling, membrane performance is reduced, operational cost, e.g. pumping costs and energy consumption are increased and risk of membrane replacement, in case of severe fouling becomes inevitable (Chen et al., 2009; Howarter and Youngblood, 2009; Lobo et al., 2006; Shen et al., 2003; Tay et al., 2003; Vernhet et al., 2003; Mohammadi et al., 2002; Nicolaisen, 2002; Srijaroonrat et al., 1999; Field, 1996; Scott, 1996; Wenten, 1995; Field et al., 1994; Roesink et al., 1991; Gekas and Hallström, 1990; Wakeman and Tarleton, 1986). In the following two sections, these two phenomena are further discussed.

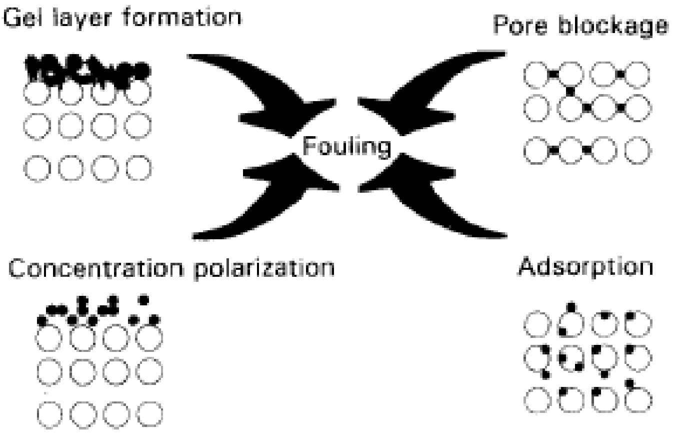


Fig. (4.14): Membrane fouling mechanisms (Tansel et al., 2000).

4.4.1 Concentration Polarization

As far as the filtration process is concerned, some molecules/particles of the liquid/colloid to be filtered will pass through the membrane while others will be retained depending on their size and membrane pore size distribution. Those retained, due to their larger size than membrane pores and under the influence of process conditions, will deposit on the membrane surface and eventually a layer of these deposits will build-up and work as a secondary membrane, as shown in Fig. (4.15) (Salahi et al., 2010; de Morais Coutinho et al., 2009; Del Colle et al., 2007; Mohammadi et al., 2003; Herath et al., 2000; Srijaroonrat et al., 1999; Al-Malack and Anderson, 1997; Akay and Wakeman, 1996; Wenten, 1995; Akay and Wakeman, 1994b; Akay and Wakeman, 1994a; Belfort et al., 1994; Wakeman and Tarleton, 1986). Mathematical models that illustrate the development of this secondary membrane are described by Akay and Wakeman (Akay and Wakeman, 1996). The thickness of this layer at steady-state is constant with time but it builds up with the distance from the membrane (Romero and Davis, 1988). One important aspect of this layer is that its high concentration of solute molecules (particles) at the side that’s adjacent to the membrane surface, with this concentration diminishes as the distance to the membrane surface increases. As a result, a concentration gradient generates in the perpendicular direction to the membrane surface (Concentration polarization/concentration boundary layer) as shown in the schematic diagrams below Fig. (4.15-16) (Herath et al., 2000; Wakeman and Akay, 1997; Field, 1996;

Parvatiyar, 1996; Akay and Wakeman, 1994a; Belfort et al., 1994; Schulz and Ripperger, 1989; Romero and Davis, 1988; Wakeman and Tarleton, 1987; Baker et al., 1985; van Gassel and Ripperger, 1985). Understanding the behavioural nature of this layer is a key in membrane processes.

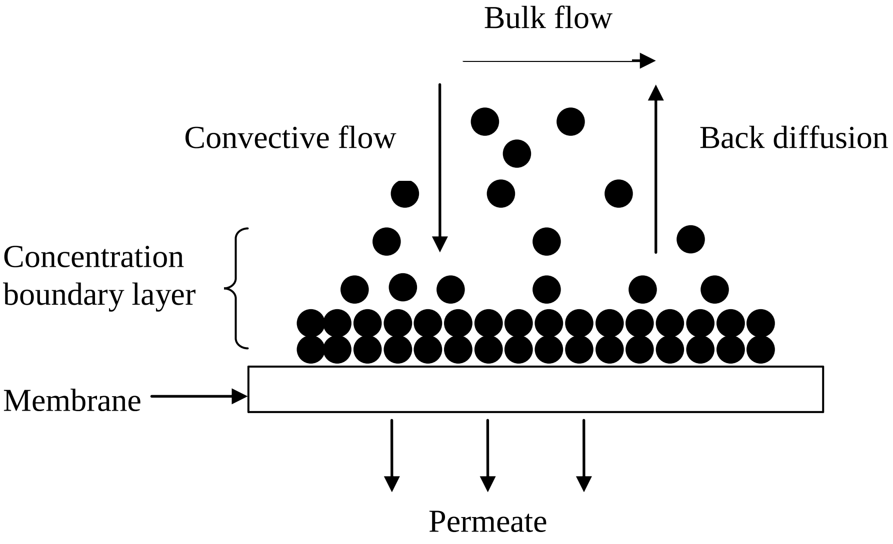


Fig. (4.15): Schematic diagram of concentration polarization. Reproduced from (Herath et al., 2000).

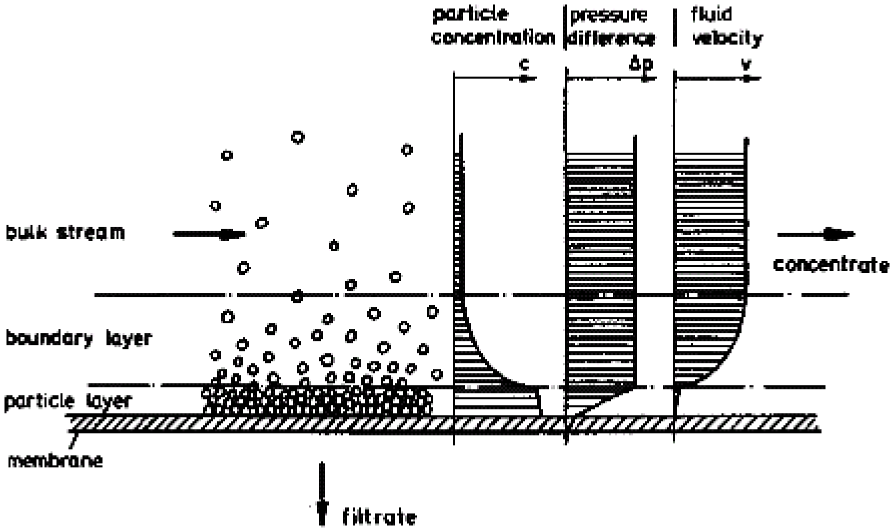


Fig.(4.16): Schematic diagram of concentration polarization (van Gassel and Ripperger, 1985).

Once this layer has established, which usually does not require a long time (Del Colle et al., 2007; Field, 1996; Fell et al., 1990; Gatenholm et al., 1988), it acts as a new membrane (dynamic membrane) for smaller molecules which normally would not be retained by the original membrane. In fact, this layer leads to a performance decay (permeate reflux degradation) of microfiltration membranes through the alteration of interactions between solvent, solutes and membrane surface (Mohammadi et al., 2003; Akay and Wakeman, 1994b). The properties of the liquid to be filtered, such as: its particle size distribution, concentration and viscosity along with filtration operational factors including membrane pore size, feed velocity and TMP, have an important effect on the development of this layer (Akay and Wakeman, 1994b; Fell et al., 1990; Schulz and Ripperger, 1989). Under steady-state conditions, the concentration gradient is constant since the same amount of large deposits diffuses back to the bulk lending their place, on the membrane surface, to new deposits brought in under convective flow (Wakeman and Williams, 2002; Elmaleh et al., 1998; Benkahla et al., 1995; Fell et al., 1990; van Gassel and Ripperger, 1985). In another detailed studies by Romero and Davis (1990; 1988), a deeper insight into this layer, suggests that depending on the flow conditions on the membrane surface (Tarleton and Wakeman, 1993), it comprises two layers; a flowing layer and a stagnant layer, the latter layer is beneath and more concentrated than the former one. This layer increases the hydraulic resistance to flow which means a declined flux (Herath et al., 2000; Field, 1996; Wu and Howell, 1992; Schulz and Ripperger, 1989; Romero and Davis, 1988; van Gassel and Ripperger, 1985). In addition, with regards to the non-linear velocity profile within this layer that molecules/particles close to the membrane surface are stationary i.e. their velocity is zero; however, the difference in velocity diminishes with the distance from the membrane surface until it becomes nil in regions away from the surface where the dominant velocity is the bulk one (Field, 1996; Gatenholm et al., 1988; van Gassel and Ripperger, 1985). However, an opposite trend is reported on viscosity, as this layer is characterized with higher viscosity at the membrane surface compared to that of the bulk stream (Field, 1996; Fell et al., 1990; Gatenholm et al., 1988; Romero and Davis, 1988).

4.4.2 Membrane Fouling

Membrane fouling means reduced membrane permeability, it has the units of: permeate volume/ (membrane area) (time) (pressure) (Cornel and Krause, 2008). There are two mechanisms that lead to membrane fouling: membrane pore blocking and cake formation; the former, as filtration time elapses, results in the latter. Membrane pore blocking by retained particles contributes to the sharp flux decline that takes place in the early stage of filtration through increased membrane resistance. Long-term and gradual flux degradation; however, is attributed to the formation and growth of cake layer which performs as an additional layer of resistance to the permeate flow. Solute adsorption, particle deposition within membrane pores and changes in the cake layer can further complicate/simplify membrane fouling (de Morais Coutinho et al., 2009; Howarter and Youngblood, 2009; Srijaroonrat et al., 1999; Song, 1998).

Prior to membrane pore blocking; once filtration has commenced, permeate flux rate is virtually a maximum since all membrane pores are available (unblocked). As filtration proceeds, a time will come when membrane pores are blocked. Shape and relative size of particles and membrane pores dictate the degree of blockage. For instance, complete pore blocking occurs when both particles and pores are of comparable shape and size. Further particles retention by the membrane body with pre-blocked pores leads to the formation of a growing cake layer on the membrane surface. Due to this layer, permeate flux rate further declines through increased resistance to the permeate flow (Tay et al., 2003; Song, 1998).

This resistance is largely influenced by membrane properties and its tendency to pore blockage as well as by the permeability of the formed fouling layer on the membrane surface. Chemical compatibility, wettability and resistance to temperature, pressure and pH may help tackle the problems associated with membrane properties and its susceptibility to pore blocking. The permeability of the resultant layer is a sensitive function of some operational parameters, which have considerable effect on the filtration hydraulic system, such as: feed velocity, pressure, temperature and concentration, as they determine the extent of turbulence, shear stresses and layer thickness (Koltuniewicz et al., 1995). Both pore blocking and cake formation have been used to explain flux decline mechanism(s) in filtration processes. For this, several physical models based on constant pressure filtration (Hermia's model) and surface renewal model have been developed. According to Hermia's model the mechanism of flux decline in microfiltration can be explained by the following (Saxena et al., 2009; Mohammadi et al., 2003; Waniek et al., 2002; Field, 1996; Koltuniewicz and Field, 1996; Koltuniewicz et al., 1995; Belfort et al., 1994):

4.4.2.1 Complete Pore Blocking Model

This model postulates that each particle participates in blocking of membrane pores and particles are not superimposed upon one another as depicted in Fig. (4.17- a). The blocked surface area is proportional to the permeate volume.

4.4.2.2 Standard Pore Blocking Model

According to this model, Fig.(4.17- b), the particle diameter is much less than the pore diameter; therefore, particles can enter most pores, deposit on the pore walls and; thus, reduce the pore volume. The decrease of pore volume is also proportional to the permeate volume.

4.4.2.3 Intermediate Pore Blocking Model

In this model, see Fig. (4.17- c), it is assumed that the number of blocked pores is also proportional to the permeate volume, but it is less restrictive in such a way that not every particle necessarily blocks the pores and particles may settle on other particles.

4.4.2.4 Cake Filtration Model

This model states that the permeate flow is reduced by increasing the resistance on the membrane surface where retained solute is accumulated as shown in Fig. (4.17- d). The total resistance is; therefore, the sum of membrane resistance and resistance of the cake layer that's proportional to the mass of solute accumulated and consequently to the volume of filtrate.

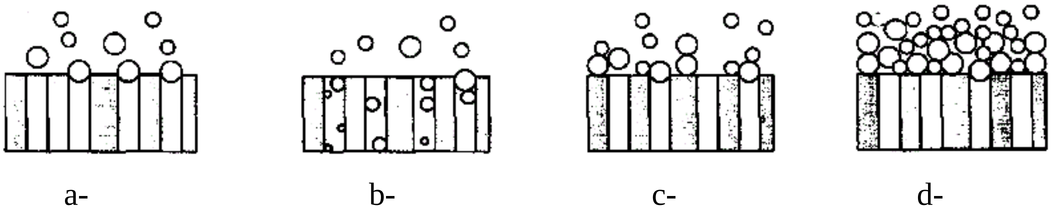


Fig. (4.17): Mechanisms of pore blocking: a- complete blocking, b- standard blocking, c- intermediate blocking and d- cake filtration. Reproduced from (Koltuniewicz and Field, 1996)

4.5 Measures for Reducing Concentration Polarization and Membrane Fouling

Flux decline, due to concentration polarization and membrane fouling, is a common and inevitable phenomenon in filtration processes. There have been a number of methods to improve microfiltration by reducing concentration polarization and membrane fouling. Generally, high crossflow velocities can be employed to reduce or mitigate this problem, as was demonstrated in a study by Wu and Howell (Wu and Howell, 1992); the higher the flow rates, the lower the concentrations of deposits are. Furthermore, moderate/low TMP can be applied as another measure to overcome this problem as high pressures were found to increase the amount of deposited material (Wu and Howell, 1992). Low pressure is also desirable in order to avoid compaction of the deposits on the membrane surface (Wakeman and Williams, 2002). Membrane surface modification to alter the membrane-molecules/particles interaction characteristics may also be useful in this regard (Srijaroonrat et al., 1999; Gatenholm et al., 1988; Anderson et al., 1987). A summary of some suggested techniques is given in Table (4.2) which is based mainly on a study by Wakeman and Williams (Wakeman and Williams, 2002).

Several strategies can be implemented in order to reduce both concentration polarization and membrane fouling. By doing so, membrane cleaning can be considered as non-compulsory requirement. Factors that lead to concentration polarization and membrane fouling reduction include; physical and chemical feed treatment/conditioning, membrane properties, flow conditions, enhancement of filtration performance through coupling filtration with some external electrical/ultrasonic fields and/or back-flow. An assortment of these techniques used to reduce membrane fouling is listed in Table (4.2), which is based on some studies and suggestions from some researchers (Fakhru'l-Razi et al., 2009; Cornel and Krause, 2008; Nicolaisen, 2002; Wakeman and Williams, 2002; Srijaroonrat et al., 1999; Akay et al., 1998; Holdich et al., 1998; Akay and Wakeman, 1996; Field, 1996; Scott and Hughes, 1996; Belfort et al., 1994; Bowen and Sabuni, 1991; Trägårdh, 1989; Hsieh et al., 1988).

Table (4.2): Measures for reducing concentration polarization and membrane fouling.

No.	Technique	Approach/procedure	Contribution	Influence	Reference(s)
1-	Feed pre-treatment a- Physical processes b- Chemical processes.	-Centrifugation. - Pre-filtration. - pH adjustment. - Precipitation. - Coagulation. - Flocculation. - Use of proprietary chemicals (antiscalants/ disinfectants).	- To remove suspended macromolecules, particulates or solids. - To keep molecular/colloidal foulants away from their isoelectric point.	- To avoid deposits on membrane surface and clogs in the membrane. - To reduce molecular/colloidal foulants propensity to form a gel layer.	(Cornel and Krause, 2008; Nicolaisen, 2002; Wakeman and Williams, 2002; Belfort et al., 1994; Bowen and Sabuni, 1991; Trägårdh, 1989; Hsieh et al., 1988).
2-	Appropriate membrane selection.	- Membrane material with low solute interaction character as possible (hydrophilicity-hydrophobicity), compatibility with feed pH, temperature and chemical composition.	- To weaken solute(s)-membrane surface attachment.	- To enhance membrane permeability. -To make membrane cleaning easier since the solute is loosely attached to the membrane surface.	(Fakhru'l-Razi et al., 2009; Matsumoto et al., 1999; Belfort et al., 1994; Bowen and Sabuni, 1991; Trägårdh, 1989; Tarleton and Wakeman, 1988).
3-	Flow manipulation (adjustment).	- Turbulence (instability) and local vortex promoters via	- To disturb foulants. - To induce fluid mixing	- To increase shear rate at the membrane surface via	(Cornel and Krause, 2008; Wakeman and

		rotational, leakage, helical, tortuous or corkscrew flow (through inserts), static mixing and oscillation (pulsation).	at membrane-solution interface.	high feed flow rates.	Williams, 2002; Akay et al., 1998; Holdich et al., 1998; Belfort et al., 1994; Bowen and Sabuni, 1991).
4-	Dynamic filtration.	- Rotating membrane. - Vibrated membrane.	- To develop high shear stress (higher than that obtained via high flow rates) at the membrane surface and pores.	- Increased filtration rate.	(Wakeman and Williams, 2002; Belfort et al., 1994).
5-	Gas spargeing.	- Gas spargeing.	- To disrupt polarization concentration layer.	- Increased filtration rates.	(Wakeman and Williams, 2002).
6-	Electric field.	- Electric field.	- To supply stream particles/molecules with electrophoretic velocity.	- Increased filtration rates.	(Wakeman and Williams, 2002; Akay and Wakeman, 1996; Bowen and Sabuni, 1991; Tarleton, 1988; Tarleton and Wakeman, 1988; Wakeman and Tarleton, 1986).
7-	Ultrasonic field.	- Ultrasonic field.	- To reduce stream viscosity and bring changes in particles surface properties.	- Increased filtration rates.	(Wakeman and Williams, 2002; Tarleton, 1988).
8-	Combined electrical and ultrasonic fields.	- Simultaneous electric and ultrasonic fields.	- Refer to the above.	- Increased filtration rates.	(Wakeman and Williams, 2002; Akay et al., 1998;

					Tarleton, 1988).
9-	Periodic backflushing.	- Use of chemicals. - Reversing flow direction.	To clean the membrane by removing deposited material(s) from membrane surface To clean the membrane by removing pore fouling if deposits are not firmly adhering to pores walls.	To restore original membrane performance characteristics.	(Cornel and Krause, 2008; Wakeman and Williams, 2002; Srijaroonrat et al., 1999; Hsieh et al., 1988; Tarleton and Wakeman, 1988).

In fact, some of these techniques might not be applicable due to some process constraints; others may not have a significant effect. According to Tarleton (Tarleton, 1992) such techniques, due to either economic grounds or practical difficulties, have been considered as 'technologies awaiting applications'. Although with turbulence flow inserts, energy saving of 20 % can be achieved and that membrane fluxes are 50-300 % enhanced in comparison to conventional microfiltration processes. However, employing such inserts does not appear widely applied in commercial applications. The gas sparging technique is less efficient (60-270 % flux rates improvement) than turbulence/vortex promoters and with some complexity that's imposed by gas injection. Also, with respect to backflushing, it may only be able to deal with membrane-surface deposits; however, this technique becomes limited when severe foulants adhesion or pore fouling has taken place. Furthermore, in the two available cleaning approaches; cleaning-in-place (CIP) and cleaning-out-off-place (COP), downtimes are present; they are shorter in CIP than COP. In addition, when considering backflushing with chemicals, care should be taken to select an appropriate cleaning solution that's efficient to remove membrane foulant(s) whilst being compatible with membrane material(s) as; otherwise, membrane swelling/damage is envisaged (Wakeman and Williams, 2002; Schulz and Ripperger, 1989).

4.5.1 Enhancement of Membrane Crossflow Microfiltration by External Electric Field

As demonstrated in Sec.4.4 flux decline in crossflow microfiltration due to concentration polarization and membrane fouling is a serious problem and seems inevitable. Techniques to enhance permeate flux rates through a membrane are; therefore, essential. Many of these techniques were listed in Table (4.2). Among of these techniques was the application of an external electric field to the unit of crossflow microfiltration (electro-microfiltration), which can be through a continuous or pulsed application. Enhancements based on electrical field application have significant potential than other enhancements techniques which rely on changing membrane modules and/or hydrodynamic conditions (Huotari et al., 1999a; Akay and Wakeman, 1996). To this end, throughout this study these enhancements were introduced so as to improve the membrane performance. On the other hand; however, due to some restrictions this approach has not found wide commercial applications. These restrictions include unavailability of cheap and corrosion-resistant electrodes, high power consumption in some circumstances and inefficiency in case of processing streams with relatively low conductivity levels as well as unavailability of engineering aspects to design a suitable module by which the cost can be reduced (Wakeman and Williams, 2002; Huotari et al., 1999b; Huotari et al., 1999a; Bowen and Sabuni, 1991).

There are two possibilities by which an electrical field can be applied in an electrofiltration cell. The electric field can be applied across the membrane with one electrode on either side of the membrane. Alternatively, the electric field can be applied between the membrane that's made of a conductive material, and another electrode, i.e., the membrane here serves as an electrode (Wakeman and Williams, 2002; Huotari et al., 1999b; Huotari et al., 1999a). In this latter setup, energy consumption can be reduced and module construction can be simpler (Huotari et al., 1999a). Electro-microfiltration induces the movement of particles away from the membrane at a rate dependable on their electrophoretic mobility (Wakeman and Williams, 2002; Huotari et al., 1999a; Bowen and Sabuni, 1991; Bowen et al., 1989). This movement; therefore, can help reduce membrane fouling (cake formation) and; therefore, can increase membrane permeate flux rate (Saxena et al., 2009; Wakeman and Williams, 2002; Bowen et al., 1989; Wakeman and Tarleton, 1987). Applying an electrical field across a microfiltration system can further help prevent membrane fouling by gas bubbles, such as hydrogen and oxygen at the cathode and anode; respectively, which may generate by electrolysis (Wakeman and Williams, 2002; Huotari et al., 1999b; Akay and Wakeman, 1996; Scott, 1996). Furthermore, Wakeman and Williams (2002) stated that applying an electrical field to a microfiltration system is more influential when coupled with fairly low feed crossflow velocities. This in addition can directly lead to reduced pumping costs.

The effect of an electric field on the microfiltration behaviour was also examined by Wakeman and Williams (2002), Tarleton and Wakeman (1990) and Wakeman and Tarleton (1987). They observed that introducing an electrical field across the filtration system, as long as it is higher than the threshold current necessary to lift the particles away from the membrane surface, *does* result in enhanced flux rate compared to that obtained with no electric field. Tarleton and Wakeman (1990) have also examined the combined effect of both acoustic and electric fields. Their conclusions show that simultaneous application of the two fields through a synergic effect, further enhances the flux rate with no sharp drop due to fouling. Furthermore, Wakeman and Williams (2002) observed that the enhancement of flux rate through the application of the latter fields (acoustic and electric) is constantly largely greater, in particular in case of small suspension particles with high zeta potentials, than that obtained via the application of the former field (electrical field only). In addition, Tarleton and Wakeman (1990) analyzed the flux decline behaviour in microfiltration of two different suspensions with and without an acoustic field. At the examined conditions, microfiltering both suspensions with no acoustic field gave a lower flux rates in comparison to when an acoustic field was applied. Flux decline was obvious in both cases, i.e. with and without the application of the acoustic field. It was also shown that the distance between the acoustic field source and the membrane is of great importance since higher flux rates were obtained as this distance was shortened. The contribution of acoustic fields in improving the membrane flux rate can be viewed by the high internal forces (vibratory input) being produced near the membrane surface upon its application. Such forces include particle dispersion, viscosity reduction, alterations in particle surface properties and cavitation (Pangu and Feke, 2004; Robins et al., 2002; Wakeman and Williams, 2002; Mason and Cordemans, 1996; Tarleton and Wakeman, 1992). These forces may be able to carry the fouling particles through the filtered stream away from the membrane surface which in turn may help reduce pore blockages.

4.6 Membrane Cleaning

Trägårdh (1989) defined membrane cleaning as ‘a process where material is relieved of a substance which is not an integral part of the material’. Membrane cleaning is usually used in an attempt to restore the original membrane performance characteristics as far as possible. It can be achieved mechanically, thermally and/or chemically. In addition, as it was stated, in the previous section, Sec. 4.5.1, applying an electrical field across a microfiltration system can further help prevent membrane fouling or serve the purpose of membrane cleaning by the microscopic H_2 or O_2 bubbles that generate from a conducting membrane by which fouling deposits on the membrane surface are dislodged (Scott, 1996). Mechanical cleaning relies on introducing a high shear rate at the membrane surface by; for instance, reversing the flow direction (back-flush) so that a part of the permeate/water is forced to flow back through the membrane (Lipp et al., 2005; Cakl et al., 2000; Srijaroonrat et al., 1999; Belfort et al., 1994; Gekas and Hallström, 1990; Trägårdh, 1989; van Gassel and Ripperger, 1985) as shown in Fig. (4.18). Air can also be used to enhance cleaning efficiency and minimize the use of chemicals, if required (Lipp et al., 2005). This should be achieved at a higher circulation flow rate as well as a lower pressure than those applied during the actual filtration procedure.

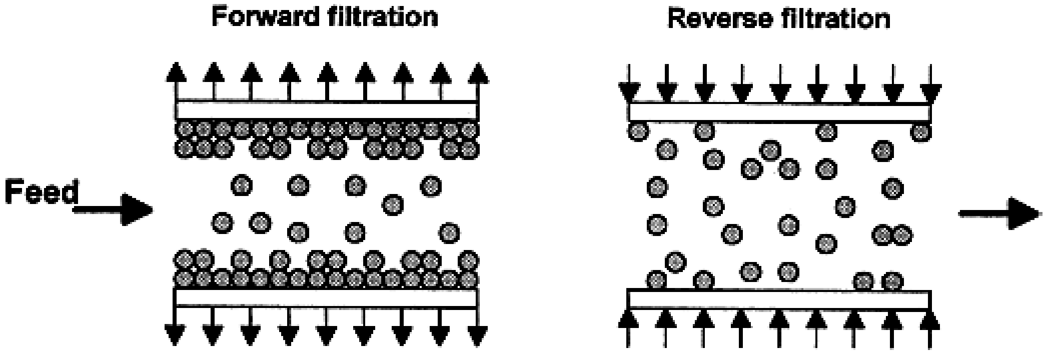


Fig. (4.18): Schematic representation of back-flushing technique (Srijaroonrat et al., 1999).

Reversible fouling, that as mentioned earlier, takes place on the membrane surface and can be dealt with by a physical washing with water. Chemical cleaning procedures; however, have to be employed to conquer irreversible fouling (that may persist after air/water washing) which is encountered in membrane pores (Howarter and Youngblood, 2009; Cornel and Krause, 2008). In chemical cleaning, some chemicals (agents) are employed to restore the original separation membrane characteristics, usually in a negative flow direction (Lipp et al., 2005; Cakl et al., 2000). For this purpose, various chemicals have been used with respect to fouling material and nature. Examples of these chemicals are: bases such as sodium and potassium hydroxides, acids such as nitric acid, different types of surfactants and disinfectants (Mohammadi et al., 2002; Trägårdh, 1989; Hsieh et al., 1988). These chemicals should perform the cleaning task by dissolving and loosening the foulant(s). However, they should not bring new foulant(s) nor damage the filtration system; that’s the membrane itself and the rest of the equipment within the filtration unit (de Morais Coutinho et al., 2009; Mohammadi et al., 2002; Trägårdh, 1989). Therefore, selection of cleaning agent, which is usually carried out by trial and error, must take into account not only the fouling material’s nature, but also the chemical and thermal resistance limits of the membrane system (Mohammadi et al., 2002; Trägårdh, 1989). In addition, these chemicals should be chemically in-reactive with the membrane, cheap, safe and washable with water (Mohammadi et al., 2002; Scott, 1996).

In fact, although with high crossflow velocities and back-flush technique permeate flux in microfiltration processes can be increased, a high velocity requires a higher energy consumption; which entails further cost and complexity (Mohammadi et al., 2004), and is also accompanied with high pressure losses. Furthermore, despite the fact that by back-flushing original permeate flux characteristics can be restored, it diminishes the effective filtration time and when permeate, in particular, is employed for back-flushing, it leads to the contamination of some of the permeate with the feed solution (Mohammadi et al., 2004; Nicolaisen, 2002; Cakl et al., 2000; Wenten, 1995).

4.7 Influence of Operating Conditions and Membrane Properties on Membrane Permeate Flux Rate

Although there are different cleaning techniques, as was shown in Sec. 4.6, that can be used to restore original membrane performance characteristics as possible, these techniques are generally not always quite efficient or easy to employ, depending on the complexity of the filtration system. In response to this, preventive measures by means of a collection of some optimum operational conditions of TMP, feed velocity, feed concentration and membrane properties, may help reduce fouling and; therefore, enhance membrane flux. It is important to mention that in order to attain these optimum conditions, a trade-off amongst these conditions is required. However, it cannot by no means be claimed that these optimal conditions will render filtration processes fouling-free, but they may retard fouling making the need for cleaning process(es) less frequent.

The influence of these operational conditions on the performance of membrane processes is briefly touched upon in the following sections.

4.7.1 Effect of Transmembrane Pressure (TMP)

With the TMP, the membrane flux rate substantially changes. Kocherginsky et al. (2003) in their investigation of w/o demulsification via membrane filtration, claimed that increasing TMP increases membrane flux rate. This is in line with Darcy's law which states that a membrane flux rate is directly proportional to the applied pressure gradient, as explained in Sec. 4.3.1 (Wakeman and Tarleton, 1991). They discovered that membranes with bigger pore size at higher pressures gave a higher flux rates. However, they produced more water in the permeate stream than other membranes with smaller pores. One explanation for this is that increasing the TMP in membranes with big pore size reduces the residence time of emulsion droplets on the membrane surface. This; therefore, leads to reduced coalescence and; thus, reduced demulsification efficiency (more water in the product). On the other hand, results reported by Sun et al. (1998) suggest that increasing the TMP increases flowing speed of the emulsions, rupture of the droplets and coalescence of internal aqueous phase inside membrane pore; hence, demulsification efficiencies increase. Nevertheless, excessive TMP increase can result in reduced demulsification efficiencies as it will lead to water droplets desorption which means reduced water droplets adsorption and coalescence. Higher TMP gives higher permeation flux due to the fact that water droplets will pass through the membrane pore very quickly. According to this, a balance should be made between high permeation flux and demulsification efficiencies. However, Chakrabarty et al. (2008); Srijaroonrat et al. (1999); Song (1998) and Riesmeier et al. (1987) stated that higher TMP than a critical pressure leads to a fast membrane pore blockage, cake layer formation and alteration in the critical surface tension, contact angle and pore size of the membrane; thus, increased membrane rejection, i.e. membrane flux deterioration. This was also demonstrated by Koltuniewicz et al. (1995) and Riesmeier et al. (1987) and was ascribed to the fact that the applied pressures were able to entrap oil droplets into the membrane pores but were not high enough to make them sweep away from the membrane, which in turn leads to pore blocking; hence, membrane flux decline (increased membrane rejection) (Chakrabarty et al., 2008). Furthermore, it was also demonstrated that the flux declined at higher rates at high pressures.

In another study by Scott et al. (2001), dependency of membrane flux rate on TMP was categorized into three trends, refer to Fig. (4.19). Initially, increasing TMP gave increased fluxes; this was then followed by a reversal effect of TMP on the flux at which concentration polarization layer is formed and membrane pores are blocked by water droplets. This effect dominates the process until a pressure called breakthrough pressure is applied by which pore blockers (water droplets) can break through with the permeate. Ohya et al. (1998) pointed out a similar style of behaviour, that at a particular pressure it was shown that the flux declines over time. Initially, this particular pressure was able to force oil droplets to settle on the membrane surface to permeate through. However, there was a stage where oil droplets are no longer dependant on the applied pressure and instead of being pushed out through the membrane they underwent a partial deformation, which in turn promotes oil layer compaction; hence, flux decline.

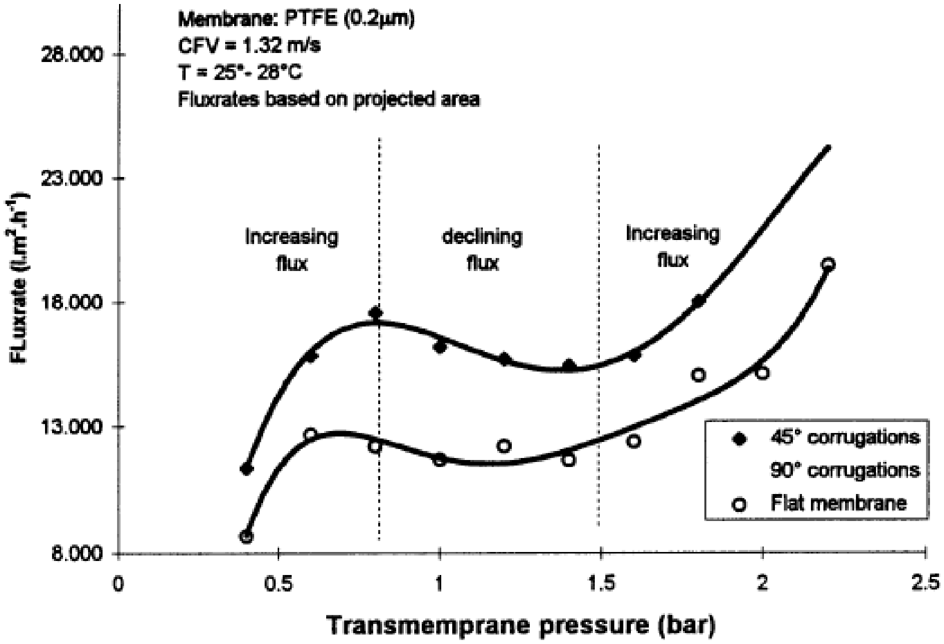


Fig. (4.19): The effect of transmembrane pressure on flux for corrugated membranes. 90º angle of corrugation (Scott et al., 2001)

4.7.2 Effect of Feed Crossflow Velocity (CFV)

There have been several studies investigating the relationship between membrane flux rate and the feed CFV. Generally, higher flux rates are obtained when running the filtration experiments at high velocities (Scott et al., 2001; Tarleton and Wakeman, 1994a; Jiao and Sharma, 1994; Riesmeier et al., 1987). Increasing the feed CFV corresponds to higher Reynolds number values (turbulence). Hence, concentration boundary layer and membrane fouling can be reduced; therefore, higher permeate fluxes are secured. A slightly different behaviour was demonstrated by Ohya et al. (1998) in which they reported a slight flux reduction with time as the feed CFV increased particularly at lower velocities. This was due to the fact that there was no shift towards turbulent flow conditions by which the flux may be improved (de Morais Coutinho et al., 2009; Gomez and Lin, 2004; Mohammadi et al., 2004; Ohya et al., 1998; Benkahla et al., 1995; Koltuniewicz et al., 1995; Fell et al., 1990). Tarleton and Wakeman (1992) produced an unchangeable filtrate flux rate of the suspensions they examined, regardless of the feed CFV utilized. In their study, no interpretation of such a trend was given.

4.7.3 Effect of Feed Concentration

Generally, increasing emulsion concentration leads to flux decline due to a fouling layer being formed on the membrane surface (Wakeman and Tarleton, 1991; Wakeman and Tarleton, 1986). This layer may be so rigid and; therefore, influential in term of fouling if flow forces are too low to remove it. In addition, the nature of the membrane (hydrophilic/hydrophobic) *does* help minimize interactions between this layer and membrane body so that flux decline is minimized accordingly (Mohammadi et al., 2004). Also, in a study by Kocherginsky et al. (2003) the effect of initial dispersed water content on the flux rate at different TMPs and on the amount of water in the separated stream was studied. It was found that irrespective of the TMPs applied, streams with higher initial dispersed water slightly gave lower fluxes. However, the amount of initial dispersed water was found with no effect on the final amount of water in the permeate. The effect of emulsion concentration on flux decline was also studied by Ohya et al. (1998). They found that the lower the emulsion concentration is, the higher the flux rate is, at a moderate pressure and feed CFV. However, there was a decrease in flux rates over time regardless of the feed concentration. This may suggest that there is a minimum concentration below which fouling layer formation on the membrane surface is insignificant; hence, fouling concentration has no effect on flux rate. Experimental results reported by Sun et al. (1998) in their work on demulsification of w/o emulsions by using glass membranes also support this trend.

4.7.4 Effect of Membrane Properties

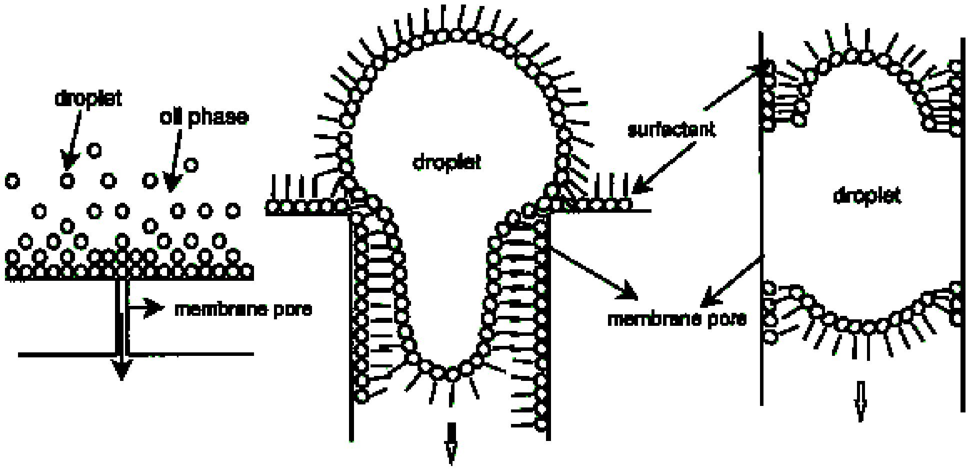
Broadly speaking; for a given membrane, the permeate flux is expected to increase in accordance with the increase of its pore size. Experimental evidence demonstrated that membranes with bigger pore size produced higher permeate fluxes (Kocherginsky et al., 2003; Fell et al., 1990). However, bigger membrane pores may result in more contamination of the permeate stream (Kocherginsky et al., 2003). In fact, it should be emphasized that this relationship between a membrane performance and its pore size distribution seems rather a system specific property; thus, cannot be generalized. For instance, although Le et al. (1984) in their analysis of the flux behaviour with time of three membranes of different nominal pore sizes (0.2, 0.45 and 0.6 µm) but similar membrane material (Asypor) have observed that a 0.6 µm membrane gave a 20 % higher permeate flux than that obtained via a 0.2 µm membrane. On the other hand, they also found that a 0.45 µm membrane gave a flux almost twice higher than that produced by a 0.6 µm over the entire duration of the filtration experiment. An explanation of this pattern was attributed to the variation in the size of solute particles relative to the membrane pore size and pore-pore proximity. In the 0.6 µm membrane, particles had a greater opportunity to penetrate through the membrane surface than in the 0.45 µm membrane; therefore, greater fouling (reduced flux) in the former membrane in comparison to the latter one. Similar findings were also reported by Waeger et al. (2010) and Tarleton and Wakeman (1993) in their investigation of microfiltration/ultrafiltration of particle removal from feed suspension and anaerobic digester effluents through ceramic membranes, respectively. Membrane material, through membrane-solute interactions, in particular during the initial stages of filtration, is also an important parameter to enhance membrane performance, i.e. increased flux/reduced rejection. This membrane-solute interaction, through solute adsorption on membrane surface or within its pores, results in an increased polarization which results in an increased membrane rejection capacity as the filtration advances (Wakeman and Williams, 2002; Wakeman and Akay, 1997; Tarleton and Wakeman, 1994b; Wakeman and Tarleton, 1991; Fell et al., 1990).

4.8 Application of Crossflow Microfiltration in Water-in-Oil Emulsions

Crossflow microfiltration has increasingly seen continuous developments which have led to widening its applicability in several applications including w/o emulsions. There has been a wealth of information on o/w separation in multiple studies through different processes including: hydrocyclones (Hashmi et al., 2004), ultrafiltration (UF) (Salahi et al., 2010; Chakrabarty et al., 2008; Belkacem et al., 2007; Li et al., 2006b; Lobo et al., 2006; Gomez and Lin, 2004; Hu et al., 2002; Chang et al., 2001; Faibish and Cohen, 2001; Briscoe et al., 2000; Kong and Li, 1999; Srijaroonrat et al., 1999; Lin and Lan, 1998), microfiltration (MF) (Zhao et al., 2005; Mohammadi et al., 2004; Hong et al., 2002; Holdich et al., 1998; Mueller et al., 1997; Koltuniewicz and Field, 1996; Marc, 1995; Scott et al., 1994), dissolved air flotation (DAF) (Li et al., 2007; Rodrigues and Rubio, 2007; Al-Shamrani et al., 2002b; Al-Shamrani et al., 2002a; Rubio et al., 2002; Zouboulis and Avranas, 2000), electro-flotation (Bande et al., 2008; Mostefa and Tir, 2004), electrical demulsification (Tsuneki, 2007; Ichikawa et al., 2004; Ichikawa and Nakajima, 2004) and electrochemical processes (Chen-Lu, 2007). In membrane processes, although mainly membranes with hydrophobic characters were used, hydrophilic membranes were also employed. On the other hand; however, few studies, to the best of this thesis author's knowledge, have described w/o emulsions separation (topic of this work) through microfiltration processes (Hu and Scott, 2008; Hu and Scott, 2007; Ezzati et al., 2005; Kocherginsky et al., 2003; Scott et al., 2001; Dezhi et al., 1999; Sun et al., 1998). It should be noted that the mechanism by which membranes function in the destabilization of oil emulsions is different from that in the separation of colloidal suspensions. In the latter systems, separation is dependent on sieving mechanism as demonstrated in 4.2.6, whereas in w/o emulsion systems membranes encourage emulsion droplets, which are usually of trivial size, to coalesce so that larger droplets are formed where gravity separation can then be applied (de Morais Coutinho et al., 2009; Chakrabarty et al., 2008; Hong et al., 2002). Explanation of this mechanism is the task of the following paragraphs.

Ezzati et al. (2005) in an effort to attain low water content in the permeate side used a porous hydrophobic membrane to demulsify w/o emulsion in the presence of an emulsifier (Span 80). Hu and Scott (2007) experimentally found that water-in-kerosene (oil) emulsion with an oil soluble surfactant (Span 80) can be separated by hydrophilic and hydrophobic membranes by crossflow filtration. Of the former membrane (hydrophilic), permeate flux rate was much lower than that obtained from the different hydrophobic membranes examined. This low flux was as a result of low surfactant (hydrophobic)-membrane (hydrophilic) interaction. This membrane; however, exhibited a gradual flux decline. Turbulence promoters by means of half-cylinder or triangular corrugations were also shown to further enhance flux rates in comparison to flat membranes. They enhance mass transfer in regions away from the membrane leading to reducing concentration polarization, increase shear rate on the membrane surface leading to reducing membrane fouling as well as increase membrane filtration area and improve energy consumption. Corrugation was found to be very influential at higher feed flow velocities (Scott et al., 2000). Similar results were also obtained in a study by Scott et al. (2001). In another study, Hu and Scott (2008) compared their results of microfiltration of a w/o emulsion, using a variety of hydrophobic and hydrophilic membranes of different pore size, with Hermia’s models at different experimental conditions. They found that, in both membranes (PVDF; hydrophobic and regenerated cellulose; hydrophilic), flux decline was due to two predominant behaviours, namely, cake formation and intermediate pore blocking, respectively.

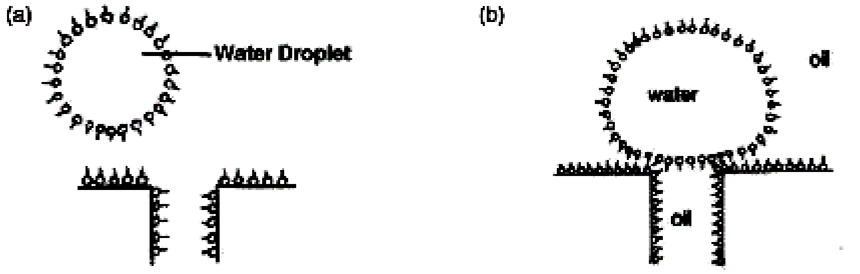
Successful demulsification work on w/o emulsions using a hydrophilic porous glass membrane that functions as a wetting and coalescing medium has also been carried out by Kukizaki and Goto (2008) and Sun et al. (1998). Glass membranes were employed in these studies due to their high strength, narrow pore size distribution, rigid pore structure as well as ease of cleaning. Due to some interactive forces between membrane surface (hydrophilic) and emulsion water droplets, emulsion droplets; with the protective surfactant film, begin to congregate on the membrane surface. Under the influence of TMP, this collection of droplets will be forced to enter the membrane pores. Three scenarios are then envisaged: a- emulsion droplets diameter (D_d) is smaller than the membrane pore diameter (D_p) i.e. ($D_d/ D_p<1$), this will permit droplet(s) to pass through the membrane, as a result, no demulsification or at most ineffective demulsification will occur, b- when emulsion droplets are in the same range as that of the membrane pore diameter ($D_d/ D_p \approx 1$), only part of the droplets can pass through the membrane which accordingly will be partially demulsified and c- better demulsification efficiencies but lower permeation fluxes are obtained if emulsion droplets size is larger than membrane pore diameter ($D_d/ D_p>1$) (de Morais Coutinho et al., 2009). Droplet deformation is a mandatory process for this last mechanism by which droplets enter the membrane pore and can be squeezed and collided, leading to destroying their protective film. As a result, the internal phase (water) is released and contacts with the hydrophilic pore wall. As the process advances, water droplets will wet, adsorb and coalesce on the internal surface of the porous hydrophilic membrane wall creating larger water droplets. The latter (water droplets) will be pushed out of the membrane pore under the influence of TMP at a velocity similar that of the permeate stream (Cumming et al., 2000). By this mechanism, w/o emulsions are separated into water phase and oil phase. The sequence of this demulsification process is presented in Fig (4.20) below.



(a) (b) (c)

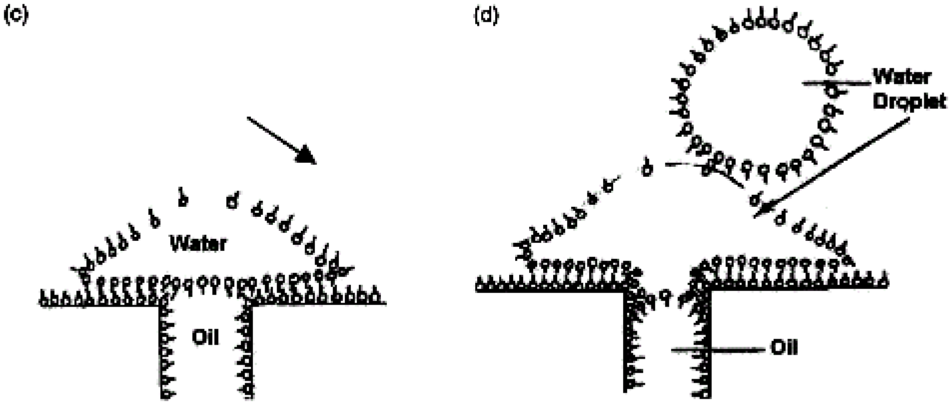
Fig. (4.20): Schematic diagram of demulsification by porous glass membranes: (a) emulsion droplets with the protective surfactant film congregate on the membrane surface, (b) droplet deformation and (c) larger droplets are formed. Reproduced from (Sun et al., 1998).

Comparable results were also reported by Kocherginsky et al. (2003) in their investigation of the demulsification of w/o emulsions through filtration via a hydrophilic nitrocellulose polymeric membrane. The emulsion was made up from kerosene with di-2-ethylhexyl phosphoric acid as a surfactant comprising the oil phase while the aqueous phase was NaOH solution. The emulsion droplet size distribution was wide (0.5- 50) µm. The membrane pore size was between (0.05-0.45) µm. Therefore, there were two possibilities when the emulsion was fed against the hydrophilic membrane to which water droplets are attached. Droplets that are smaller than the membrane pore size will go through easily and coalescence occurs inside the pores. However, larger droplets have to deform in order to pass through the membrane under the effect of TMP that’s higher than the critical pressure (Kocherginsky et al., 2003; Park et al., 2001). Critical pressure is defined as the least TMP at which droplets are permeated through a membrane (Park et al., 2001; Kong and Li, 1999). Adsorption of these larger emulsion droplets on the membrane surface is also probable, leading to droplet coalescence creating a thin layer of water on membrane surface. This is granted by the interactions between the membrane surface and water droplets and the surfactant film around water droplets. Hence, the top surface of the droplet becomes flatter losing its surfactant molecules. Thus, this flat surface (attached to the membrane surface) in turn would have its surface area reduced and; therefore, would have a higher surface tension than that of other parts of the droplets that's not physically in contact with the membrane surface (Park et al., 2001). This leads to surface instability, droplet fusion and transport through the membrane. As a result of surfactant film destruction and increased surface tension (instability), more interaction and fusion with the incoming new droplets take place as shown in Fig. (4.21). Therefore, emulsion droplets are not stabilized anymore (demulsified). Larger water droplets will then form, which eventually will settle down forming a water phase. Meanwhile the oil phase will form the top layer.



Water droplet near the surface of the membrane.

Water droplet arriving at the surface of the membrane.



Water droplet spreads on the hydrophilic surface. The top of the surface loses surfactant molecules giving rise to a high local surface tension.

Second water droplet approaches the high surface tension surface and fuses with droplet on the suface. Coalescence takes place and a bigger droplet is formed.

Fig. (4.21): Schematic diagram of demulsification by hydrophilic nitrocellulose membrane (Kocherginsky et al., 2003).

Moreover, Dezhi et al. (1999) investigated the use of hydrophilic coalescence materials in stirred/packed columns to breakdown w/o emulsions of kerosene in aqueous HCl solution with Span80 as an emulsifier. Due to good wetting properties, mechanical strength and low capital cost, silica gel, porous glass and some other natural fibers were utilized in this study. Their experimental findings demonstrated that demulsification of this emulsion under study is feasible. In such a technique, emulsion droplets are captured within the fibrous bed until larger droplets are formed, which later can be separated by gravity settlers (Daiminger et al., 1995). In addition, they also concluded that silica gel and porous glass in stirred-column set-up gave lower demulsification rates than that obtained via natural fibrous wetting materials. This was explained by the fact that natural fibrous wetting materials are relatively characterized by higher surface area than inorganic ones. Similar results were also obtained in the packed-column configuration using natural fibrous wetting materials and inorganic materials, as they gave good demulsification results. However, higher pressure differences throughout the column were necessary when using the latter one (inorganic materials). It is; therefore, concluded that inorganic materials have poorer wetting properties for the emulsion droplets than natural fibers.

Chapter Five

Apparatus, Experimental Procedure and Analytical Methods

Chapter Five

Apparatus, Experimental Procedure and Analytical Methods

> When you are inspired by some great purpose, some extraordinary project, all your thoughts break their bounds. Your mind transcends limitations, your consciousness expands in every direction and you find yourself in a new, great and wonderful world. Dormant forces, faculties and talents become alive, and you discover yourself to be a greater person by far than you ever dreamed yourself to be.
>
> Patanjali (150 BCE)

> Better is the enemy of the good.
>
> Voltaire
> (1694-1778)

5.1 Introduction

In this Chapter, details of the experimental procedures followed to achieve the main aim of this study, that's, microfiltration of w/o emulsions through the use of a hydrophilic membrane in the absence and presence of electric fields (process intensification technique) in which various electrical fields were applied are presented and provided. The analytical techniques which were employed to characterize the prepared w/o emulsions and the produced PHP membranes, along with the chemicals and other resources used, are also discussed. The experimental work in this study was carried out in three stages: emulsion formation, preparation of PHP membranes and microfiltration experiments. In the latter stage, two kinds of experiments were performed, microfiltration and electro-microfiltration in which a DC electric field was applied, so as to investigate what effect an electrical field may have on permeate flux rate.

Part of this experimental work was devoted to the formation of w/o emulsions using the supplied BP crude oil and model sea water. Throughout this task, in an effort to reflect various w/o emulsions that are widely encountered in the petroleum industry, emulsions were made with two different water contents. Having prepared these emulsions, measurements of their stabilities extent and conductivities were performed.

Next, in order to carry out the microfiltration experiments on the prepared w/o emulsions, several batches of hydrophobic PHP membranes with various pore sizes were prepared. Manipulation of operational parameters such as: dosing and mixing time, impeller speed or temperature of the aqueous phase/mixing vessel can allow the production of PHP membranes with different pore sizes (Calkan, 2007). These PHP membranes were then cut into a shape according to the microfiltration module dimensions. In an attempt to alter the surface chemistry of these hydrophobic PHP membranes, a sulphonation procedure was carried out on them and then they were employed to perform the microfiltration tests.

Microfiltration experiments were conducted at different operating conditions of emulsion water content, filtration duration, feed CFV and membrane pore size. These filtration experiments were then repeated at identical operating conditions to those used in the first set of experiments but in the presence of a DC electrical field to investigate the flux enhancement. Equally important, to fulfil the aims of this investigation it was also necessary to perform some analytical techniques, such as environmental scanning electron microscopy (ESEM) investigations, on both fresh un-sulphonated and sulphonated membranes. ESEM imaging of oil-fouled membranes (used membranes after microfiltration experiments) may give an idea of the extent of deposition of surfactants and/or any other crude oil constituent's on the PHP membrane and/or within the pores, in an effort to correlate the PHP performance to its internal structure. However, due to some restrictions of appropriate use of an ESEM microscope such as contamination and damage of the column by oil vaporization during analysis, it was not possible to take any ESEM images of oil-fouled membranes. In addition, surface area analysis (SAA) was performed on fresh PHP membranes.

5.2 Materials

The crude oil implemented in this work was obtained from a BP-field in the North sea and used as supplied. The aqueous phase of the prepared w/o emulsions was simulated sea water which was prepared by dissolving some salts such as $CaCl_2$, $MgCl_2$ and NaCl in double distilled water. The filter used was a PHP polymer prepared in Newcastle University laboratory. Chemicals required for PHP preparation included: DVB (crosslinker), span80 (surfactant), styrene (monomer), potassium persulphate (polymerization initiator) and 98 % concentrated sulphuric acid which was also used for PHP sulphonation. In addition, isopropanol was also required for PHP washing. All required chemicals for this study were purchased from Sigma-Aldrich (Gillingham-Dorset, UK) and used as received without further purification/modification. These chemicals according to their application in this investigation are listed in Table (5.1).

Table (5.1): Chemicals used in this study and their applications.

Material	Application
Crude oil	Emulsion formation/oil phase
$CaCl_2$	Emulsion formation/aqueous phase
$MgCl_2$	
NaCl	
DVB (hydrophobic crosslinker)	Membrane preparation/organic phase
Span80 (surfactant)	
Styrene (water-immiscible monomer)	
potassium persulphate (polymerization initiator)	Membrane preparation/aqueous phase
98 % conc. H_2SO_4	
Isopropanol	Membrane washing
98 % conc. H_2SO_4	Membrane sulphonation

5.3 Methods

5.3.1 Formation of Water-in-oil Emulsions

A crude oil, provided by BP-Amoco, was employed in preparing the w/o emulsions. Relevant physical properties of this crude are given in Table (5.2). In this work, the continuous phase was the crude oil in which model sea water containing 0.6 g/l CaCl2, 5 g/l MgCl2 and 28.1 g/l NaCl was dispersed (w/o emulsion). Since in real applications, depending on crude composition, emulsions are comprised of various ratios of internal and external phases; in this work, emulsions were prepared with two different compositions, to reflect the influence of emulsion water content on emulsion stability level and; therefore, on the extent of emulsion destabilization by means of microfiltration. Although in real applications emulsions are also formed due to different mixing conditions; however, in this study this has not been considered and only a mixing rate of 1000 rpm (revolution per minute) was used. Since indigenous crude oil surfactants in preliminary experiments have sufficiently stabilized the emulsion over a period of time, it was decided not to add any other emulsifiers. All emulsification experiments were conducted at laboratory temperature.

Table (5.2): Physical properties of BP-Amoco crude oil (Noor, 2006).

Property	Value/colour
Specific gravity	0.80
Dynamic viscosity, cP at 25 ºC	153
Colour	Dark brown to black

Prior to the emulsion formation procedure, the crude oil in its metal container was warmed in a 60-70 ºC water bath to attain good mixing of the contents of the container. Then, the crude oil was poured from its metal supplier container into a well-sealed metal vessel, to avoid spillage of the crude throughout the course of mixing. Here the crude was thoroughly homogenized, using an ABB motor attached to an ACS-150 drive (Lowara, CE) at 300 rpm for 2.5 hr. Mixing of the crude was made in an attempt to ensure that the crude contents are uniformly distributed prior to the emulsification process. The homogenization process is schematically shown in Fig. (5.1). Stirring was carried on until the crude oil was loaded into the emulsification setup, refer to Fig. (5.2). W/o emulsions with different model seawater concentrations, as required, were prepared according to the following procedure.

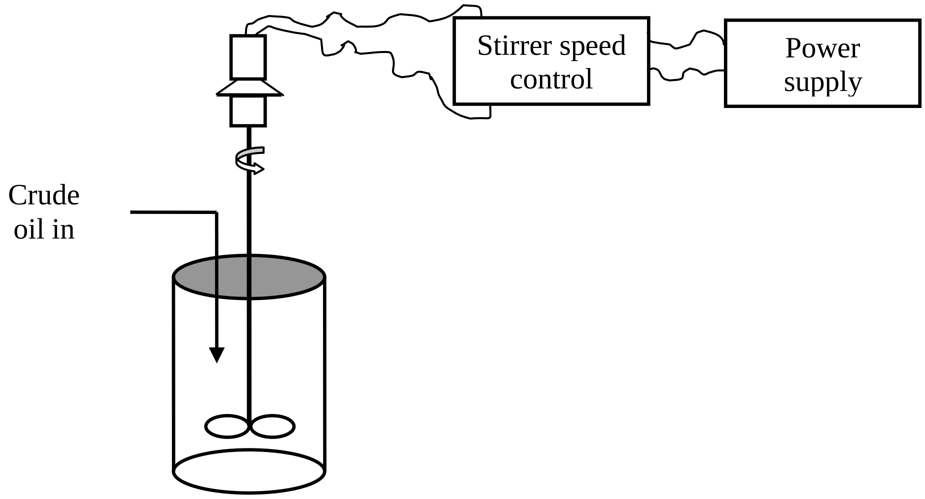


Fig. (5.1): A schematic representation of crude oil homogenization process.

This model seawater was made by dissolving salts such as $CaCl_2$, $MgCl_2$ and NaCl at concentrations of 0.6 g/l, 5 g/l and 28.1g/l, respectively, in deionized water (brine). Such a brine was made in an effort to imitate the brine that’s normally in contact with the crude in an oil field (Noor, 2006). In order to form emulsions with different water contents, the water content in the emulsion was varied from 30 to 50 vol. % (EI and EII, respectively). Within the emulsification setup, shown in Fig. (5.2), a preset volume of model seawater (6 L in case of EI emulsions and 10 L in case of EII emulsions) was gradually added to a preset volume of crude oil (14 L in case of EI emulsions and 10 L in case of EII emulsions) which was previously contained in a 35 L PTFE rectangular feed tank (F) with a lid. In order to create the desired w/o emulsions, vessel contents were then re-circulated through a by-pass recycle loop by a pump (model U30), Lowara, CE, at 1000 rpm for 2 hr. This flow diversion (by-pass) was facilitated by completely opening valve V1 meanwhile completely closing valve V2. Although it was possible to run the pump at higher speeds, the assigned pump speed of 1000 rpm and the duration of 2 hr were chosen on the basis of the stability of the synthesized emulsions, as will be shown in Chapter 6, Sec. 6.5. This pump speed was also chosen to avoid any vibrations that *did* occur at higher speeds within the system. To avoid the formation of a stagnant layer of water and/or oil at the bottom of the vessel and to attain stream uniformity, the pump suction line was always positioned in a way that was not too away from the vessel's bottom. The experimental set-up used for emulsion preparation is shown in Fig. (5.2) along with a synopsis of the processes carried out on the crude in order to produce the desired w/o emulsion represented in Fig. (5.3). Pictorial representation of the experimental rig is given in Appendix C. Specimens from the prepared emulsions were allowed to age for some days, until no phase separation was observed, during which their separation profiles were carefully monitored and recorded. Fresh prepared emulsions were directly used in the microfiltration experiments. Two routines were implemented; the first one is microfiltration experiments in the absence of an electrical field; and in the second one, microfiltration was coupled with the application of electrical fields at different intensities. Details of the microfiltration unit will be given in Sec. 5.3.4 of this Chapter and in Fig. (5.8).

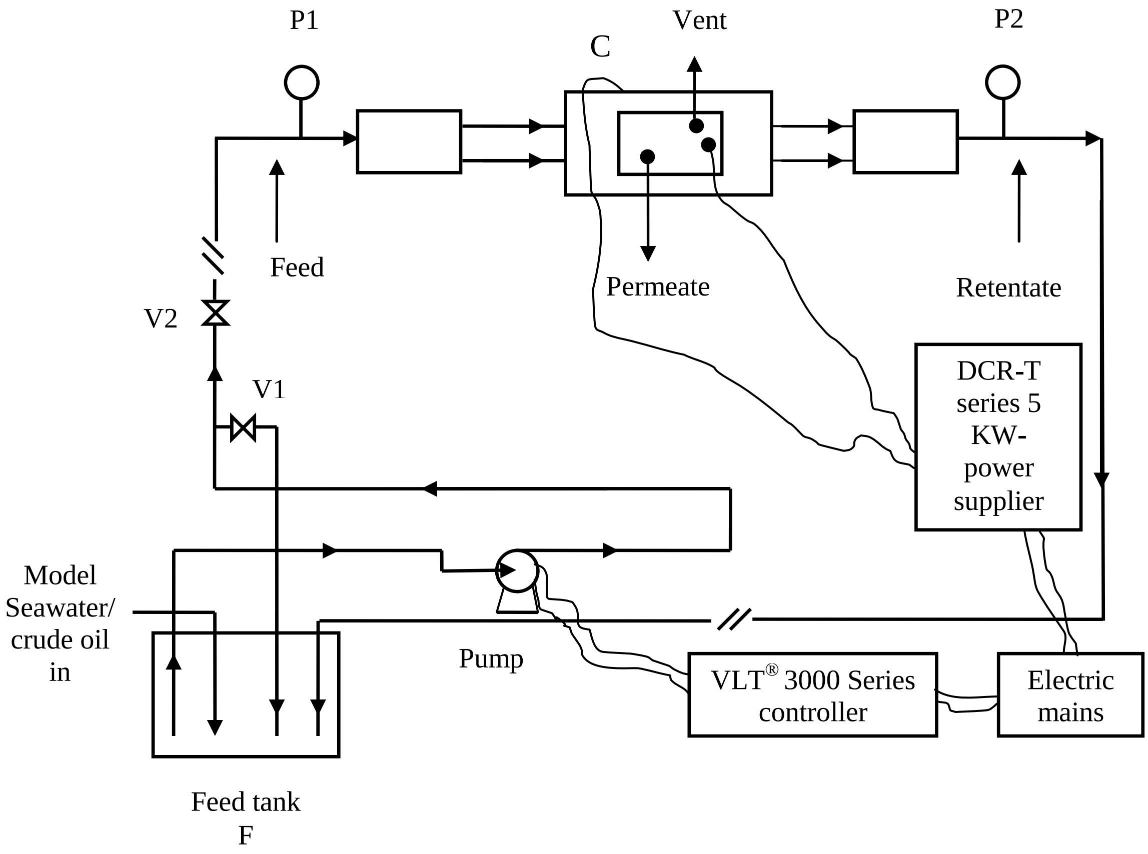


Fig. (5.2): A schematic representation of the emulsification process.
F: feed tank and V1/V2: valves.

$$\text{Crude oil} \xrightarrow{\text{Homogenization}} \text{+ model Sea water} \xrightarrow{\text{Stirring}} \text{emulsion}$$

Fig. (5.3): A synopsis of the processes of w/o emulsion formation.

5.3.2 Measurement of the Stability of the Prepared Emulsions and Permeate Samples with Time

In order to examine their stabilities, prepared w/o emulsions with different water contents were analyzed for their stability by bottle tests under gravity at laboratory temperature. Bottle test analysis provides a measure of the extent of phase separation, if there is any, monitored over time. Samples were transferred into plastic tubes, of 50 ml graduated in 2.5 ml graduations and tightly stoppered with PTFE lids to avoid any escape of crude components. Samples were then allowed to stand under gravity for some days (until no further water was separated). During this period of time, separated water volume, which is a measure of the emulsion stability, was registered at regular time intervals. This procedure was also followed for permeate samples to examine the demulsification capability of the prepared PHPs. Figs. (5.4) and (5.5) schematically represent a summary of this procedure giving sample(s) volume of the prepared fresh emulsions and demulsified permeate streams vs. phase separation time, respectively.

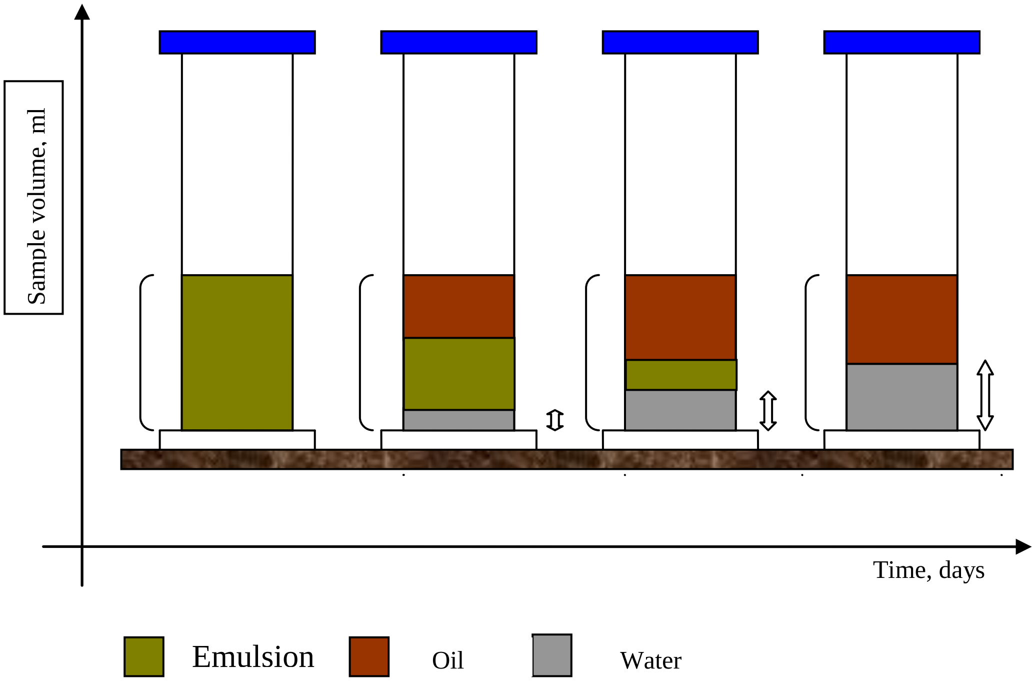


Fig. (5.4): Sample volume of the prepared fresh emulsions vs. phase separation time.

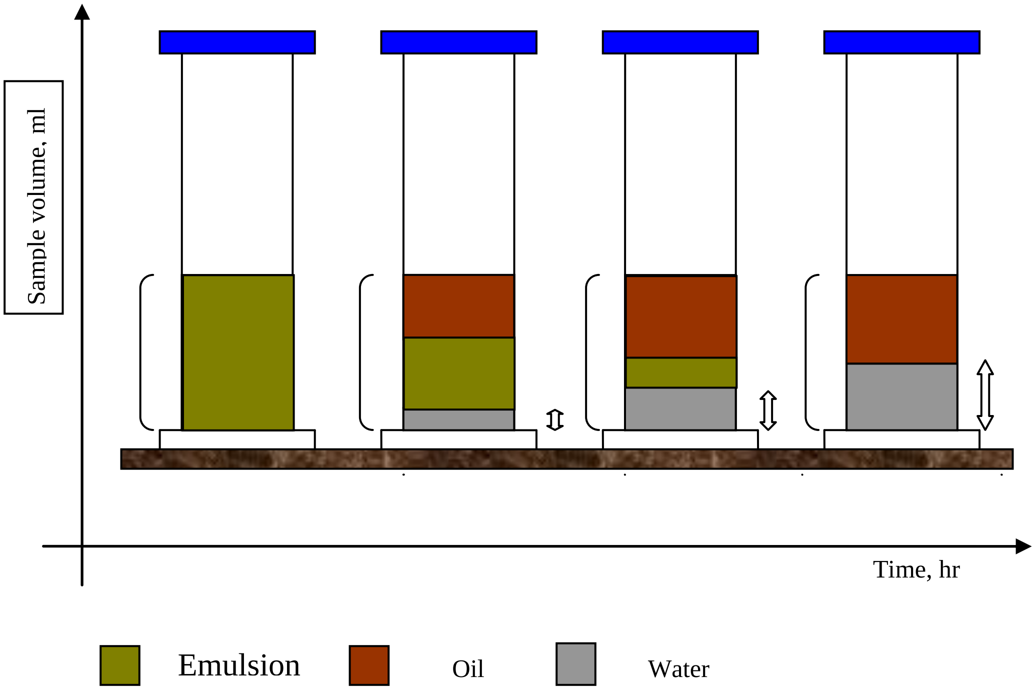


Fig. (5.5): Sample volume of permeates vs. phase separation time.

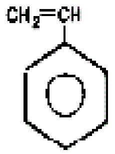
5.3.3 Preparation, Processing and Post-functionalization of PHP

The preparation of PHP polymers has been described by several workers elsewhere (Ergenekon et al., 2011; Livshin and Silverstein, 2008; Haibach et al., 2006; Menner et al., 2006; Akay et al., 2005; Barbetta et al., 2005; Cameron, 2005; Krajnc et al., 2005; Zhang and Cooper, 2005; Deleuze et al., 2002; Sergienko et al., 2002; Brown et al., 1999; Akay, 1998; Wakeman et al., 1998; Hoisington et al., 1997; Walsh et al., 1996; Hainey et al., 1991). PHP is a highly porous material that is prepared through a high internal phase emulsion (HIPE) polymerization route of the monomeric continuous phase. The development of a PHP polymer involves three stages. These are HIPE formation, polymerization of this emulsion and then, according to the final application, final post-functionalization, respectively. Among the ingredients of the continuous phase were:

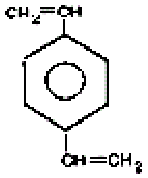
monomer(s), a cross-linker and a suitable surfactant. All PHP membranes used in this work were prepared in-house in a Newcastle University laboratory. In this study, in line with procedures described by Akay and co-workers (Akay et al., 2005; Akay et al., 2004; Akay, 1998), PHP polymer was prepared by mixing the 'oil phase' (25 ml) which consisted of styrene as a monomer, divinyl benzene (DVB) as a cross linker and sorbitan monooleate (Span80) as a surfactant (w/o emulsifier); and the 'aqueous phase' (225 ml) which comprised double distilled water, potassium persulphate as the aqueous phase initiator and concentrated sulphuric acid (98 %). Chemical formulas of oil phase components are given in Fig. (5.6) below. The recipe for preparing the PHP is listed in Table (5.3). The PHP was prepared by adding the aqueous phase drop-wise by two peristaltic pumps to the organic phase in a mixing vessel.

Table (5.3): Recipe for PHP preparation.

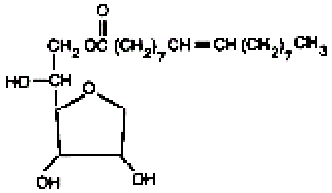
	Compound	Volume, ml	Percentage, %
Organic phase	Styrene	19	76
	DVB	2.50	10
	Span80	3.50	14
Total		25	100
Aqueous phase	Double distilled water	211.50	94
	Potassium persulphate	2.25	1
	98 % conc. H_2SO_4	11.25	5
Total		225	100



Styrene



Divinyl benzene (DVB)



Sorbitan monooleate (Span 80)

Fig. (5.6): Chemistry of oil phase components (Hoisington et al., 1997)

The detailed procedure for preparing PHP was as follows: the oil phase of 25 ml (10 vol. % of the total emulsion) was prepared first by commingling its aforementioned components according to the recipe given in Table (5.3). A typical oil phase composition was styrene 76 %, DVB 10 % and Span 80 14 % (by volume). This mixture was then placed at the bottom of a mixing vessel (internal diameter = 12 cm). All the aqueous phase of 225 ml (90 vol. % of the total emulsion) that contains 211.50 ml double distilled water, 2.25 ml potassium persulphate and 11.25 ml H_2SO_4 was then dosed drop-wise to the vessel by using two peristaltic pumps within 5 min, while constant mixing to break up large droplets. Mixing is facilitated by two flat impellers (8 cm in diameter) which were stacked at right-angles to each other with the bottom impeller positioned as close to the bottom of the vessel as possible. Rotational speed of the impellers was kept constant at 300 rpm. The impeller was started at the same time as dosing the aqueous phase into the mixing vessel. Since polymerization factors such as temperature of emulsification and mixing speed and duration are decisive with regards to the structure and pore size of the produced PHP. Control of pore size and structure of a produced PHP has been described in previous works of Akay and others (Akay et al., 2004; Akay et al., 1995). Mixing time was changed when preparing each polymer. Stirring of both phases was continued for an additional 1 min after dosing all the aqueous phase (225 ml) into the mixing vessel. A simplified schematic diagram of the experimental setup used to produce PHPs is given Fig. (5.7).

Once the emulsion has been prepared, it was then transferred to plastic containers through an outlet situated at the bottom of the vessel. To ensure wasted emulsion is minimal, having no emulsion is collected from the bottom of the vessel, the vessel was taken apart to recover any trapped emulsion within the vessel and on the impellers. The plastic containers were then placed in a pre-heated oven at 60 ºC for at least 8 hr for polymerization. Once the HIPE is polymerized, solidified PHP blocks were removed from plastic containers and sliced with care with a bandsaw into rectangular sheets of dimensions that fit into the filtration cell ready for further processing and modification. Water was rapidly removed from the produced PHP by drying in a fume cupboard overnight, reflecting its open-cell structure.

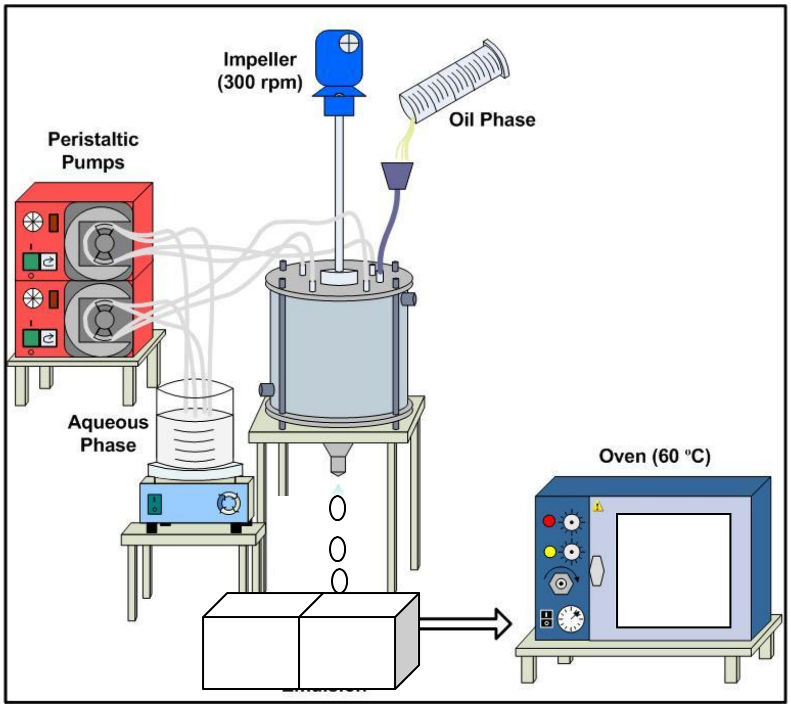


Fig. (5.7): A simplified schematic diagram of the experimental setup used for the preparation of PHP.

Any residues of chemicals such as surfactants and initiators, which may have remained in the pores and interconnects of the produced PHP following drying, were removed by soaking the PHP with isopropanol for 2 hr and then washing with double distilled water for 8 hr followed by drying a fume cupboard overnight. Once washed and dried, surface chemistry of the produced PHP was modified by means of sulphonation in an attempt to improve its hydrophilicity (water up-take), increase its surface area and render it a conductive media. Of the first point with regards to sulphonation, since in w/o emulsions oil (continuous phase) content is by definition higher than, or equal to, that of water (dispersed phase) content, it is; therefore, intuitive that using a hydrophobic membrane instead of a hydrophilic one, in treating such emulsions, may lead to the production of massive amounts of oil in the permeate side with greater susceptibility to membrane fouling by oil droplets. In addition, for a given process, in which a hydrophobic membrane is used, this means that a larger membrane area may be required. Therefore in this work, in an attempt to make the filtration process more viable, a hydrophilic PHP membrane with which oil attraction is minimal was required in order to reduce membrane fouling by oil droplets; thus, increasing membrane flux rate. However, it should not be expected that hydrophilicity/ hydrophobicity is the only means towards an optimum membrane system. Other filtration operational factors should also be considered.

A sulphonation process was carried out according to the procedure described by Akay and co-workers (Akay et al., 2005). PHP sheets were placed in a 500 ml beaker that contained 98 % concentrated sulphuric acid for 2 hr without stirring at laboratory temperature. Next, PHP sheets were microwaved until cooked. To ensure the removal of surfactants and initiators as well as the excess sulphuric acid, double distilled water was then used to wash the PHP for 2 hr in a 500 ml beaker with stirring with a magnetic bar. During these two hours, used distilled water was disposed of in a specified container and replaced with a fresh one every 30 min. Finally, sulphonated PHP sheets were left in a fume cupboard overnight to dry out ready for use in the filtration experiments.

5.3.4 Filtration Equipment and Procedure

In order to investigate the capability of the hydrophilic polymeric membranes (PHP) that were prepared and processed according to the procedures outlined in Sec. 5.3.3, the emulsion formed through the steps shown in Sec. 5.3.1 was passed through a micro/electro-filtration separation cell mounted in a closed circuit crossflow rig, as shown in Fig. (5.8). There were two modes followed whilst performing the experiments, namely, microfiltration and electro-microfiltration. As the names imply, in the former practice no electrical field was applied; nevertheless, in the latter there was. Experiments were conducted on fresh emulsions i.e. immediately used following formation. In microfiltration experiments, the effect of factors which have an influence on the extent of stability of the emulsion such as water content of w/o emulsion and upon the membrane performance (flux and retention) of microfiltration of w/o emulsions was investigated. This was accomplished by examining the effect of changing the following parameters: emulsion water content, filtration duration, feed CFV and membrane pore size. The influence of these parameters was also studied in a second set of crossflow electro-microfiltration experiments in the presence of an electrical potential which is thought can help reduce the flux decline caused by membrane fouling. In this work, an electrical field corresponds to the voltage applied (0-300) V across a crossflow space of a 0.30 cm sandwiched between the hydrophilic polymeric membrane and the other electrode. This distance was measured by a depth micrometer.

Filtration cell (C) is constructed from clear acrylic, trade name ‘Perspex’. ‘Perspex’ was first disclosed in a patent in 1932 by I.C.I. research laboratories (UK). ‘Perspex’ is fabricated in clear/ coloured acrylic sheets, blocks, rods or corrugated sheets. Due to good properties such as light weight, toughness, transparency, moderate heat resistance up to 130-150 ºC and resistance to chemical attack by concentrated solutions and organic liquids at both normal and elevated temperatures, ’Perspex’ has been suitable for many applications, including this work.

The cell consists of two rectangular compartments/blocks assembled together with eight brass screws and bolts and has the dimensions of 26.30*9.80*8.25 cm (length*width*depth) measured by a vernier caliper. On each block, two channels were drilled for feed inlets and another two channels for feed outlets. On one block, a channel for permeate outlet and another one for ventilation outlet were machined. A ventilation outlet is to allow the escape of electrolysis gases that may generate following applying an electrical field through the system. To prevent any emulsion leakage from between the blocks, O-rings were used. In between the blocks, there was a gap of 30 mm (0.30 cm) which was meant to be the distance for the electrical field intensity. One block has a cavity with an area of 48 cm^2 (8 cm * 6 cm) and a depth of 1.75 cm, which was measured by depth micrometer. This cavity precisely accommodates the flat hydrophilic polymeric membrane (PHP) sheets which, due to their conductivity, were used as an electrode (EC1). Underneath where a polymeric membrane sheet sits, some rectangular grooves (flow channels) on the surface of the block were made to assist the permeate stream to flow out of the cell. To ensure that all the liquid (emulsion) to be filtered only passes thorough the membrane, avoiding any escape out side of the membrane, borders of the membrane were thoroughly sealed to the adjacent cell surface with silicon. On this block, an electrode (hydrophilic polymeric membrane) contact point was also machined. The other block carried a foil sheet that was 20 µm thick and acted as an electrode (EC2) which can be negative or positive as required. Both electrodes were wired up for connection to a voltage source (DCR-T series 5 KW-power supplier supplied by Sorensen). All metal elements in the system were grounded. The following items were also among the essential elements included in the rig:

1- A Waukesha model U30 pump 200 V which was utilized to deliver the emulsion from the feed tank (F) into the membrane unit and to pressurize and re-circulate the emulsion, connected to a variable speed gear motor drive unit model VLT$^{®}$ 3000 Series controller supplied by Danfoss to adjust the emulsion flow rate by changing the revolutions of the gear pump.
2- In-line bypass valves (V2 and V2) to control the transmembrane pressure.
3- Two digital pressure manometers (P1 and P2) model XML-F, supplied by Nautilus were fitted at the inlet/outlet of the membrane unit; respectively, to

monitor the transmembrane pressure. The experimental equipment used in the filtration experiments is illustrated schematically in Fig. (5.8).

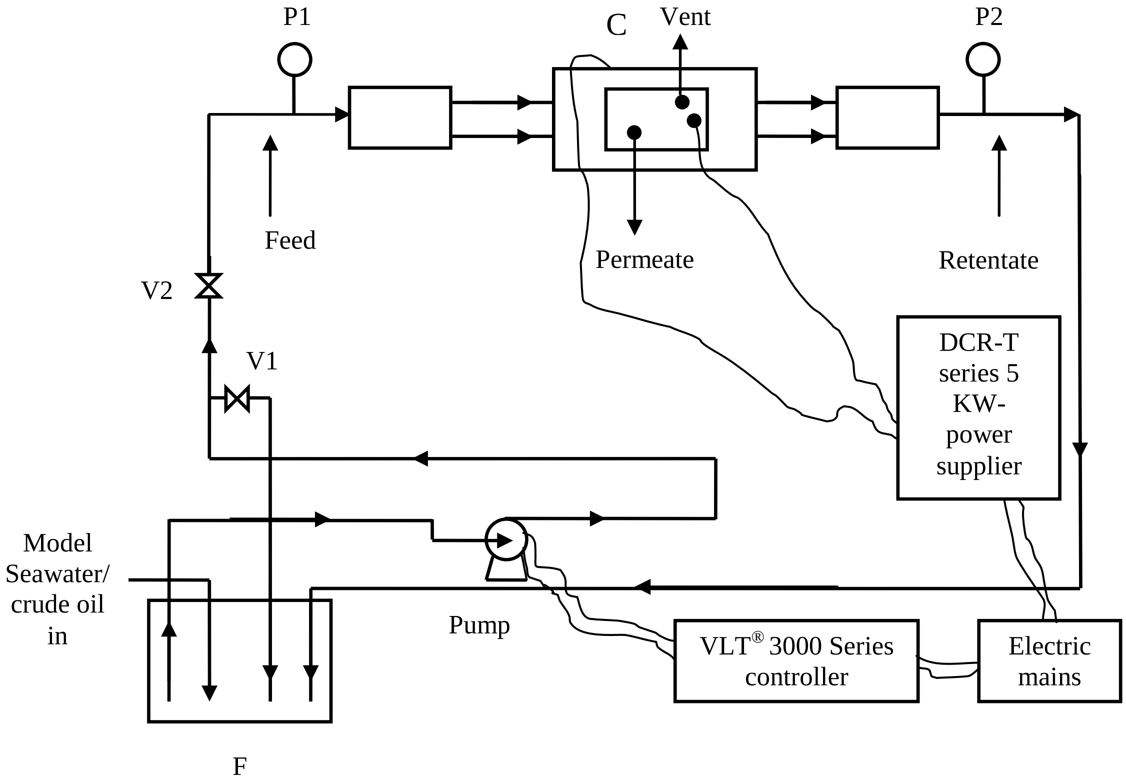


Fig. (5.8): Schematic diagram of the MF experimental apparatus.
F: feed tank; V1/V2: valves; P1/P2 pressure manometers and C: filtration cell.

By completely opening valve V2, meanwhile gradually closing the by pass valve V1, the emulsion was pumped from the feed tank (F) to the membrane unit tangentially across the membrane surface through two inlets and the retentate was continuously recycled to the feed tank (F). Feed samples prior to and after filtration were collected in plastic tubes, 50 ml graduated in 2.5 ml graduations, and tightly stoppered with PTFE lids to measure their stability and conductivity. Filtration experiments were run for 30 min throughout which permeate samples were collected in similar tubes as those used for feed samples every 5 min, so as to monitor the initial and final permeate fluxes throughout the filtration experiment, and then analyzed for their conductivity and emulsion stability over a period of time. Once permeate analysis was finished, permeate was then returned to the feed tank (F) in an effort to keep the emulsion's water content approximately constant. This procedure was repeated at different emulsion flow rates using the different prepared PHP membranes. For all samples taken, volume of separated water was recorded as a function of time at laboratory temperature, in order to calculate the efficiency of the separation experiments according to the phase collected. Feed flow rate was changed between 4.8 and 57 L/min. For each experiment, a fresh PHP membrane was used. Also, the pressure on the permeate manometer was measured whilst the permeate was being collected. Throughout the course of the filtration experiments, feed and permeate flow rates were recorded. All experiments were carried out at laboratory temperature. At certain time intervals, the filtration flux, J (L/m^2 hr) was calculated by dividing the permeate volume (L) by the product of the effective membrane area A (m^2) and sampling time τ (hr). Immediately, at the end of each experiment, the PHP membrane was taken out from the cell.

In electro-microfiltration experiments, as a contingency step, the rig was designed to electrically disconnect through an interlock switch, if the guard, that covers the whole system was left while the experiment is running. Also, attention was carefully paid when taking samples while the electrical field was applied, making sure that no direct hand-emulsion contact occurs. In addition, as a precautionary measure, insulated gloves were worn. As a summary, the ranges of parameters were as follows:
Crossflow velocity: 1-12 m/sec
Water contents of w/o emulsions: 30-50 vol. %
Electric field: 0-666.70 V/cm, and
Filtration duration: 30 min

Prior to the operation, it was essential to ensure that the rig is assembled in a correct manner that complies with the safety procedures, as the power supplier used is designed for use at up to 300 V. In addition, to ensure safe operation to avoid an electrical shock, the following guidelines were followed:

1- Before any work is carried out on cell connections from DC power supplier, ensure all system power is isolated.

2- Make sure that the guard is down otherwise there will be no power across the rig.
3- Turn on system power when all guard's and system interlocks are in place.
4- Put the pump on first and then the power supplier unit.
5- Using manufacturer's guide, turn on the power supply and select the power intensity as required via the adjustment knob/key. Voltage and current knobs should always be fully counter clockwise before start.
6- In case of an emergency, push the emergency button immediately and ask the technician for keys to re-activate the circuit again once the problem is rectified.

5.3.5 Cleaning Procedure

In order to ensure that no emulsion has remained within the filtration system which may cause measurement error(s) or damage the pump sealings or piping connections, a cleaning procedure was adopted. Immediately following each set of experiments, the emulsion was completely drained out from the system. The unit is then flushed with used isopropanol in a recycling mode at 300 rpm for 30 min. Next, the same procedure was repeated with warm tap water. Both isopropanol and water were then disposed of in specified waste containers.

5.4 Analytical Methods

Among the analytical techniques employed in this study were the following:

1- Water-in-Oil Emulsions Analytical Measurements:

I- Conductivity Measurements; and
II- Transmission Electron Microscope (TEM).

2- Membrane Analytical Methods:

I- Surface Area Analysis (SAA), and
II- Environmental Scanning Electron Microscope (ESEM).

5.4.1 Water-in-Oil Emulsions Analytical Measurements:

5.4.1.1 Conductivity Measurements

The conductivity (G) of a solution is an important property. Conductivity represents an indication of how conductive a solution is, that's able to carry an electrical current or not. To a large extent it depends on the amount and nature of the ions present in the solution. The higher the ion concentration, the higher the solution conductivity. However, there are also conditions at which conductivity is not linearly dependant on the solution concentration; this may be attributed to the ionic interactions that may modify the conductivity-solution concentration behaviour.

Conductivity, on this basis, is the reverse of the solution resistance which embodies the electrical field impedance. Therefore, Ohm's law can be re-written as:

$$\mathbf{G}= \frac{1}{R}\ \mathbf{(Ohm^{-1}) =} \frac{I(A)}{E(V)}$$

Where: G is the conductivity, Ohm^{-1}.

R is the resistance, Ohm.

I is the current, A; and

E is the electrical field, V.

As shown above from the definition, the unit of the conductivity is Ohm^{-1} which can be read reversely as mho. Currently, this unit is no longer used and has been replaced with Siemens/cm or more commonly micro/milli-Siemens/cm (µ/m-S/cm).

Conductivity is mainly used as a measure of the total impurities present in a solution. However, conductivity measurements do not give a specific identification of an ion present in a solution. In fact, it provides a collective measure of all of the ions found in the solution in one reading. In emulsion systems, the conductivity can be used to distinguish w/o from o/w emulsions because it is a well known fact that in emulsions of which the oil is the continuous medium (w/o emulsion), the conductivity is expected to be low compared to that of water itself, or in the case where water is the continuous phase, of an o/w emulsion (Schramm 1992).

Feed and permeate conductivities were measured immediately after sampling. They were measured by using an InoLab, Terminal level 3 manufactured by Wissenschaftlich Technische Werk Staten German Company. The conductivity probe was a WTW Tetracon$^{®}$ Model 325, see Fig. (5.9).

Fig. (5.9): Conductivity meter.

5.4.1.2 Transmission Electron Microscope (TEM)

In this section, the principle of operation of a TEM is summarized. Generally, a TEM operates much like an overhead projector. In a projector, a beam of light is shone through the slide. Depending upon the structure and objects present on the slide, certain part(s) of the beam of light would pass through the slide. A TEM works in the same way, but it sends a beam of electrons, instead of light, through an ultra thin specimen. Part of this beam transmits on a fluorescent screen (phosphor) which represents the image. Darker areas of the image indicate that fewer electrons were transmitted through the specimen indicating that those areas are thick/dense. By contrast, lighter areas of the image indicate thinner or less dense areas of the specimen through which more electrons were transmitted. With its low wavelength of electrons, a TEM produces a very high image resolution.

Technically, a virtual source of electrons (electron gun) produces a beam of monochromatic electrons. By means of condenser lenses (lenses 1 and 2), refer to Fig. (5.10), this beam of electrons is narrowed to a small, thin and coherent beam. Lens 1 determines the general size of the final spot that hits the sample. The second lens changes the beam from a wide dispersed spot to a pinpoint beam. This beam is then restricted by the condenser aperture after which it hits the specimen where parts of it are transmitted. These transmitted parts are focused by the objective lens into an image. The contrast of this beam can be enhanced by the objective aperture by blocking out high-angle diffracted electrons. Selected area aperture enables the user to examine the periodic diffraction of electrons by ordered arrangements of atoms in the sample. Next, through the intermediate and projector lenses, the image passes down through the column by which it can be enlarged. Finally, the image strikes the fluorescent image screen where a light is generated, producing the image.

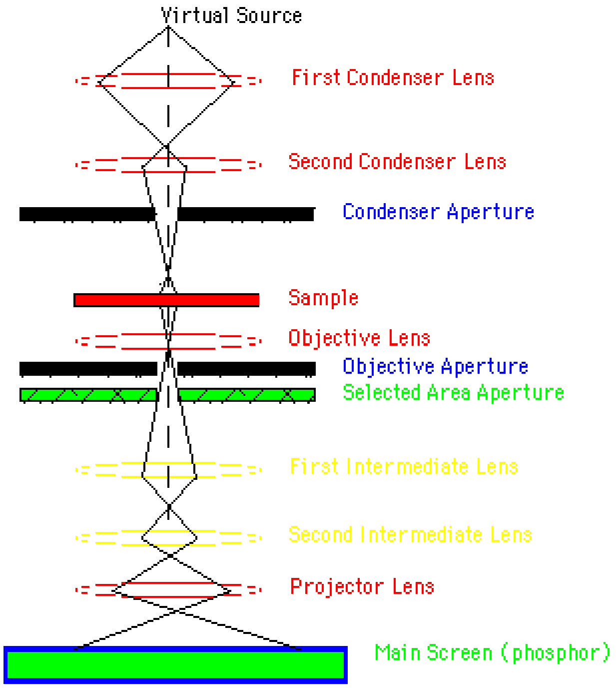


Fig. (5.10): Schematic drawing of a transmission electron microscope (TEM).

In this work, the microscope used was a Philips CM 100 Compustage (FEI) Transmission Electron Microscope with digital images collected using an ATM CCD camera (Deben). Pictorial representation of the microscope is shown in Fig. (5.11).

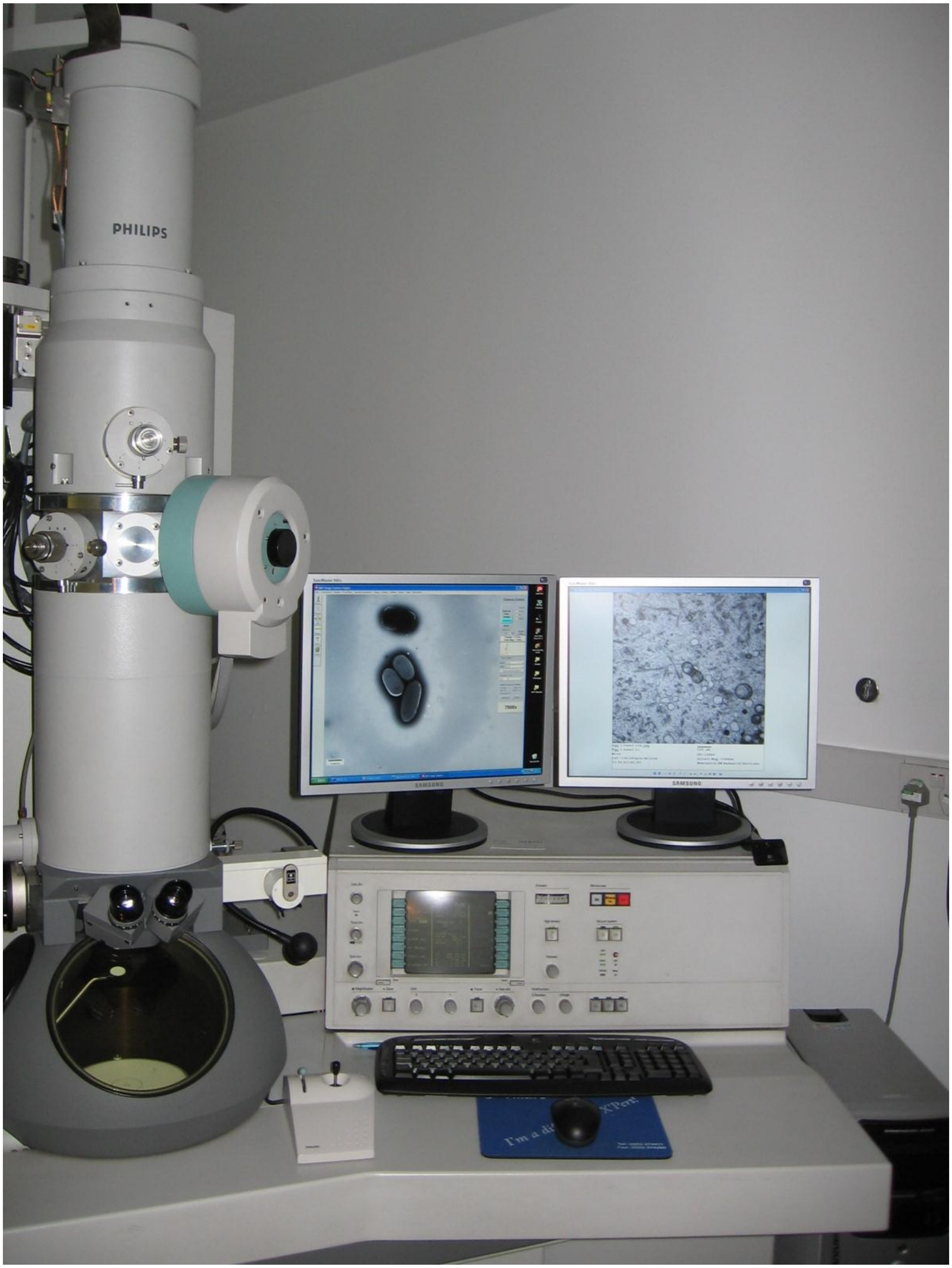


Fig. (5.11): Photograph of Philips CM 100 Compustage (FEI) TEM.

5.4.2 Membrane Analytical Methods:

5.4.2.1 Surface Area Analysis (SAA)

Surface area is one of the main physical features of a PHP. Based on the value of its surface area, more information can be drawn about a particular PHP material such as physical structure and water/solvent (depending on the polarity of the polymer) uptake capacity. Although it is not always the case, a PHP material with high surface area usually has high water/solvent uptake capacity to match. Since the PHP efficiency to absorb water is important in the oil/water separation experiments, surface area of the PHP materials utilized in the experiments needs to be evaluated. The measurement of surface area may be performed in several different ways but gas sorption by far is the most widely used and accurate method for total surface area measurements. Furthermore, this method can also be applied to measure pore size distributions within the approximate range of 0.4 to 200 nm. This method provides very high resolution data and has a vast applicability. In this study, the instrument used to measure the surface area of the PHP material was a Coulter SA 3100 analyzer Fig. (5.12), which is manufactured by the Beckman-Coulter company.

This instrument uses a gas sorption technique to obtain the surface area and pore size distributions. This technique may be defined as the physical characterization of material structures using a process where gas molecules of known volume, at fairly low temperatures (cryogenic conditions), are condensed and the resultant sample pressures are recorded and used for subsequent calculation. Within low temperature environment, molecular attractive forces are weak; hence, gas molecules will find it easy to attach to the solid surface. This data, when measured at a constant temperature, allows an isotherm to be constructed.

Fig. (5.12): Coulter SA 3100 analyzer.

Materials such as powders and solid pieces of inorganic and organic compounds or mixtures are capable of retaining amounts of gases and vapours within their structure which may occur through either of two processes; absorption or adsorption. Absorption is a process where a material such as gas, vapour or liquid is retained within the body of a material. On the other hand, adsorption occurs when material(s) attach to the surface of another material. During the adsorption process, the adsorbate molecules (the molecules that attached themselves to the surface of the other material) are retained by either physisorption or chemisorption forces. Different adsorbates are used, depending on the application, including: argon, krypton or nitrogen. Differences in these two mechanisms are summarized in Table (5.4).

Table (5.4): Differences between physisoprtion and chemisorption.

Physisorption	Chemisorption
Readily reversible process at adsorption temperature	Irreversible process at adsorption temperature
Bonding is a result of physical attraction	Bonding is formed chemically
Involves lower energy due to process condensation	Involves much higher energy of adsorption due to covalent bonding

The adsorption of nitrogen and other gases such as argon and krypton used in the SA 3100 analyzer may be characterized as physisorption processes. It assumes that all adsorption detected is due to the physically adsorbed gas. No calculation models are provided to account for adsorption caused by chemisorption processes.

The surface area and pore size distribution of a sample are calculated from all or part of the adsorption and desorption isotherms. The adsorption isotherms are an incremental set of data which describe the amount of adsorbate gas (in volume) which condense on to a material at a given pressure and at a fixed temperature specifically at STP condition (Standard Temperature and Pressure). The volume is reported by the SA 3100 analyzer in units of cm^3/g. Desorption on the other hand, is the exact reverse process and is a decremental set of data reported in the same unit. In order to form accurate isotherms, the saturation vapour pressure of the adsorbate gas during analysis needs to be known precisely. The saturation vapour pressure may be considered to be the boiling pressure of the liquid gas, which is temperature-dependent. Typical analysis setup usually requires liquid nitrogen as the sample coolant bath. However, the bath temperature will change with atmospheric pressure and the purity of the nitrogen used. Since the liquid nitrogen is usually put in an open container throughout the duration of the analysis, the liquid tends to be contaminated by the atmospheric gases. In order to obtain accurate results, the saturation vapour pressure is measured during the whole length of sample analysis.

The adsorption process is measured volumetrically with a static fully equilibrated procedure. The adsorption and desorption isotherms can be formed from a few to more than a hundred individual data points. The isotherm volume data (Y-axis) is calculated by subtracting the free space of the sample tube (volume of the tube that is not occupied by sample) which is measured using helium gas, from the total volume of gas closed to the sample. Each data point processed is calculated by calculating the volume adsorbed and measuring the sample pressure which is then divided by the saturation vapour pressure. This is known as the relative pressure and is recorded as the X-axis.

Since the absorption process is reported at STP, the Ideal Gas Law can be applied for the calculation of both free space and the volume of adsorptive dosed. Then, the volume of the adsorbed gas by the sample can be determined by the following equation:

$$P_M V_M = nRT_M$$

Where:
P_M = Pressure of the dose manifold
V_M = Volume of the dose manifold
T_M = Temperature of the dose manifold, and
R = Gas Constant

Helium gas is used to measure the free space of the sample tube. Since free space is the volume in the sample tube, it tends to vary with the volume occupied by the sample itself. The volume of helium dosed to the sample tube, i.e. the free space is calculated after opening and closing the sample valve. The free space may be found from the resultant pressure drop. The temperature or the volume of the intermediate space above the level of the liquid nitrogen or below the manifold volume is not accounted for. This intermediate volume varies with the sample tube, room temperature and also with the level of the liquid nitrogen; therefore, the free space value will change over the course of a long measurement as the liquid nitrogen level drops due to evaporation. However, this effect is minimized by the instrument during a long analysis.

Volume dosed Vd_n, is calculated from the equation below:

$$Vd_n = \frac{(P_{M1} - P_{M2}) \times V_M}{T_M} \times \frac{273.15}{760} + Vd_{n-1}$$

Where:

P_{M1} = Initial manifold pressure

P_{M2} = Final manifold pressure

V_M = Volume of the dose manifold

T_M = Manifold temperature

Vd_{n-1} = Volume dosed from previous data point, and

273.15/760 = Standard temperature and pressure conversion

The helium data points are measured at incremental pressure to ensure accuracy. The helium free space correction is obtained from the linear plot of volume dosed vs. sample pressure. The slope of this line is equivalent to the volume of the sample tube per unit of sample tube pressure. After the helium measurement has been completed, the adsorption isotherm is measured. The volume of adsorptive dosed to the sample is calculated the same way as for the helium free space dose. The volume of gas adsorbed by the sample $Vads_n$, is calculated for each measured data point using the following equation:

$$Vads_n = Vd_n - (P_{Sn} \text{ x slope + intercept})$$

Where:

$Vads_n$ = Volume adsorbed

$\mathrm{Vd_n}$ = Volume dosed

$\mathrm{P_{Sn}}$ = Sample pressure

slope = Free space measurement slope, and

intercept = Free space measurement intercept

A complete isotherm data can now be plotted. Isotherm data is then subjected to a variety of mathematical models to obtain surface area and pore size distribution results, respectively. There are several other mathematical models that may be used to calculate the surface area from the isotherm data but BET (Brunaeur, Emmet and Teller) is the most commonly used technique since it was first introduced in 1938. However, Barret, Joyner and Halenda (BJH) is the only calculation model that is used by this instrument to determine the pores size distributions. The BET surface area which includes all internal structure is calculated from a multilayer adsorption theory which is based upon the assumption that the first layer of molecules adsorbed on the surface involves adsorbate-adsorbent energies, and subsequent layers of molecules adsorbed involve the energies of vaporization of the adsorbate-adsorbate interaction.

At relative pressures from 0.05 to 0.2, the BET adsorption isotherm normally produces straight line plot (in linear form) which usually is represented as the following relation:

$$\frac{P_s}{V_A(P_0 - P_S)} = \frac{1}{V_M C} + \left[\frac{C-1}{V_M C}\right] \times \frac{P_S}{P_0}$$

Where:

V_m = Volume of monolayer
$Vads_n$ = Volume adsorbed
P_S = Sample pressure
P_0 = Saturation pressure, and
C = Constant related to the enthalpy of adsorption

The BET surface area, S_{BET} in m^2/g is then evaluated from the following expression:

$$S_{BET} = \frac{V_m \times N_A \times A_M}{M_V}$$

Where:

N_A = Avogadro’s number

A_M = Cross-sectional area occupied by each adsorbate molecule (A_M = 0.162 m^2 for nitrogen), and
M_V = Gram molecular volume (22414 ml)

In this study, the surface area analysis of the PHP samples was conducted by placing the sample in the sample tube, which comes in three different sizes namely 3 cm^3, 9 cm^3 and 12 cm^3 (depending on the amount of sample required where a minimum of weight of 1.00 g per analysis is ideal in order to obtain an accurate result), after being pre-heated in the oven at 60^oC for a few hours. Then the sample (in the tube) was out-gassed for another five hours at a particular temperature (for PHP samples, out-gassed temperature of 40 to 60^oC was normally used). Nitrogen was used as an adsorbate in this analysis. This was immediately followed by the analysis which was carried out by connecting the out-gassed sample in the tube to the analytical port and immersing the tube in the liquid nitrogen while the BET surface area was calculated by the equipment. Depending on the nature of the sample and the type of analysis performed (BET or BET and BJH), the analysis would usually take from half an hour up to two hours. After the analysis was completed the results were displayed on the screen of the equipment.

5.4.2.2 Environmental Scanning Electron Microscope (ESEM)

In addition to surface area analysis, among the analytical investigations carried out on the prepared PHPs is the morphological characterization by means of environmental scanning electron microscopy (ESEM). Both un-sulphonated and sulphonated PHPs were ESEMed. Although SEM was first discovered in 1930's, with the first SEM image taken by Max Knoll, it took decades for commercial marketing, until 1965 when Charles Oatley and Gary Stewart first introduced it to the market by the Cambridge Instrument Company under the name of Stereoscan. Since then, SEM has seen continuous improvements in terms of the image resolution and image recording time. To this end, its use has become widespread, both in terms of production by different companies worldwide and the extent of the application for material research laboratories.

Due to multiple signals generated in a SEM analysis, a wide (low/high 3-150,000 times or more) magnification range, simple image formation of the morphology of a specimen with high resolution and great depth of field (300 times higher than that of an ordinary light microscope) which facilitates more exposure of the specimen at different distances from the lens which gives the image three-dimensional information, have made ESEM a good candidate for imaging techniques. The actual magnification results from the ratio of the area scanned on the specimen to the area of the television screen, rather than by the lens. A photograph of an ESEM is illustrated in Fig. (5.13).

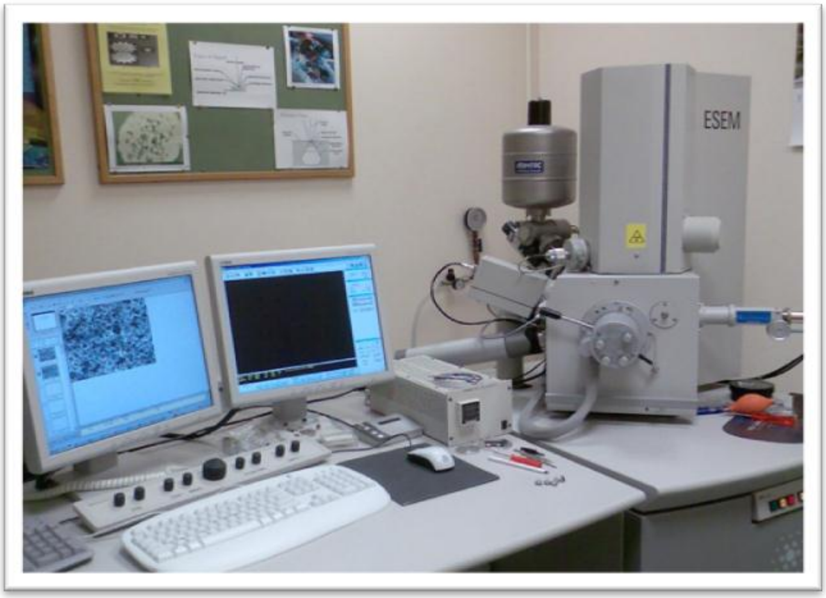


Fig. (5.13): Photograph of an Environmental Scanning Electron Microscope (ESEM).

Therefore, ESEM was used to reveal the internal architecture of the post-functionalized fresh PHP membranes such as the PHP pore size distribution, interconnecting structure and the wall porosity. Depending on the possibility of having the oil-fouled membrane(s) compatible with the normal requirement of use of an ESEM microscope that a sample should be dry and that no volatile component(s) of oil might vaporize and contaminate the unit, some ESEM images may also be taken for these membranes. The electron microscope used in this present work was a FEI XL30 ESEM, field emission gun (FEG) at the Advanced Chemical and Materials Analysis (ACMA) Centre at Newcastle University, UK. This instrument can analyze wet and nonconductive samples due to its capability to work at high vacuums. Although it is intuitive to coat

ESEM non-conductive specimens with a conductive media to attain the necessary conductivity, usually with carbon/gold. In this work; however, specimens were examined after being processed, modified and dried as they are without any coating since they are hydrophilic and; therefore, conductive. Each specimen was cut and mounted on stainless pin stub 12.7 mm diameter.

The principle of operation of a SEM is as follows. An electron microscope uses an electron beam (not light as in traditional microscopes) to generate a highly magnified image of the specimen under analysis. This electron beam is fired from a gun which sits at the top of the microscope. This beam then, in a vertical direction, enters a chamber which is maintained at a vacuum pressure to allow the effective travel of an electron beam. Within this chamber, the electron beam passes a series of: an electrode (anode), a magnetic lens (to focus the electron beam onto the sample surface) and scanning coils. Having passed these consecutive stages, but still within the vacuum chamber, the electron beam finally strikes the sample/specimen resulting in electron and x-ray ejection from the sample. These electrons are the primary back-scattered, secondary and Auger electrons. A detector then collects these electrons and x-rays into a signal which is then sent to a TV screen to represent the specimen image. Fig. (5.14) illustrates this procedure schematically.

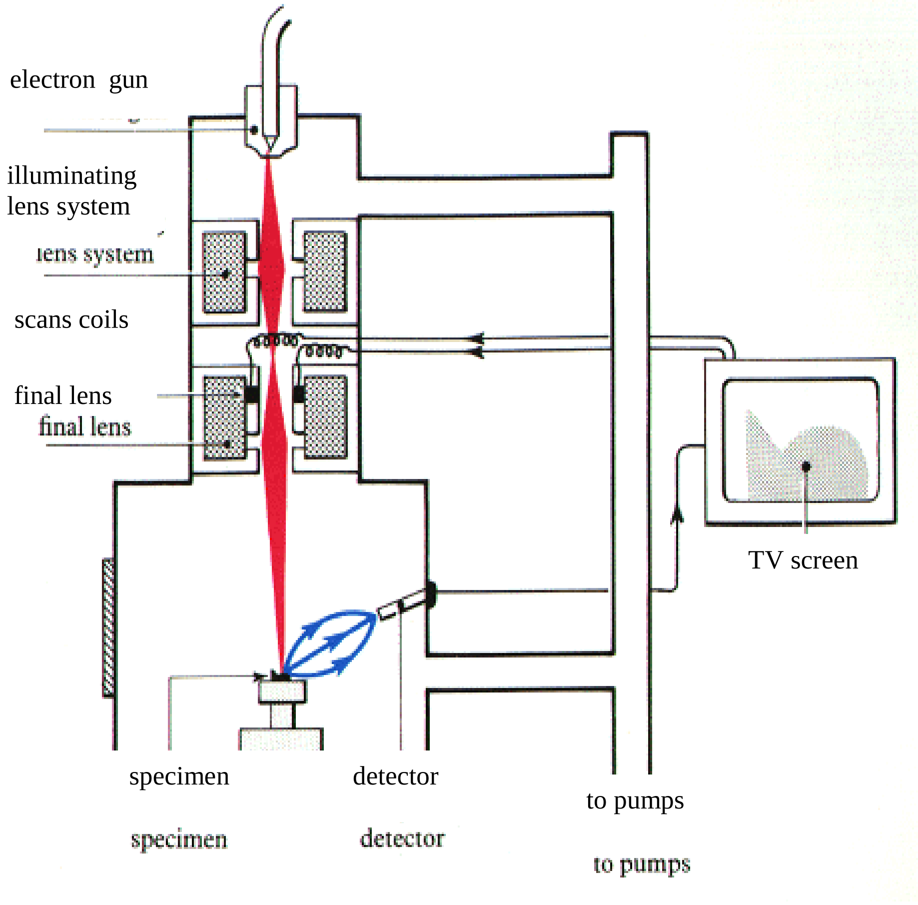


Fig. (5.14): Schematic drawing of a scanning electron microscope with secondary electrons forming the images on the TV screen.

The secondary electrons are selectively attracted to a grid held at a low (50 volt) positive potential with respect to the specimen. Behind the grid there is a disc held at about 10 kilovolts and positive with respect to the specimen. The disc consists of a layer of scintillant, coated with a thin layer of aluminium. The strength of this voltage depends on the number of secondary electrons that are striking the disc. Thus, the secondary electrons produced from a small area of the specimen gives rise to a voltage signal of a particular strength. The voltage is led out of the microscope column to an electronic console, where it is processed and amplified to generate a point of brightness on a cathode ray tube (television) screen.

Chapter Six

Results and Discussion

Chapter Six

Results and Discussion

> Whatever course you decide upon there is always someone
> to tell you that you are wrong. There are always difficulties
> arising which tempt you to believe that your critics are right.
> To map out a course of action and follow it to an end
> requires courage.
>
> Ralph Waldo Emerson
> (1803-1882)

6.1 Introduction

Several w/o emulsions demulsification processes including chemical, thermal and electrical and microfiltration have been reviewed and discussed in Chapters 3 and 4, respectively. Being the main aim of this study, water phase separation from w/o emulsion by membrane technology was tested with a hydrophilic membrane, prepared ‘in-house’, by the methods explained in Chapter 5 and the results are represented and discussed in this Chapter. This Chapter starts first by referring to the measurement of pump flow rate for the system (pump and emulsion) used in this work as well as some related calculations including calculation of total crossflow velocity (CFV), permeate flux rate (J) and electrical field intensity (E). Results of bottle test analysis to measure the extent of phase separation of the prepared emulsions are also provided. Next, measurements of feed and permeate conductivities are also given. The effect of influent emulsion water content, filtration duration, feed CFV, electric field and membrane pore size on the permeate flux rate was studied. This was then followed by an investigation of the effect of these filtration variables on demulsification efficiency. Investigations were carried out using two emulsions of two different water contents, namely 30 and 50 vol. % of water (dispersed phase), referred to henceforth as EI and EII, respectively. Unless stated otherwise, data for all tests are given in Appendices (A-B).

6.2 Measurement of Pump Flow Rate

Having turned on the pump and allowed the circulation of the emulsion EI for 15 min; to ensure steady state operation, a procedure of pump flow rate measurement based on its rpm as explained in Sec. 5.31 in Chapter 5 was followed. The pump drive speed was used to alter the operational speed gradually from 100 to 1000 rpm. Although the pump is designed to operate at higher speeds it was only run up to this maximum (1000 rpm) to avoid any vibrations. To ensure the reproducibility of the results at each rpm, measurements were repeated twice and the average reported. Details of these measurements are tabulated in Table (6.1) below which reveal a linear relationship, with a slight deviation from linearity, between the pump rpm's (up to 700 rpm) and the obtained flow rate. According to Fig. (6.1), a non-linear behaviour; however, is noticed at higher rpms. This means, at higher rpm levels, changing the pump speed to attain a change of flow, is rather different and dependent upon the correspondent rpm. For instance, increasing the pump rpm from 800 to 900 has led to increasing the flow rate from 1485 to 1980 L/hr ($4.125*10^{-4}$ to $5.5*10^{-4}$ m^3/sec), whereas the flow rate increased to 3420 L/hr ($9.5*10^{-4}$ m^3/sec) when the rpm was increased from 900 to 1000 rpm. It should also be mentioned that measurements curves obtained from both emulsions (EI and EII) are with a very trivial difference in terms of the obtained flow rate. To this end, the measurement curve of emulsion EI has been considered as a typical one for both emulsions in this study.

Table (6.1): Measurements of pump flow rate with respect to emulsion EI.

Rpm	Volume, ml		Time, sec	Flow arte, ml/sec		Average flow rate, m1/sec	Average flow rate, l/hr
	1st attempt	2nd attempt		1st attempt	2nd attempt		
1000	900	1000	1	900	1000	950	3420
900	1100	1100	2	550	550	550	1980
800	820	830	2	410	415	412.50	1485
700	810	830	2	405	415	410	1476
600	1050	1100	3	350	366.70	358.40	1290.20
500	860	860	3	286.70	286.70	286.70	1032.10
400	780	800	3	260	266.70	263.40	948.20
300	680	690	3	226.70	230	228.40	822.20
200	520	530	3	173.30	176.70	175	630
100	400	400	5	80	80	80	288
50	380	380	10	38	38	38	136.80
0	0	0	0	0	0	0	0

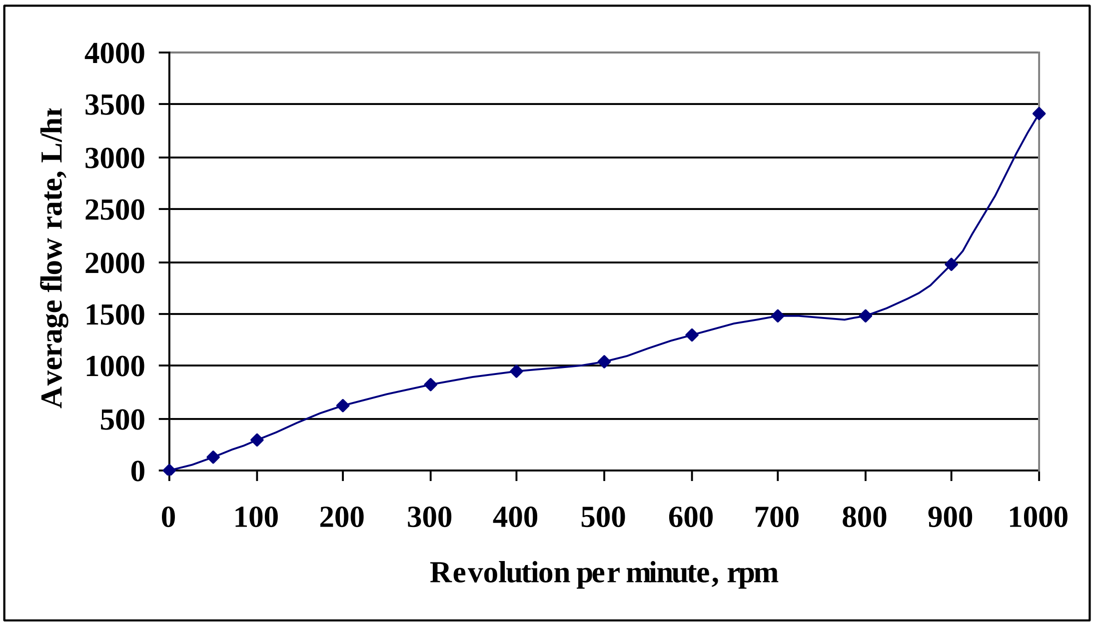


Fig. (6.1): Average pump flow rate vs. pump rpms.

6.3 Calculation of Total Crossflow Velocity (CFV)

The total volumetric flow rate of a fluid in a system of *n* pipes connected to a reservoir in parallel, as the pressure drop is the same, is the sum of the flow in each individual pipe. Such a system is schematically depicted in Fig. (6.2).

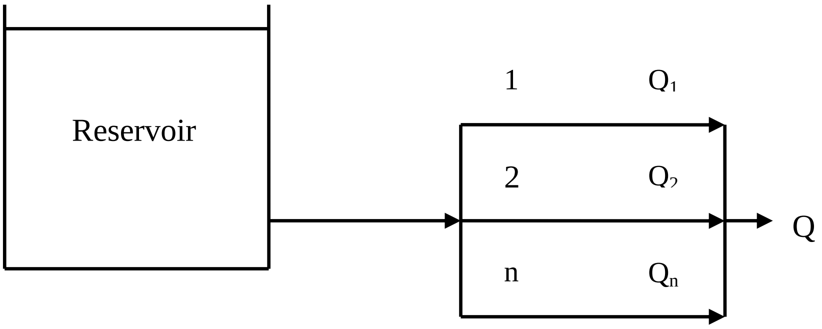


Fig. (6.2): Pipes in parallel (Kothandaraman and Rudramoorthy, 2007).

$$Q = Q_1+Q_2 + Q_3 +\ldots\ldots+ Q_n$$

Where Q denotes the total volumetric flow rate whereas Q_1 through Q_n denote flow rate through pipes 1 through n, respectively (Kothandaraman and Rudramoorthy, 2007).

In this work, the number of pipes is two, i.e.:

Therefore: $Q = Q_1+Q_2$

Since the two pipes are of identical diameter, it can be assumed that individual volumetric flow rate in each pipe is equal, i.e., $Q_1 = Q_2.$

Since: $Q = Q_1 + Q_1$

Thus: $Q = 2 Q_1$

Solving for $Q1$, gives: $Q_1 = ½ Q= Q_2$

In order to convert a volumetric flow rate of whatever fluid through a pipe into a crossflow velocity, V, the former is simply divided by the cross-sectional area of that pipe.

$$V_1= Q_1/ A_p = V_2$$

Where V_1 and V_2 are the velocity of the fluid in pipe 1 and pipe 2, m/sec, respectively, A_p is the cross-sectional area of the pipe, m^2.

Finally, the total crossflow velocity (CFV) that the emulsion is fed by to the cell is:

$$V = V_1 + V_2$$

Therefore, the CFV at a flow rate of 3420 l/hr, which is equivalent to 1000 rpm, see Table (6.1), has been calculated as follows:

$$V_1= Q_1/ A_p$$

$$Q= 1000\ rpm= 3420\ l/hr= 9.50*10^{-4}\ m^3/sec=2\ Q_1=2\ Q_2$$

Therefore:

$$V_1= (9.50*10^{-4})/2/ (\pi*(0.005*0.005))$$

$$=6\ m/sec= V_2$$

Thus: $V = 6 +6$

$$=12\ m/sec.$$

Accordingly, the remainder of CFVs at lower rpms have been calculated and are tabulated in the following table, Table (6.2).

Table (6.2): Conversion of pump rpms onto feed CFV.

Rpm	Total CFV, m/sec
900	7
800	5.25
700	5.20
600	4.60
500	3.65
400	3.35
300	2.90
200	2.25
100	1
50	0.50
0	0

6.4 Calculation of Permeate Flux Rate (*J*) and Electrical Field Intensity (E)

Although the permeate flux rate has already been defined in Sec. 4.3.1 in Chapter 4, it might be useful in this Chapter to repeat its definition again. The permeate flux rate *(J)* measures the permeate volume, *V (L)* collected during the filtration process per unit of cross sectional area of membrane, $A\ (m^2)$ that's perpendicular to the direction of the feed flow as a function of time, τ *(hr)* as expressed in the following equation (Cheryan, 1998):

$$J = V\,(L) / (A, m^2)\ (\tau, hr)$$

In this work, as has been previously mentioned in Sec. 5.3.4 in Chapter 5, τ was randomly chosen in a way it allowed the collection of a readable volume of the sample on the tube's scale, and also to ensure that the sampling tube can accommodate the entire permeate sample without a risk of flooding since the valve used *did* require a time to fully close. To take this into account, the following tables were constructed. The cross sectional area of membranes used was always constant at 38.5 cm^2 (7cm length *5.5 width). The permeate flux rate of emulsion EI when using no electrical field, as shown in the first row from top in Table (6.6) below, was calculated through the equation given below as shown next. The volume of permeate sample collected was 2.70 ml/sec (which is equivalent to 9.72 L/hr) which was then divided by the membrane cross sectional area (0.00385 m^2). This yields a permeate flux rate of 2524.70 L/m^2. hr as indicated in Tables (6.6-23).

$$J = 9.72(L)/\ 0.00385(m^2)\ 1(hr)$$

$$= 2524.70\ \mathrm{l/m^2\ hr}$$

Also, the electric field *(E)* across the cell has been calculated by dividing the voltage applied by the DCR-T power supplier by the distance between the electrodes (3 mm = 0.3 cm). Therefore, the correspondent *E* when for example applying *10 V* is as follows:

$$E = 10/0.30$$

$$= 33.30\ V/cm.$$

The following table, Table (6.3), shows the complete range of electrical fields applied.

Table (6.3): Electric field vs. voltage applied.

Voltage, V	0	10	25	50	100	200
Electric field, V/cm	0	33.30	83.30	166.70	333.30	666.70

6.5 Assessment of Phase Separation of Fresh Emulsions

As stated earlier in the methodology section in Chapter 5, Sec. 5.3.2, the bottle test method was utilized to assess the stability of the prepared w/o emulsion(s) by monitoring water phase separation against time. The amount of resolved water is the most suitable measure of the emulsion stability of w/o emulsions, since the coalescence of the droplet phase is the limiting step in the demulsification process (Xia et al., 2004). Typical water phase separation data against settling time for fresh emulsions EI and EII are reported in Table (6.4) and Fig. (6.3). Prepared emulsions have remained intact over a period of time, in which no water phase separation was observed until 79/71 days (1896/1704 hr) in the case of emulsion EI/EII; respectively, have elapsed. In the case of emulsion EI, a maximum percentage of 43 vol. % of the collected sample was water, and in the case of emulsion EII, the sample contained 48 vol. % water, see Fig. (6.3). It is also of interest to observe that emulsion EI, that originally had a lower water content than emulsion EII, when broken down has ultimately exhibited less water than emulsion EII and that it required longer time to do so.

Table (6.4): Bottle test results of phase separation observed as a function of time for both EI and EII w/o emulsions.

Water phase separation, %		
Settling time, days	Emulsion water content, vol. %	
	30	50
0	0	0
Up to 14	0	0
Up to 28	0	0
Up to 42	0	0
Up to 56	0	0
Up to 70	0	0
Up to 84	43	48
Up to 98	43	48

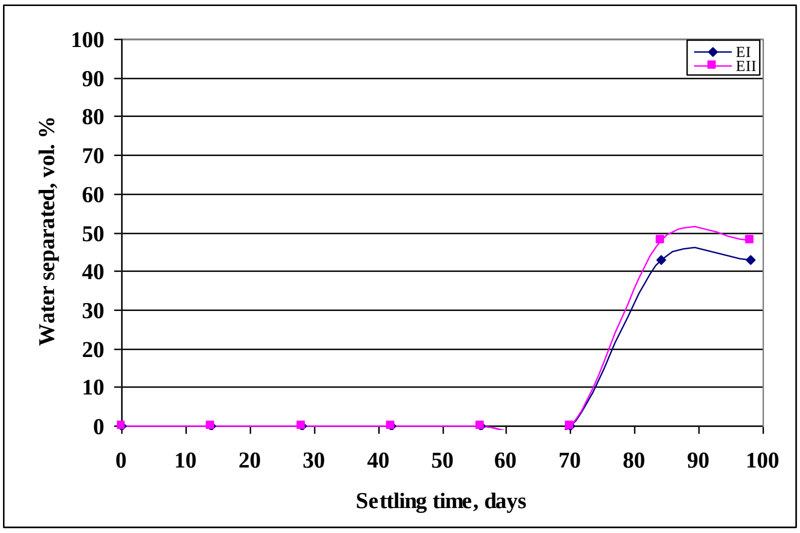


Fig. (6.3): Bottle test results of phase separation observed as a function of time for both EI and EII w/o emulsions.

6.6 Conductivity Measurements

Conductivities of feed and permeate samples were recorded once collected. Table (6.5) gives the obtained conductivities, with respect to feed EI and EII stream using membrane MI, at different filtration conditions. It is clear that samples of fresh emulsion EII (50 % vol. water content) have higher conductivities than those of samples of fresh emulsion EI (only 30 % vol. water content). This difference in conductivity value can be attributed to the corresponding amount of water in each emulsion, since the higher the water content in an emulsion is, the higher the conductivity would be (Becher, 2001). In fact, w/o emulsions are characterized with very low conductivities, whereas o/w emulsions have a very high conductivity very close to that of water (Schramm 1992). Conductivities of permeate samples are generally higher than those of the parallel fresh feed samples. This indicates that permeate samples are with higher water content than that of feed samples, see Tables (6.25-38). A good reason for this water content is perhaps the hydrophilicity of the PHP membrane that has resulted in more water in the permeate stream.

Table (6.5): Conductivities of feed and permeate samples from memebrane MI.

Stream	Conductivity, µs/cm		
Feed EI	0.4		
Feed EII	0.52		
Permeate Based on E1 using MI	No current and 1 m/sec	With 33.30 V/cm and 1 m/sec	With 83.30 V/cm and 1 m/sec
	0.51	0.51	0.53
Permeate Based on E2 using MI	No current and 1 m/sec	With 33.30 V/cm and 1 m/sec	With 83.30 V/cm and 1 m/sec
	0.52	0.54	0.58

6.7 Results of Transmission Electron Microscope (TEM)

Figs. (6.4-a-b) show TEM micrographs of permeate samples. Presence of coalescing oil droplets in the separated water layer in permeate is shown, see Fig. (6.4-a). Presence of water droplets in the separated oil phase in permeate possibly showing that the water phase is stabilized by a thick layer of surface active material (asphaltenes and resins), see Fig. (6.4-b). Figs. (6.5-a-b) show TEM micrographs of retentate samples. Fig. (6.5-b) shows the presence of small oil phase droplets. Distortion is possibly due to sample preparation as a result of spreading it on the grid.

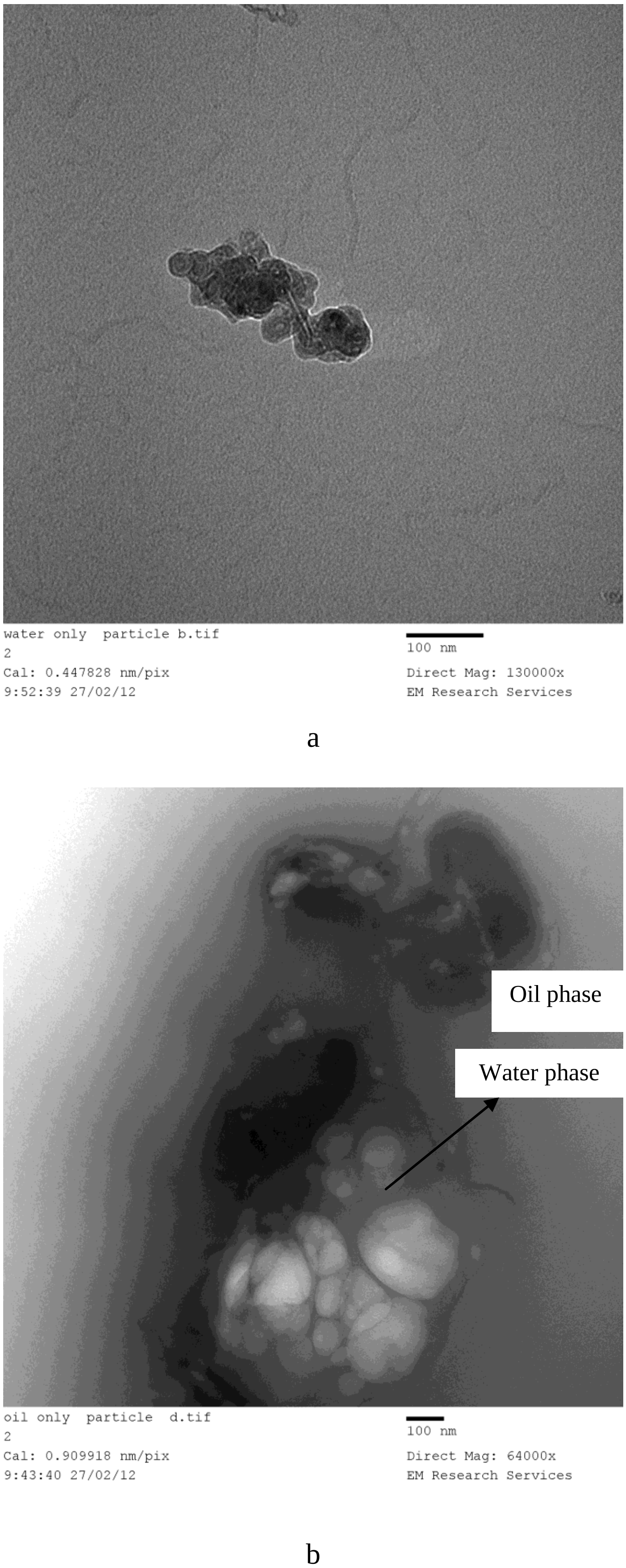


Fig. (6.4): TEM micrographs of permeate samples.

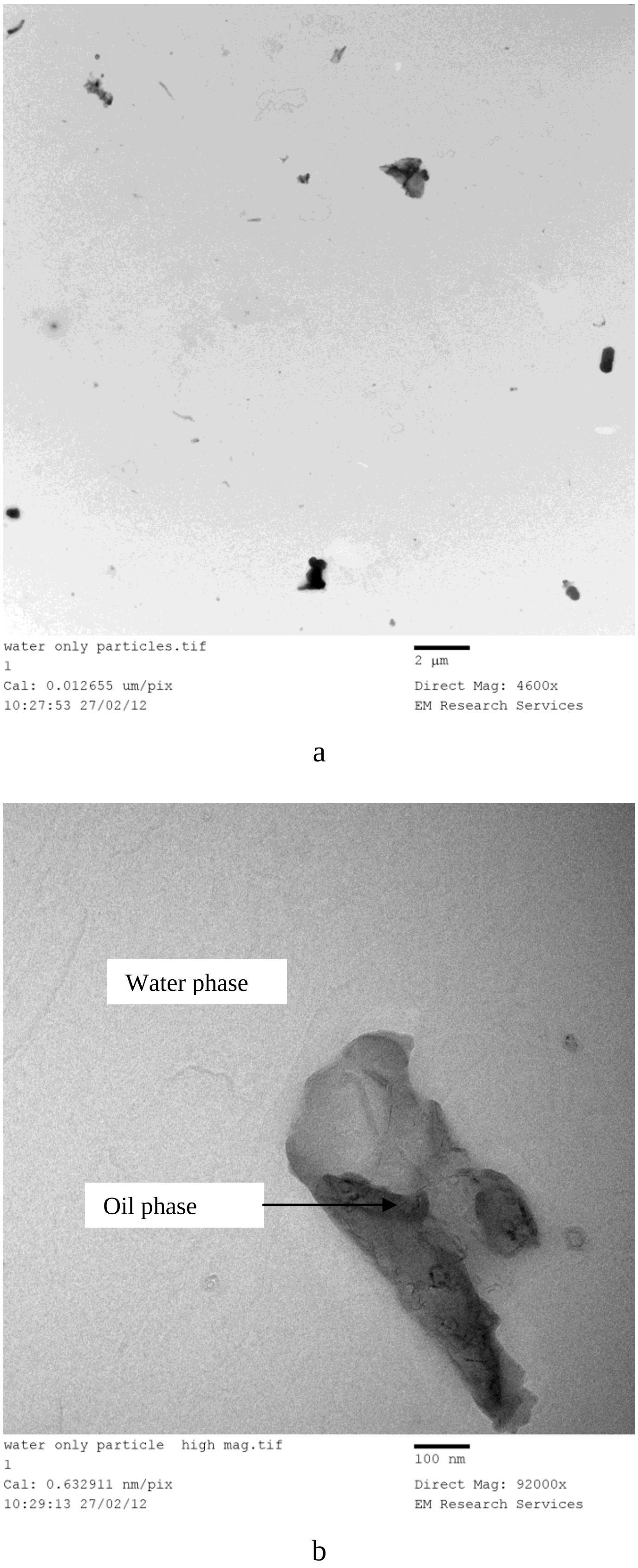
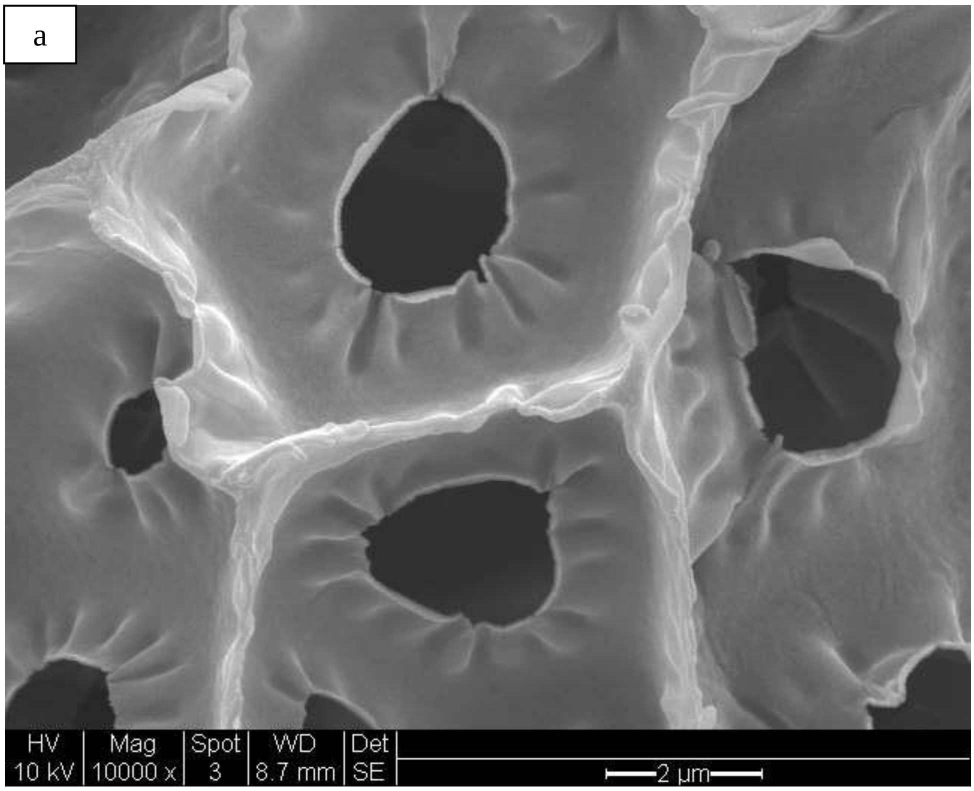
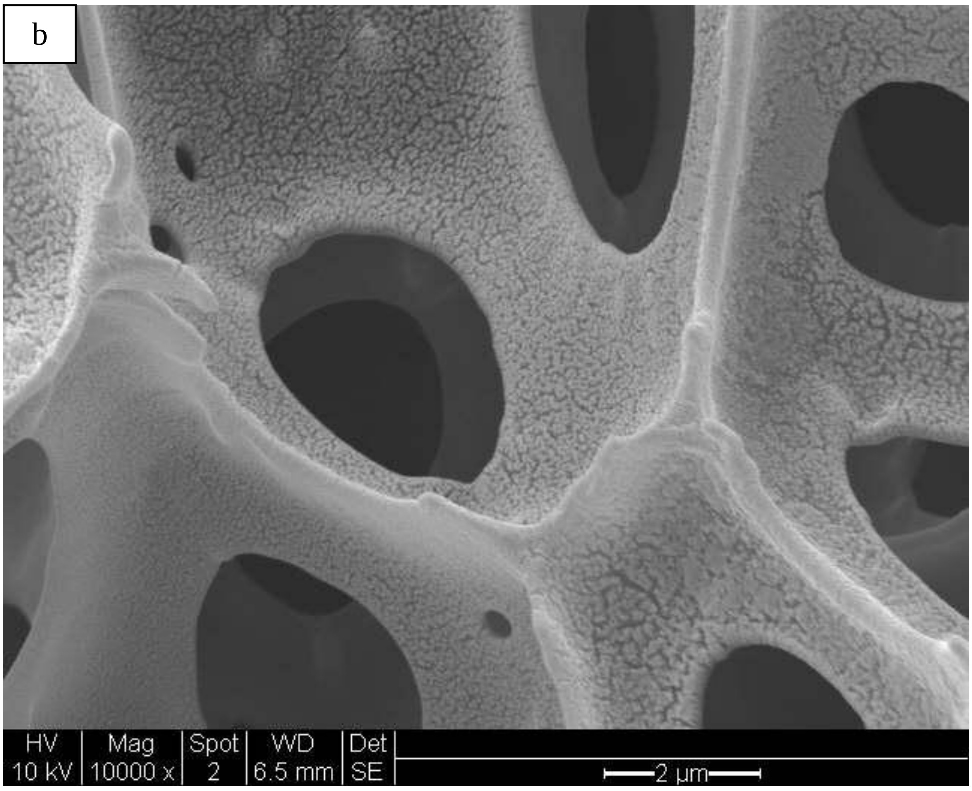


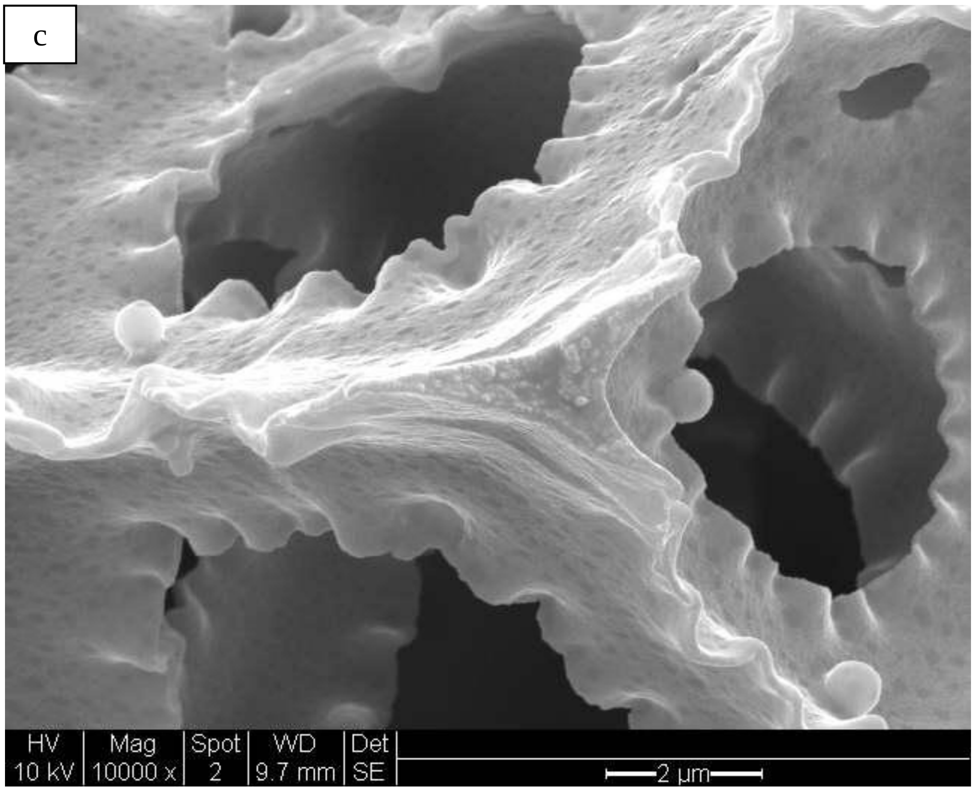
Fig. (6.5): TEM micrographs of retentate samples.

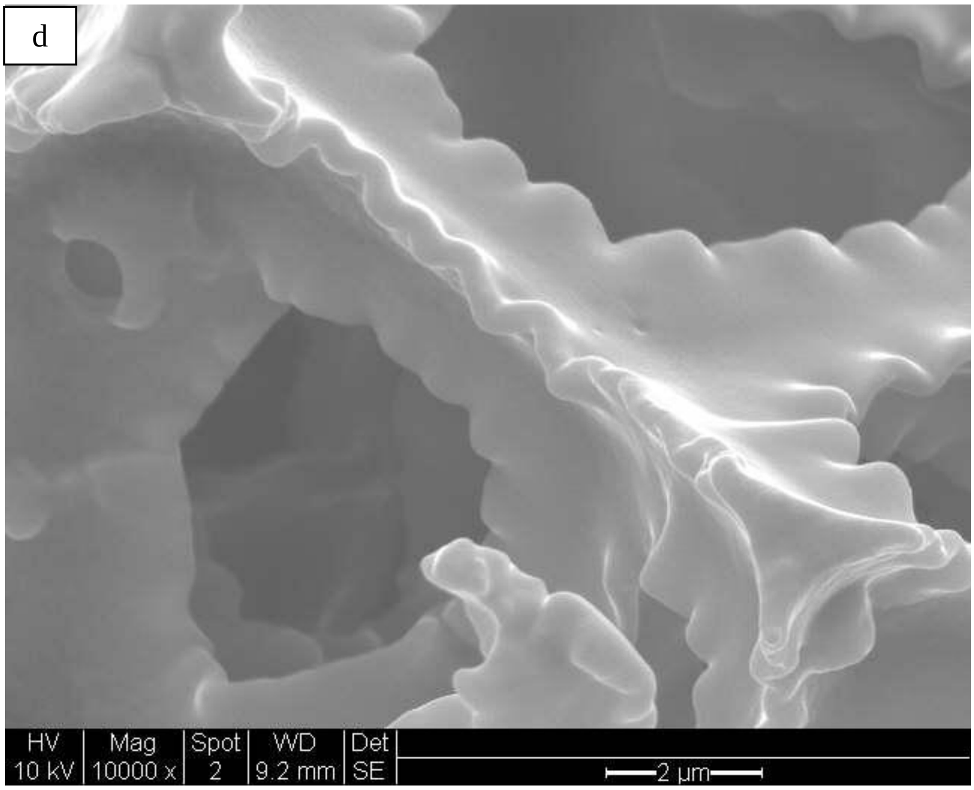
6.8 Results of Environmental Scanning Electron Microscope (ESEM)

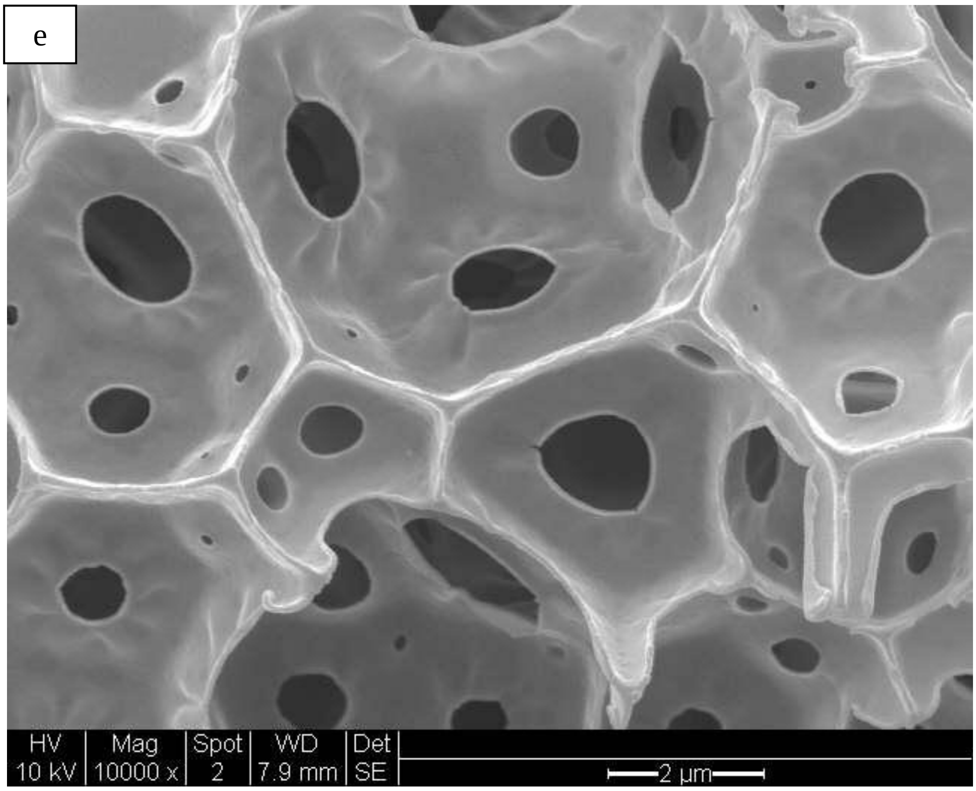
In Figs. (6.6-a-c), the ESEM micrographs for un-sulphonated PHPs (membranes: MI, MII and MIII) are shown; respectively. Similarly, Figs. (6.6-d-f) show the effect of sulphonation by sulphuric acid on the morphology of sulphonated membranes. In the first set of these micrographs (a-c), a typical PHP microstructure showing the pores and the interconnects between them is shown. The rest of these micrographs evidently demonstrate a morphological change in the structure of the relevant PHPs. Generally, such a change causes the PHP to expand and renders it with larger pore sizes, wider walls whilst maintaining the holes on them. This may result in higher absorption capability and improved permeate flux rates as filtration processes are concerned.




b
HV 10 kV
Mag 10000 x
Spot 2
WD 6.5 mm
Det SE
2 µm


c
HV 10 kV
Mag 10000 x
Spot 2
WD 9.7 mm
Det SE
2 µm


d
HV 10 kV
Mag 10000 x
Spot 2
WD 9.2 mm
Det SE
2 µm


e
HV 10 kV
Mag 10000 x
Spot 2
WD 7.9 mm
Det SE
2 µm

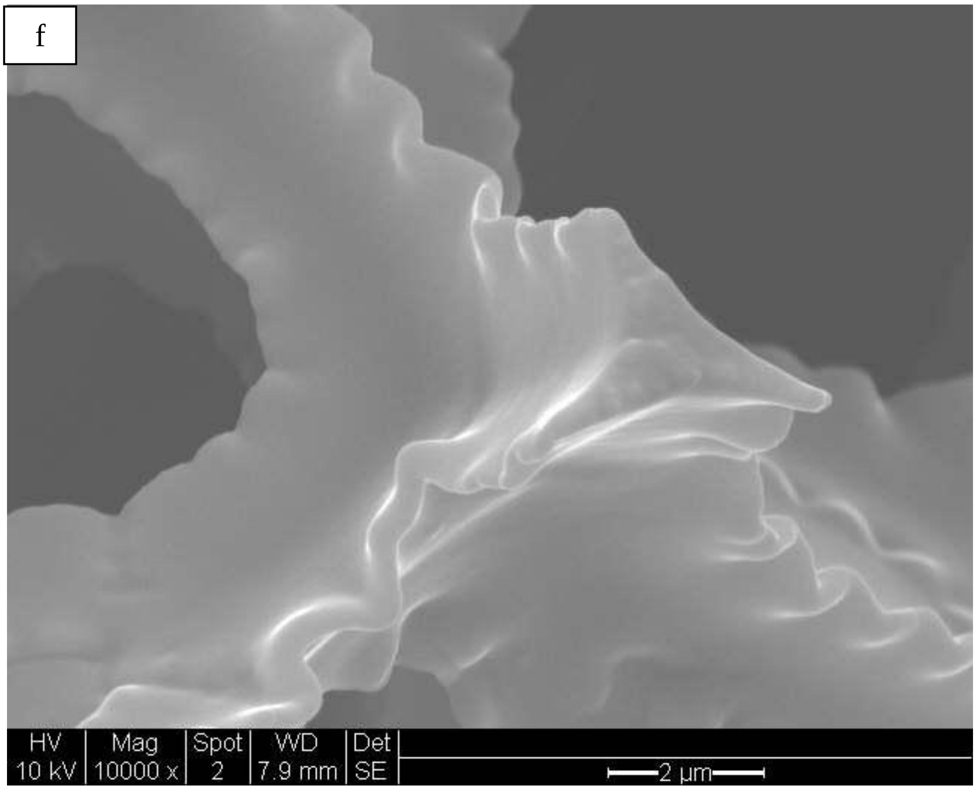


Fig. (6.6): ESEM micrographs for un-sulphonated and sulphonated PHPs. a- Membrane MI un-sulphonated; b- Membrane MII un-sulphonated; c- Membrane MIII un-sulphonated; d- Membrane MI sulphonated; e- Membrane MII sulphonated and f- Membrane MIII sulphonated. Magnification 10000X.

6.9 Effect of Influent Emulsion Water Content on Permeate Flux Rate

The effect of feed water content on membrane permeation was tested at different feed flow rates ($8*10^{-5}$-$9.5*10^{-4}$ m^3/sec) and electric field intensities (0-666.70 V/cm) using three different membranes in terms of their pore sizes for invariable filtration duration of 30 min. This investigation was carried out on both emulsions EI and EII. The influence of influent emulsion water content on the permeate flux rate from membrane MI at flow rate of $8*10^{-5}$ m^3/sec and electric fields of 0, 33.30 and 83.30 V/cm as a function of filtration time has been placed in the main body of this study as shown in Table (6.6) and Fig. (6.7), respectively. Similarly, permeates obtained from membranes MII and MIII at the same conditions are also presented in Tables (6.7-8) and Figs. (6.8-9), respectively. However, further experimental results of these investigations at higher conditions are collated in Appendix A.

Table (6.6): Effect of emulsion water content on permeate flux rate for membrane MI for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

Filtration time, min	Permeate flux rate, l/m^2. hr					
	Electric field, V/cm					
	0		33.30		83.30	
	Emulsion water content, vol. %		Emulsion water content, vol. %		Emulsion water content, vol. %	
	30	50	30	50	30	50
0	2524.7	2646.2	2922.1	3272.7	3039	3422.3
5	2758.4	2898.7	3272.7	3581.3	3422.3	3889.8
10	2945.5	3039	3506.5	3740.3	3581.3	4516.4
15	1963.6	2103.9	2197.4	2487.3	2571.4	2954.8
20	1753.3	1963.6	2010.4	2337.7	2103.9	2646.2
25	1355.8	1552.2	1402.6	1963.6	1711.2	2337.7
30	1192.2	1402.6	1262.3	1636.4	1355.8	1870.1

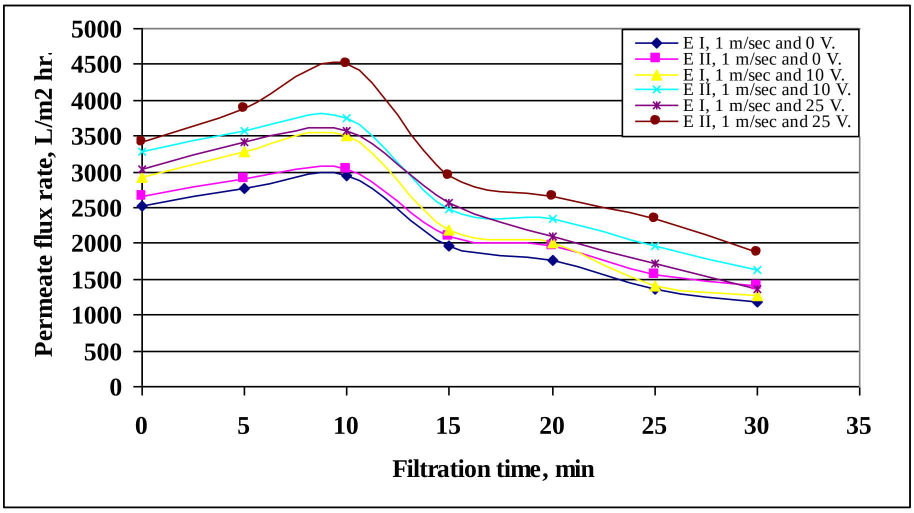


Fig. (6.7): Effect of emulsion water content on permeate flux rate for membrane MI for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

Table (6.7): Effect of emulsion water content on permeate flux rate for membrane MII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

Permeate flux rate, l/m^2. hr						
Filtration time, min	Electric field, V/cm					
	0		33.30		83.30	
	Emulsion water content, vol. %		Emulsion water content, vol. %		Emulsion water content, vol. %	
	30	50	30	50	30	50
0	2244.2	2337.7	2646.2	2805.2	2805.2	3113.8
5	2618.2	2618.2	3039	3113.8	3113.8	3272.7
10	2758.4	2898.7	3113.8	3422.3	3740.3	4048.8
15	2178.7	2337.7	2459.2	2805.2	2805.2	3272.7
20	2010.4	2178.7	2057.1	2646.2	2487.3	2898.7
25	1916.9	2103.9	2010.4	2103.9	2487.3	2805.2
30	1711.2	1870.1	1870.1	1870.1	2057.1	2646.2

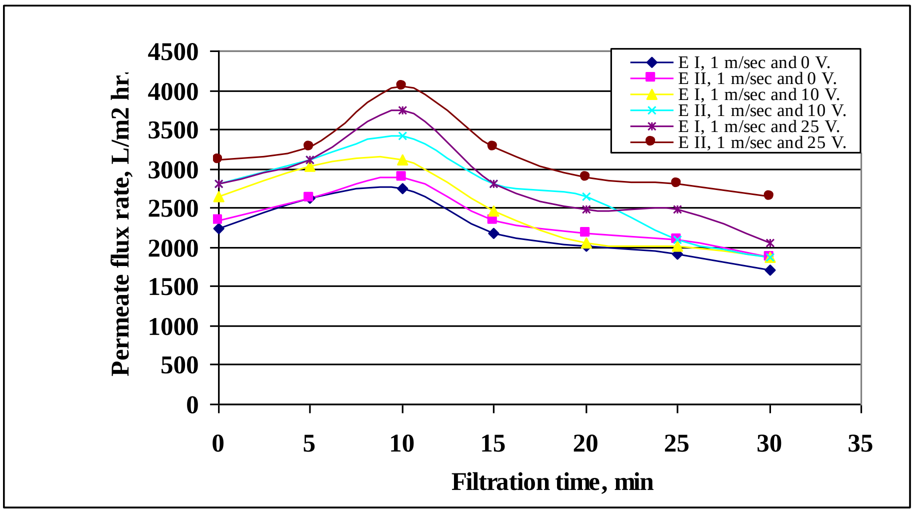


Fig. (6.8): Effect of emulsion water content on permeate flux rate for membrane MII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

Table (6.8): Effect of emulsion water content on permeate flux rate for membrane MIII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

Permeate flux rate, l/m^2. hr						
Filtration time, min	Electric field, V/cm					
	0		33.30		83.30	
	Emulsion water content, vol. %		Emulsion water content, vol. %		Emulsion water content, vol. %	
	30	50	30	50	30	50
0	2618.2	2805.2	3039	3422.3	3272.7	3581.3
5	3422.3	3740.3	3740.3	4207.8	4048.8	4768.8
10	3553.3	3974	4048.8	4909.1	4675.3	5451.4
15	3506.5	3581.3	3740.3	4357.4	4357.4	4675.3
20	2711.7	2898.7	3039	3581.3	3506.5	3974
25	2178.7	2337.7	2487.3	3039	2646.2	3272.7
30	1309.1	1552.2	1711.2	1963.6	1870.1	2337.7

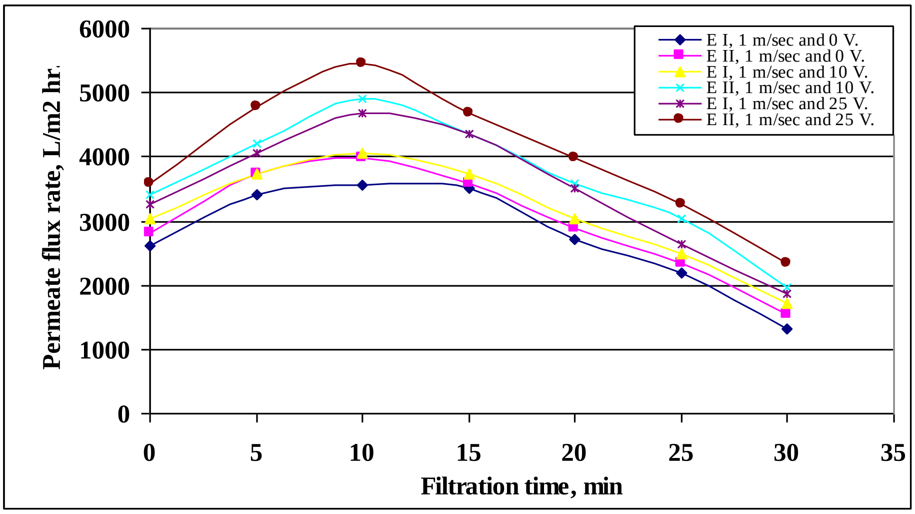


Fig. (6.9): Effect of emulsion water content on permeate flux rate for membrane MIII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

Throughout the course of microfiltration of both emulsions, that's with 30 and 50 vol. % water content, using membrane MI for half an hour, Fig. (6.7) indicates that there was an increase in the membrane flux for the first ten minutes from 2524.7 to 2945.5 l/m^2 hr in case of emulsion EI and from 2646.2 to 3039 l/m^2 hr in case of emulsion EII . This was also the case with other membranes MII and MIII as they initially produced 2244.2 and 2337.7 l/m^2 hr following microfiltering emulsion EI and 2618.2 and 2805.2 l/m^2 hr following microfiltering emulsion EII, respectively. With reference to that, by the end of the first third of filtration time for emulsions EI and EII, these membranes produced 2758.4 and 2898.7 l/m^2 hr and 3553.3 and 3974 l/m^2 hr; respectively. This was then followed by a decrease in flux rate as filtration time elapsed until it mostly became independent of filtration time. For instance, by using membrane MI it reached a plateau of 1192.2 and 1402.6 l/m^2 hr for emulsion EI and EII by the end of the filtration time, respectively. A similar trend was also observed on the permeation-time relationship for membranes MII and MIII.

The declination of permeate flux rate with time is perhaps due to the increase of membrane resistance as a result of the development of an oily layer on the membrane surface or within its pore structure (Wakeman and Tarleton, 1991; Wakeman and Tarleton, 1986). In fact, larger oil droplets than the membrane pores may have attached to the membrane surface, whereas smaller ones would have penetrated throughout the membrane structure leading to internal pore fouling. These phenomena can modify the surface properties of the hydrophilic membrane as well as diminish the effective available pore diameter prior to membrane fouling, respectively, which in turn results in a reduced membrane flux.

The application of an electric field(s) (33.30 and 83.30 V/cm) to both emulsions resulted in increased permeates obtained from all used membranes. In comparison to filtration with no electrical field, permeate flux rates after 15 minutes of filtration of emulsion EI, from membranes MI, MII and MIII were 1963.6, 2178.7 and 3506.5 l/m^2 hr, respectively. By comparison, the permeate flux rate was 2197.4 l/m^2 hr from membrane MI, 2459.2 l/m^2 hr from membrane MII and 3740.3 l/m^2 hr from membrane MIII when applying an electric field of 33.30 V/cm. Also, following increasing the electric field to 83.30 V/cm using membranes MI, MII and MIII, the permeate flux rate at 15 minutes of filtration increased to 2571.4, 2805.2 and 4357.4 l/m^2 hr, respectively. Likewise when using emulsion EII, the permeate flux rate obtained from membrane MI; for example, at 15 minutes of filtration, with no electric field and with 33.30 and 83.30 V/cm, was 2103.9, 2487.3 and 2954.8 l/m^2 hr, respectively. For the permeates collected from MII and MIII, the reader is referred to Tables (6.7-8). A later section in this Chapter shall examine such effect of electric field on permeate flux rate. Among the two emulsions filtered at all conditions, it is obvious that the emulsion with higher oil content (70 vol. %) produced a lower membrane flux rate throughout the entire period of filtration than that obtained in case of microfiltering the emulsion with only 50 vol. % oil content. An increase in the oil content in the feed stream leads to an increased oil concentration in the boundary layer of oil droplets on the hydrophilic membrane and; thus, a lower membrane flux rate would be the outcome as the filtration proceeds. These hydrophobic rejected oil droplets, or at least with no strong affinity towards the membrane surface, compared to water droplets, will gather at the membrane surface and build a boundary layer, which perhaps is mainly composed of oil. With time, these retained oil droplets, to an extent, tend to accumulate at the membrane surface which eventually has the sequence of reducing the membrane flux.

6.10 Effect of Filtration Time on Permeate Flux Rate

In order to investigate the effect of filtration time on permeate flux rate at various filtration conditions, several experiments at various conditions of emulsion water contents, flow rates and electric fields strengths using three PHP membranes with different pore sizes were performed. In these experiments, two emulsions with different water contents were used, namely, 30 and 50 vol. % of water content. Inlet flow rate was changed in the range of ($8*10^{-5}$-$9.5*10^{-4}$ m^3/sec) with applying electric fields of (0-666.70 V/cm). A sample of the results of these experiments for each membrane is separately shown below in Tables (6.9-11) and Figs. (6.10-15). For a complete set of results, refer to Appendix A. Initially, for both emulsion water contents, the flux increased as filtration time increased, and then it started to decline with time until it underwent no change with filtration time, i.e., steady state operation.

The permeate flux rate declination may be caused by membrane pore blockage and/or settlement of emulsion droplets on the membrane surface as filtration time increases. Based on these graphs in Figs. (6.10-15), it seems that emulsion water content, membrane pore size, flow rate, or presence of electric field with different intensities, has no influence on the shape of the relationship between membrane permeation rate and filtration time, as the trend of variation of permeate flux rate from each membrane examined, with time, is almost identical, irrespective of emulsion water content, membrane pore size, flow rate or presence of an electric field. However, using a membrane with larger pore size, increasing the flow rate and/or applying an electrical field across the filtration module *does* increase the value of the permeate flux rate accordingly over the whole period of filtration time. Interpretations of this increment of permeate flux rate with membrane pore size, feed flow rate and/or electric field will be discussed in later sections of this Chapter.

With time, where a secondary membrane of deposits (surfactants) appears to have formed on the membrane surface, it seems that membrane-solute interactions, which are mainly the driving force for emulsion filtration, have become less active. This can be understood from the drop in difference in membrane permeates in the second half of filtration, in comparison to the first half. By way of example, not exhaustive enumeration, the difference in permeate flux rate at 15 min of filtration through membrane MI, with an electrical field of 83.30 V/cm and without an electrical field, at $8*10^{-5}$ m^3/sec was 1009.9 and 981.9 l/m^2 hr for emulsion EI and 1561.6 and 935.1 l/m^2 hr for emulsion EII, respectively. However, this difference by the end of the filtration period under the same filtration conditions was only 355.4 and 163.6 l/m^2 hr, for emulsion EI and 467.6 and 149.6 l/m^2 hr, for emulsion EII, respectively. Under higher filtration rate conditions of feed CFV and/or electrical field, this observation is also applicable.

Table (6.9): Time dependent-permeate flux rate for membrane MI for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 2.25 and 2.90 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

Permeate flux rate, l/m^2. hr																		
Filtration time, min	CFV, m/sec																	
	1						2.25						2.90					
	Emulsion water content, vol. %						Emulsion water content, vol. %						Emulsion water content, vol. %					
	30			50			30			50			30			50		
	Electric field, V/cm			Electric field, V/cm			Electric field, V/cm			Electric field, V/cm			Electric field, V/cm			Electric field, V/cm		
	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30
0	2524.7	2922.1	3039	2646.2	3272.7	3422.3	5919	6919.5	7013	6077.9	7321.6	7480.5	10594.3	11220.8	11529.4	10902.9	12389.6	12857.1
5	2758.4	3272.7	3422.3	2898.7	3581.3	3889.8	6264.9	8228.6	8724.2	6386.5	7574	8097.7	11875.3	13090.9	14026	12155.9	13867	14493.5
10	2945.5	3506.5	3581.3	3039	3740.3	4516.4	6639	8415.6	9116.9	6779.2	8724.2	9350.7	12857.1	14026	14334.6	13090.9	14727.3	15194.8
15	1963.6	2197.4	2571.4	2103.9	2487.3	2954.8	6358.4	7013	7246.8	6545.5	7574	7948	7901.3	8415.6	8883.1	8415.6	9724.7	10594.3
20	1753.3	2010.4	2103.9	1963.6	2337.7	2646.2	5292.5	5610.4	5844.2	5610.4	6311.7	6779.2	6639	7480.5	8097.7	7013	7948.1	8565.2
25	1355.8	1402.6	1711.2	1552.2	1963.6	2337.7	5049.4	5329.9	5703.9	5142.9	5919	6227.6	5563.6	6227.5	6386.5	5844.2	6854	7480.5
30	1192.2	1262.3	1355.8	1402.6	1636.4	1870.1	4909.1	5142.9	5292.5	5142.9	5610.4	5919	5292.5	5919	6227.5	5610.4	6639	6854

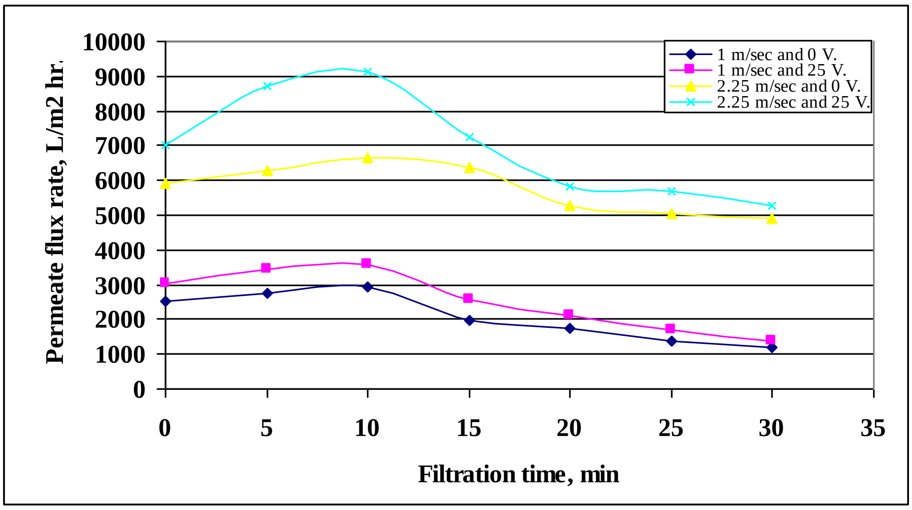


Fig. (6.10): Time dependent-permeate flux rate for membrane MI for 30 minutes filtration for emulsion water content of 30 vol. %; CFV: 1 and 2.25 m/sec; electric field: 0 and 83.30 V/cm.

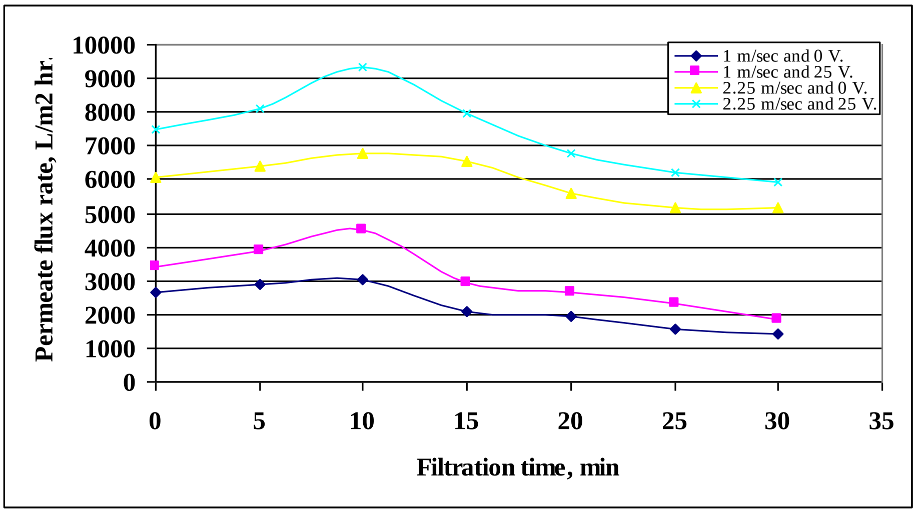


Fig. (6.11): Time dependent-permeate flux rate for membrane MI for 30 minutes filtration for emulsion water content of 50 vol. %; CFV: 1 and 2.25 m/sec; electric field: 0 and 83.30 V/cm.

Table (6.10): Time dependent-permeate flux rate for membrane MII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 2.25 and 2.90 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

	Permeate flux rate, l/m^2. hr																	
Filtration time, min	CFV, m/sec																	
	1						2.25						2.90					
	Emulsion water content, vol. %						Emulsion water content, vol. %						Emulsion water content, vol. %					
	30			50			30			50			30			50		
	Electric field, V/cm			Electric field, V/cm			Electric field, V/cm			Electric field, V/cm			Electric field, V/cm			Electric field, V/cm		
	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30
0	2244.2	2646.2	2805.2	2337.7	2805.2	3113.8	4862.3	5610.4	5844.2	4983.9	5919	6227.5	9350.7	10285.7	11529.4	9818.2	11314.3	12623.4
5	2618.2	3039	3113.8	2618.2	3113.8	3272.7	5423.4	6227.5	6854	5610.4	6386.5	6854	10052	11594.8	12464.4	10379.2	12389.6	12932
10	2758.4	3113.8	3740.3	2898.7	3422.3	4048.8	5844.2	6854	7597.4	6077.9	6779.2	7789.1	10519.5	11837.9	13090.9	10902.9	13090.9	13708.1
15	2178.7	2459.2	2805.2	2337.7	2805.2	4048.8	5516.9	5919	6854	5703.9	6386.5	7321.6	7293.5	7948	8649.4	7480.5	8724.2	9032.7
20	2010.4	2057.1	2487.3	2178.7	2646.2	2898.7	4161	4488.3	4909.1	4675.3	5610.4	5844.2	4909.1	5236.4	5844.2	5292.5	6077.9	6545.5
25	1916.9	2010.4	2487.3	2103.9	2103.9	2805.2	3927.3	4357.4	4675.3	4048.8	4909.1	4983.9	4161	4675.3	5292.5	4357.4	5142.9	5703.9
30	1711.2	1870.1	2057.1	1870.1	1870.1	2646.2	3646.8	4114.3	4207.8	3974	4357.4	4768.8	4048.8	4301.3	4909.1	4207.8	4768.8	5292.5

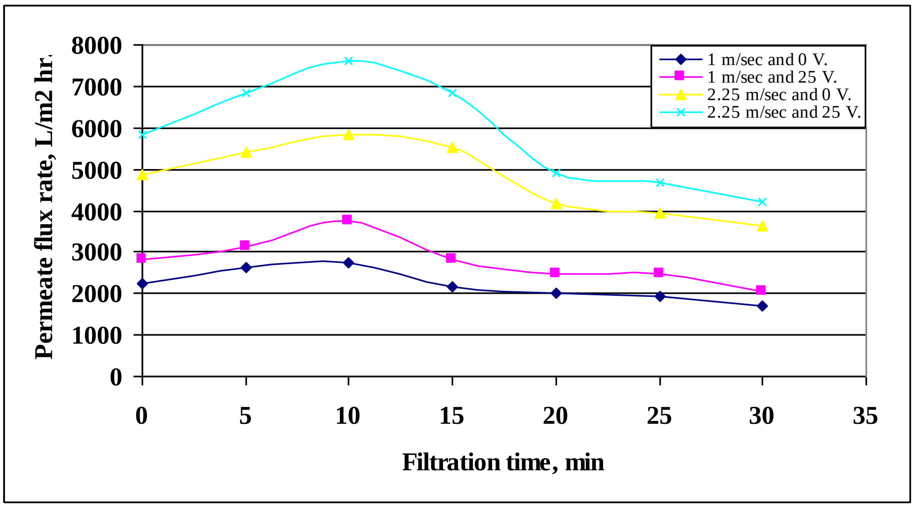


Fig. (6.12): Time dependent-permeate flux rate for membrane MII for 30 minutes filtration for emulsion water content of 30 vol. %; CFV: 1 and 2.25 m/sec; electric field: 0 and 83.30 V/cm.

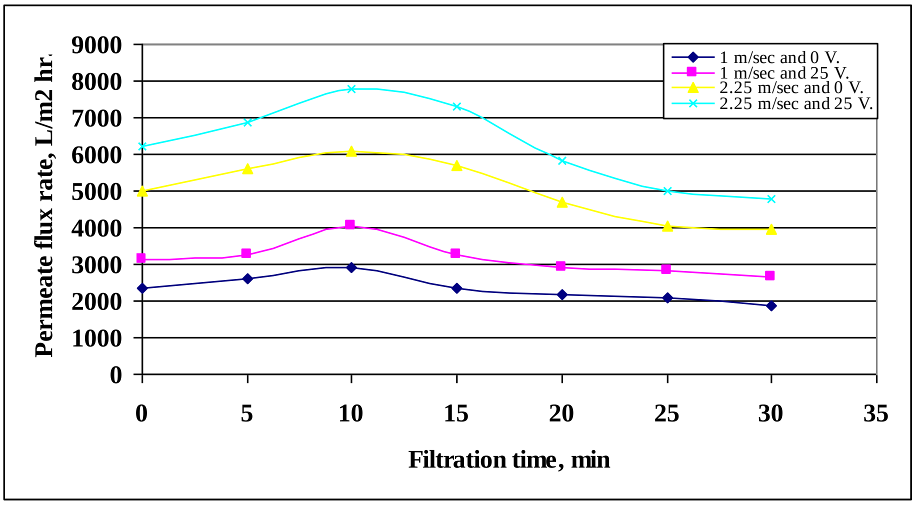


Fig. (6.13): Time dependent-permeate flux rate for membrane MII for 30 minutes filtration for emulsion water content of 50 vol. %; CFV: 1 and 2.25 m/sec; electric field: 0 and 83.30 V/cm.

Table (6.11): Time dependent-permeate flux rate for membrane MIII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1 2.25 and 2.90 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

Permeate flux rate, l/m^2. hr																		
Filtration time, min	CFV, m/sec																	
	1						2.25						2.90					
	Emulsion water content, vol. %						Emulsion water content, vol. %						Emulsion water content, vol. %					
	30			50			30			50			30			50		
	Electric field, V/cm			Electric field, V/cm			Electric field, V/cm			Electric field, V/cm			Electric field, V/cm			Electric field, V/cm		
	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30
0	2618.2	3039	3272.7	2805.2	3422.3	3581.3	6779.2	7480.5	7854.6	7321.6	8649.4	9350.7	10285.7	11061.8	11529.4	10902.9	12773	13090.9
5	3422.3	3740.3	4048.8	3740.3	4207.8	4768.8	7013	8097.7	8649.4	7574	9116.9	9818.2	11922.1	12623.4	13867	12623.4	14493.5	15194.8
10	3553.3	4048.8	4675.3	3974	4909.1	5451.4	8228.6	9818.2	10285.7	9191.7	11220.8	11529.4	12464.4	13324.7	13558.4	13558.4	15269.6	15896.1
15	3506.5	3740.3	4357.4	3581.3	4357.4	4675.3	6854	8415.6	9584.4	7480.5	9818.2	10126.8	7948.1	8649.4	9191.7	8883.1	10594.3	11220.8
20	2711.7	3039	3506.5	2898.7	3581.3	3974	6358.4	7162.6	7789.1	6854	8097.7	8649.4	6545.5	7321.6	7574	7162.6	8256.6	8883.1
25	2178.7	2487.3	2646.2	2337.7	3039	3272.7	4983.9	5919	6386.5	5610.4	6779.2	7321.6	5844.2	6662.3	7013	6386.5	7714.3	8256.6
30	1309.1	1711.2	1870.1	1552.2	1963.6	2337.7	3740.3	4516.4	5142.9	4207.8	5610.4	6077.9	4488.3	5142.9	5292.5	5292.5	6311.7	6545.5

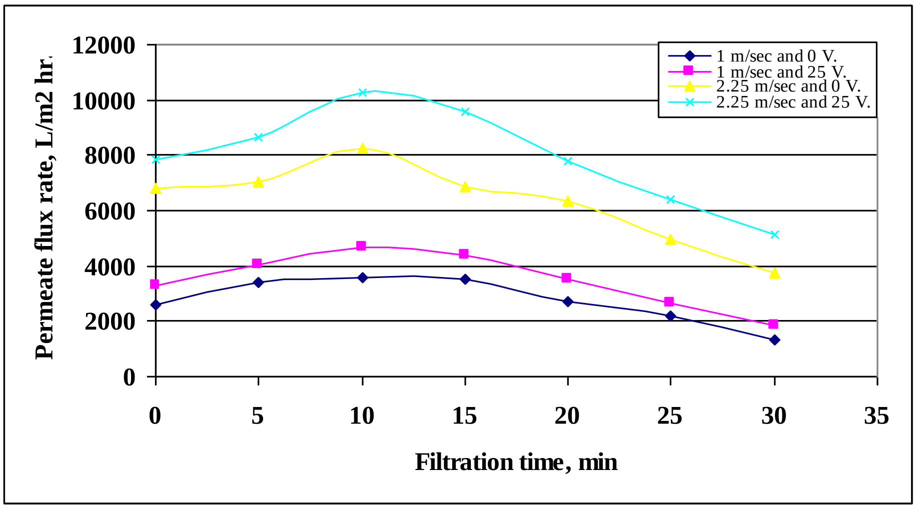


Fig. (6.14): Time dependent-permeate flux rate for membrane MIII for 30 minutes filtration for emulsion water content of 30 vol. %; CFV: 1 and 2.25 m/sec; electric field: 0 and 83.30 V/cm.

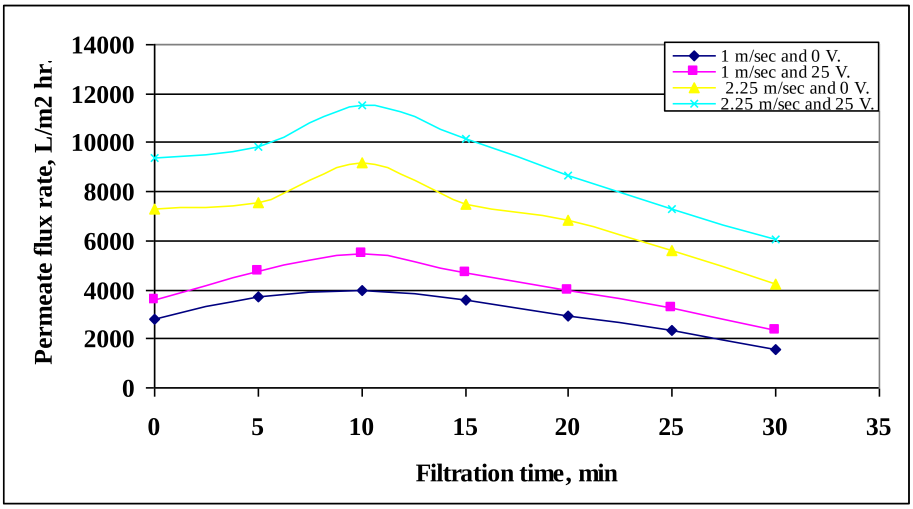


Fig. (6.15): Time dependent-permeate flux rate for membrane MIII for 30 minutes filtration for emulsion water content of 50 vol. %; CFV: 1 and 2.25 m/sec; electric field: 0 and 83.30 V/cm.

6.11 Effect of Feed Crossflow Velocity (CFV) on Permeate Flux Rate

In this section, the effect of feed CFV on membrane permeate flux rates is discussed. To accomplish this, experiments were performed whilst varying feed CFV step by step from 1 to 12 m/sec. Each experiment was repeated at different electrical fields in the range of (0-666.70 V/cm) on the two different emulsions (30 and 50 vol. % of water content) using three different PHP membranes of different pore diameter for the same duration of 30 min. The effect of feed CFV from 1 to 3.35 m/sec on membrane MI permeate flux rate for both emulsions in the absence of electrical fields is given in Table (6.12) and demonstrated in Fig. (6.16) as a function of filtration time. The effect of higher velocities (3.65-12 m/sec) is tabulated in Appendix A. Similarly, permeate flux rates obtained from membranes MII and MIII under these conditions are tabulated in Tables (6.13-14) and illustrated in Figs. (6.17-18), respectively. As was the case with membrane MI, the influence of higher feed CFVs (3.65-12) m/sec on the permeate flux rates of membranes MII and MIII is shown in Appendix A.

Table (6.12): Effect of feed CFV on permeate flux rate for membrane MI for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 2.25, 2.90 and 3.35 m/sec. No electrical field.

Permeate flux rate, l/m^2. hr								
Filtration time, min	CFV, m/sec							
	1		2.25		2.90		3.35	
	Emulsion water content, vol. %		Emulsion water content, vol. %		Emulsion water content, vol. %		Emulsion water content, vol. %	
	30	50	30	50	30	50	30	50
0	2524.7	2646.2	5919	6077.9	10594.3	10902.9	12623.4	13090.9
5	2758.4	2898.7	6264.9	6386.5	11875.3	12155.9	15194.8	15737.1
10	2945.5	3039	6639	6779.2	12857.1	13090.9	15896.1	16831.2
15	1963.6	2103.9	6358.4	6545.5	7901.3	8415.6	11688.3	12623.4
20	1753.3	1963.6	5292.5	5610.4	6639	7013	9967.8	10753.3
25	1355.8	1552.2	5049.4	5142.9	5563.6	5844.2	6545.5	7321.6
30	1192.2	1402.6	4909.1	5142.9	5292.5	5610.4	6031.2	6545.5

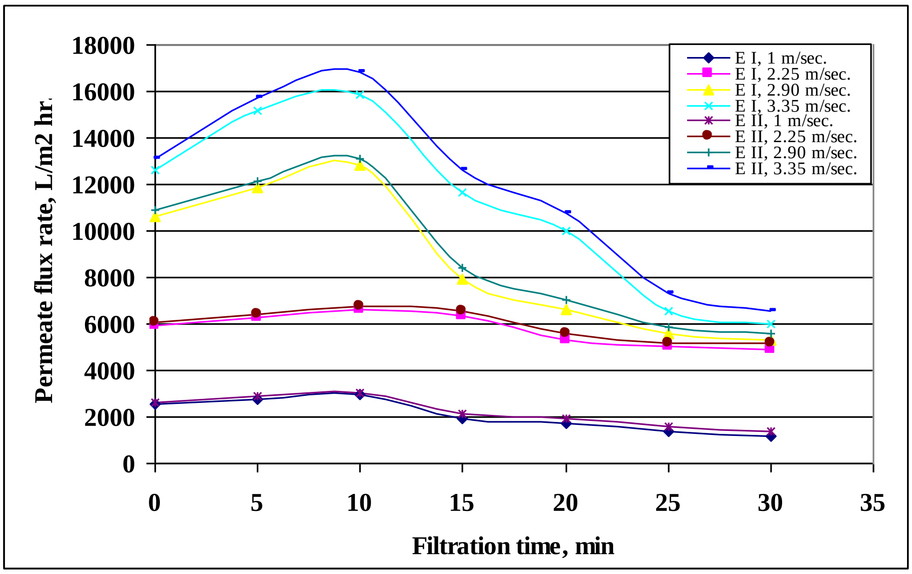


Fig. (6.16): Effect of feed CFV on permeate flux rate for membrane MI for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 2.25, 2.90 and 3.35 m/sec. No electrical field.

Table (6.13): Effect of feed CFV on permeate flux rate for membrane MII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 2.25, 2.90 and 3.35 m/sec. No electrical field.

Permeate flux rate, l/m^2. hr								
Filtration time, min	CFV, m/sec							
	1		2.25		2.90		3.35	
	Emulsion water content, vol. %		Emulsion water content, vol. %		Emulsion water content, vol. %		Emulsion water content, vol. %	
	30	50	30	50	30	50	30	50
0	2244.2	2337.7	4862.3	4983.9	9350.7	9818.2	15428.6	15989.6
5	2618.2	2618.2	5423.4	5610.4	10052	10379.2	16597.4	17064.9
10	2758.4	2898.7	5844.2	6077.9	10519.5	10902.9	19870.1	20412.5
15	2178.7	2337.7	5516.9	5703.9	7293.5	7480.5	12623.4	13184.4
20	2010.4	2178.7	4161	4675.3	4909.1	5292.5	11220.8	11837.9
25	1916.9	2103.9	3927.3	4048.8	4161	4357.4	7293.5	7714.3
30	1711.2	1870.1	3646.8	3974	4048.8	4207.8	6639	7480.5

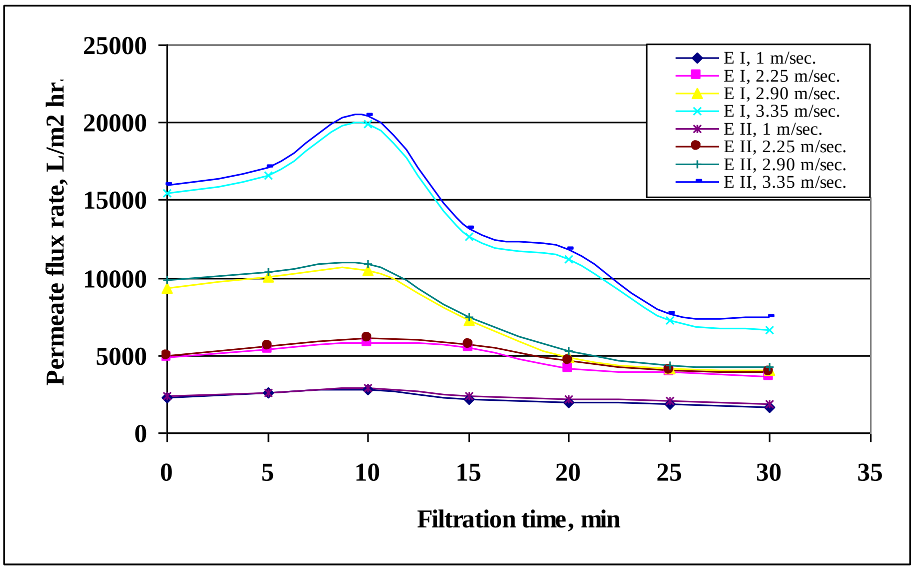


Fig. (6.17): Effect of feed CFV on permeate flux rate for membrane MII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 2.25, 2.90 and 3.35 m/sec. No electrical field.

Table (6.14): Effect of feed CFV on permeate flux rate for membrane MIII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 2.25, 2.90 and 3.35 m/sec. No electrical field.

Permeate flux rate, l/m^2. hr								
Filtration time, min	CFV, m/sec							
	1		2.25		2.90		3.35	
	Emulsion water content, vol. %		Emulsion water content, vol. %		Emulsion water content, vol. %		Emulsion water content, vol. %	
	30	50	30	50	30	50	30	50
0	2618.2	2805.2	6779.2	7321.6	10285.7	10902.9	16204.7	17298.7
5	3422.3	3740.3	7013	7574	11922.1	12623.4	16831.2	18383.4
10	3553.3	3974	8228.6	9191.7	12464.4	13558.4	18233.8	20571.4
15	3506.5	3581.3	6854	7480.5	7948.1	8883.1	12932	14119.5
20	2711.7	2898.7	6358.4	6854	6545.5	7162.6	10285.7	11688.3
25	2178.7	2337.7	4983.9	5610.4	5844.2	6386.5	7013	7789.1
30	1309.1	1552.2	3740.3	4207.8	4488.3	5292.5	5610.4	6386.5

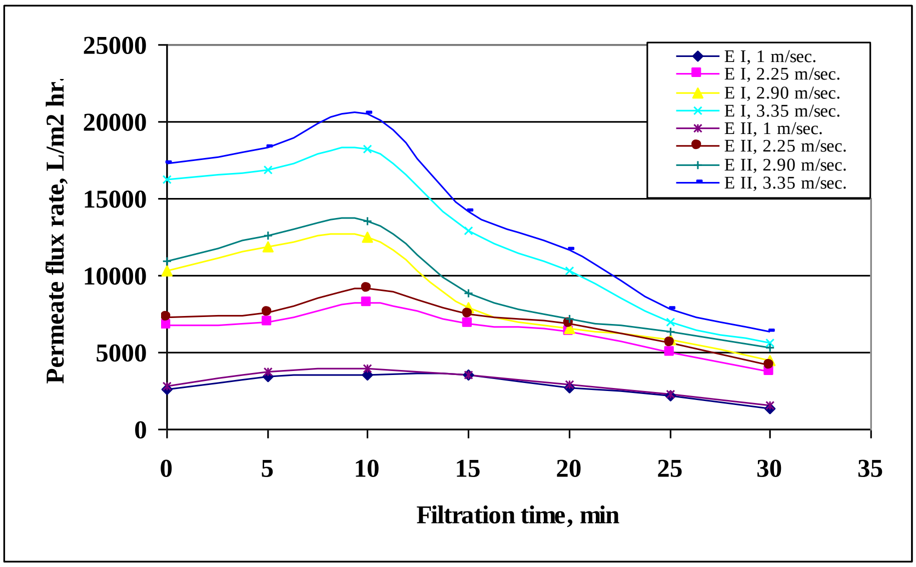


Fig. (6.18): Effect of feed CFV on permeate flux rate for membrane MIII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 2.25, 2.90 and 3.35 m/sec. No electrical field.

According to theses figures, the effect of feed CFV on membrane flux is evident. As can be observed, increasing the CFV increased the permeate flux rate for both emulsions. For instance, the permeate rate from membrane MI at the middle of filtration time, 15 min, was 1963.6 l/m^2 hr at CFV of 1 m/sec and 6358.4 l/m^2 hr at CFV of 2.25 m/sec for emulsion EI and 2103.9 l/m^2 hr at CFV of 1 m/sec and 6545.5 l/m^2 hr at CFV of 2.25 m/sec for emulsion EII. Doubling the feed CFV from 1 to 2.25 m/sec corresponded to an increase of more than 3 fold in the permeate for both emulsions. This observation also applies to membranes MII and MIII when using either emulsion as a filtration media; doubling the CFV led to doubling the permeate flux rate. The collected permeates, after 15 min of filtration of emulsion EI at 1 m/sec, were 2178.7 and 3506.5 l/m^2 hr, 5516.9 and 6854 at 2.25 m/sec, respectively. Employing emulsion EII has made no difference, as feeding it at a CFV of 1 m/sec to membranes MII and MIII, the permeates at 15 min were 2337.7 and 3581.3 l/m^2 hr. Similarly, with increasing the CFV to 2 m/sec, membrane MII gave 5703.9 and membrane MIII 7480.5 l/m^2 hr.

In addition, Figs. (6.19-20) below show the quantitative correlation between the permeate flux rates of the examined membranes and feed CFV in the range of 1 to 3.35 m/sec for both emulsions. Overall, it is clear that membranes MI and MII did not produce a linear relationship between their permeate flux rates and feed CFVs for both of the emulsions tested. In the case of membrane MIII; however, a slightly linear relationship can be observed. Deviation from linearity in the relationship between a membrane's permeate flux rate and the applied feed CFV can be explained by the possibility of emulsion droplet deformation as well as their interactions/rejection with/by the membrane surface.

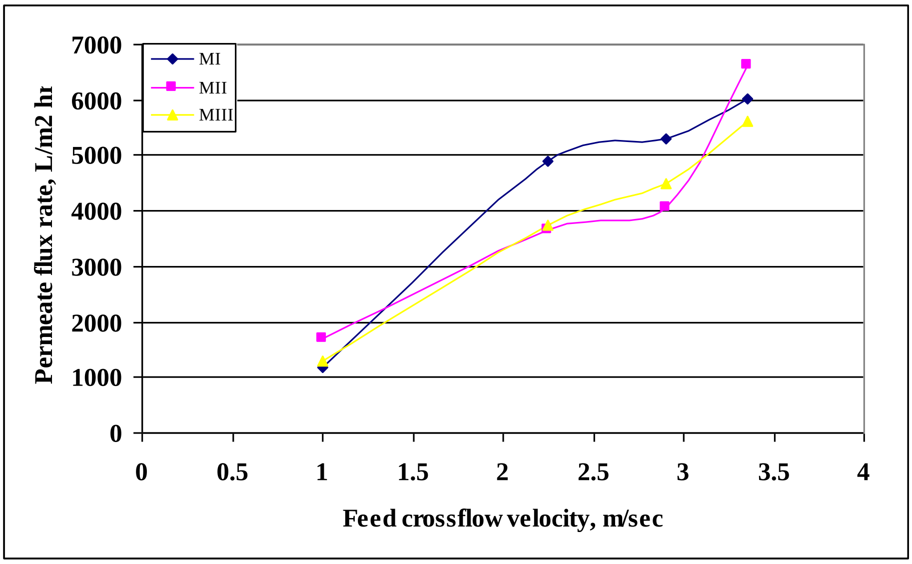


Fig. (6.19): Correlation of membranes MI, MII and MIII permeate flux rates and feed CFV after 30 min of filtration of emulsion EI.

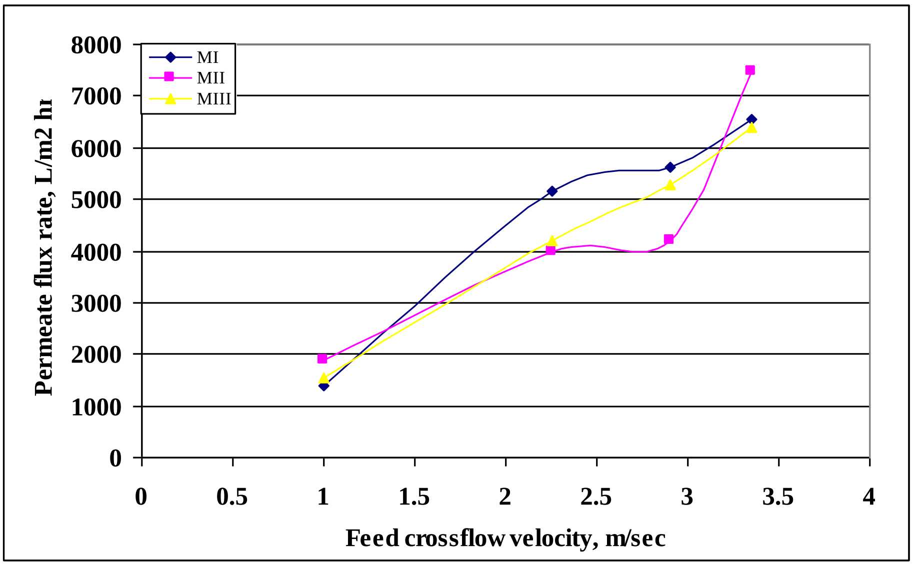


Fig. (6.20): Correlation of membranes MI, MII and MIII permeate flux rates and feed CFV after 30 min of filtration of emulsion EII.

However, it seems that the composition of the emulsion does not have a role to play in determining the nature of dependence of permeation rate on feed CFV, since both emulsions responded quite similarly to the alterations in feed CFV irrespective of their water contents. The success of higher feed CFVs in increasing the membrane permeate flux rate may be attributed to the higher shear forces that may be generated on the membrane surface which limits the thickness of the oily layer which may develop on the membrane surface due to membrane rejection, resulting in increased permeate flux rate. Increased turbulence and mass transfer rates and removal of oil droplets from the membrane surface back to the bulk stream, which can lead to a reduced level of concentration polarization can also be achieved by increasing the CFV (Kong and Li, 1999). In fact, this can maintain a high membrane permeate flux rate over a prolonged period of time. Therefore, it can be concluded that increasing the CFV of the feed leads to improvements in the membrane flux rate (Scott et al., 2001; Tarleton and Wakeman, 1994a; Jiao and Sharma, 1994; Riesmeier et al., 1987).

Furthermore, it is interesting to observe that the effect of feed CFV on membrane permeation flux for both emulsions, in the absence or presence of an electrical field, is identical, as shown below in Tables (6.15-17) and Figs. (6.21-23) for membranes MI, MII and MIII, respectively. These tables and figures show the permeates obtained from all membranes (MI, MII and MIII), as a function of filtration time, at a randomly chosen electrical field of 83.30 V/cm. For example; at 10 min of filtration, increasing the feed CFV from 1 to 2.25 m/sec, while using membrane MI for both emulsions, led to a doubling of the permeate flux rate from 3581.3 to 9116.9 l/m^2 hr, in the case of emulsion EI, and from 4516.4 to 9350.7 l/m^2 hr, in the case of emulsion EII. This was also the case when doubling the feed CFV from 1 to 2 m/sec while applying no electric field in which the membrane permeate flux rate increased from 2945.5 to 6639 l/m^2 hr and from 3039 to 6779.2 l/m^2 hr, for emulsion EI and EII, respectively. These results are also true with regard to the permeates collected from membranes MII and MIII. The contribution of increasing the electrical field to improve the membrane flux rate at a given feed CFV will be discussed in the following section.

Table (6.15): Effect of feed CFV on permeate flux rate for membrane MI for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 2.25, 2.90 and 3.35 m/sec; electric field: 83.30 V/cm.

	Permeate flux rate, l/m^2. hr							
Filtration time, min	CFV, m/sec							
	1		2.25		2.90		3.35	
	Emulsion water content, vol. %		Emulsion water content, vol. %		Emulsion water content, vol. %		Emulsion water content, vol. %	
	30	50	30	50	30	50	30	50
0	3039	3422.3	7013	7480.5	11529.4	12857.1	14493.5	15989.6
5	3422.3	3889.8	8724.2	8097.7	14026	14493.5	17607.3	19168.8
10	3581.3	4516.4	9116.9	9350.7	14334.6	15194.8	21188.6	19944.9
15	2571.4	2954.8	7246.8	7948	8883.1	10594.3	13867	15428.6
20	2103.9	2646.2	5844.2	6779.2	8097.7	8565.2	11688.3	13184.4
25	1711.2	2337.7	5703.9	6227.6	6386.5	7480.5	7789.1	9191.7
30	1355.8	1870.1	5292.5	5919	6227.5	6854	7321.6	8097.7

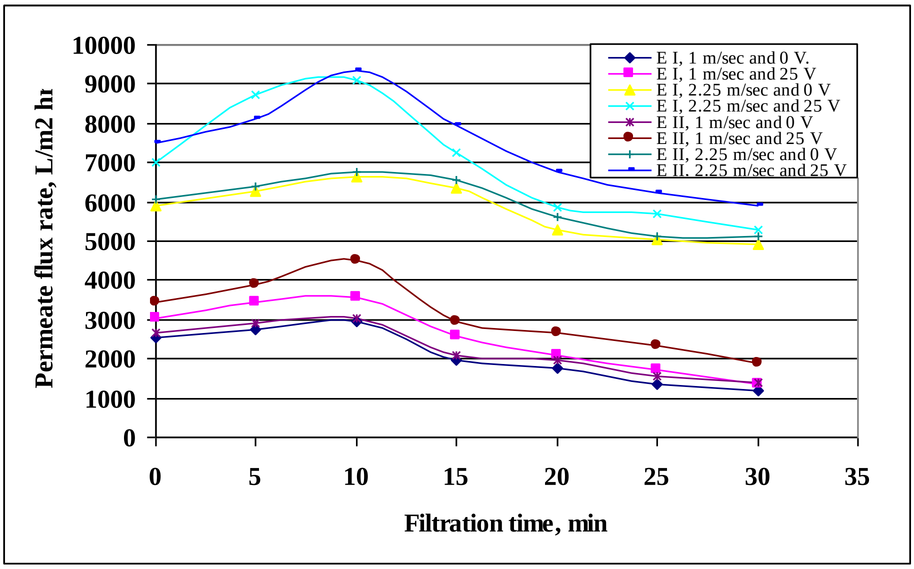


Fig. (6.21): Effect of feed CFV on permeate flux rate for membrane MI for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 2.25, 2.90 and 3.35 m/sec; electric field; 0 and 83.30 V/cm.

Table (6.16): Effect of feed CFV on permeate flux rate for membrane MII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 2.25, 2.90 and 3.35 m/sec; electric field: 83.30V/cm.

Permeate flux rate, l/m^2. hr								
Filtration time, min	CFV, m/sec							
	1		2.25		2.90		3.35	
	Emulsion water content, vol. %		Emulsion water content, vol. %		Emulsion water content, vol. %		Emulsion water content, vol. %	
	30	50	30	50	30	50	30	50
0	2805.2	3113.8	5844.2	6227.5	11529.4	12623.4	17766.2	19636.4
5	3113.8	3272.7	6854	6854	12464.4	12932	19636.4	20664.9
10	3740.3	4048.8	7597.4	7789.1	13090.9	13708.1	21974	24077.9
15	2805.2	3272.7	6854	7321.6	8649.4	9032.7	15428.6	15896.1
20	2487.3	2898.7	4909.1	5844.2	5844.2	6545.5	13399.5	14119.5
25	2487.3	2805.2	4675.3	4983.9	5292.5	5703.9	8883.1	9116.9
30	2057.1	2646.2	4207.8	4768.8	4909.1	5292.5	7789.1	8724.2

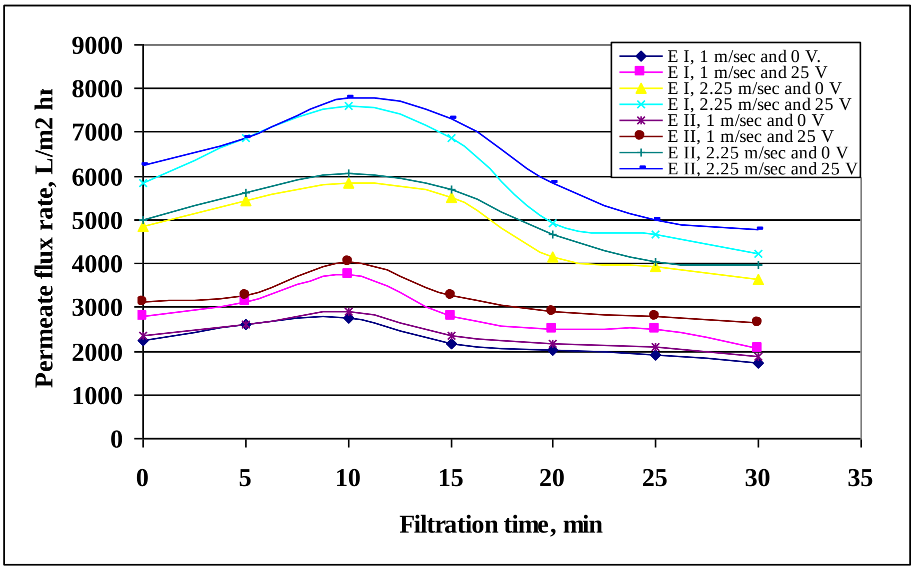


Fig. (6.22): Effect of feed CFV on permeate flux rate for membrane MII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 2.25, 2.90 and 3.35 m/sec; electric field: 0 and 83.30 V/cm.

Table (6.17): Effect of feed CFV on permeate flux rate for membrane MIII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 2.25, 2.90 and 3.35 m/sec; electric field: 83.30 V/cm.

Filtration time, min	Permeate flux rate, l/m^2. hr							
	CFV, m/sec							
	1		2.25		2.90		3.35	
	Emulsion water content, vol. %		Emulsion water content, vol. %		Emulsion water content, vol. %		Emulsion water content, vol. %	
	30	50	30	50	30	50	30	50
0	3272.7	3581.3	7854.6	9350.7	11529.4	13090.9	18233.8	21039
5	4048.8	4768.8	8649.4	9818.2	13867	15194.8	19870.1	23376.6
10	4675.3	5451.4	10285.7	11529.4	13558.4	15896.1	21347.5	24779.2
15	4357.4	4675.3	9584.4	10126.8	9191.7	11220.8	15428.6	17298.7
20	3506.5	3974	7789.1	8649.4	7574	8883.1	12773	15194.8
25	2646.2	3272.7	6386.5	7321.6	7013	8256.6	8415.6	10285.7
30	1870.1	2337.7	5142.9	6077.9	5292.5	6545.5	6639	8097.7

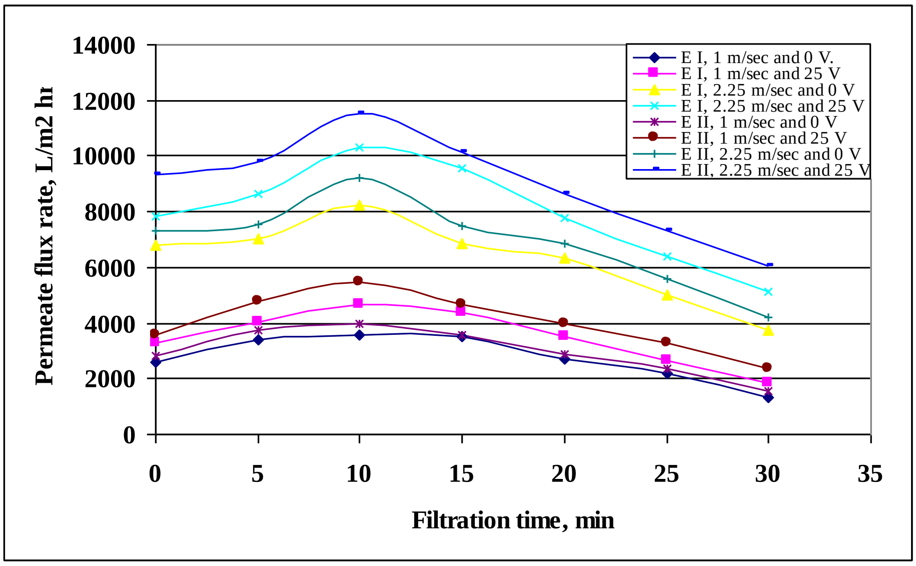


Fig. (6.23): Effect of feed CFV on permeate flux rate for membrane MIII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 2.25, 2.90 and 3.35 m/sec; electric field: 0 and 83.30 V/cm.

6.12 Effect of Electric Field (E) on Permeate Flux Rate

The effect of electric field strength on membrane permeate flux rate of both emulsions (30 and 50 vol. % of water content) was tested at three levels: low, medium and high, as indicated in Table (6.18) below. The medium level was used to provide a simulation of any possible curvature in the permeate value in between the low and high levels chosen. At each electric field, eight feed CFVs, ranging from 1 to 12 m/sec, were tested. This procedure was performed using three PHP membranes of different pore sizes for 30 min in each run. The effect of electric field on the permeation of both emulsions from each membrane at 0, 83.30 and 333.30 V/cm (that's the onset of each level) with 1 and 4.60 m/sec as a function of filtration time is provided in this section, see Tables (6.19-20) and Figs. (6.24-35). Due to the similarity of the results, the rest of the results obtained from these runs are given in Appendix A.

Table (6.18): Grades of applied electric fields.

Level of electric field	Value of electric field, v/cm
Low	0-33.30
Medium	83.30-166.70
High	333.30-666.70

Table (6.19): Effect of electric field on permeate flux rate for membranes MI, MII and MIII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec.

Permeate flux rate, l/m^2. hr																		
Filtration time, min	Electric field, V/cm																	
	0						83.30						333.30					
	Emulsion water content, vol. %						Emulsion water content, vol. %						Emulsion water content, vol. %					
	30			50			30			50			30			50		
	MI	MII	MIII	MI	MII	MIII	MI	MII	MIII	MI	MII	MIII	MI	MII	MIII	MI	MII	MIII
0	2524.7	2244.2	2618.2	2646.2	2337.7	2805.2	3039	2805.2	3272.7	3422.3	3113.8	3581.3	4207.8	3740.3	4207.8	4048.8	3974	4441.6
5	2758.4	2618.2	3422.3	2898.7	2618.2	3740.3	3422.3	3113.8	4048.8	3889.8	3272.7	4768.8	4441.6	4675.3	5376.6	4768.8	4768.8	5703.9
10	2945.5	2758.4	3553.3	3039	2898.7	3974	3581.3	3740.3	4675.3	4516.4	4048.8	5451.4	4768.8	4675.3	5919	4983.9	4983.9	6386.5
15	1963.6	2178.7	3506.5	2103.9	2337.7	3581.3	2571.4	2805.2	4357.4	2954.8	3272.7	4675.3	3113.8	3422.3	5292.5	3422.3	3833.8	5610.4
20	1753.3	2010.4	2711.7	1963.6	2178.7	2898.7	2103.9	2487.3	3506.5	2646.2	2898.7	3974	2646.2	3039	3974	3272.7	3422.3	4516.4
25	1355.8	1916.9	2178.7	1552.2	2103.9	2337.7	1711.2	2487.3	2646.2	2337.7	2805.2	3272.7	2178.7	2805.2	3422.3	2898.7	3272.7	3833.8
30	1192.2	1711.2	1309.1	1402.6	1870.1	1552.2	1355.8	2057.1	1870.1	1870.1	2646.2	2337.7	1776.6	2571.4	2103.9	2646.2	2898.7	2805.2

Table (6.20): Effect of electric field on permeate flux rate for membranes MI, MII and MIII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 4.60 m/sec.

Permeate flux rate, l/m^2. hr																		
Filtration time, min	Electric field, V/cm																	
	0						83.30						333.30					
	Emulsion water content, vol. %						Emulsion water content, vol. %						Emulsion water content, vol. %					
	30			50			30			50			30			50		
	MI	MII	MIII	MI	MII	MIII	MI	MII	MIII	MI	MII	MIII	MI	MII	MIII	MI	MII	MIII
0	14643.1	18383.4	18074.8	14961	19477.4	19477.4	17859.7	22441.6	21974	19318.4	24545.5	24545.5	24928.8	29604.2	29763.1	25714.3	31792.2	32727.3
5	16597.4	20384.4	19636.4	17298.7	21272.7	21188.6	20412.5	26490.4	23376.6	22282.6	27584.4	26022.9	26649.4	29922.1	31792.2	29454.6	32961	35214.6
10	18383.4	23096.1	21815.1	19636.4	24311.7	23376.6	22441.6	28052	25246.8	25087.8	30389.6	28828.1	29220.8	34129.9	33662.3	31885.7	36561	37243.6
15	15428.6	20412.5	17298.7	16831.2	21506.5	19009.9	19636.4	25087.8	20103.9	21506.5	27584.4	23470.1	22441.6	28052	26181.8	26649.4	30857.2	29604.2
20	12857.1	13090.9	15194.8	13867	14643.1	16672.2	15428.6	16513.3	18074.8	17766.2	19009.9	21039	19009.9	20571.4	23993.8	22441.6	24311.7	27116.9
25	12155.8	12389.6	11454.6	13090.9	13558.4	12932	14961	16129.9	14119.5	16924.7	18383.4	16363.6	17766.2	19168.8	17298.7	20664.9	21974	20664.9
30	10005.2	8724.2	8883.1	11061.8	11220.8	10126.8	11837.9	11688.3	11220.8	14727.3	15578.2	13090.9	13090.9	14961	12623.4	15428.6	18383.4	15896.1

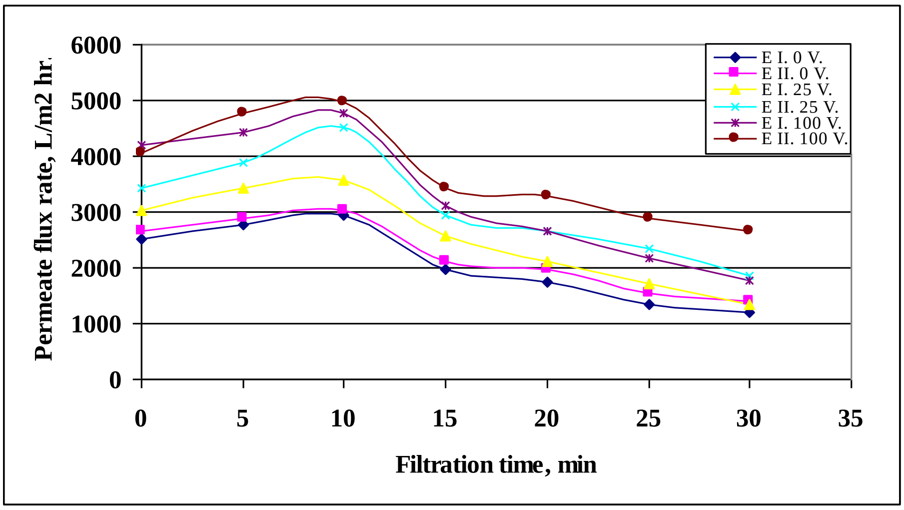


Fig. (6.24): Effect of electric field on permeate flux rate for membrane MI for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec.

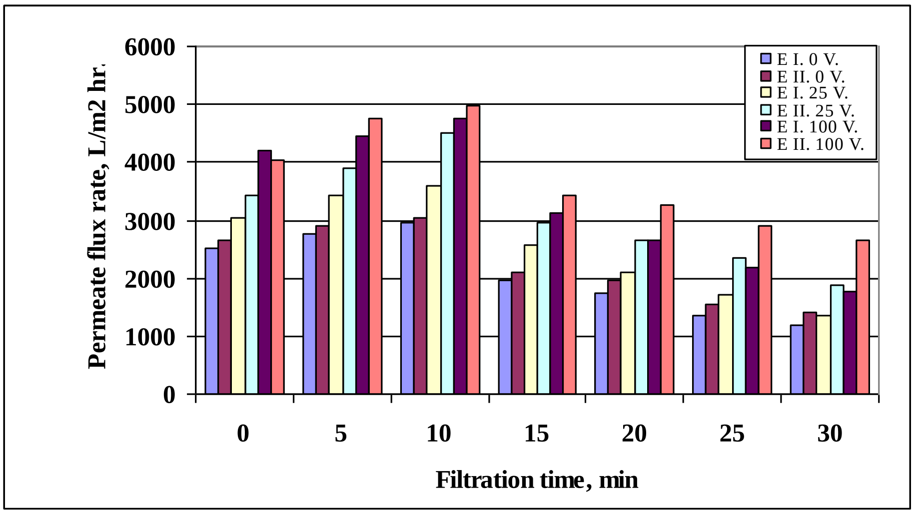


Fig. (6.25): Effect of electric field on permeate flux rate for membrane MI for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec.

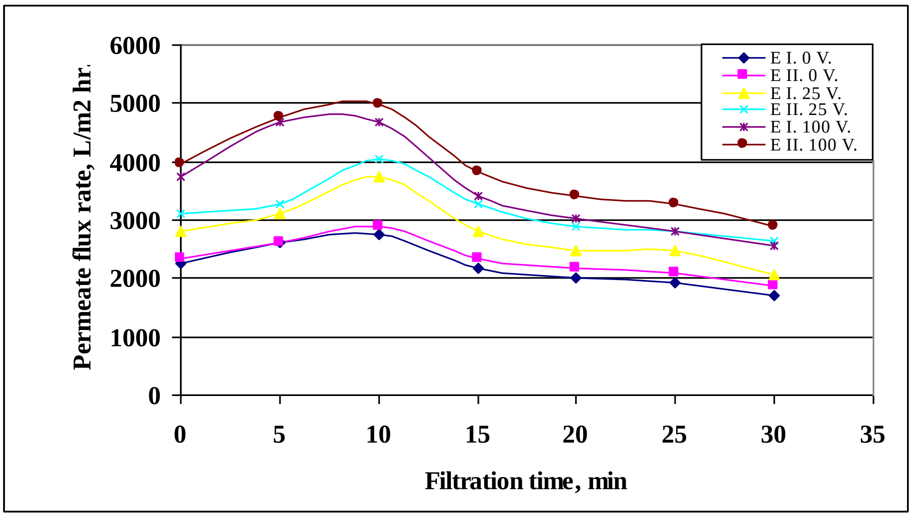


Fig. (6.26): Effect of electric field on permeate flux rate for membrane MII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec.

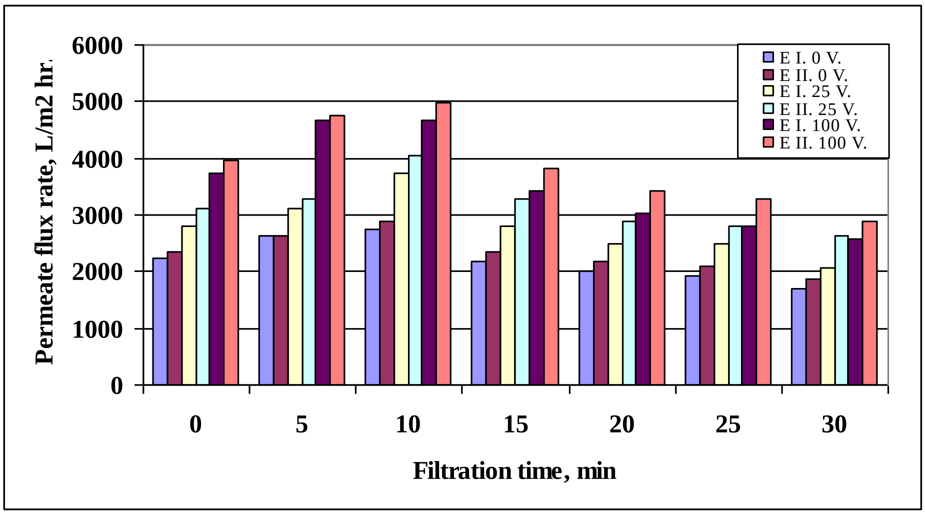


Fig. (6.27): Effect of electric field on permeate flux rate for membrane MII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec.

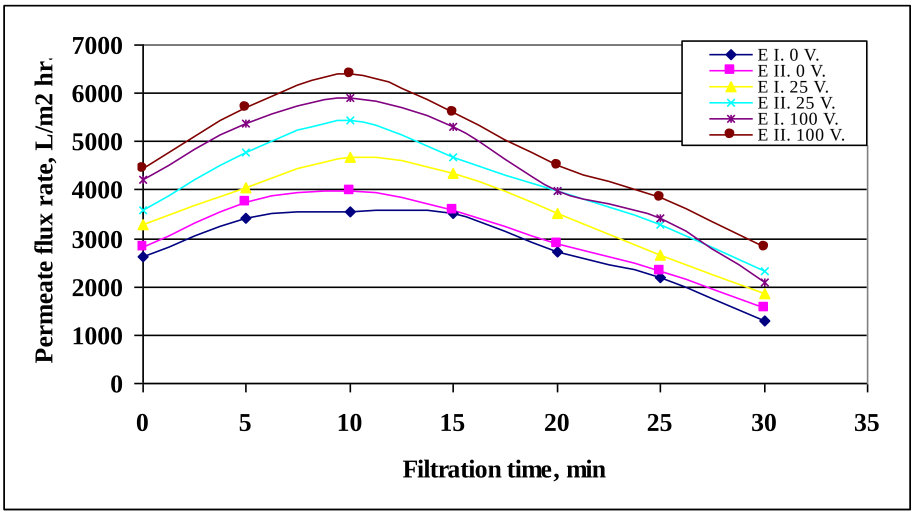


Fig. (6.28): Effect of electric field on permeate flux rate for membrane MIII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec.

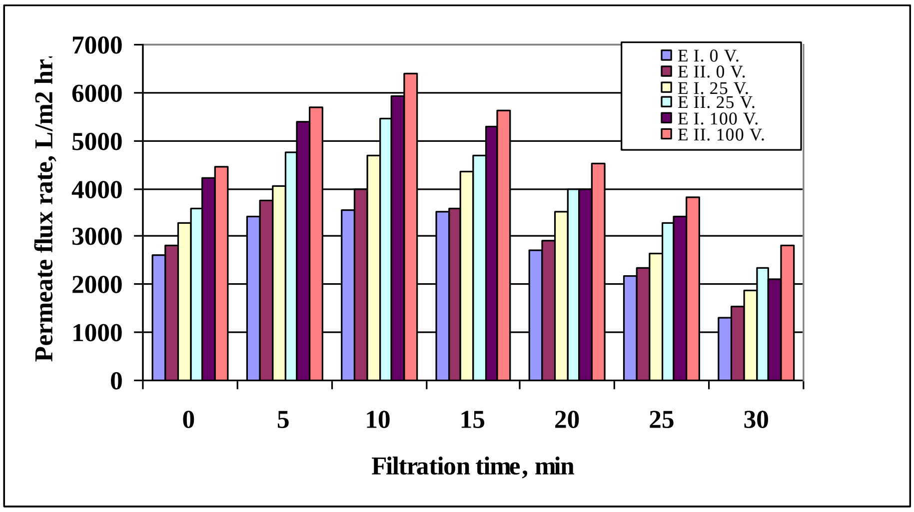


Fig. (6.29): Effect of electric field on permeate flux rate for membrane MIII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec.

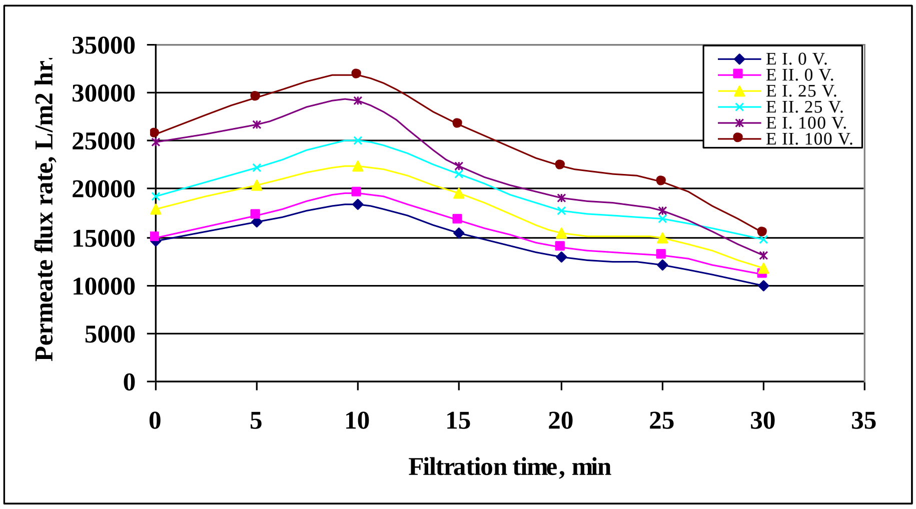


Fig. (6.30): Effect of electric field on permeate flux rate for membrane MI for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 4.60 m/sec.

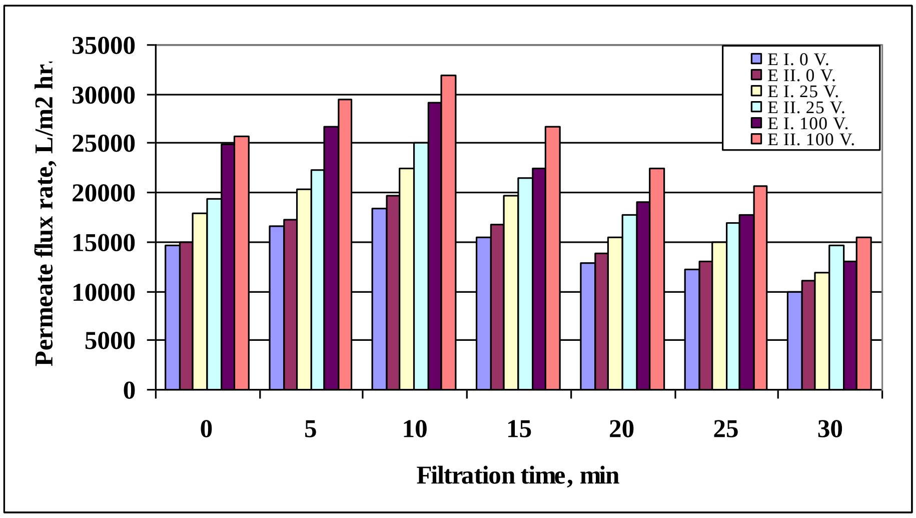


Fig. (6.31): Effect of electric field on permeate flux rate for membrane MI for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 4.60 m/sec.

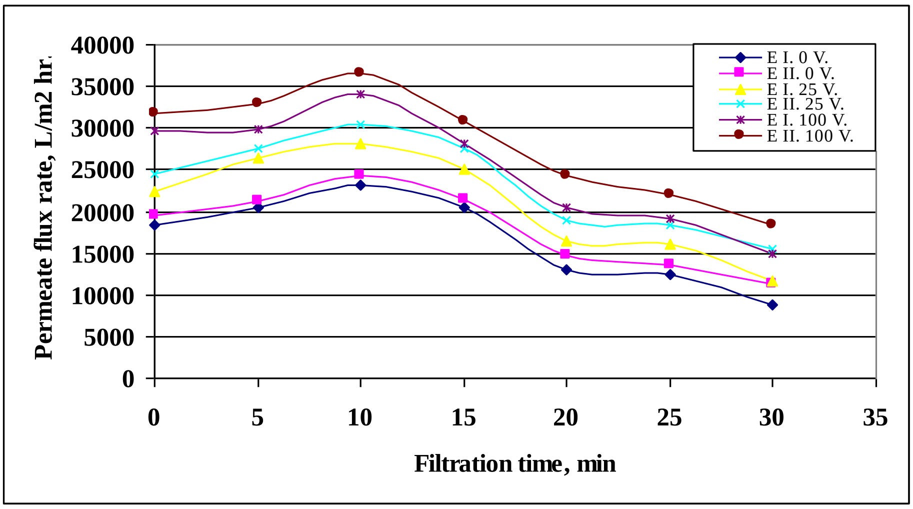


Fig. (6.32): Effect of electric field on permeate flux rate for membrane MII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 4.60 m/sec.

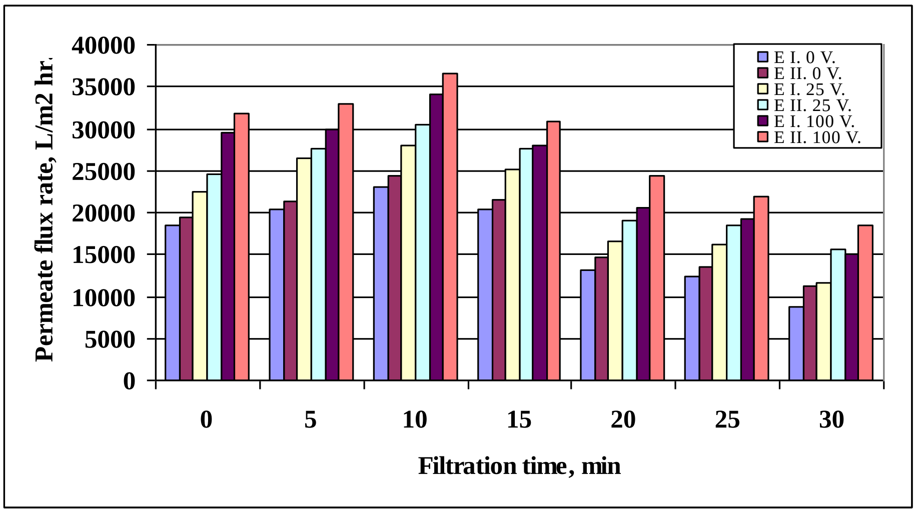


Fig. (6.33): Effect of electric field on permeate flux rate for membrane MII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 4.60 m/sec.

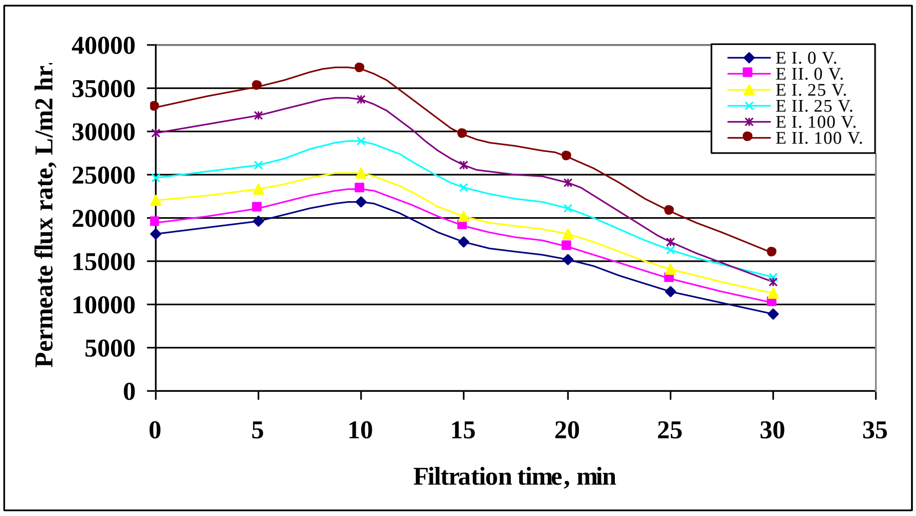


Fig. (6.34): Effect of electric field on permeate flux rate for membrane MIII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 4.60 m/sec.

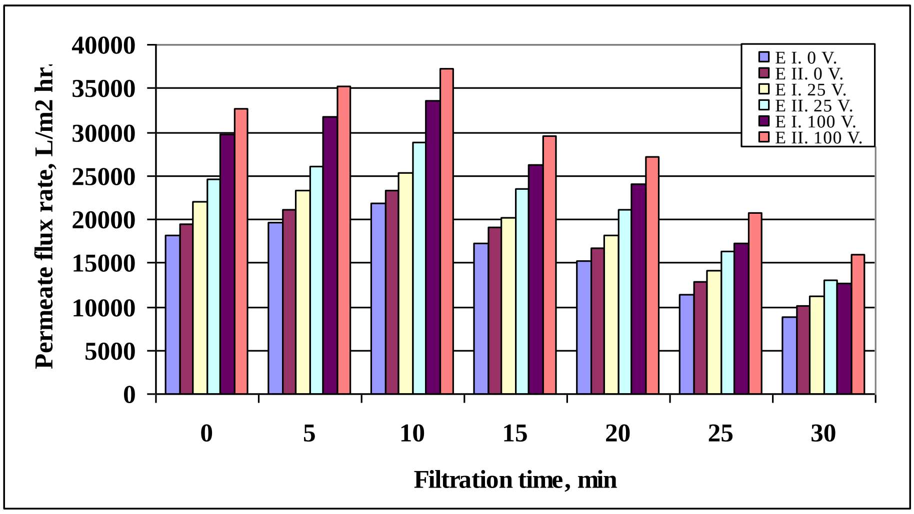


Fig. (6.35): Effect of electric field on permeate flux rate for membrane MIII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 4.60 m/sec.

The effect of electric field on the permeate flux rate from membranes MI, MII and MIII at 0, 83.30 and 333.30 V/cm with 1 and 4.60 m/sec of CFV as a function of filtration time is shown in Tables (6.19-20) and Figs. (6.24-35); respectively. At a given CFV, it can be seen that, the permeate from all membranes tested always increased during the first third of operation time. This increase reached a plateau and then started to decline with filtration time until almost a constant permeate value was attained regardless of time. It seems that applying an electrical field tends to augment the permeate flux rate at a given set of filtration condition(s). For example, the permeate flux rate after the first twenty minutes increased from 1753.3 l/m^2 hr to 2103.9 l/m^2 hr when employing membrane MI to filter emulsion EI (30 vol. % water) at 1 m/sec with no electric field and with electric field of 83.30 V/cm, respectively (see Table (6.19)). Likewise, it increased from 2010.4 to 2487.3 l/m^2 hr and from 2711.7 to 3506.5 l/m^2 hr when using membranes MII and MIII to filter emulsion EI at the same conditions stated previously, respectively. Membrane permeate flux rate augmentation is perhaps due to membrane surface cleaning, while the filtration is running, due to gas evolution through electrolysis (Akay and Wakeman, 1996)

In addition, as illustrated in Figs. (6.24-27), the change in membrane permeate flux rate of both membranes MI and MII with both emulsions at a feed CFV of 1 m/sec, is somewhat retarded at the end of filtration time compared to that observed at earlier filtration times. For example, the decline in permeate flux rate at the middle of the filtration time when applying 83.30 V/cm across emulsion EI using membrane MI, was 1009.9 l/m^2 hr, and at the end of filtration was only 355.4 l/m^2 hr. Similarly, in the case of emulsion EII, the decline was 1561.6 l/m^2 hr at the middle of filtration time and only 467.6 l/m^2 hr at the end of filtration period. This observation could also be made at higher fields (e.g. 333.30 V/cm) when using membrane MII at these voltages. However, membrane MIII, possibly due to its larger pore diameter, followed a different trend, in which the decline was higher at the end of filtration than that obtained at the middle of filtration time. For instance, in case of emulsion EI it was 776.1 and 317.9 l/m^2 hr at the end and middle of filtration time, respectively and 935 and 776.1 l/m^2 hr at these filtration times for emulsion EII. An explanation to this pattern of permeate change could be that, with the progress of filtration time the concentration of oil in the emulsion is relatively increased. Since most of the collected permeates is always water, i.e. the volume ratio of oil to water in the emulsion increases, and as a result, the emulsion’s water content is lowered restricting the effect of the applied electrical field. Another possible reason for this decline in membrane permeates flux rates change is perhaps the increased membrane fouling as filtration time elapses.

In addition, as it has been shown in Sec. 6.11 that increasing feed CFV improved the obtained permeate flux rates from all membranes tested; it is likely that the combination of simultaneously increasing both feed CFV and electrical field further increases the membrane flux rate. For instance, at the beginning of the filtration period, increasing the feed CFV from 1 to 4.60 m/sec with no electrical field applied, resulted in increasing the permeate flux rate from 2524.7, 2244.2 and 2618.2 to 14643.1, 18383.4 and 18074.8 l/m^2 hr from membranes MI, MII and MIII, respectively. On the other hand; however, increasing the feed CFV from 1 to 4.60 m/sec while applying an electrical field of 83.30 V/cm, increased the permeate flux rate to 17859.7, 22441.6 and 21974 l/m^2 hr, from membranes MI, MII and MIII, respectively.

Furthermore, it appears that the influence of an electric field is further prominent in the case of emulsion EII in comparison to emulsion EI, perhaps due to its higher water content of 50 vol. % instead of only 30 vol. % in emulsion EI. From Fig. (6.24) using a CFV of 1 m/sec, a filtration time of 0 minutes. it is observed that the permeate flux rate of emulsion EI from membrane MI with an electrical field of 83.30 V/cm was 3581.3 l/m^2 hr, whereas that obtained from the same membrane and at the same electric field, but with emulsion EII, was 4516.4 l/m^2 hr. With reference to Figs. (6.26) and (6.28), under the same set of conditions as given above, similar findings were also observed for membranes MII and MIII. For membrane MII, 3740.3 l/m^2 hr were obtained using emulsion EI and 4048.8 l/m^2 hr using emulsion EII. Likewise, membrane MIII produced 4675.3 l/m^2 hr and 5451.4 l/m^2 hr when filtering emulsion EI and EII, respectively. It is a matter of fact that emulsions with higher water content tend to pass electrical current more efficiently than those emulsions with lower water contents (Becher, 2001).

In terms of the allocated electrical field levels at both feed CFVs (1 and 4.60 m/sec) as shown in Figs. (6.32-33), increasing the applied electric field from low to high through medium levels across both emulsions EI and EII, did not show a quite linear relationship with the collected permeate flux rate. In fact, a linear relationship is demonstrated only by membrane MII at a feed CFV of 1 m/sec with both emulsions, and at a feed CFV of 4.60 m/sec only by membrane MIII.

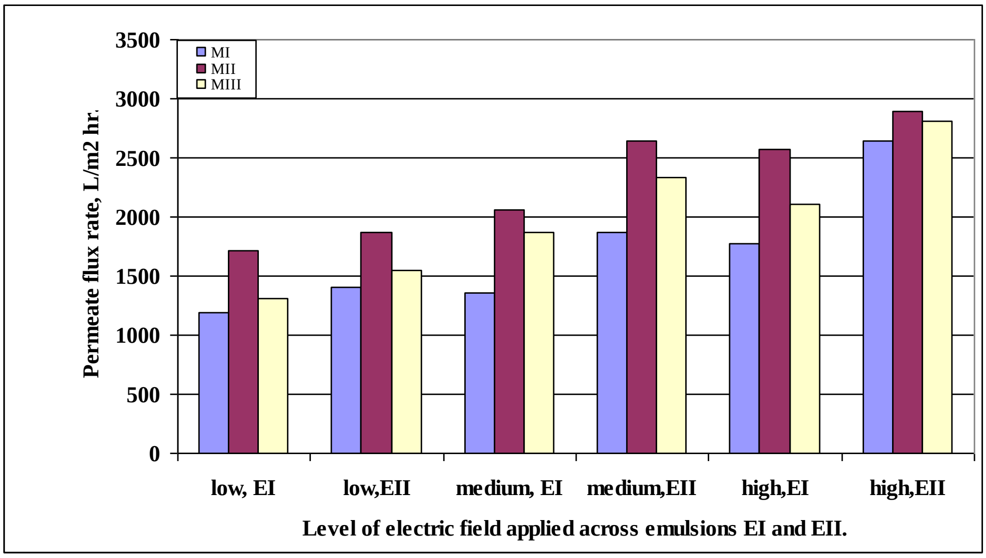


Fig. (6.36): Permeate flux rate of membranes MI, MII and MIII at different electric field grades after 30 min of filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec.

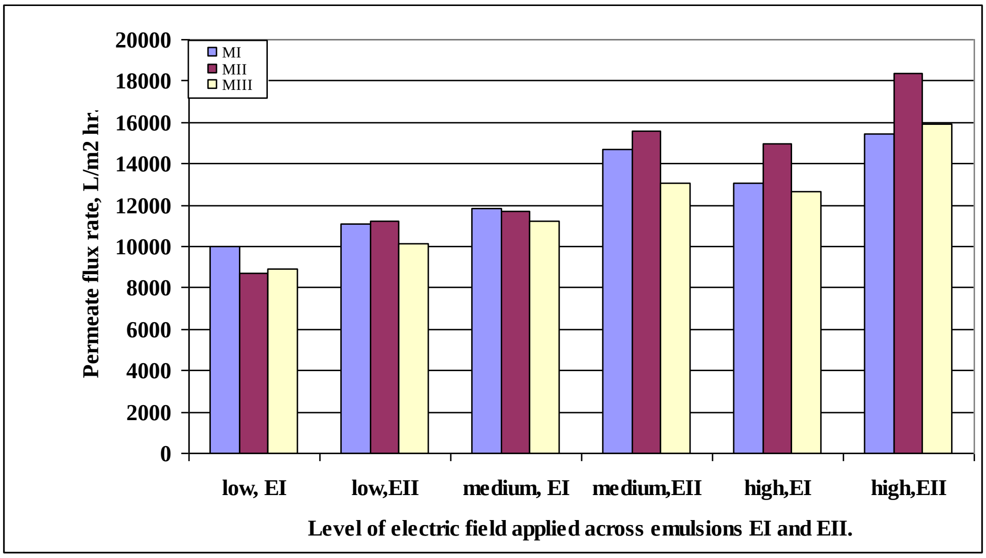


Fig. (6.37): Permeate flux rate of membranes MI, MII and MIII at different electric field grades after 30 min of filtration. Emulsion water content: 30 and 50 vol. %; CFV: 4.60 m/sec.

6.13 Effect of Membrane Pore Size on Permeate Flux Rate

Among the important membrane properties is the average pore size as it, to a great extent, determines the membrane performance. In this part of this study, the effect of membrane pore size on membrane permeate flux rate is investigated. For this purpose, three PHP membranes of different pore sizes were used in microfiltering two emulsions of different water contents (30 and 50 vol. %). In each experiment, a fresh membrane was used, the feed CFV was changed from 1 to 12 m/sec and the electric field from 0 to 666.70 V/cm; however, the filtration time was always kept constant at 30 minutes. The variation of membrane permeate flux rate with filtration time with respect to membrane pore size for membranes MI, MII and MIII at 1, 4.60 and 12 m/sec for both emulsions using no electric field is given in Table (6.21) and shown in Figs. (6.38-39), while those data obtained with the application of 333.30 and 666.70 V/cm are tabulated separately in Tables (6.22-23) and shown in Figs. (6.40-43).

Table (6.21): Effect of membrane pore size on permeate flux rate for membranes MI, MII and MIII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 4.60 and 12 m/sec. No electric field.

	Permeate flux rate, l/m^2. hr																	
Filtration time, min	Membrane																	
	MI						MII						MIII					
	CFV, m/sec																	
	1	4.60	12	1	4.60	12	1	4.60	12	1	4.60	12	1	4.60	12	1	4.60	12
	Emulsion water content, vol. %																	
	30			50			30			50			30			50		
0	2524.7	14643.1	18383.4	2646.2	14961	19477.4	2244.2	18383.4	21600	2337.7	19477.4	23058.7	2618.2	18074.8	23685.2	2805.2	19477.4	25555.3
5	2758.4	16597.4	20103.9	2898.7	17298.7	21188.6	2618.2	20384.4	24779.2	2618.2	21272.7	26181.8	3422.3	19636.4	25714.3	3740.3	21188.6	27734
10	2945.5	18383.4	24311.7	3039	19636.4	25246.8	2758.4	23096.1	26181.8	2898.7	24311.7	28285.7	3553.3	21815.1	28285.7	3974	23376.6	31885.7
15	1963.6	15428.6	21272.7	2103.9	16831.2	22441.6	2178.7	20412.5	25555.3	2337.7	21506.5	26649.4	3506.5	17298.7	22441.6	3581.3	19009.9	24311.7
20	1753.3	12857.1	19075.3	1963.6	13867	20571.4	2010.4	13090.9	20571.4	2178.7	14643.1	22535.1	2711.7	15194.8	21039	2898.7	16672.2	22909.1
25	1355.8	12155.8	16480.5	1552.2	13090.9	18000	1916.9	12389.6	18074.8	2103.9	13558.4	19636.4	2178.7	11454.6	19402.6	2337.7	12932	21039
30	1192.2	10005.2	15054.5	1402.6	11061.8	15896.1	1711.2	8724.2	13792.2	1870.1	11220.8	15194.8	1309.1	8883.1	17607.3	1552.2	10126.8	19636.4

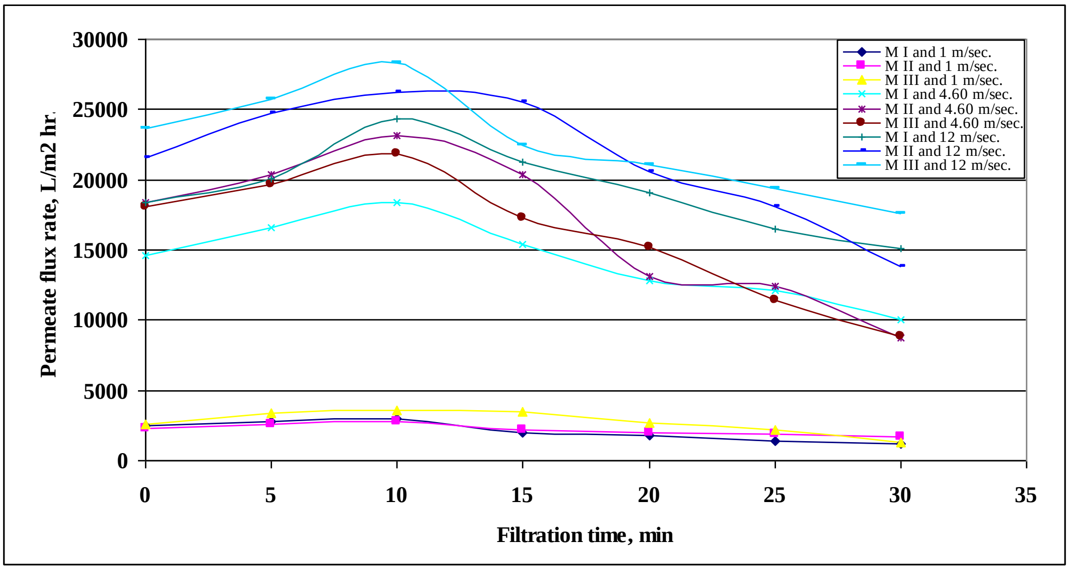


Fig. (6.38): Effect of membrane pore size on permeate flux rate for membranes MI, MII and MIII for 30 minutes filtration. Emulsion water content: 30 vol. %; CFV: 1, 4.60 and 12 m/sec. No electric field.

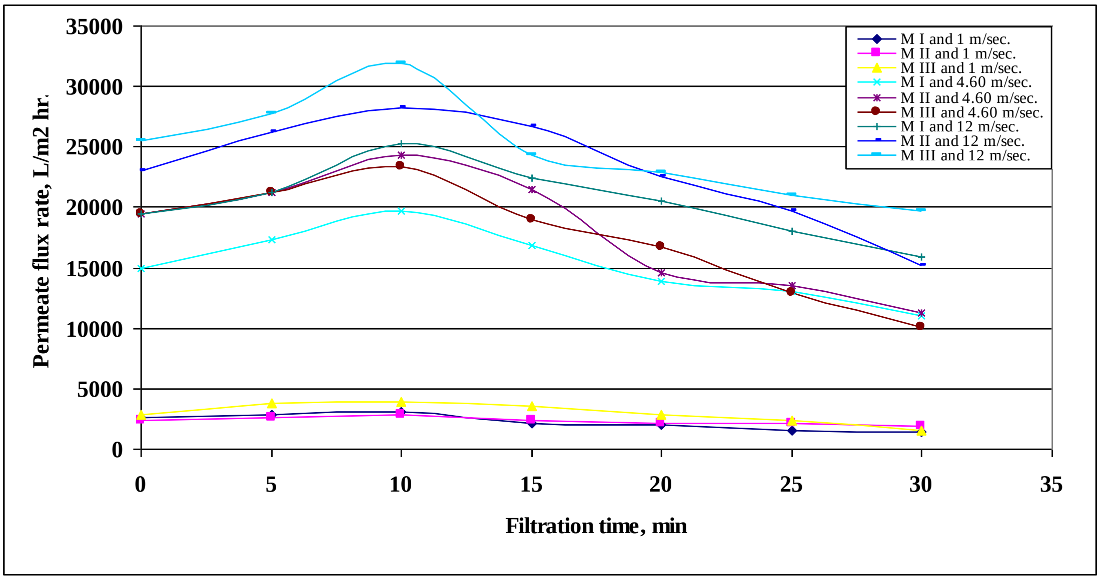


Fig. (6.39): Effect of membrane pore size on permeate flux rate for membranes MI, MII and MIII for 30 minutes filtration. Emulsion water content: 50 vol. %; CFV: 1, 4.60 and 12 m/sec. No electric field.

Generally, with reference to Figs. (6.38-43), whether with/without an electrical field, at a given set of filtration conditions, the data suggest that there was no common trend with regards to the permeates obtained from various membranes used when dealing with both emulsions. Initially, considering emulsion EI at 1 m/sec, membrane

MI gave 2524.7, membrane MII 2244.2 and membrane MIII 2618.2 l/m^2 hr (i.e., MIII>MI>MII). Likewise, in case of emulsion EII, membrane MI produced 2646.2, membrane MII 2337.7 and membrane MIII 2805.2 l/m^2 hr in which the order again is as following: MIII>MI>MII. Increasing the feed CFV to 4.6 m/sec shuffled the order of obtained permeates to: MII>MIII>MI in case of both emulsions. Further increasing the feed CFV to 12 m/sec produced another pattern among the collected permeates, according to the following order: MIII>MII>MI with respect to both emulsions. At the end of filtration time for both emulsions, a different order of permeate flux rate was again observed.

The variation of permeate flux rate among the various membranes employed can be partly attributed to differences in their morphological structure which may eventually result in different membrane porosity. Permeate variation can also be due to differences in the degree of hydrophilicity of each membrane. Under such conditions, it is envisaged that the oily layer that may form on the membrane surface, or within its pores, may be of different thickness, according to which the membrane permeate flux rate is proportional. The thicker the oil layer is, the lower the permeate flux rate would be, and vice versa. Another possible reason for permeate flux rate variation is swelling of the membrane. Depending on emulsion water content and/or membrane pore diameter, oil droplets may settle on the membrane surface creating an obstacle for permeate flow and/or sit at its pores leading to pore blockage. Amongst the tested membranes which were of different pore sizes, flux rate was not observed to be proportional to pore size. In this regard, it should not be expected that membranes with larger pore diameter will always deliver higher permeate flux rates than those with smaller pore diameter, as it is expected that the former membranes are more vulnerable to internal blocking by smaller droplets, by which membrane permeation can accordingly decline (Wakeman and Williams, 2002; Wakeman and Akay, 1997; Tarleton and Wakeman, 1994b; Wakeman and Tarleton, 1991; Fell et al., 1990).

With regard to flux declination as demonstrated in Figs. (6.38-43), it can be understood that each membrane has experienced different pattern of flux declination with time. In membrane MI, the flux declined nearly 40 % when feeding emulsion EI at a CFV of 1 m/sec from 1963.6 to 1192.2 l/m^2 hr in the last fifteen minutes of filtration. Flux deterioration was lesser at higher feed CFVs of 4.60 and 12 m/sec, in which it was 35 and less than 30 %, respectively. Generally, at all feed CFVs used, emulsion EII exhibited a smaller flux decrease with time, as the declination percentages were less than 30 to 34 % at the used feed CFVs. However, during the same period of filtration, the percentages of flux declination in membrane MII was 21.5-57 % in case of emulsion EI and 20-48 % in case of emulsion EII. For membrane MIII the corresponding figures were 21.5-49 % in case of emulsion EI and 20-57 % in case of emulsion EII, respectively.

Table (6.22): Effect of membrane pore size on permeate flux rate for membranes MI, MII and MIII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 4.60 and 12 m/sec; electric field 333.30 V/cm.

	Permeate flux rate, l/m^2. hr																	
Filtration time, min	Membrane																	
	MI						MII						MIII					
	CFV, m/sec																	
	1	4.60	12	1	4.60	12	1	4.60	12	1	4.60	12	1	4.60	12	1	4.60	12
	Emulsion water content, vol. %																	
	30			50			30			50			30			50		
0	4207.8	24928.8	27893	4048.8	25714.3	30230.7	3740.3	29604.2	34597.4	3974	31792.2	37870.1	4207.8	29763.1	39272.7	4441.6	32727.3	43480.5
5	4441.6	26649.4	30389.6	4768.8	29454.6	32409.4	4675.3	29922.1	38337.7	4768.8	32961	41142.9	5376.6	31792.2	40207.8	5703.9	35214.6	44415.6
10	4768.8	29220.8	36000	4983.9	31885.7	38805.2	4675.3	34129.9	39272.7	4983.9	36561	43789.1	5919	33662.3	41376.6	6386.5	37243.6	48305.5
15	3113.8	22441.6	32727.3	3422.3	26649.4	34129.9	3422.3	28052	37870.1	3833.8	30857.2	41376.6	5292.5	26181.8	35532.5	5610.4	29604.2	40207.8
20	2646.2	19009.9	28669.1	3272.7	22441.6	31090.9	3039	20571.4	30230.7	3422.3	24311.7	35064.9	3974	23993.8	33662.3	4516.4	27116.9	38337.7
25	2178.7	17766.2	25246.8	2898.7	20664.9	26957.9	2805.2	19168.8	25863.9	3272.7	21974	29080.5	3422.3	17298.7	31090.9	3833.8	20664.9	35373.5
30	1776.6	13090.9	22909.1	2646.2	15428.6	22909.1	2571.4	14961	22282.6	2898.7	18383.4	24779.2	2103.9	12623.4	27116.9	2805.2	15896.1	31792.2

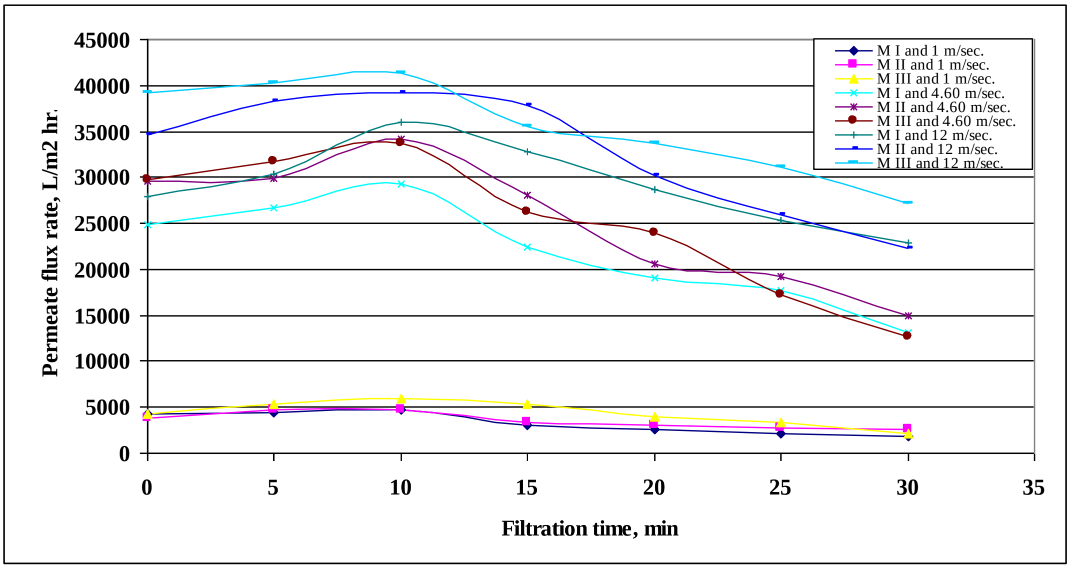


Fig. (6.40): Effect of membrane pore size on permeate flux rate for membranes MI, MII and MIII for 30 minutes filtration. Emulsion water content: 30 vol. %; CFV: 1, 4.60 and 12 m/sec; electric field: 333.30 V/cm.

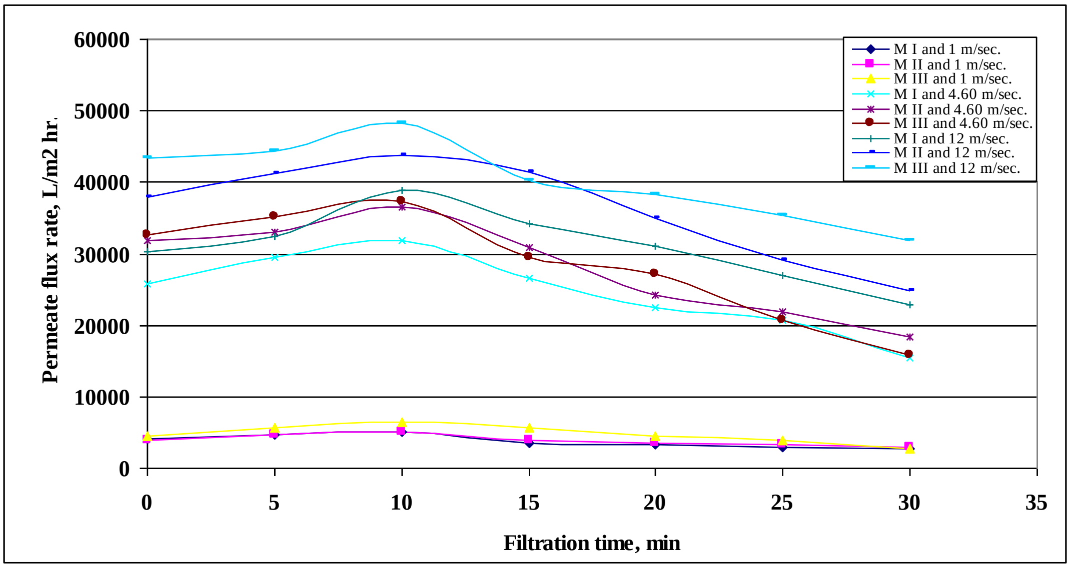


Fig. (6.41): Effect of membrane pore size on permeate flux rate for membranes MI, MII and MIII for 30 minutes filtration. Emulsion water content: 50 vol. %; CFV: 1, 4.60 and 12 m/sec; electric field: 333.30 V/cm.

Table (6.23): Effect of membrane pore size on permeate flux rate for membranes MI, MII and MIII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 4.60 and 12 m/sec; electric field 666.70 V/cm.

Permeate flux rate, l/m^2. hr																		
Filtration time, min	Membrane																	
	MI						MII						MIII					
	CFV, m/sec																	
	1	4.60	12	1	4.60	12	1	4.60	12	1	4.60	12	1	4.60	12	1	4.60	12
	Emulsion water content, vol. %																	
	30			50			30			50			30			50		
0	5292.5	31792.2	52363.6	5703.9	33503.4	52204.7	4516.4	35841	53298.7	5142.9	38805.2	57974	4983.9	33194.8	61555.3	5610.4	36467.5	69035.9
5	5610.4	35373.5	49867	6077.9	37711.2	53607.3	5451.4	40824.9	57974	5451.4	43480.5	63677.9	5610.4	40048.8	64828.1	6386.5	43480.5	71532.5
10	6077.9	43013	49090.9	6386.5	40207.8	58909.1	5844.2	48155.9	55168.8	6227.5	51737.2	64519.5	7013	44883.1	63677.9	8097.7	48155.9	75272.7
15	3974	32727.3	45818.2	4441.6	36701.3	50727.3	4516.4	42077.9	53607.3	4983.9	46285.7	57506.5	6545.5	36467.5	48932	6854	41142.9	54233.8
20	3581.3	26957.9	41919	3740.3	30857.2	46126.8	4048.8	31792.2	47370.4	4516.4	36467.5	53766.2	5292.5	31792.2	45350.7	5844.2	35064.9	51522.1
25	2646.2	24077.9	38337.7	3113.8	27893	41610.4	3506.5	27584.4	43480.5	4207.8	30857.2	48857.2	4207.8	22282.6	40675.3	4675.3	25863.9	46126.8
30	2178.7	19636.4	36935.1	2646.2	22441.6	37496.1	3366.2	18383.4	31792.2	3740.3	24311.7	37084.7	2487.3	16831.2	38337.7	3113.8	19636.4	43480.5

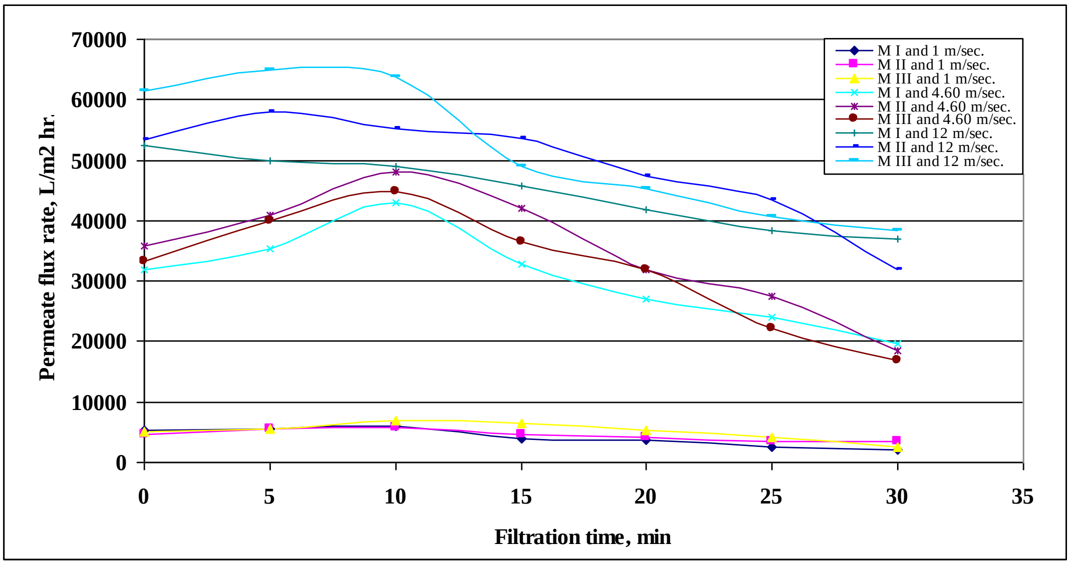


Fig. (6.42): Effect of membrane pore size on permeate flux rate for membranes MI, MII and MIII for 30 minutes filtration. Emulsion water content: 30 vol. %; CFV: 1, 4.60 and 12 m/sec; electric field: 666.70 V/cm.

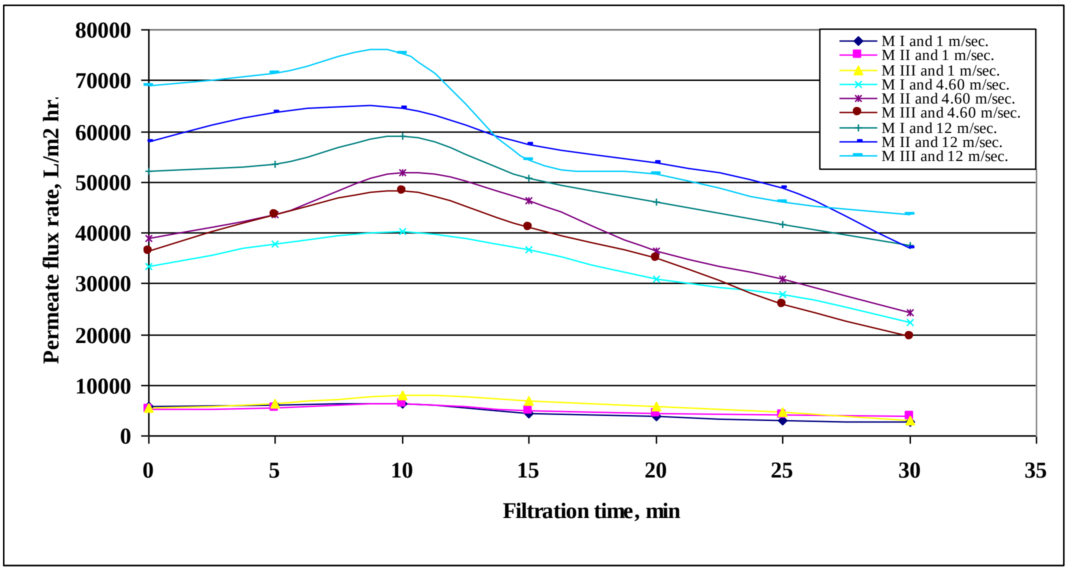


Fig. (6.43): Effect of membrane pore size on permeate flux rate for membranes MI, MII and MIII for 30 minutes filtration. Emulsion water content: 50 vol. %; CFV: 1, 4.60 and 12 m/sec; electric field: 666.70 V/cm.

6.14 Evaluation of Permeate Flux Rate

Membrane flux rate is an important performance characteristic to determine. In fact, as was explained in Secs. 4.3.1 and 4.3.2, the performance of a membrane is described by the flux rate of the liquid through it and the retention/selectivity of that membrane for a part of the treated stream, respectively. In this work, a range of operational conditions using different membrane sizes including: 1-emulsion water content, 2-filtration duration, 3-feed CFV and 4-electric field, has been thoroughly scrutinized. It was found that with increasing the oil content in an emulsion, the permeate flux rate decreases. Nevertheless, with increasing both feed CFV and/or electric field, it was found that the permeate flux rate from all membranes tested generally increases, although with different patterns. However, despite the efforts been made to optimize the permeate flux rate, obtained fluxes still correspond to no more than 5.50 % of the total inlet flow rate to the filtration unit. However, if permeate flux rate and demulsification efficiency (as will be shown next) are the important goals regardless of the economics, such permeate percentage(s) can be accepted. According to some work available in the literature concerned with microfiltration of w/o emulsions (Hu and Scott, 2008; Hu and Scott, 2007; Ezzati et al., 2005; Kocherginsky et al., 2003; Scott et al., 2001; Dezhi et al., 1999; Sun et al., 1998; Akay and Wakeman, 1996), details of permeate flux rate with respect to the total inlet were not disclosed. However, emulsions investigated and/or membranes used might have been system-specific and; therefore, such a comparison between the results of this work and those reported in the literature may not be valid.

According to the literature, emulsion viscosity, water content and droplet size relative to membrane pores and phenomena like: concentration polarization at the membrane surface, membrane fouling within its pores; membrane-emulsion droplets interactions and membrane internals can accordingly influence the performance of a membrane and ; therefore, can be held responsible to this limitation in permeate flux rate encountered in this study (Huang et al., 2012; de Morais Coutinho et al., 2009; Fakhru'l-Razi et al., 2009; Mohammadi et al., 2004; Cornelissen et al., 1998; Akay and Wakeman, 1994a; Scott et al., 1994). Details of fluxes obtained at these conditions are given in previous sections of this Chapter. To avoid repetition, only selective values are repeated in Table (6.24) below for citation purposes only. This table has been constructed with the highest permeates obtained from each membrane according to emulsion water content at the top of the table, scrolling down to lower ones. The last column of the table represents the percentage of the permeate collected relative to the total inlet flow rate (pro-rata).

Table (6.24): Percentage of obtained permeate flux rates at various filtration conditions relative to the total inlet flow rate.

Membrane	Emulsion	Filtration condition(s)	Permeate flux rate, l/m^2 hr, after 30 min of filtration	Total inlet flow rate, l/hr.	Total inlet flow rate, l/m^2 hr,	Percentage, %
MI	EII	333.30 V/cm & 4.60 m/sec	15428.60	1290.20	335116.90	4.60
	EI		13090.90			3.90
	EII	333.30 V/cm & 1 m/sec	2646.20	288	74805.20	3.50
	EI		1776.60			2.40
MII	EII	333.30 V/cm & 4.60 m/sec	18383.40	1290.20	335116.90	5.50
	EI		14961			4.50
	EII	333.30 V/cm & 1 m/sec	2898.70	288	74805.20	3.90
	EI		2571.40			3.45
MIII	EII	333.30 V/cm & 4.60 m/sec	15896.10	1290.20	335116.90	4.70
	EI		12623.40			3.80
	EII	333.30 V/cm & 1 m/sec	2805.20	288	74805.20	3.75
	EI		2103.90			2.80

6.15 Trend of Permeate Flux Rate

Based on the results obtained, as reported in Secs. 6.9-13, a number of typical stages of permeate flux rate behaviours can be identified. With reference to the schematic given in Fig. (6.44), a description of physical processes and fouling effects believed to have taken place is given below. Each stage is clearly labelled on this figure.

1- Saturation of the membrane with emulsion droplets: Initially during this stage, it seems that membrane pores are more prone to adsorb emulsion droplets within their internal structure rather than permeating them. However, towards the end of this period (after 10 min of filtration), it is obvious that permeate flux rate is increasing maxima, indicating that membrane pores are no longer adsorbing emulsion droplets, but start to push them out of the membrane body once a pore is fully occupied and that cannot accommodate further droplet(s). The chemistry of the membrane surface with respect to emulsion droplets, membrane pore size and filtration conditions are vital for this stage.

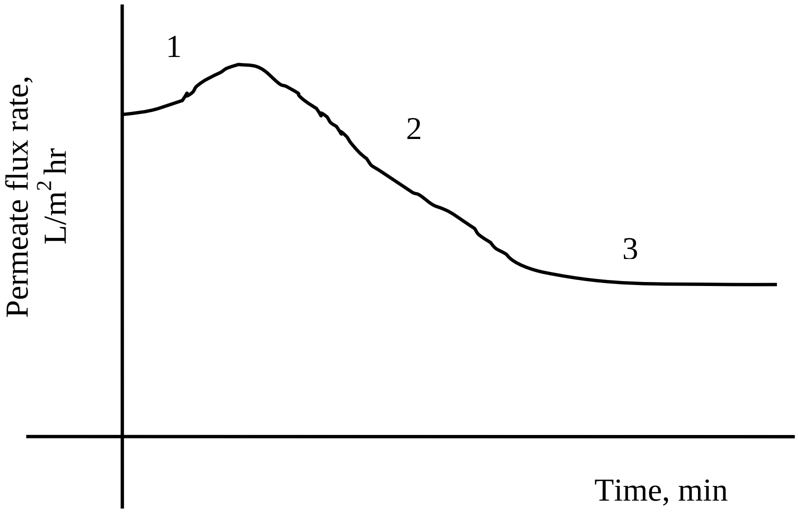


Fig. (6.44): Stages of permeate flux rate behaviour.

2- Build-up of a secondary membrane: Following the first stage, emulsion droplets seem have begun to deposit onto the membrane surface creating what’s known as secondary membrane. Eventually, such a trend weakens the chemistry of interaction between the primary membrane surface and emulsion droplets. Further, this secondary membrane, which is composed of emulsion droplets, clogs the pores of the primary membrane. As a result, the permeate flux rate begins to substantially decline. This declination is; of-course, a function of the filtration conditions.

3- Densification/compaction of secondary membrane: During this final stage in which the growth of secondary membrane seems to have finalized, permeation rate declination is somewhat retarded in comparison to that observed in the former stage. As the name implies, densification owing to the crossflow filtration principle of feed tangential flow, involves no deposition of additional/newer emulsion droplets but rather a re-arrangement. This; in turn, brings no much change to the permeate flux rate (plateau).

6.16 Effect of Influent Emulsion Water Content on Demulsification

The effect of water phase content in w/o emulsion on demulsification using three different PHP membranes in terms of their pore sizes was investigated at different feed flow rates ($8*10^{-5}$-$9.5*10^{-4}$ m^3/sec) and electric field intensities (0-666.70 V/cm) for a fixed filtration duration of 30 min. This investigation was carried out using two emulsions of two different water contents, namely 30 and 70 vol. % of water (dispersed phase). The influence of water phase content in w/o emulsion on demulsification using membrane MI at flow rate of $8*10^{-5}$ m^3/sec and electric fields of 0, 33.30 and 83.30 V/cm as a function of settling time, has been shown in Table (6.25) and Fig. (6.45), respectively. Similarly, demulsification profiles following the use of membranes MII and MIII using the same conditions, are presented in Tables (6.26-27) and Figs. (6.46-47), respectively. However, detailed experimental results of these investigations at higher conditions are collated in Appendix B.

In this study as shown in the preceding Chapter, the extent of separation (demulsification) efficiency has been calculated by working out the percentage of volume of water that comes out of the permeate sample as a watery layer at the bottom of the sample as a fraction of the total volume of the whole sample.

$$DE = W\,(ml)/\,S\,(ml) * 100$$

Where *DE* is the demulsification efficiency; *W* is the volume fraction of water in the permeate sample and *S* is the total volume of permeate sample. The demulsification efficiency was recorded as a function of settling time until no more water has come out. Substituting the results obtained from the experimental studies in this thesis into this equation can directly lead to the generation of the tables referred to hereafter. For instance, the demulsification efficiencies using membrane MI with no any electrical field, when demulsifying emulsion EI,, as shown in Table (6.25) are 0, 19.60, 23.50, 31.40 and 54.90 vol. %, after 0, 2, 4, 6, 7 hr of emulsion settling, respectively.

$$\begin{aligned} DE &= 0.7\,(ml)/\,1.275\,(ml)*100 \\ &= 54.90\,\% \end{aligned}$$

Table (6.25): Bottle test results of phase separation of water as a function of time for membrane MI. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

Separation efficiency, %						
Time, hr	Electric field, V/cm					
	0		33.30		83.30	
	Emulsion water content, vol. %		Emulsion water content, vol. %		Emulsion water content, vol. %	
	30	50	30	50	30	50
0	0	0	0	0	0	0
2	19.60	33.30	18.50	57.10	17.20	50
4	23.50	50	29.60	57.10	34.50	50
6	31.40	56.70	44.40	57.10	51.70	62.50
7	54.90	56.70	55	57.10	55.20	62.50

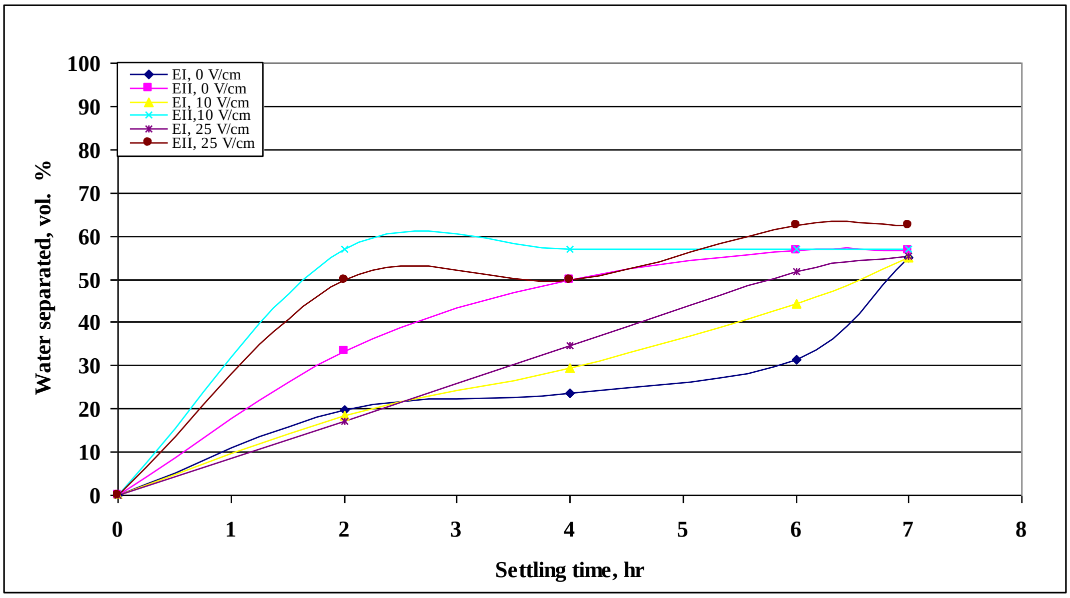


Fig. (6.45): Phase separation of water as a function of time for EI and EII w/o emulsions using memebrane MI. CFV: 1 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

Table (6.26): Bottle test results of phase separation of water as a function of time for membrane MII. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

Time, hr	Separation efficiency, %					
	Electric field, V/cm					
	0		33.30		83.30	
	Emulsion water content, vol. %		Emulsion water content, vol. %		Emulsion water content, vol. %	
	30	50	30	50	30	50
0	0	0	0	0	0	0
2	27.30	50	25	50	22.70	53
4	41	50	50	50	45.50	53
6	41	50	50	50	54.50	61.80
7	43.70	50	50	50	54.50	61.80

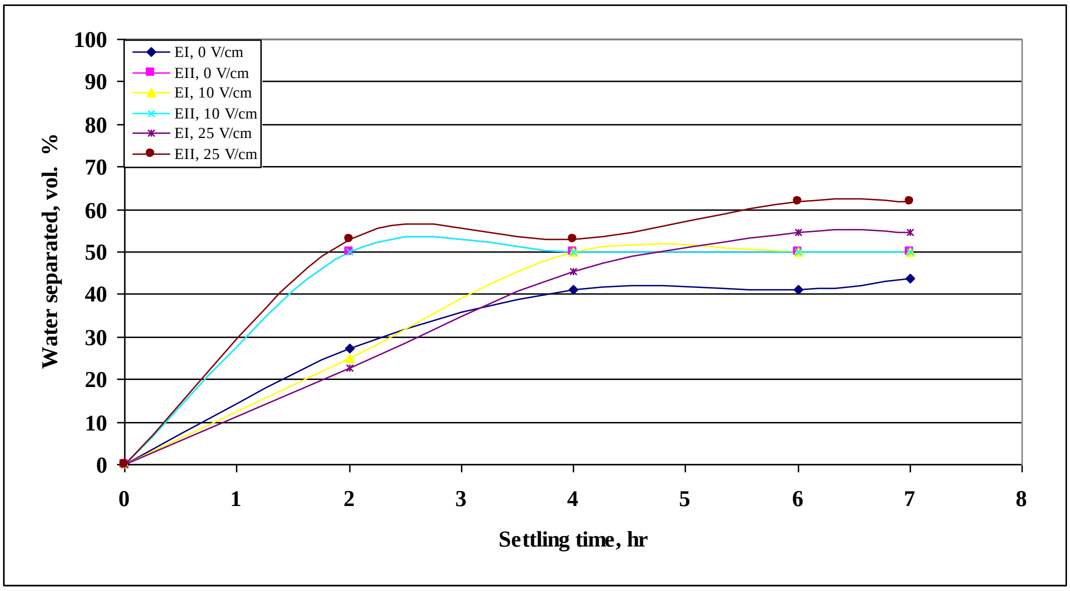


Fig. (6.46): Phase separation of water as a function of time for EI and EII w/o emulsions using membrane MII. CFV: 1 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

Table (6.27): Bottle test results of phase separation of water as a function of time for membrane MIII. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

Separation efficiency, %						
Time, hr	Electric field, V/cm					
	0		33.30		83.30	
	Emulsion water content, vol. %		Emulsion water content, vol. %		Emulsion water content, vol. %	
	30	50	30	50	30	50
0	0	0	0	0	0	0
2	35.70	0	54.60	47.60	25	60
4	35.70	45.20	54.60	57.10	50	60
6	35.70	54.20	54.60	57.10	55	60
7	53.60	54.20	54.60	57.10	55	60

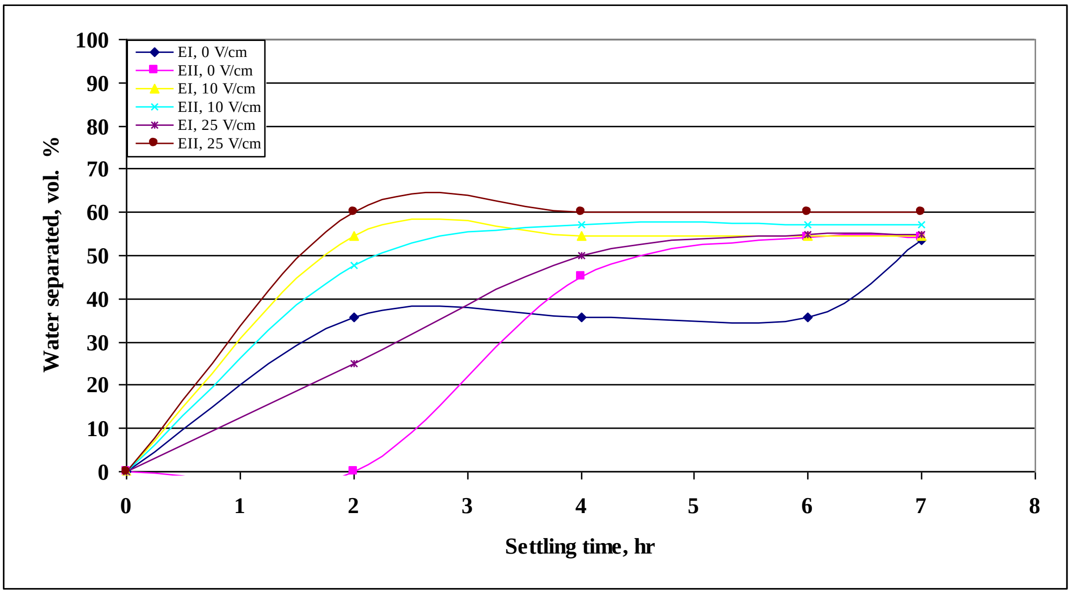


Fig. (6.47): Phase separation of water as a function of time for EI and EII w/o emulsions using memebrane MIII. CFV: 1 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

As shown in Figs. (6.45-47), water content had an effect on demulsification efficiency. It is obvious that the higher the water content in the emulsion, the higher the demulsification efficiency. For example, using membrane MI with applying no external electrical field, emulsion EI exhibited water phase separation percentage of 54.90 vol. % whereas 56.70 vol. % of the demulsified sample of emulsion EII was water. Applying an electrical field across the emulsions led to further increase in the water being separated in comparison to that when no electrical field applied. It should also be noted that when applying an electrical field emulsion EII again produced more water than emulsion EI. For example, by applying 33.30 V/cm to emulsion EI, it gave 55 vol. % and that emulsion EII gave 57.10 vol. %. This observation is also valid for both membranes MII and MIII. A likely explanation to this finding is that the stability of an emulsion that's originally with higher water phase content is lower than that of an emulsion with lower water content (higher oil content) which in turn would render the former emulsion to be more vulnerable to destabilize than the latter one. Higher oil content means more emulsion stabilizers (asphaltenes/resins) which accordingly result in an increased level of stability; that's more difficult to demulsify. With this in mind, it is fairly logic; therefore, to have the demulsification efficiency increased with the increase in the water content, and vice versa.

6.17 Relationship between Settling Time and Demulsification

To understand the relationship between settling time and demulsification efficiency at various filtration conditions, a number of experiments at various conditions of emulsion water contents, flow rates and electric fields strengths using three PHP membranes with different pore sizes were performed. These experiments were based on using two emulsions with different water contents, namely, 30 and 50 vol. % of water content. Inlet flow rate was changed in the range of ($8*10^{-5}$-$9.5*10^{-4}$ m^3/sec), whilst applying electric fields of (0-666.70 V/cm). A sample of the results of these experiments for each membrane is separately shown below in Tables (6.28-30) and Figs. (6.48-53). For a complete set of results, refer to Appendix B.

It is clear from these figures that, as settling time elapsed, demulsification efficiency of both emulsions increased at each voltage or feed CFV used. In other words, no water separation was noticed at the onset of settling time and that a water layer was gradually developing at the bottom of the sample. For example, in case of emulsion EI, running the filtration experiment at 1 m/sec using membrane MI in the absence of any electrical field, the demulsification efficiency was increasing from zero to 54.90 vol. %. Applying an electrical field of 33.30 V/cm through emulsion EI has also produced a similar trend in which the demulsification efficiency was nil at the start of settling time and was 55 vol. % at the end of settling time. It can also be noted that the demulsification rate was somewhat retarded towards the end of the settling time for both emulsions examined. It is very likely that the sample collected with time, approached its final distribution with which there is a suppression in the tendency towards a further change in its composition. After some time, an apparent upper oil phase and a distinctive lower water phase were visually identified.

Table (6.28): Demulsification efficiency vs. settling time using membrane MI for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 2.25 and 2.90 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

	Demulsification efficiency, %																	
Settling time, hr	Emulsion EI									Emulsion EII								
	CFV, m/sec									CFV, m/sec								
	1			2.25			2.90			1			2.25			2.90		
	Electric field, V/cm			Electric field, V/cm			Electric field, V/cm			Electric field, V/cm			Electric field, V/cm			Electric field, V/cm		
	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	19.60	18.50	17.20	9.50	13.60	35.30	13.30	11.80	26.30	33.30	57.10	50	36.40	50	31.60	33.30	42.30	27.30
4	23.50	29.60	34.50	24.80	31.80	44.20	26.50	15.80	37.50	50	57.10	50	63.60	66.70	55.30	37.50	49.30	54.60
6	31.40	44.40	51.70	38.10	40.90	57.40	35.30	31.60	45	56.70	57.10	62.50	63.60	70.80	71.10	65	73.90	75
7	54.90	55	55.20	55.20	56.40	57.40	58.30	58.50	58.60	56.70	57.10	62.50	63.60	70.80	71.10	65	73.90	75

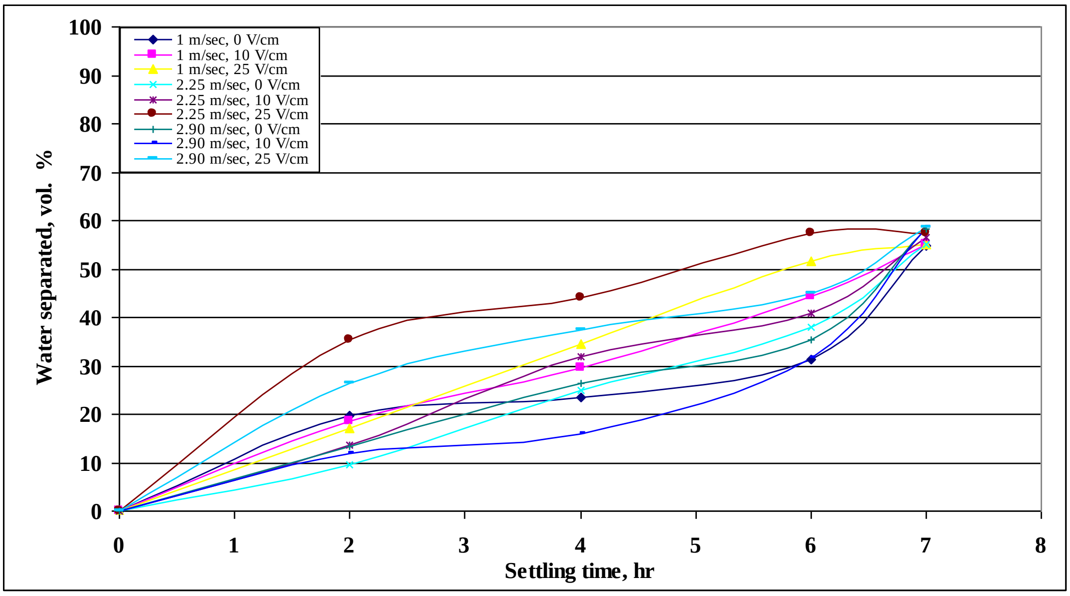


Fig. (6.48): Demulsification efficiency vs. settling time using membrane MI for 30 minutes filtration for emulsion with water content of 30 vol. %; CFV: 1, 2.25 and 2.90 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

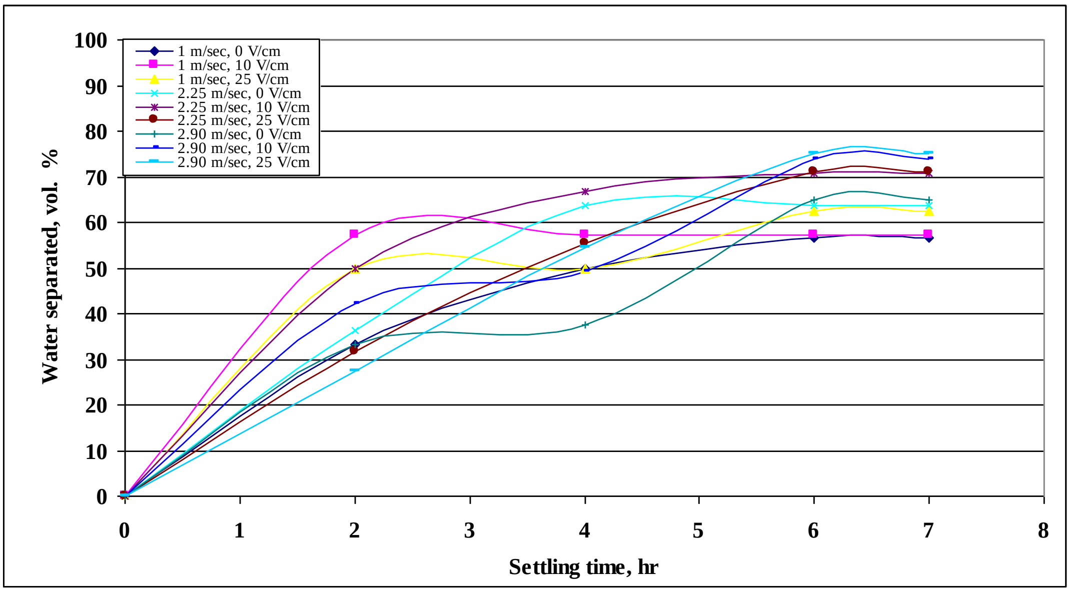


Fig. (6.49): Demulsification efficiency vs. settling time using membrane MI for 30 minutes filtration for emulsion with water content of 50 vol. %; CFV: 1, 2.25 and 2.90 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

Table (6.29): Demulsification efficiency vs. settling time using membrane MII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 2.25 and 2.90 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

Demulsification efficiency, %																		
Settling time, hr	Emulsion EI									Emulsion EII								
	CFV, m/sec									CFV, m/sec								
	1			2.25			2.90			1			2.25			2.90		
	Electric field, V/cm			Electric field, V/cm			Electric field, V/cm			Electric field, V/cm			Electric field, V/cm			Electric field, V/cm		
	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	27.30	25	22.70	25.60	22.70	22.20	23.10	21.70	28.60	50	50	53	47.10	32.20	39.20	33.30	19.60	26.50
4	41	50	45.50	51.30	34.10	55.60	34.60	27.20	28.60	50	50	53	58.80	42.90	49	44.40	49	53
6	41	50	54.50	51.30	45.50	55.60	34.60	43.50	38.10	50	50	61.80	58.80	59	62.70	61.10	63.70	66.30
7	43.70	50	54.50	51.30	56.80	57.80	52	59.80	61.90	50	50	61.80	58.80	59	62.70	61.10	63.70	66.30

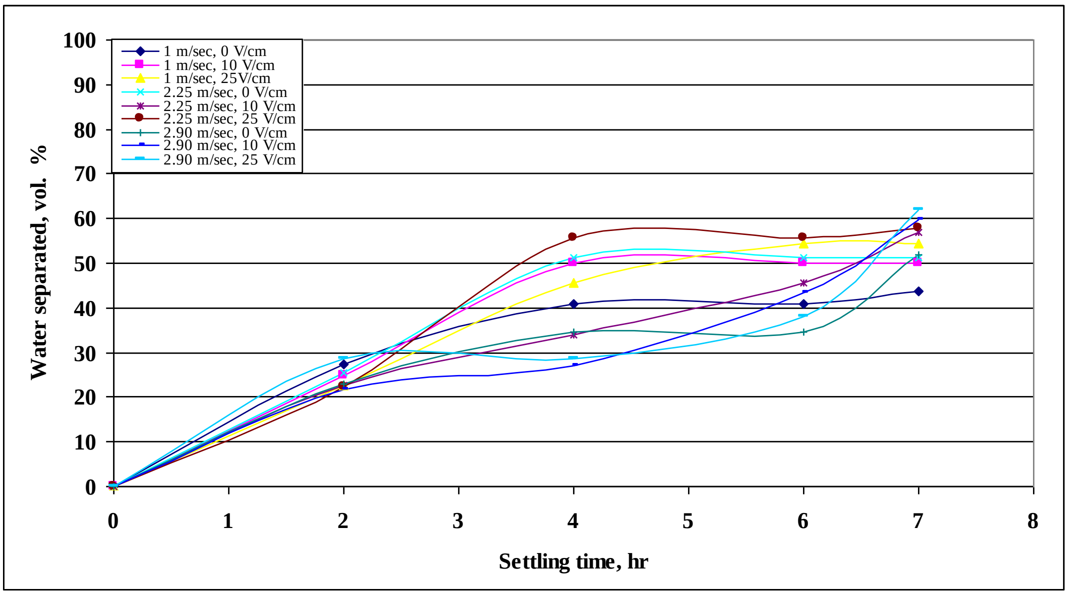


Fig. (6.50): Demulsification efficiency vs. settling time using membrane MII for 30 minutes filtration for emulsion with water content of 30 vol. %; CFV: 1, 2.25 and 2.90 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

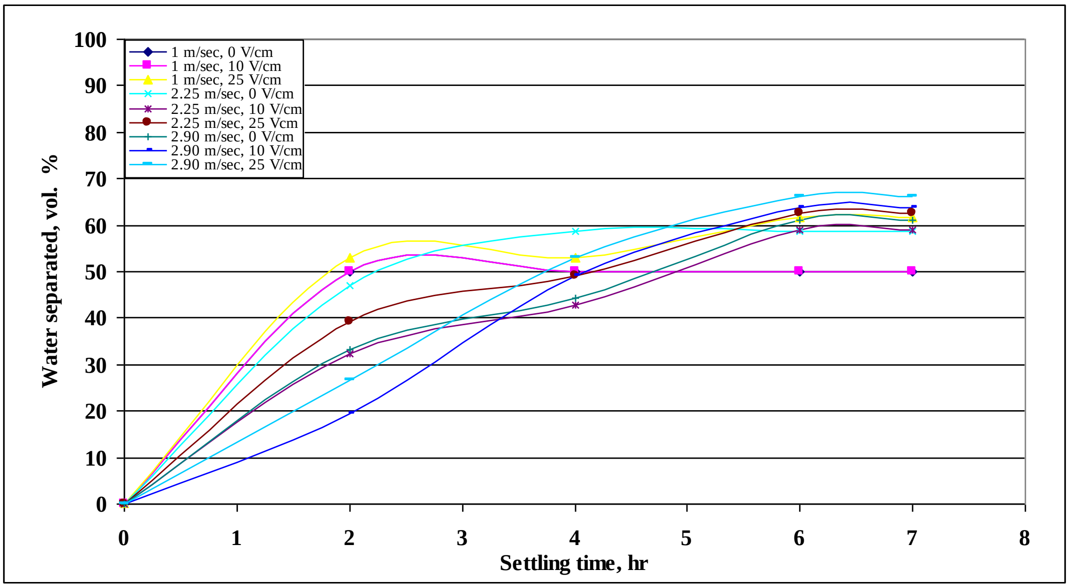


Fig. (6.51): Demulsification efficiency vs. settling time using membrane MII for 30 minutes filtration for emulsion with water content of 50 vol. %; CFV: 1, 2.25 and 2.90 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

Table (6.30): Demulsification efficiency vs. settling time using membrane MIII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 2.25 and 2.90 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

Demulsification efficiency, %																		
Settling time, hr	Emulsion EI									Emulsion EII								
	CFV, m/sec									CFV, m/sec								
	1			2.25			2.90			1			2.25			2.90		
	Electric field, V/cm			Electric field, V/cm			Electric field, V/cm			Electric field, V/cm			Electric field, V/cm			Electric field, V/cm		
	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30	0	33.30	83.30
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	35.70	54.60	25.00	12.50	0	27.30	20.80	18.20	17.70	0	47.60	60.00	33.30	16.70	15.40	26.50	22.20	42.90
4	35.70	54.60	50.00	25	31.10	36.40	31.30	45.50	35.30	45.20	57.10	60.00	55.60	41.70	46.20	53	66.70	50
6	35.70	54.60	55.00	50	41.40	54.50	52.10	45.50	44.20	54.20	57.10	60.00	61.10	62.50	65.40	61.80	66.70	67.90
7	53.60	54.60	55.00	55	55.90	56.40	57.30	58.20	58.30	54.20	57.10	60.00	61.10	62.50	65.40	61.80	66.70	67.90

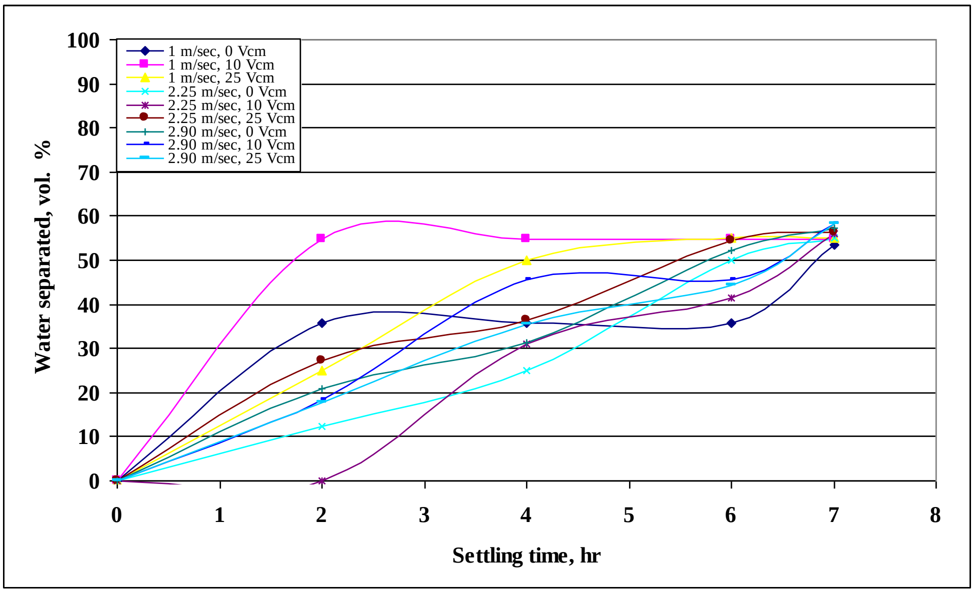


Fig. (6.52): Demulsification efficiency vs. settling time using membrane MIII for 30 minutes filtration for emulsion with water content of 30 vol. %; CFV: 1, 2.25 and 2.90 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

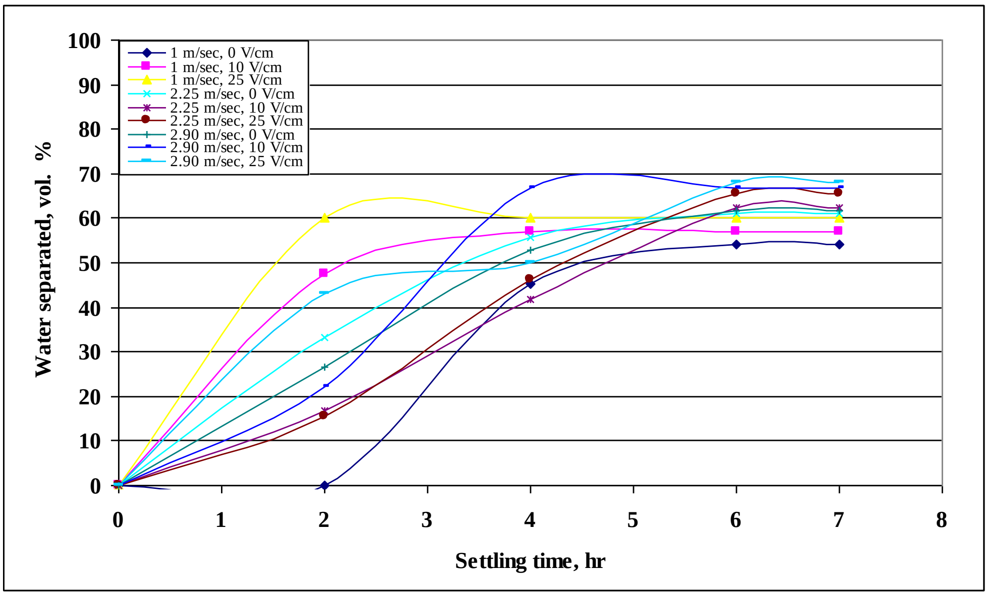


Fig. (6.53): Demulsification efficiency vs. settling time using membrane MIII for 30 minutes filtration for emulsion with water content of 50 vol. %; CFV: 1, 2.25 and 2.90 m/sec; electric field: 0, 33.30 and 83.30 V/cm.

6.18 Effect of Feed Crossflow Velocity (CFV) on Demulsification

The effect of feed CFV on demulsification efficiency of w/o emulsions was investigated. For this purpose, filtration experiments were performed within a feed CFV range of (1-12 m/sec). Each experiment was repeated at different electrical fields in the range between (0-666.70 V/cm) on the two different emulsions (30 and 50 vol. % of water content) using three different PHP membranes of different pore diameter for the same duration of 30 min. The effect of feed CFVs from 1 to 3.35 m/sec on the demulsification efficiency using membrane MI for both emulsions in the absence of electrical fields is given in Table (6.31) and demonstrated in Figs. (6.54-55) as a function of settling time. The effect of higher velocities (3.65-12 m/sec) is tabulated in Appendix B. Likewise, demulsification profiles obtained when using membranes MII and MIII under these conditions are tabulated in Tables (6.32-33) and illustrated in Figs. (6.56-59), respectively. As is the case with membrane MI, the influence of higher velocities (3.65-12 m/sec) on demulsification efficiency using membranes MII and MIII is shown in Appendix B.

Table (6.31); Effect of feed CFV on demulsification efficiency of emulsions EI and EII using membrane MI for 30 minutes filtration. CFV: 1, 2.25, 2.90 and 3.35 m/sec. No electrical field.

Settling time, hr	Demulsification efficiency, %							
	Feed CFV, m/sec							
	1		2.25		2.90		3.35	
	Emulsion water content, vol. %	Emulsion water content, vol. %	Emulsion water content, vol. %	Emulsion water content, vol. %	Emulsion water content, vol. %	Emulsion water content, vol. %	Emulsion water content, vol. %	Emulsion water content, vol. %
	30	50	30	50	30	50	30	50
0	0	0	0	0	0	0	0	0
2	19.60	33.30	9.50	36.40	13.30	33.30	34.90	57.10
4	23.50	50	24.80	63.60	26.50	37.50	42.60	64.30
6	31.40	56.70	38.10	63.60	35.30	65	46.50	75
7	54.90	56.70	55.20	63.60	58.30	65	58.90	75

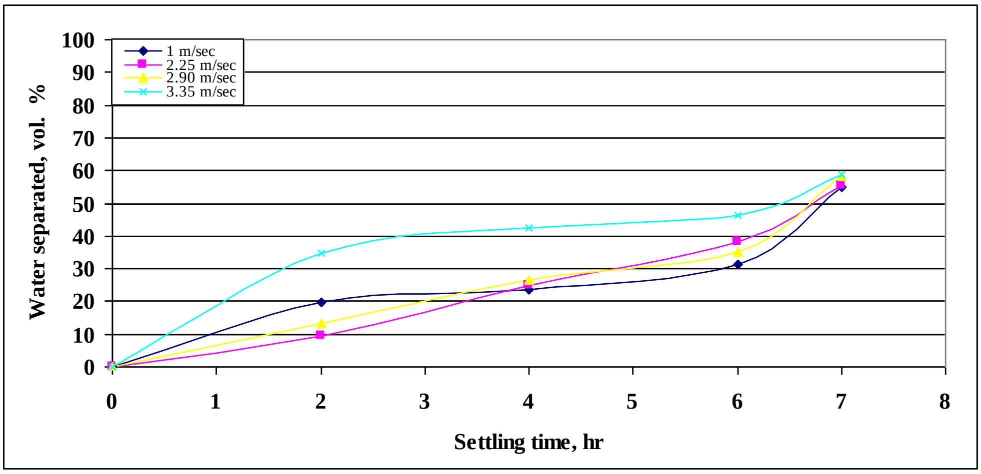


Fig. (6.54): Demulsification efficiency vs. settling time using membrane MI for 30 minutes filtration for emulsion EI. CFV: 1, 2.25, 2.90 and 3.35 m/sec. No electrical field.

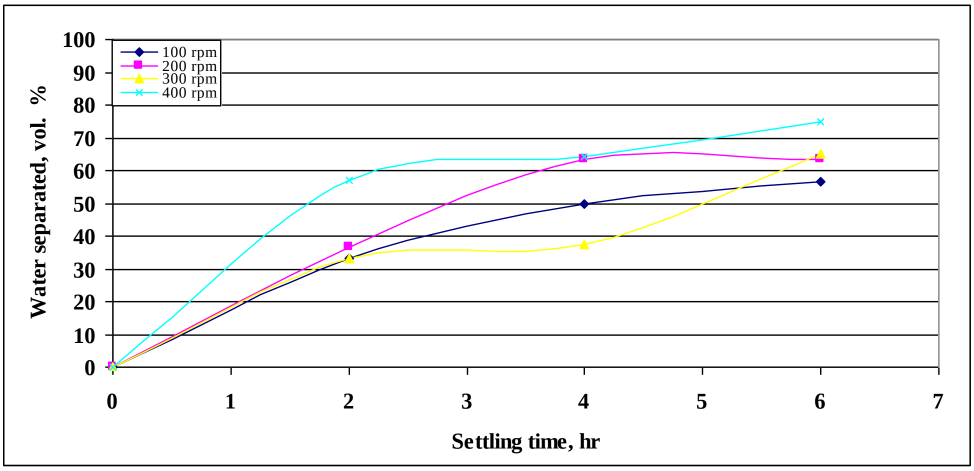


Fig. (6.55): Demulsification efficiency vs. settling time using membrane MI for 30 minutes filtration for emulsion EII. CFV: 1, 2.25, 2.90 and 3.35 m/sec. No electrical field.

With respect to demulsification, it can be assumed that emulsion droplets are at least of two sizes in comparison to membrane pore diameter; these are smaller or larger than membrane pore diameter. Emulsion droplets that are smaller than membrane pore diameter would easily pass through the membrane; of course, at an increased rate at higher feed CFVs, see Figs. (6.54-59). No demulsification is expected to have taken place on these small emulsion droplets and that passed as they are into the permeate side. Thus, these droplets can be considered as the main oil source in the permeate side, the rest of oil in the permeate side can be linked with the carry over by water droplets while filtration is running. Larger emulsion droplets than the membrane pore diameter inlets; however, have to deform to adopt the shape of membrane pores after which membrane-droplet interactions occur. It seems that at a low feed CFV, these droplets did not have enough force to deform, have their oil film stripped by the pore walls, coalesce, adsorb on the pore walls and then pass through the membrane pore outlets, i.e. a lower demulsification efficiency in comparison to that obtained as the feed CFV is increased. For example, using membrane MI with a CFV of 1 m/sec with no electrical field applied across either emulsion, EI or EII, the demulsification efficiency at maximum was 54.90 and 56.70 vol. %, respectively. The demulsification efficiency; however, with a CFV of 3.35 m/sec increased to 58.90 vol. % in the case of emulsion EI, and to 75 vol. %, in the case of emulsion EII. In fact, higher feed CFVs one can argue that emulsion droplets may swiftly leave the membrane pore internals resulting in a relatively decreased demulsification efficiency. On the other hand, it may be expected that as the feed CFV is increased, emulsion droplet collision rate and deformation within membrane pores are expected to increase accordingly, by which demulsification efficiency is ultimately improved. Therefore, the overall effect of higher feed CFV can be considered as a means of improving demulsification efficiency and not the opposite.

Table (6.32); Effect of feed CFV on demulsification efficiency of emulsions EI and EII using membrane MII for 30 minutes filtration. CFV: 1, 2.25, 2.90 and 3.35 m/sec. No electrical field.

Settling time, hr	Demulsification efficiency, %							
	Feed CFV, m/sec							
	1		2.25		2.90		3.35	
	Emulsion water content, vol. %	Emulsion water content, vol. %	Emulsion water content, vol. %	Emulsion water content, vol. %	Emulsion water content, vol. %	Emulsion water content, vol. %	Emulsion water content, vol. %	Emulsion water content, vol. %
	30	50	30	50	30	50	30	50
0	0	0	0	0	0	0	0	0
2	27.30	50	25.60	47.10	23.10	33.30	35.20	18.80
4	41	50	51.30	58.80	34.60	44.40	42.30	50
6	41	50	51.30	58.80	34.60	61.10	56.30	68.80
7	43.70	50	51.30	58.80	52	61.10	59.90	68.80

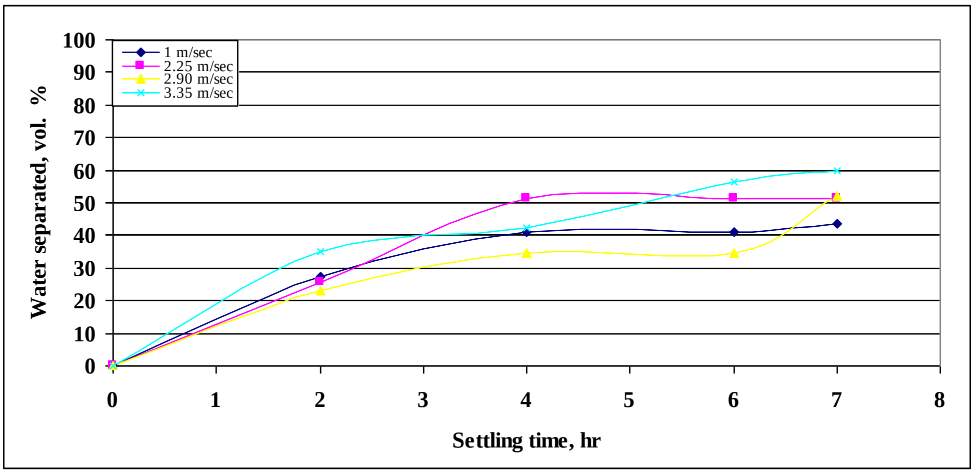


Fig. (6.56): Demulsification efficiency vs. settling time using membrane MII for 30 minutes filtration for emulsion EI. CFV: 1, 2.25, 2.90 and 3.35 m/sec. No electrical field.

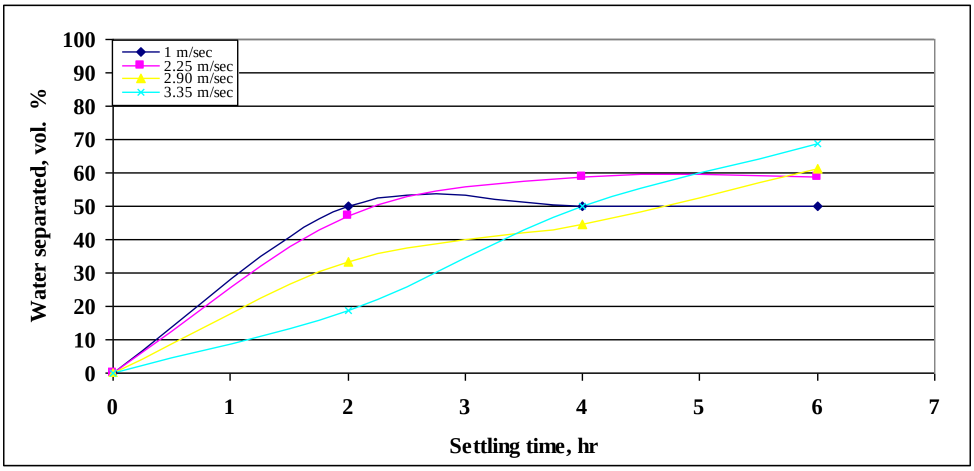


Fig. (6.57): Demulsification efficiency vs. settling time using membrane MII for 30 minutes filtration for emulsion EII. CFV: 1, 2.25, 2.90 and 3.35 m/sec. No electrical field.

Table (6.33); Effect of feed CFV on demulsification efficiency of emulsions EI and EII using membrane MIII for 30 minutes filtration. CFV: 1, 2.25, 2.90 and 3.35 m/sec. No electrical field.

Settling time, hr	Demulsification efficiency, %							
	Feed CFV, m/sec							
	1		2.25		2.90		3.35	
	Emulsion water content, vol. %	Emulsion water content, vol. %	Emulsion water content, vol. %	Emulsion water content, vol. %	Emulsion water content, vol. %	Emulsion water content, vol. %	Emulsion water content, vol. %	Emulsion water content, vol. %
	30	50	30	50	30	50	30	50
0	0	0	0	0	0	0	0	0
2	35.70	0	12.50	33.30	20.80	26.50	8.30	36.60
4	35.70	45.20	25	55.60	31.30	53	33.30	58.60
6	35.70	54.20	50	61.10	52.10	61.80	50	73.20
7	53.60	54.20	55	61.10	57.30	61.80	58.30	73.20

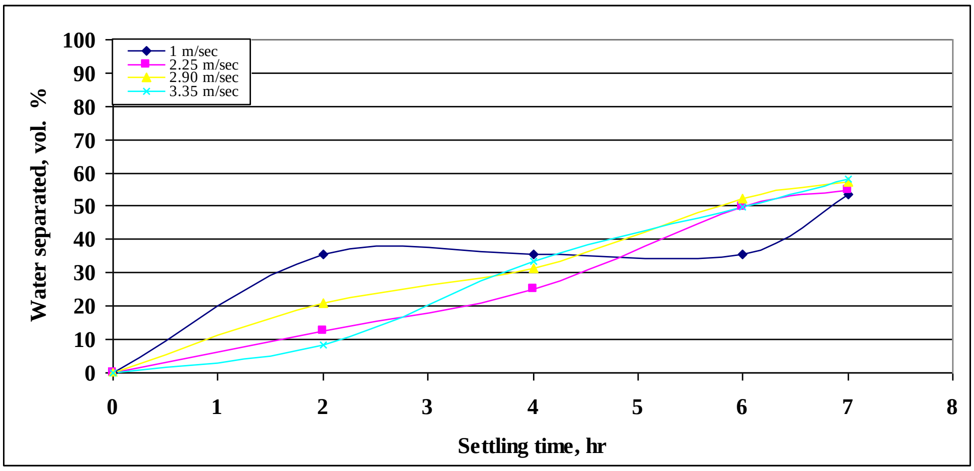


Fig. (6.58): Demulsification efficiency vs. settling time using membrane MIII for 30 minutes filtration for emulsion EI. CFV: 1, 2.25, 2.90 and 3.35 m/sec. No electrical field.

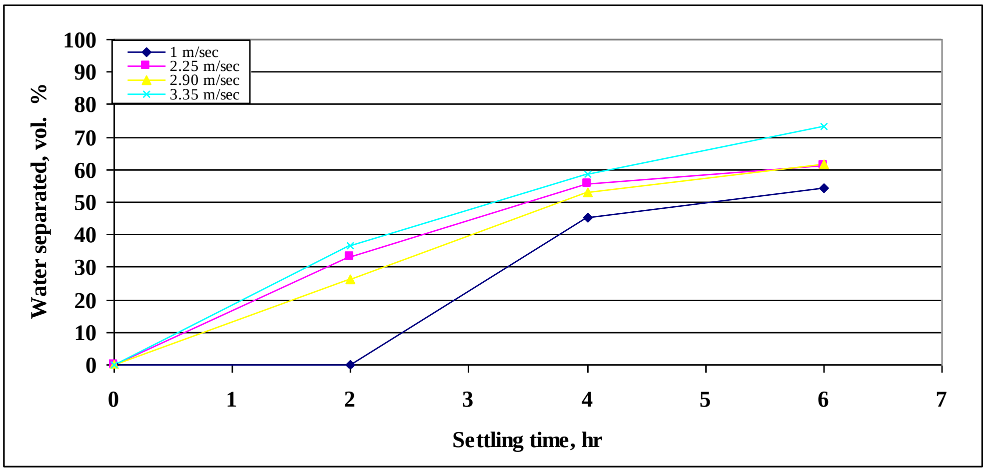


Fig. (6.59): Demulsification efficiency vs. settling time using membrane MIII for 30 minutes filtration for emulsion EII. CFV: 1, 2.25, 2.90 and 3.35 m/sec. No electrical field.

6.19 Effect of Electric Field (E) on Demulsification

The effect of electric field strength on demulsification efficiency when filtering both emulsions (30 and 50 vol. % of water content) was tested at three levels: low, medium and high as indicated previously in Table (6.18) in Sec. 6.12. At each electric field strength, eight feed CFVs, ranging from 1 to 12 m/sec, were tested. This procedure was performed using three PHP membranes of different pore sizes for 30 min in each run. The effect of electric field on demulsification efficiency of both emulsions by each membrane at 0, 83.30 and 333.30 V/cm (that's the onset of each level) with a CFV of 1 and 4.60 m/sec, as a function of settling time is provided in this section, see Tables (6.34-35) and Figs. (6.60-65). Due to the similarity of the results, the rest of the results obtained from these runs are given in Appendix B.

Table (6.34): Effect of electric field strength on demulsification efficiency by membranes MI, MII and MIII after 30 minutes of filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec.

Demulsification efficiency, %																		
Settling time, hr	Electric field, V/cm																	
	0						83.30						333.30					
	Emulsion water content, vol. %						Emulsion water content, vol. %						Emulsion water content, vol. %					
	30			50			30			50			30			50		
	MI	MII	MIII	MI	MII	MIII	MI	MII	MIII	MI	MII	MIII	MI	MII	MIII	MI	MII	MIII
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	19.60	27.30	35.70	33.30	50	0	17.20	22.70	25	50	53	60	13.20	36.40	22.20	35.30	48.40	33.30
4	23.50	41	35.70	50	50	45.20	34.50	45.50	50	50	53	60	39.50	54.50	44.40	70.70	64.50	50
6	31.40	41	35.70	56.70	50	54.20	51.70	54.50	55	62.50	61.80	60	57.90	63.60	57.80	74.20	64.50	66.70
7	54.90	43.70	53.60	56.70	50	54.20	55.20	54.50	55	62.50	61.80	60	57.90	63.60	57.80	74.20	64.50	66.70

Table (6.35): Effect of electric field strength on demulsification efficiency by membranes MI, MII and MIII after 30 minutes of filtration. Emulsion water content: 30 and 50 vol. %; CFV: 4.60 m/sec.

Demulsification efficiency, %																		
Settling time, hr	Electric field, V/cm																	
	0						83.30						333.30					
	Emulsion water content, vol. %						Emulsion water content, vol. %						Emulsion water content, vol. %					
	30			50			30			50			30			50		
	MI	MII	MIII	MI	MII	MIII	MI	MII	MIII	MI	MII	MIII	MI	MII	MIII	MI	MII	MIII
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	9.30	21.40	26.30	29.60	33.30	18.50	31.60	24	25	25.40	24	7.10	23.20	21.90	37	27.30	12.70	32.40
4	23.40	37.50	42.10	50.70	45.80	46.20	43.40	32	29.20	41.30	39	32.10	50	53.10	48.10	48.50	40.70	47.10
6	30.40	42.90	52.60	78.20	72.90	76.20	55.30	44	50	81	75	78.60	67.90	68.80	64.80	83.30	76.30	80.90
7	63.10	61.60	62.10	78.20	72.90	76.20	64	66	64.60	81	75	78.60	67.90	68.80	64.80	83.30	76.30	80.90

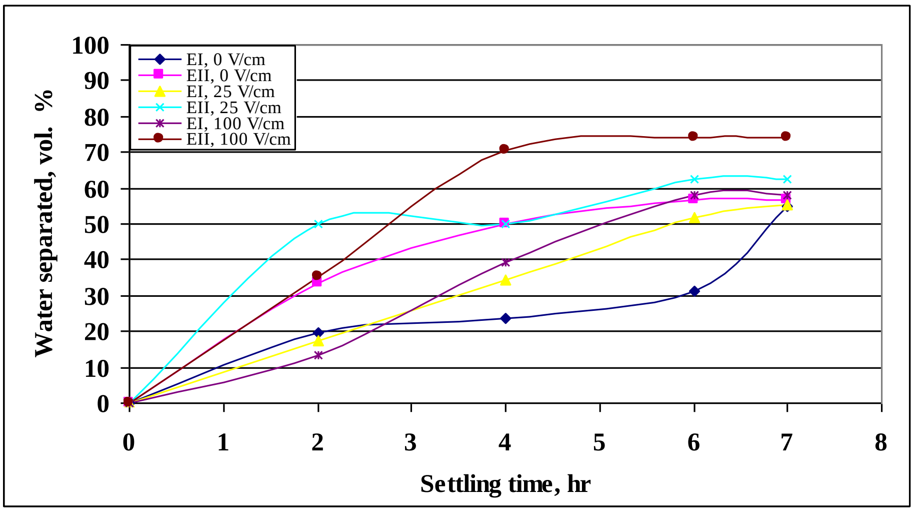


Fig. (6.60): Effect of electric field on demulsification efficiency by membrane MI after 30 minutes of filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec.

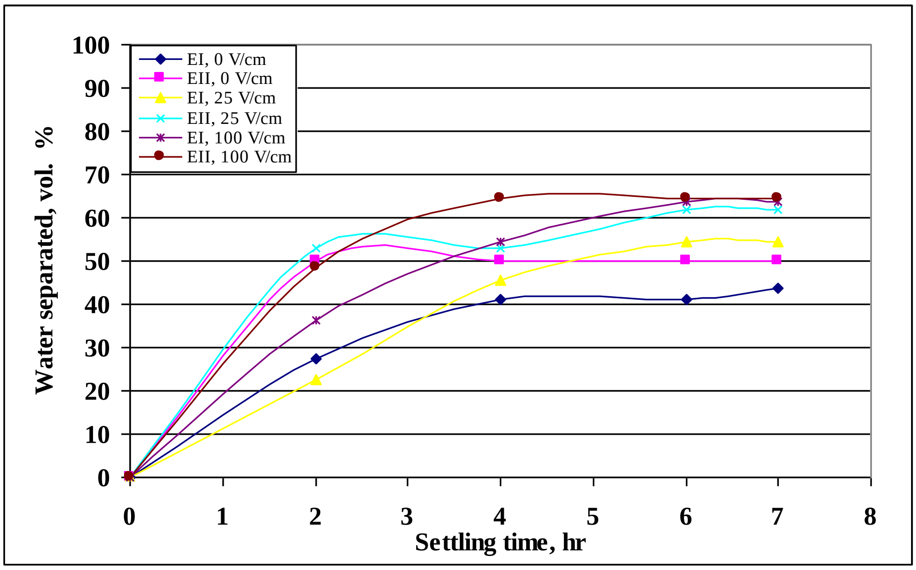


Fig. (6.61): Effect of electric field on demulsification efficiency by membrane MII after 30 minutes of filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec.

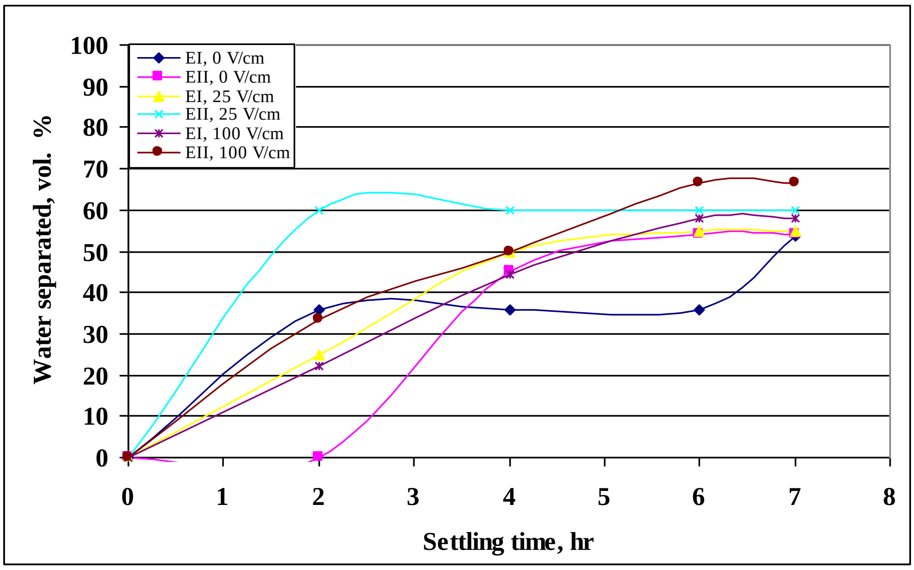


Fig. (6.62): Effect of electric field on demulsification efficiency by membrane MIII after 30 minutes of filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1 m/sec.

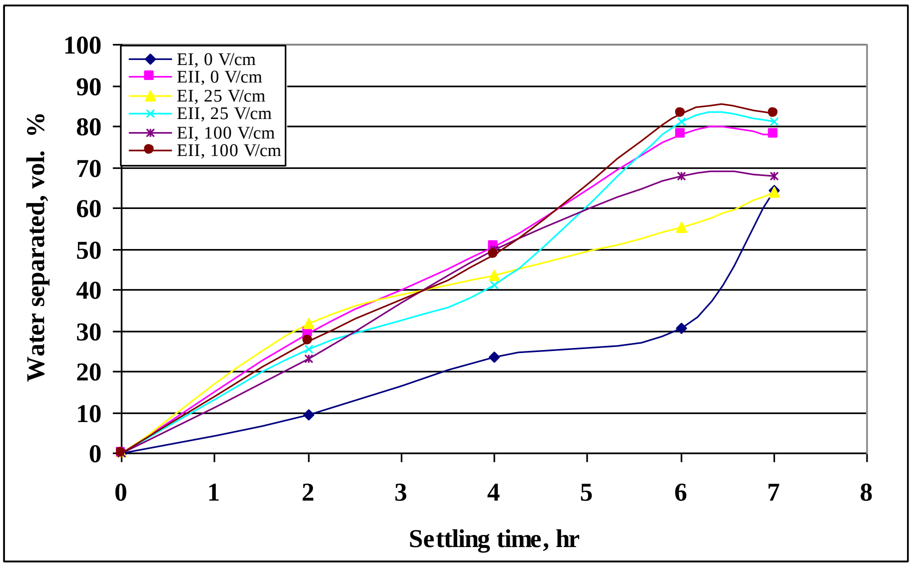


Fig. (6.63): Effect of electric field on demulsification efficiency by membrane MI after 30 minutes of filtration. Emulsion water content: 30 and 50 vol. %; CFV: 4.60 m/sec.

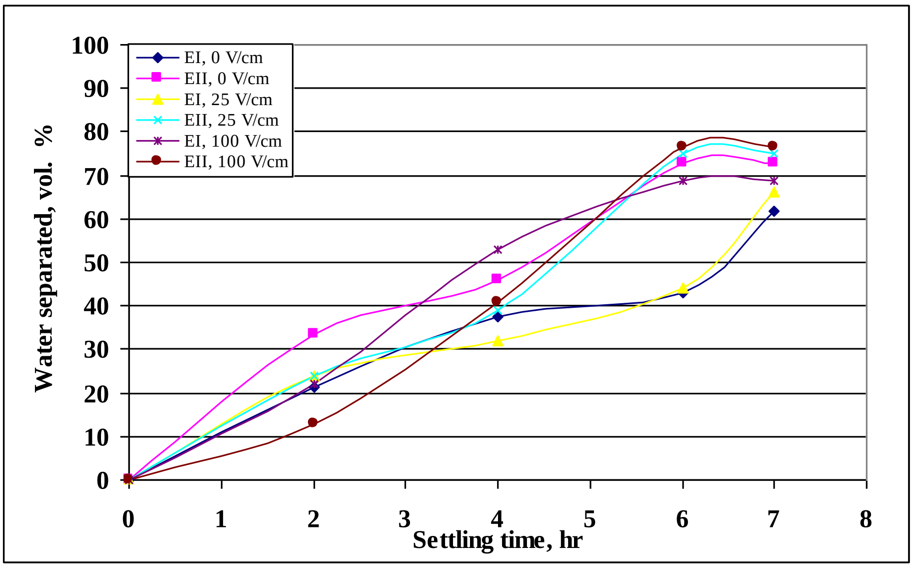


Fig. (6.64): Effect of electric field on demulsification efficiency by membrane MII after 30 minutes of filtration. Emulsion water content: 30 and 50 vol. %; CFV: 4.60 m/sec.

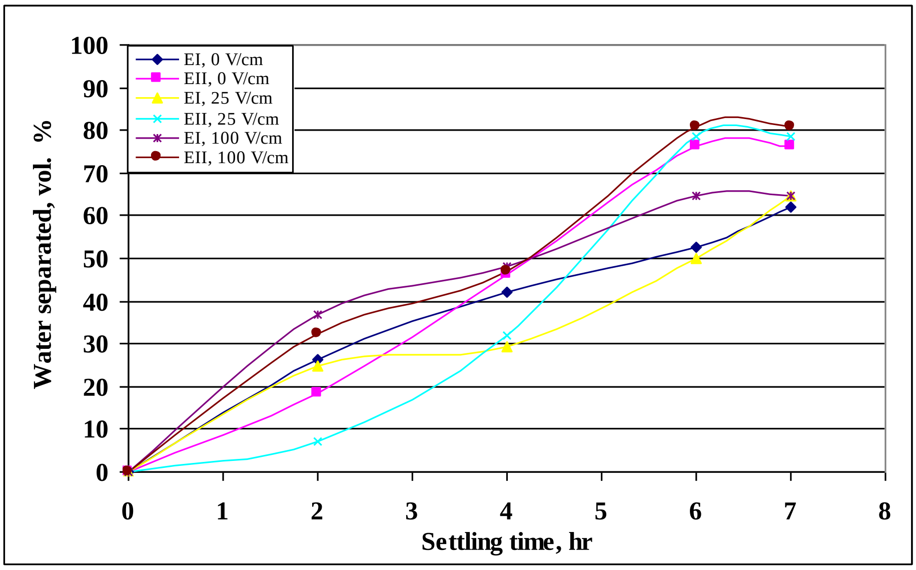


Fig. (6.65): Effect of electric field on demulsification efficiency by membrane MIII after 30 minutes of filtration. Emulsion water content: 30 and 50 vol. %; CFV: 4.60 m/sec.

When using a membrane to filter a given emulsion at a certain feed CFV, it can be generally noted that increasing the applied electrical field led to higher demulsification efficiency. For example, the demulsification efficiency by membrane MI when running the filtration experiment at 1 m/sec increased from 55.20 vol. % to 57.90 vol. % when the applied electrical field was increased from 83.30 to 333.30 V/cm, respectively. This pattern of increasing demulsification efficiency when increasing the applied electrical field is more pronounced in the case of emulsion EII. For example, the demulsification efficiency increased from 62.50 vol. % to 74.20 vol. % following application of electrical fields of 83.30 and 333.30 V/cm, respectively. This finding may be explained by the fact that emulsion EII originally contains more water (50 vol. %) than emulsion EI (30 vol. %), and this was another factor for this emulsion (EII) to be more prone to be further demulsified and producing more water. Applying an electrical field across emulsion droplets can aid emulsion demulsification by increasing the chance of water droplets colliding (Kim et al., 2002). On this basis; therefore, the emulsion is to an extent easier to be dealt with by the hydrophilic membrane, resulting in an increased demulsification efficiency, when compared to that obtained when no electrical field is applied, refer to Tables (6.34-35).

6.20 Effect of Membrane Pore Size on Demulsification

The effect of membrane pore size on demulsification efficiency was investigated. To achieve this, three PHP membranes of different pore sizes were employed to microfilter two emulsions of different water contents (30 and 50 vol. % of water content). In each experiment, a fresh membrane was used with changing the feed CFV from 1 to 12 m/sec and the electric field from 0 to 666.70 V/cm; however, the filtration time was always kept constant at 30 minutes. The demulsification profiles with respect to membrane pore size for membranes MI, MII and MIII at 1, 4.60 and 12 m/sec for both emulsions using no electric field are given in Table (6.36) and shown in Figs. (6.66-67), while those data obtained with the application of 333.30 and 666.70 V/cm are tabulated separately in Tables (6.37-38) and shown in Figs. (6.68-71).

Table (6.36): Effect of membrane pore size on demulsification efficiency by membranes MI, MII and MIII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 4.60 and 12 m/sec. No electric field.

Demulsification efficiency, %																		
Settling time, hr	Membrane																	
	MI						MII						MIII					
	CFV, m/sec																	
	1	4.60	12	1	4.60	12	1	4.60	12	1	4.60	12	1	4.60	12	1	4.60	12
	Emulsion water content, vol. %																	
	30			50			30			50			30			50		
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	19.60	9.30	18.60	33.30	29.60	20.60	27.30	21.40	13.60	50	33.30	36.90	35.70	26.30	29.20	0	18.50	23.80
4	23.50	23.40	43.50	50	50.70	47.10	41	37.50	23.70	50	45.80	64.60	35.70	42.10	53.10	45.20	46.20	50
6	31.40	30.40	55.90	56.70	78.20	79.40	41	42.90	40.70	50	72.90	76.90	35.70	52.60	58.40	54.20	76.20	78.60
7	54.90	63.10	66.80	56.70	78.20	79.40	43.70	61.60	66.10	50	72.90	76.90	53.60	62.10	63.70	54.20	76.20	78.60

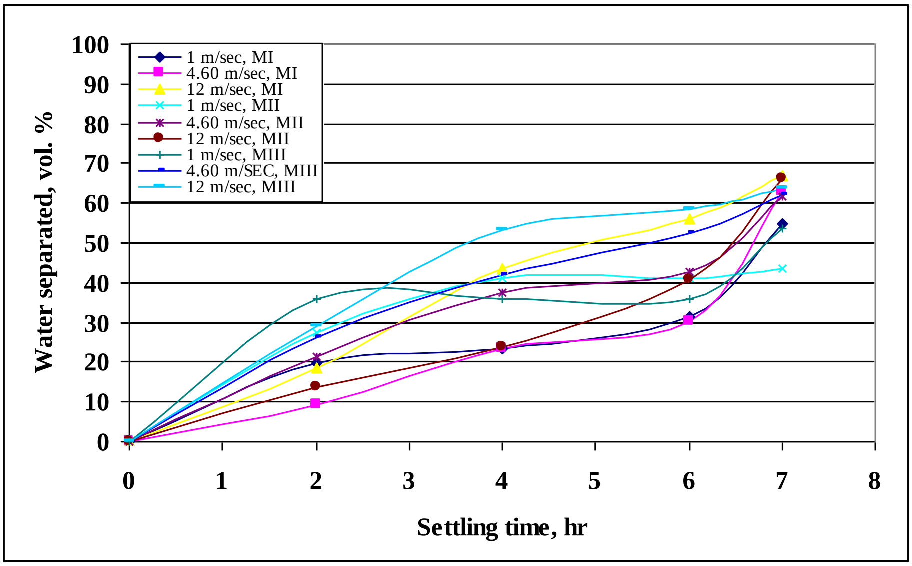


Fig. (6.66): Effect of membrane pore size on demulsification efficiency by membranes MI, MII and MIII for 30 minutes filtration. Emulsion water content: 30 vol. %; CFV: 1, 4.60 and 12 m/sec. No electric field.

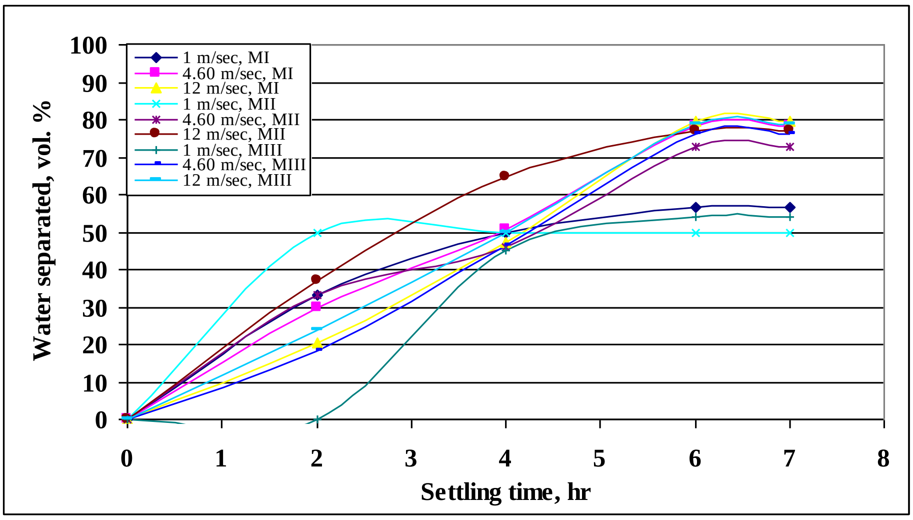


Fig. (6.67): Effect of membrane pore size on demulsification efficiency by membranes MI, MII and MIII for 30 minutes filtration. Emulsion water content: 50 vol. %; CFV: 1, 4.60 and 12 m/sec. No electric field.

By reference to Figs. (6.38-43) in Sec. 6.13 it can be generally noted that a membrane with a larger pore diameter produced a higher permeate flux rate compared to that obtained via a membrane with a smaller pore diameter. However, with regard to demulsification efficiency, membranes with larger pore diameter exhibited a lower demulsification efficiency of either emulsion in comparison to those membranes with smaller pore diameter. For instance, membrane MIII, which has a larger pore diameter than membrane MI, at feed CFV of 1 m/sec and applying no electrical field, was only capable of achieving a maximum demulsification efficiency of 53.60 vol. %, with regard to emulsion EI and 54.20 vol. % in the case of emulsion EII, as shown in Figs. (6.66-67). Whereas membrane MI, as depicted in Figs. (6.68-69) under the same conditions, achieved a relatively higher demulsification efficiency of 54.90 vol. % in case of emulsion EI and 56.70 vol. % in case of emulsion EII. The difference in performance of these membranes is more notable at higher feed CFVs. This was concluded by the pattern of increase of demulsification efficiency with feeding either of the emulsions at a feed CFV of 12 m/sec; from 66.80 vol. % to 79.40 vol. %, in the case of emulsion EI, and from 63.70 vol. % to 78.60 vol. % , in the case of emulsion EII.

Table (6.37): Effect of membrane pore size on demulsification efficiency by membranes MI, MII and MIII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 4.60 and 12 m/sec; electric field 333.30 V/cm.

Demulsification efficiency, %																		
Settling time, hr	Membrane																	
	MI						MII						MIII					
	CFV, m/sec																	
	1	4.60	12	1	4.60	12	1	4.60	12	1	4.60	12	1	4.60	12	1	4.60	12
	Emulsion water content, vol. %																	
	30			50			30			50			30			50		
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	13.20	23.20	16.30	35.30	27.30	44.90	36.40	21.90	29.40	48.40	12.70	30.20	22.20	37	27.60	33.30	32.40	23.50
4	39.50	50	38.80	70.70	48.50	57.10	54.50	53.10	39.90	64.50	40.70	64.20	44.40	48.10	41.40	50	47.10	42.60
6	57.90	67.90	69.40	74.20	83.30	86.70	63.60	68.80	70.30	64.50	76.30	79.20	57.80	64.80	66.40	66.70	80.90	83.10
7	57.90	67.90	69.40	74.20	83.30	86.70	63.60	68.80	70.30	64.50	76.30	79.20	57.80	64.80	66.40	66.70	80.90	83.10

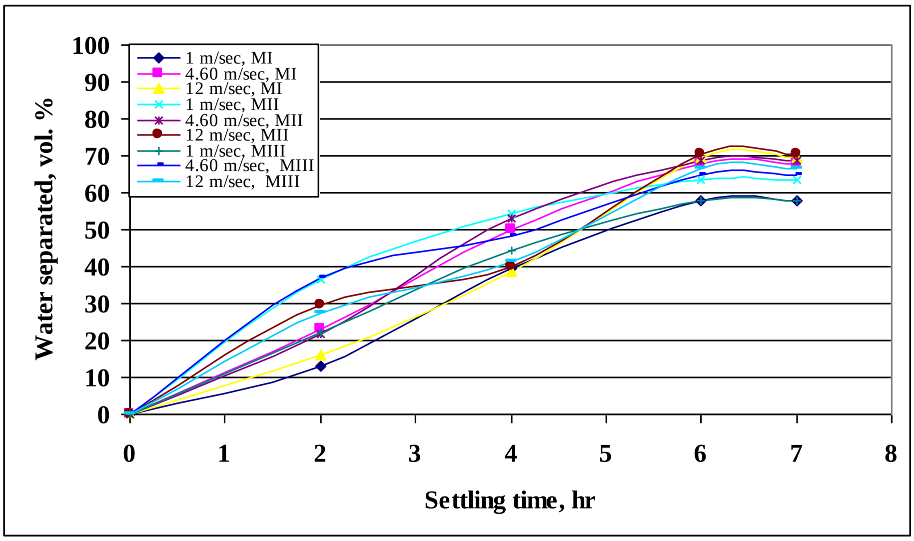


Fig. (6.68): Effect of membrane pore size on demulsification efficiency by membranes MI, MII and MIII for 30 minutes filtration. Emulsion water content: 30 vol. %; CFV: 1, 4.60 and 12 m/sec; electric field: 333.30 V/cm.

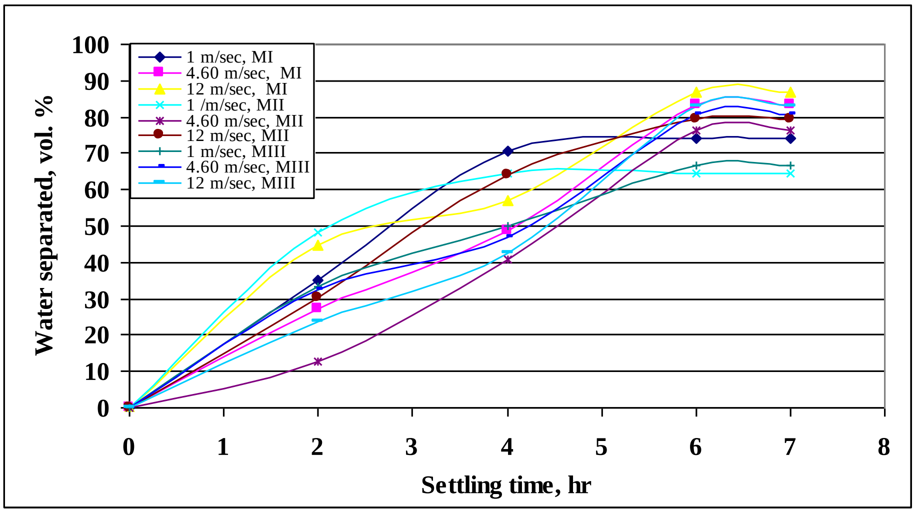


Fig. (6.69): Effect of membrane pore size on demulsification efficiency by membranes MI, MII and MIII for 30 minutes filtration. Emulsion water content: 50 vol. %; CFV: 1, 4.60 and 12 m/sec; electric field: 333.30 V/cm.

Table (6.38): Effect of membrane pore size on demulsification efficiency by membranes MI, MII and MIII for 30 minutes filtration. Emulsion water content: 30 and 50 vol. %; CFV: 1, 4.60 and 12 m/sec; electric field 666.70 V/cm.

Demulsification efficiency, %																		
Settling time, hr	Membrane																	
	MI						MII						MIII					
	CFV, m/sec																	
	1	4.60	12	1	4.60	12	1	4.60	12	1	4.60	12	1	4.60	12	1	4.60	12
	Emulsion water content, vol. %																	
	30			50			30			50			30			50		
	1 m/sec	4.60 m/sec	12 m/sec	1 m/sec	4.60 m/sec	12 m/sec	1 m/sec	4.60 m/sec	12 m/sec	1 m/sec	4.60 m/sec	12 m/sec	1 m/sec	4.60 m/sec	12 m/sec	1 m/sec	4.60 m/sec	12 m/sec
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	10.70	9.50	27.80	26.50	27.10	24.90	27.80	25.40	29.40	25	15.40	27.70	18.80	16.70	26.80	45	23.80	12.90
4	32.20	22.60	36.70	35.30	45.80	41.10	41.70	43.20	51.50	62.50	42.30	54.20	37.60	25	47.60	60.10	52.40	53.80
6	60.10	67.90	69.60	74.20	83.30	86.70	63.90	71.20	71.30	68.80	77.90	79.40	60.20	65.30	67.10	72.10	81	84.40
7	60.10	67.90	69.60	74.20	83.30	86.70	63.90	71.20	71.30	68.80	77.90	79.40	60.20	65.30	67.10	72.10	81	84.40

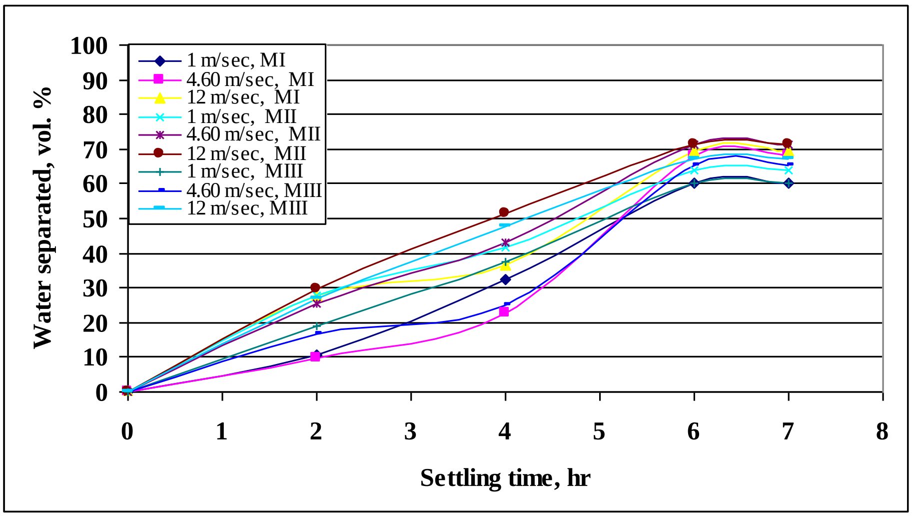


Fig. (6.70): Effect of membrane pore size on demulsification efficiency by membranes MI, MII and MIII for 30 minutes filtration. Emulsion water content: 30 vol. %; CFV: 1, 4.60 and 12 m/sec; electric field: 666.70 V/cm.

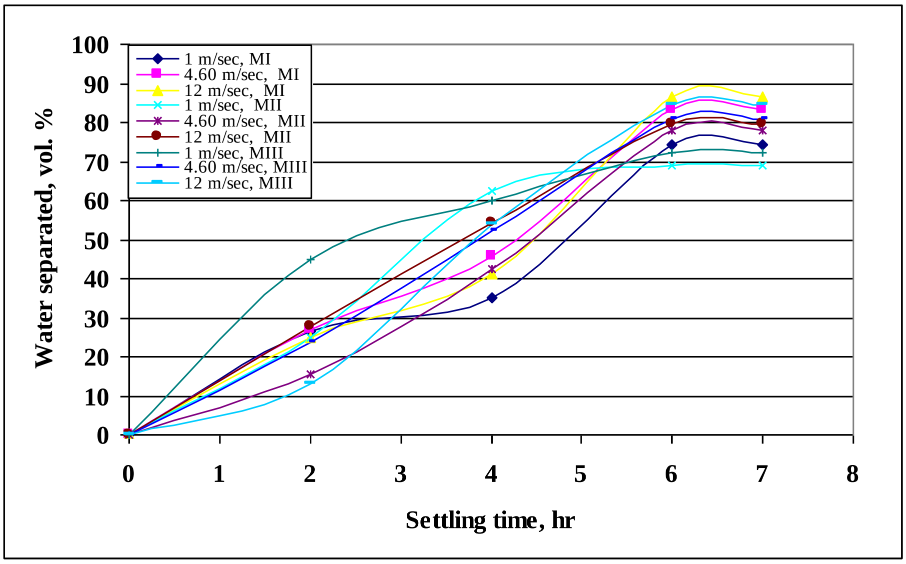


Fig. (6.71): Effect of membrane pore size on demulsification efficiency by membranes MI, MII and MIII for 30 minutes filtration. Emulsion water content: 50 vol. %; CFV: 1, 4.60 and 12 m/sec; electric field: 666.70 V/cm.

Applying an electrical field and/or increasing the feed CFV *did* increase the demulsification efficiency, but again it was higher in the case of membrane MI than in the case of membrane MIII. For instance, as shown in Figs. (6.68-69), by increasing the feed CFV from 1 to 4.60 m/sec, coupled with applying an electrical field of 333.30 V/cm across emulsion EI and EII while using membrane MIII, the demulsification efficiency increased from 57.80 to 64.80 vol. % with regard to emulsion EI and from 66.70 to 80.90 vol. % in case of emulsion EII. Under these conditions using membrane MI, the demulsification efficiency was 57.90 and 67.90 vol. % in case of emulsion EI and 74.20 and 83.30 vol. % in case of emulsion EII. It can be concluded that a membrane with a smaller pore diameter in comparison to a membrane with larger ones, seems more able to contribute to emulsion droplet deformation and tearing of the oily film around water droplets, which in turn can lead to higher demulsification efficiency.

6.21 Assessment of Phase Separation of Fresh Emulsions and Permeate Stream(s)

As stated earlier in the methodology section in Chapter 5, Sec. 5.3.2, the bottle test method was utilized to assess the stability of the prepared w/o emulsion(s) as well as of the permeate streams (demulsified emulsion), by monitoring water phase separation against time. The amount of resolved water is the most suitable measure of the emulsion stability of w/o emulsions, since the coalescence of the droplet phase is the limiting step in the demulsification process (Xia et al., 2004). Typical water phase separation data against settling time, for fresh emulsions EI and EII, were reported in Table (6.4) and Fig. (6.3). For the freshly prepared emulsion(s), no water phase separations were observed until 79/71 days (1896/1704 hr) have elapsed in the case of emulsion EI/EII, respectively. In the case of emulsion EI, a maximum percentage of 43 vol. % of the collected sample was water, and in the case of emulsion EII, the sample contained 48 vol. % water, see Fig. (6.3).

On the other hand, in the case of demulsified emulsions, owing to the interactions between the hydrophilic PHP membrane and emulsion droplets as well as to the influence of various microfiltration operating variables tested, only a few hours were required to initially observe phase separation in the permeate stream, which did not require a long time to take place and the to finalize. In general, in the permeate of both emulsions, a water layer at the bottom of the sample was observed after 2 hr of settlement, and that this layer only required 6-7 hr to completely form. Depending on the filtration conditions and/or emulsion composition, this layer required less/more time to be completely created. For instance, samples of emulsion EI collected subsequent to either membrane (MI, MII or MIII) always, apart from those taken at higher electrical fields which required 6 hr to completely form, required 7 hr to do so. In addition, when using either membrane, all samples of emulsion EII always required 6 hr to finally form. It is also worthwhile mentioning that, although higher feed CFVs *did* boost the demulsification efficiency as was previously discussed in Sec. 6.18, they did not contribute in shortening the required time for final phase separation. For instance, when using membrane MI, increasing the feed CFV from 2.25 to 3.35 m/sec while applying no electrical field, led to increasing the demulsification efficiency from 55.20 to 58.90 vol. % in case of emulsion EI and from 63.60 to 75 vol. % in case of emulsion EII. However, the time required to achieve the corresponding demulsification efficiency was the same (generally 7 hr in case of emulsion EI and 6 hr in case of emulsion EII) irrespective of feed CFV used.

A brief summary of the demulsification experiments undertaken and observations made is given here:

a) The demulsification process is carried out in two stages;
   i) passing of the emulsion through a hydrophilic micro-porous PHP in a crossflow filtration mode;
   ii) gravity settling
b) Gravity settling rate is affected by the processing conditions in Stage 1(crossflow filtration). Therefore, this investigation focuses on Stage 1 only.
c) Crossflow is carried out with or without an electric field which is orthogonally superimposed on the crossflow.
d) The crossflow filtration system is such that it has the elements of membrane filtration and flow through porous media. Although the filtration media has no active membrane layer, and that the interconnecting holes of PHP are very large compared with the molecular size of the crude oil components; nevertheless, there is ‘fouling’ of the membrane, as a result of which the permeate flux rate decays and subsequently reaches equilibrium.
e) Without the electric field, this decay starts immediately, but in the presence of the electric field permeate flux rate *does* , in fact, increase with increasing filtration time, followed by decay. Nevertheless, the equilibrium permeate flux rate when applying an electric field is always higher compared with the flux with no electric field.

f) It was found that the permeate flux rate increased with increasing PHP pore size.
g) Demulsification rate increased with decreasing PHP pore size, and
h) Permeate flux rate was higher for the water-rich emulsion (50 vol. % water) compared to the emulsion containing only 30 vol. % water.

6.22 Mechanism of Demulsification

Based on the summarized results above, a mechanism of crossflow filtration and subsequent separation is proposed.

- **Similarities of Crossflow Membrane Filtration of Water- in-Crude Oil Emulsions with the Crossflow Membrane Filtration of Solutions or Dispersions of Surface Active Molecules or Molecular Aggregates**

The results in (d) and (e) have also been observed for the crossflow filtration of dilute surfactant solutions or diluter solutions of hydrophobically modified water soluble polymers which act as surface active species without the formation of ordered structured encountered in molecular surfactants (Akay and Wakeman, 1996; Akay and Wakeman, 1994b; Akay and Wakeman, 1994a). In these studies, both non-sulphonated PHP and several different membranes were used with or without an electric field. It was concluded that a secondary membrane was formed by the surface active components on the surface and within the pores of the membrane. Secondary membrane dictated the permeate flux rate and the rejection of the surface active molecules or sub-micron/nano-sized molecular aggregates (of nano-sized) dissolved or dispersed in water. It was shown that irrespective of pore size of the membrane, ultimate equilibrium permeate flux rates and rejection of the surface active molecules (molecular or polymeric) or molecular aggregates were dictated by the nature of the secondary membrane. If the pore size of the primary membrane was small, permeate flux reached equilibrium rapidly due to rapid formation of the secondary membrane.

The effect of the electric field was three fold; it degraded some of the surfactants; rejected surface active molecules; and allowed the formation of larger pore size secondary membrane formation. It was shown that there was no real ‘gel polarization’ when permeate flux rate became zero. Therefore, both permeate flux rate and rejection were high under an electric field.

- Filtration of Whole Crude Oil from Sulphonated PolyHIPE Polymer

Filtration of various crude oils with differing indigenous surface active profiles was carried out in syringes. The chemical constituents of the crude oil before and after filtration were analyzed using GC-MS (Akay et al., in preparation). The results are shown below and indicate that sulphonated PHP retained large amounts of polar molecules.

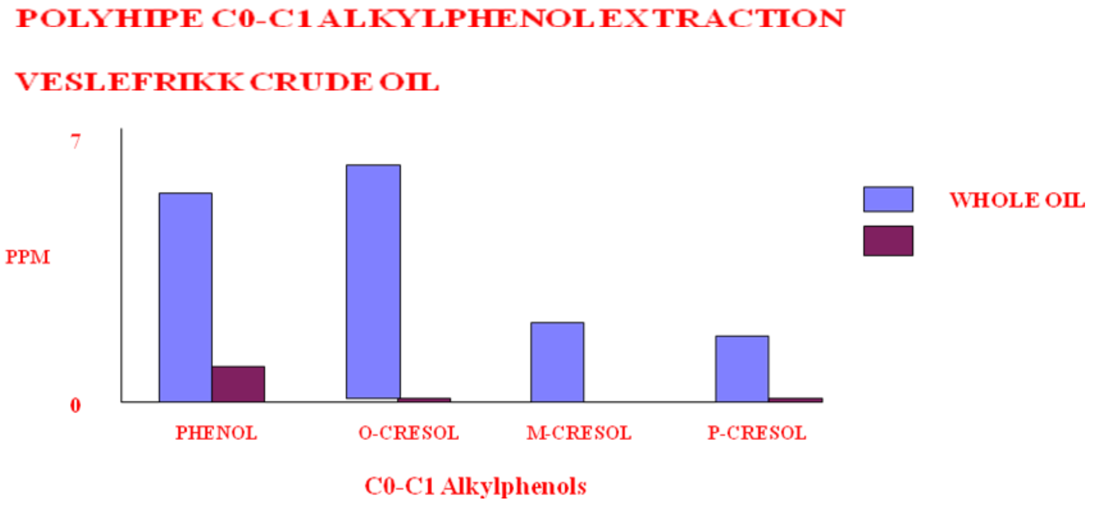


Fig. (6.72): Concntration of alkylphenols with/out PHP.

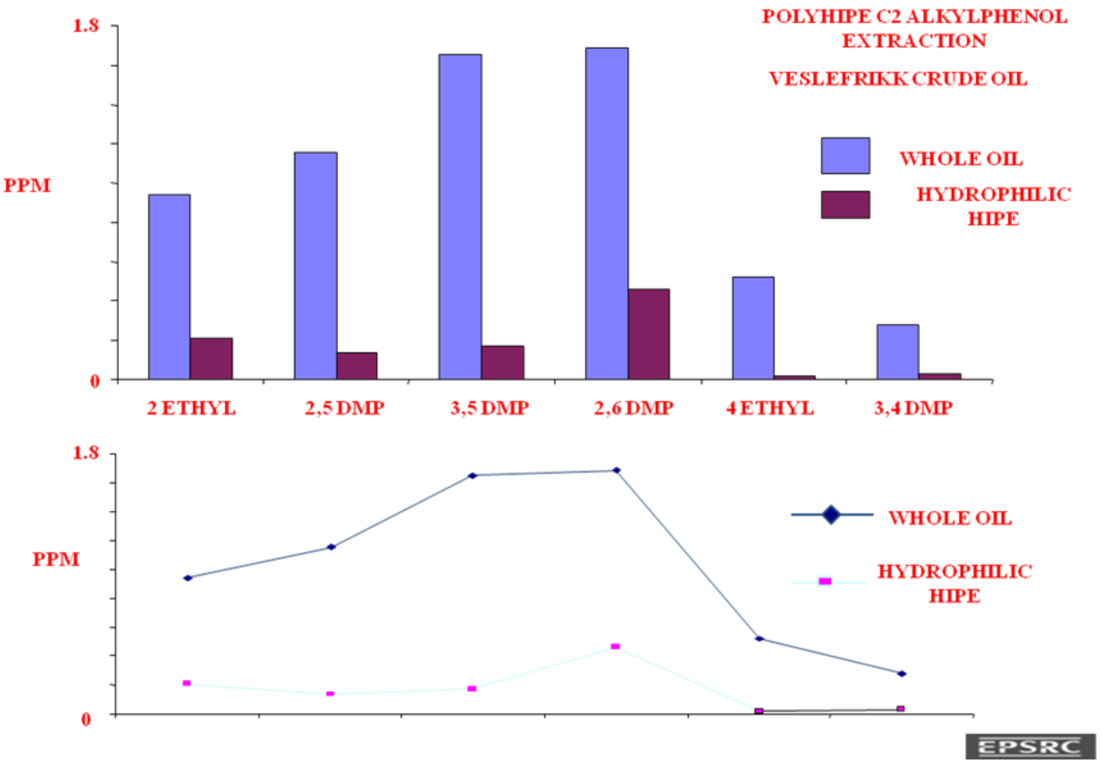


Fig. (6.73): Concntration of alkylphenols with/out PHP.

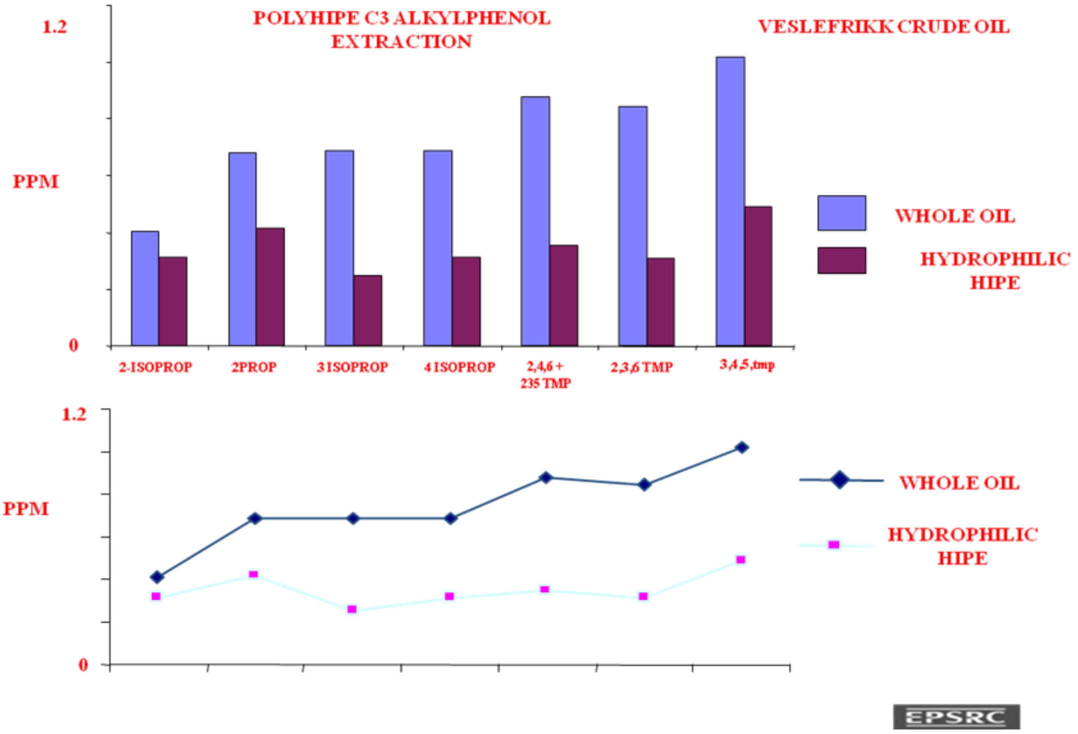


Fig. (6.74): Concntration of alkylphenols with/out PHP.

Sulphonated PHPs also retained tars from syngas generated by the gasification of biomass. The GC-MS tar profile before and after passing of syngas through a PHP bed are shown in Figs. (6.75-76) (Akay and Jordan, 2012).

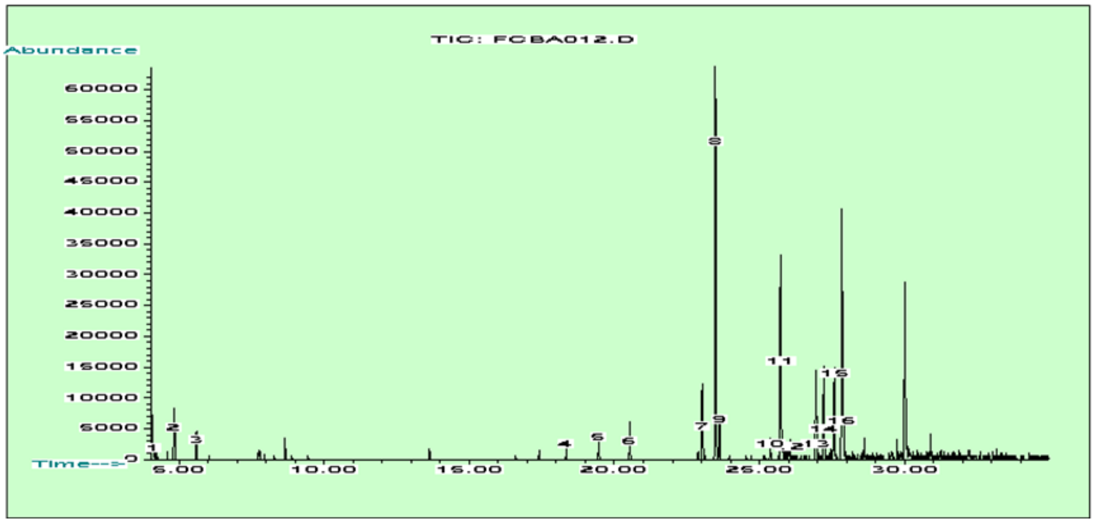


Fig. (6.75): Tar profile of syngas before cleaning with sulphonated PHP.

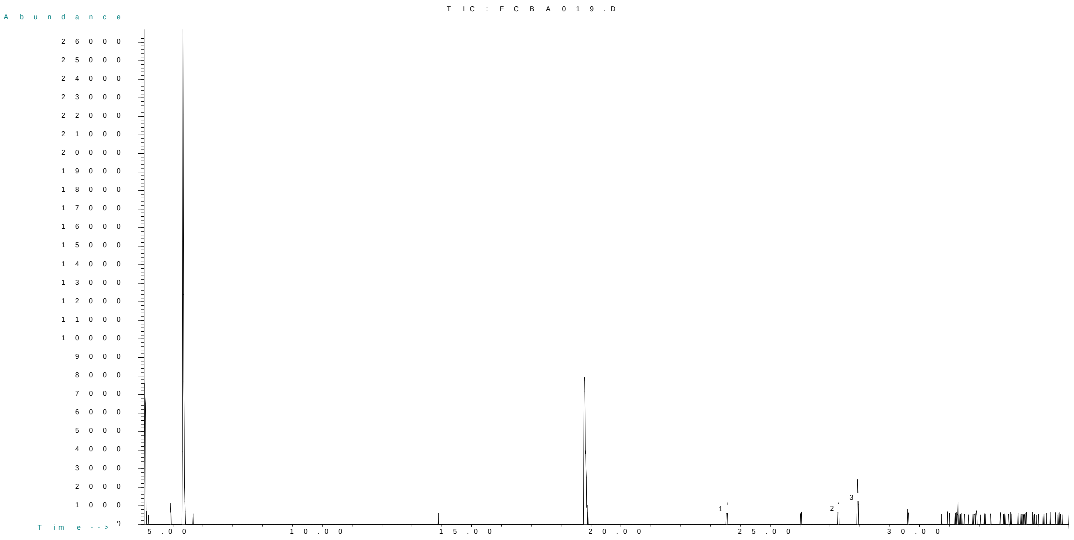


Fig. (6.76): Tar profile af syngas after cleaning with sulphonated PHP. Note that the abundance scale is approximately 50 % reduced.

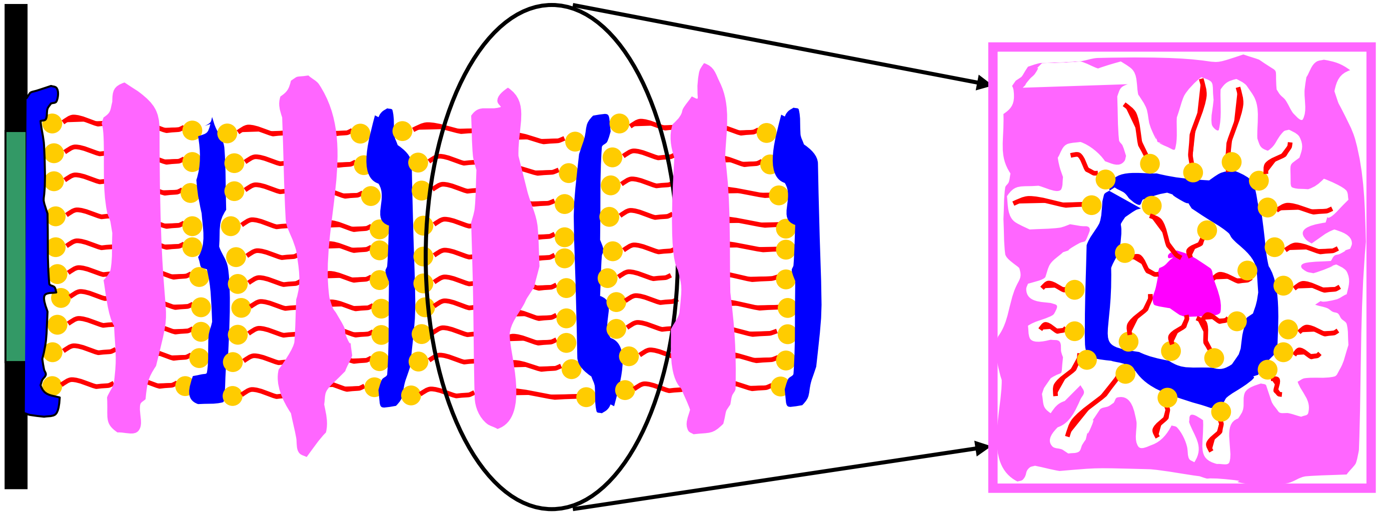
The above results indicate that, irrespective of the system, polar molecules are selectively adsorbed by PHP, as indeed has also been shown recently for emulsions stabilized by particulate matter (Akay et al., 2012). In the above results, adsorption of surface active molecules by sulphonated PHP have been explained by a ‘confinement phenomenon’ as discussed below.

- Confinement Phenomenon

The confinement phenomenon (Akay, 2006) has been utilized in process intensification including bioprocess intensification, tissue engineering, separation processes and agro-process intensification. In general terms, according to the confinement phenomenon, the behaviour of a matter is dictated by the size and biochemical structure of the confinement media in which the matter is present. Clearly, the size of the confinement media must be comparable with the size of the matter that is confined. Although the size of the individual surface active molecules is small compared to that of the pores of PHP; nevertheless, surface active molecules grow in size through aggregate or super-molecular structures. These structures are highly stable (low entropy), especially in the presence of confinement media and; hence, there is a driving force for such molecules to diffuse from the bulk fluid (liquid or gas) into the confinement media, where they are stabilized.

- Mechanism of Demulsification

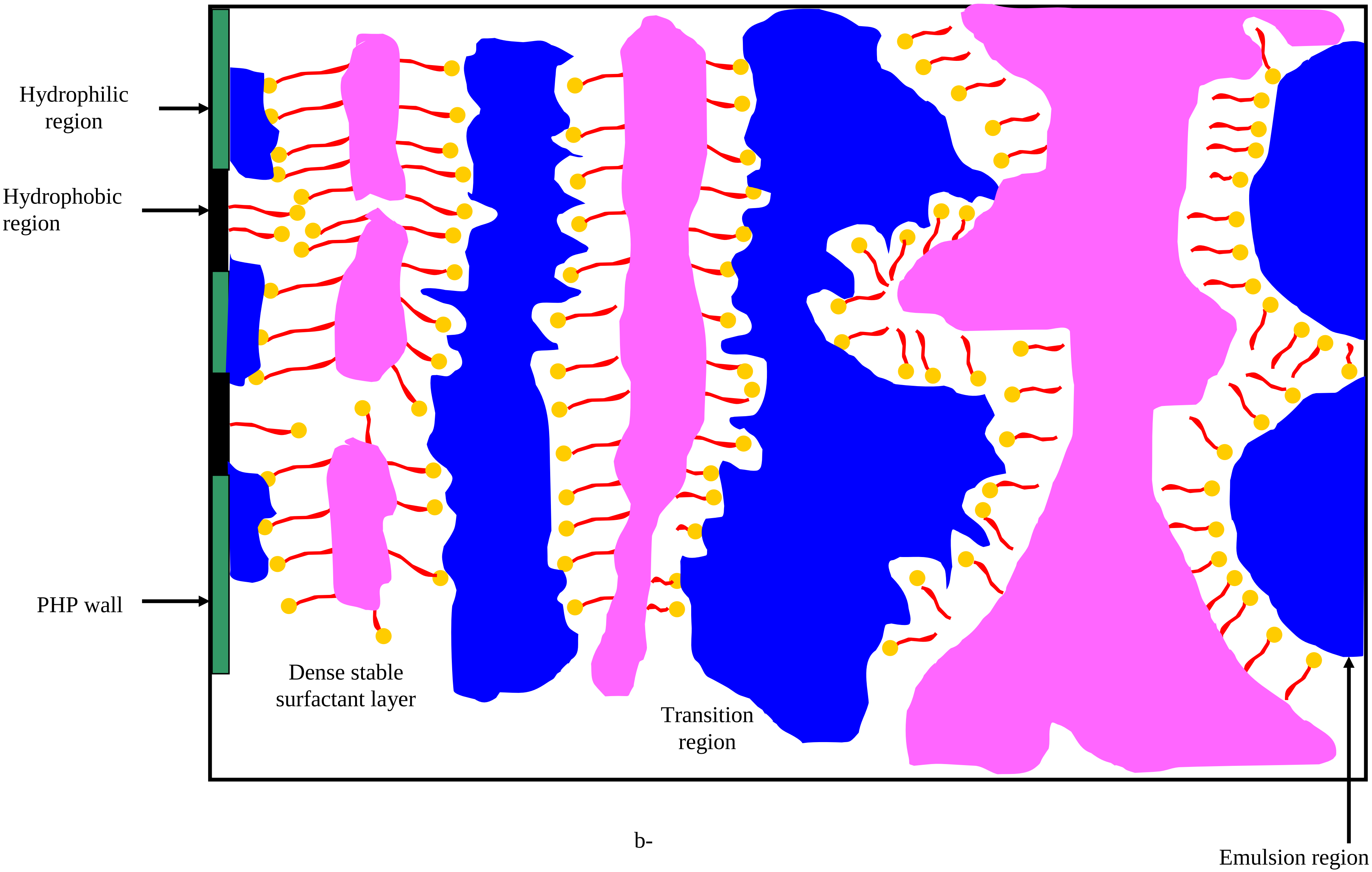
The mechanism of demulsification can be explained through a model based on the confinement phenomenon. In Fig (6.77a-c), mechanisms of surfactant migration from the bulk of crude oil and from water-oil interface to the PHP wall and subsequent formation of a [-surfactant-water-surfactant-oil-] structure are illustrated diagrammatically. Although the surface active species (resins and asphaltenes) do not have the well ordered chemical structure of molecular surfactants; nevertheless, their interactions with oil and water are similar to that of the molecular surfactants. Therefore, in Fig (6.77a-c), we represent the indigenous surfactants in crude oil as molecular surfactants.



Fracture of surfactant/water/oil structures and formation
of oil- in-water-in-oil multiple emulsions and entrapping
water which cannot be easily removed.

Oil-in-water-in-oil multiple emulsion
formation, leading to highly stable
water droplets in bulk oil.

a-


Hydrophilic region
Hydrophobic region
PHP wall
Dense stable surfactant layer
Transition region
Emulsion region

b-

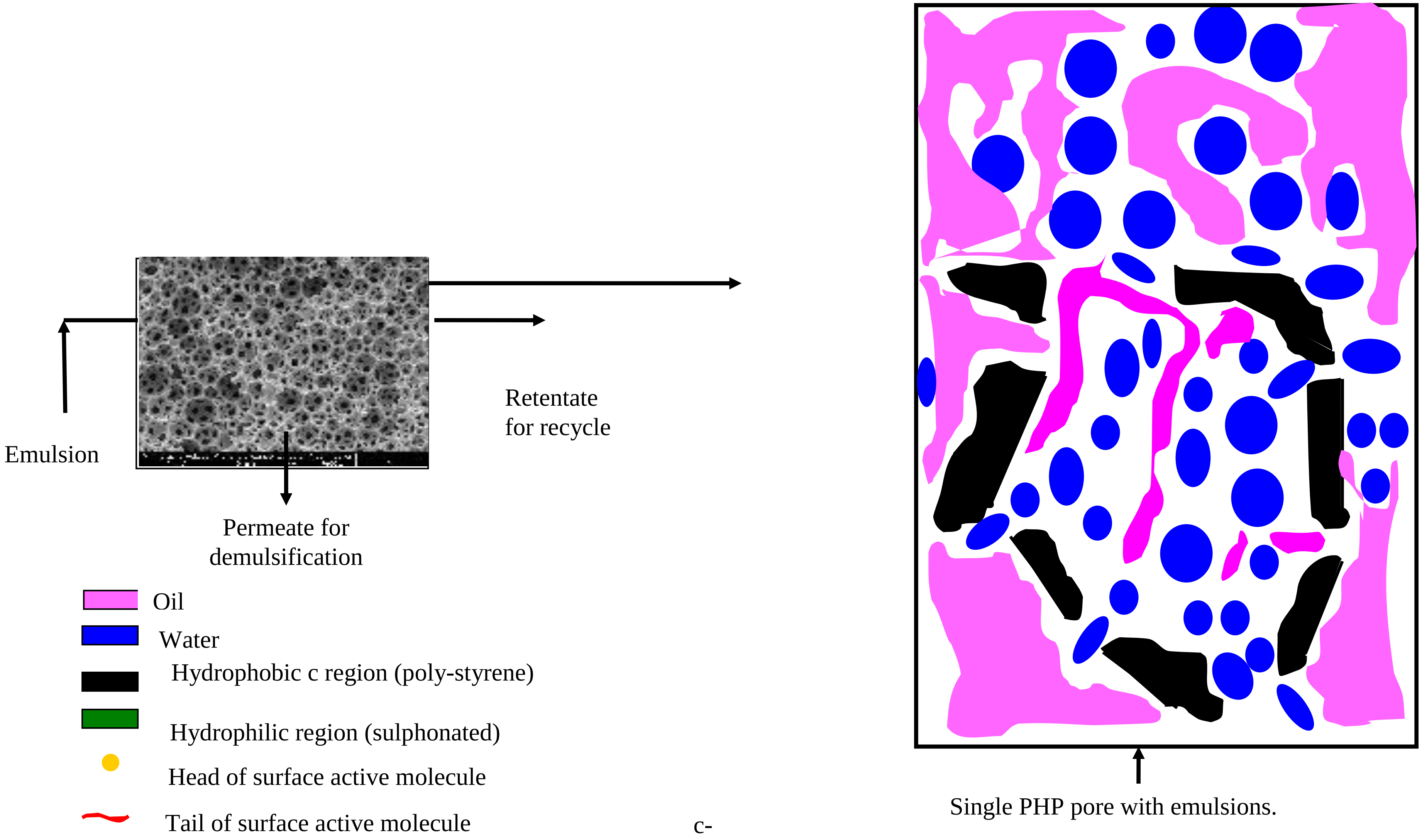


Fig. (6.77): A schematic representation of mechanism of demulsification

The chemical structure of the PHP is also like a surfactant, in which the hydrophilic and hydrophobic regions are present on the 3D-crosslinked PHP. The hydrophilic regions will be wetted by water while the hydrophobic regions will have adsorbed surface active species. Wetting of the PHP will be enhanced as water droplets deform when entering or exiting in and out of the pores of PHP during permeate flow through the separation media. Deformation of the droplets increases the surface area per unit volume of the droplets and; thus, causes instability to the emulsion (Akay, 1998).

As shown previously (Akay and Wakeman, 1994b; Akay and Wakeman, 1994a), the lamellar structure of the [-surfactant-water-surfactant-oil- surfactant-] phases can cover a large portion of the pore volume of the PHP; thus, causing flux decay. These lamellar structures are also porous due to the presence of permeate flow. However, it is likely that the volume of these lamellar structures will reach an equilibrium value through a dynamic process of building and break-up as a result of stresses generated by the permeate flow. However, when such lamellar structures breakup from the main aggregate, they will reform into spherical multi-lamellar droplets dispersed into the continuous oil-phase. This transformation will create highly stable multiple emulsions entrapping some water which will not be easily accessed. Nevertheless, this process removes the indigenous surfactants from the crude oil and; hence, de-stabilize the emulsions due to reduced surfactant concentration in the oil phase which will in turn cause water droplet coalescence. Therefore, upon standing, emulsion will separate into oil and water phases.

In this mechanism, we have utilized the fact that surface active species are more stable within the pores of PHP since they are preferentially retained and form highly stable phases. The addition of PHP particles to water-in-crude oil also causes demulsification since the surface active species selectively diffuse into the PHP pores (Akay et al., 2012; Noor, 2006) (Akay and ZZ Noor et al 2005, Akay et al 2012). In the present method, the migration of surface active species is by convection, rather than diffusion; thus, accelerating the surfactant capture process. Both methods can be combined by dispersing PHP particles into the emulsion and subjecting the resulting system to crossflow filtration. This will also help to stop surface fouling of the PHP separation media during crossflow filtration.

The application of an electric field results in enhanced permeate flux rate and shorter oil-water separation time. The function of the electric field includes the degradation of the surfactants and enhancement of flux due to the modification of the secondary membrane pore structure.

6.23 Summary of Results

- Under the emulsification conditions and according to the emulsion recipe implemented, prepared emulsions, EI/EII, have remained stable (intact) for 79/71 days (1896/1704 hr), respectively.

- Several batches of three hydrophilic PHP membranes with different pore size ratings have been developed.

- Via employing these hydrophilic membranes, permeate flux rate, in a microfiltration configuration with/without electrical field, of each membrane was evaluated against: 1-influent emulsion water content (30 and 70 vol. % of water (dispersed phase) content), 2- filtration duration, 3- feed CFV, 4- electric field and 5- membrane pore size. This study was also extended to focus on the effect of these variables on demulsification efficiency (*DE).* A summary of these results is given here:

- Higher flux permeates were favoured by increasing the feed CFV and applying an electrical field across either emulsion. Increasing the feed CFV of both emulsions demonstrated a high permeate flux rate from all membranes used. With high CFVs higher shear forces on the membrane surface are generated, by which the thickness of the oily layer that may have developed on membrane surface, is limited. Also, turbulence and mass transfer of oil droplets from the membrane surface back to the bulk stream can also help reduce the level of concentration polarization and; therefore, increases membrane flux rate. Similarly, applying an electrical field across either emulsion augmented the permeate flux rate at a given filtration condition(s). Gas evolution through electrolysis while the filtration is running, by which the membrane surface is continuously cleaned, increasing the chance of emulsion droplets collision, are believed to be a key in the successfulness of an electrical field to improving permeate flux rate. The influence of an electrical field across the emulsion with higher water content (EII), in comparison to the other emulsion with lower water content (EI), has appeared more prominent. In fact, as the water content of both emulsions is concerned, the conductivity of the former emulsion (EII) is higher than that of the latter one (EI) and; therefore, the electrical current was passed more efficiently in the former emulsion than in the latter one.

- On the other hand, flux permeates from all tested membranes were affected by emulsion water content and duration of filtration. Throughout the course of filtration, the effect of emulsion water content on membrane permeate flux rate was rather reversal. Emulsions with higher oil content produced a lower membrane flux rate. An explanation of this is that, with increasing oil concentration in an emulsion, the contamination of a hydrophilic membrane with oil droplets is increased; thus, membrane permeate flux rate is reduced. As a function of filtration time, it seems a secondary membrane made up of an oily layer (surfactants) appears to have formed on the membrane surface. In doing so, it seems that the membrane surface properties are modified. As a consequence, membrane-solute interactions, which are mainly the driving force for emulsion filtration, have become less active, leading to flux declination. Settlement of emulsion droplets on membrane pores, by which effective available membrane pore diameter may have been reduced, may also be another contributor to permeate flux rate declination.
- With regards to the effect of membrane pore size on membrane flux rates from the tested membranes with time, experimental evidence suggests that there was not a common trend when considering both emulsions. Permeates from different membranes randomly changed with respect to changes in filtration conditions. In case of both emulsions, membranes with larger pore sizes did not necessarily produce the highest permeates in comparison to those with smaller pore sizes. Differences in their morphological structure (porosity), hydrophilicity degree (concentration polarization) and also susceptibility to swelling (blocking) may have been the driving forces for such a relationship between the permeate flux rates from the used membranes and their pore sizes.

- Higher *DEs* were favoured by increasing an emulsion’s water content, settling time, feed CFVs and intensity of the applied electrical field. The higher the water content, the higher the *DE* was. Such a result is directly correlated to the stability level of the corresponding emulsion. With settling time *DE* was increasing but at a lower rate at the end of settling time, perhaps due to suppression in the tendency towards a further change in the sample composition. Due to increased droplet collision rate and deformation facilitated by higher feed CFVs, higher *DEs* were obtained. Likewise, increasing the applied electrical field produced higher *DEs.* On the other hand, demulsification efficiencies were affected when using a membrane with bigger pore sizes.

Chapter Seven

Conclusions, Suggestions and Future Work/Research

Chapter Seven

Conclusions, Suggestions and Future Work/Research

> *A conclusion is the place where you get*
> *tired of thinking.*
>
> *Steven Wright*
> *(1955-present)*

> *We are afraid of ideas, of experimenting,*
> *of change. We shrink from thinking a*
> *problem through to a logical conclusion.*
>
> *Anne Sullivan Macy*
> *(1866-1936)*

7.1 Introduction

Over the past five and half years, work has been carried out to implement a process intensification (PI) philosophy in the demulsification of w/o emulsions via crossflow microfiltration through a hydrophilic PolyHIPE Polymer (PHP). To achieve this, w/o emulsions with two different water contents, namely 30 and 50 vol. %, in an effort to imitate emulsions that are usually found in oil industry, were made. Hydrophobic PHP membranes have been prepared through an HIPE polymerization technique. These membranes were then sulphonated to render them hydrophilic. These membranes were then used for microfiltration of prepared w/o emulsions. During the course of this work, the potential of microfiltration for demulsifying w/o emulsions has been investigated. Membrane permeate flux rates and demulsification efficiencies were examined. The effect of influent emulsion concentration, filtration duration, feed crossflow velocity (CFV), electric field and membrane pore size**,** on the permeate flux rate and demulsification efficiencies, was investigated. A summary and conclusions drawn from the results obtained are given here.

7.2 Conclusions

7.2.1 Emulsions

Two kinds of w/o emulsions of different water contents were prepared and characterized. Since both emulsions (EI and EII) had been stable for 79/71 days; respectively, no other emulsifiers were added. In the case of emulsion EI, a maximum percentage of 43 vol. % of the collected sample was water, and in the case of emulsion EII, the sample contained 48 vol. % water, see Fig. (6.3). It is also of interest to observe that emulsion EI; that originally had a lower water content than emulsion EII, when broken down has, ultimately produced less water than emulsion EII and required a longer time to do so.

7.2.2 Membranes

A number of PHP membranes, modified by means of sulphonation and characterized. Sulphonation of prepared PHP membranes was carried out in an attempt to improve their hydrophilicity (water absorption). ESEM micrographs for un-sulphonated and sulphonated PHPs membranes (membranes: MI, MII and MIII) showed a morphological change in the structure of the latter PHPs. Generally, such a change causes the PHP to expand and renders it with larger pore sizes and wider walls, whilst maintaining the holes on them. This may result in higher absorption capability and improved permeate flux rates as filtration processes are concerned.

7.2.3 Membranes Flux Rates

What this investigation also proves is that membrane performance is dependent on: influent emulsion water content, filtration duration, feed crossflow velocity (CFV), electric field and membrane pore size.

- In all tested membranes, influent emulsion water content has been one of the factors that have an important effect on permeation flux rate. Out of all tested membranes, the permeation rate was found to decrease with an increase in the feed oil content. As a function of emulsion water content, the permeate flux rate from all used membranes initially increases with filtration time. However, after a while it is the opposite as filtration advances. With time where a secondary membrane made out from an oily layer (surfactants) appeared to have formed on the membrane surface, it seems that membrane surface properties are modified. As a consequence, membrane-solute interactions, which are mainly the driving force for emulsion filtration, have become less active leading to flux declination. Settlement of emulsion droplet on membrane pores, by which effective available membrane pore diameter may have been reduced, can also be another contributor to permeate flux rate declination. Through out the course of filtration, the effect of emulsion water content on membrane permeate flux rate is rather reversal. Emulsions with higher oil contents produce a lower membrane flux rate. A possible reason for this is that, with increasing oil content in an emulsion, the contamination of a hydrophilic membrane with oil droplet is increased; thus, membrane permeate flux rate is reduced.

- Irrespective of emulsion water content, increasing the feed CFV demonstrate a higher permeate flux rate from all membranes used. The relationship between feed (both emulsions) CFV and the resultant permeate flux rate from both membranes MI and MII is non-linear, but it is slightly linear in case of membrane MIII. Non-linearity of membranes MI and MII can be explained by droplet deformation and droplet interactions and/or rejection with/by the membrane surface. With high CFVs higher shear forces on the membrane surface are generated, by which the thickness of the oily layer that may have developed on membrane surface is limited. Also, turbulence and mass transfer of oil droplets from the membrane surface back to the bulk stream can also help reduce the level of concentration polarization and; therefore, increase membrane flux rate.
- Similarly, applying an electrical field across either emulsion augments the permeate flux rate at a given filtration condition(s). Gas evolution through electrolysis while filtration is running by which the membrane surface is continuously cleaned and resulting in an increased chance of emulsion droplet collision, are believed a key in the success of an electrical field to improving permeate flux rate. The influence of an

electrical field across the emulsion with higher water content (EII), in comparison to the other emulsion with lower water content (EI), has appeared more prominent. In fact, as far as the water content of both emulsions is concerned, the conductivity of the former emulsion is higher than that of the latter one and; therefore, the electrical current was passed more efficiently in the former emulsion than in the latter one.

- With regards to the effect of membrane pore size on membrane flux rates from the tested membranes with time, experimental evidence suggests that there is not a common trend when considering both emulsions. Permeates from different membranes randomly change with respect to changes in filtration conditions. In the case of both emulsions, membranes with larger pore sizes do not necessarily produce the highest permeates in comparison to those with smaller pore sizes. Differences in their morphological structure (porosity), degree of hydrophilicity (concentration polarization) and susceptibility to swelling (blocking), may have been the driving forces for such a relationship between the permeate flux rates from the used membranes and their pore sizes. In accordance to this, retained emulsion droplets will either deposit on or within the membrane surface or membrane internals, respectively. In either case, with filtration time this deposition seems to have changed the way fresh membrane pore sizes respond to the produced permeate. In fact, membranes with larger pore size in comparison to those with smaller pore sizes, might be more vulnerable to internal blocking by small emulsion droplets, by which the volume of permeate collected from such membranes might be lower than that obtained from membranes with smaller pores.
- A possible mechanism to explain the trend of obtained permeate flux rates is proposed. The trend of permeate flux rates obtained can be described through physical processes and fouling effects believed to have taken place while filtration is advancing as follows:

1- Saturation of the membrane with emulsion droplets: As filtration commences, it seems that the membrane is getting saturated with emulsion droplets during which membrane pores are more prone to adsorb emulsion droplets within their internals rather than allowing them to permeate through. However, towards the end of this period, it is obvious that permeate flux rate is increasing (maxima). This suggests that the membrane pores are no longer adsorbing emulsion droplets, but start to push them out of the membrane body once a pore is fully occupied and cannot accommodate further droplet(s). The chemistry of the membrane surface with respect to emulsion droplets, membrane pore size and filtration conditions are vital for this stage.

2- Build-up of a secondary membrane: Following the first stage, emulsion droplets seem to have begun to deposit onto the membrane surface, creating what's known as secondary membrane. Eventually, such a trend weakens the chemistry of interaction between the primary membrane surface and emulsion droplets. Further, this secondary membrane, which is composed of emulsion droplets, clogs the pores of the primary membrane. As a result, the permeate flux rate begins to substantially decline. This declination is; of- course, a function of the filtration conditions.

3- Densification/compaction of secondary membrane: During this final stage in which the growth of secondary membrane seems has finalized, permeation rate declination is somewhat retarded in comparison to that observed in the former stage. As the name implies, densification, owing to the crossflow filtration principle of feed tangential flow, involves no deposition of additional/newer emulsion droplets but rather a re-arrangement. This; in turn, brings little change in the permeate flux rate (plateau).

7.2.4 Demulsification Efficiencies

This study has confirmed that the hydrophilic membranes prepared have been capable of demulsifying the prepared emulsions. Though it may still require further consideration from both technical and economical viewpoints. During the course of this work, the effect of several factors on demulsification efficiency *(DE)* was investigated. These factors have included: emulsion water content, filtration duration, feed CFV, presence of an electrical field and membrane pore size. *DE* relates the volume fraction of water in the permeate sample to the total volume of permeate sample. It is concluded that demulsification can be influenced by emulsion water content, feed CFV, electrical field and membrane pore size. Experimental results show that emulsion water content was found to be an important factor in *DE*. The higher the water content (and consequently the lower the concentration of emulsion stabilizers), the higher the *DE.* Such a result is directly correlated to the stability level of the corresponding emulsion. With settling time, *DE* is increasing but at a lower rate at the end of the settling period, perhaps due to a suppression in the tendency towards a further change in the sample composition. Due to increased droplet collision rate and deformation, facilitated by higher feed CFVs, higher *DEs* are obtained. Likewise, increasing the applied electrical field produces higher *DEs.* It was also found that membrane pore size can significantly affect *DE.* Although membranes with larger pore diameter, in comparison to those with smaller ones, generally produce higher permeate flux rates, membranes of the latter type exhibit a much better performance in demulsification than those membranes of the former type. *DEs* of 66.80, 79.40, 69.60 and 86.70 vol. % have been obtained when using membrane MI to filter emulsions EI and EII, without and with applying an electrical field, respectively.

7.3 Suggestions and Future Work/Research

> Map out your future – but do it in pencil.
> The road ahead is as long as you make it.
> Make it worth the trip.
>
> Jon Bon Jovi (1962-present)

Future work should be targeting the following research objectives.

- Although in this work, flat sheets of PHP membranes were successfully used, other membrane configurations with similar characteristics should also be tested in future studies.
- This study was applied on synthesized emulsions with two water contents only; emulsions with lower/higher water contents should also be investigated. In addition, demulsification work should also be carried out on real emulsions.
- Since for technical reasons relating to the appropriate use of an ESEM microscope, it was not possible to carry out any ESEM observations on fouled membranes, visualization of filtration phenomena to obtain information on the permeation flow of emulsion droplets and on membrane fouling might be a good alternative.
- Although improvement in permeate flux rates from all tested membranes by introducing an electrical field across both emulsions is evident, the relative total energy consumption and associated costs should be economically assessed.
- Since using an electrical field has been demonstrated o have a positive effect on both membrane(s) flux rate(s) and demulsification efficiencies, the effect of higher electrical fields should also be tested.
- The mechanism of membrane fouling has not been thoroughly investigated in this study. To this end, a mathematical model should be developed so as to understand the mechanism of membrane fouling and to interlink it with the effect of operational parameters on flux declination.
- In order to prevent breakup of the lamellar phase in the secondary membrane; thus, causing water entrapment, it is possible to periodically wash the PHP separation media using a suitable solvent and recover the surfactants. This

can be achieved by operating in tandem using two separation filtration modules.

While one module is operating in crossflow mode, the second module can be washed to remove the surface active species.

- In case of both emulsions, since permeate flux rates obtained were relatively low, perhaps due to high emulsions viscosities, measures that restore a membrane’s original performance should be investigated. Such measures may include: periodic backflushing and efficient membrane cleaning for reuse.

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&
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Appendices

Appendix A

Permeate Flux Rate

N. B. Samples were measured in ml/sec when collected. For the purpose of calculations, this was converted to L/m^2 hr taking into account the membrane cross sectional area of (0.00385 m^2). For instance, a membrane permeate flow rate of 2.7 ml/sec can be converted to permeate flux rate (J, L/m^2 hr) as follows:

2.7 ml/sec * 3600 sec/ 1 hr * 1 L/1000 ml * 1/ 0.00385 m^2 = 2524.7 L/m^2 hr.
According to this, a conversion factor of 935.065 can be used.

A.1- Membrane MI

A.1.1- Emulsion EI

A.1.1.1- Permeate Flow Rate (ml/sec)

A.1.1.1.1- No current

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	2.7	2.95	3.15	2.1	1.875	1.45	1.275
200	6.33	6.7	7.1	6.8	5.66	5.4	5.25
300	11.33	12.7	13.75	8.45	7.1	5.95	5.66
400	13.5	16.25	17	12.5	10.66	7	6.45
500	14.75	17.1	18.4	13.25	11	9.25	7.66
600	15.66	17.75	19.66	16.5	13.75	13	10.7
800	16	18.33	20.7	17.7	15.5	13.75	12
1000	19.66	21.5	26	22.75	20.4	17.625	16.1

A.1.1.1.2- 10 kV

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	3.125	3.5	3.75	2.35	2.15	1.5	1.35
200	7.4	8.8	9	7.5	6	5.7	5.5
300	12	14	15	9	8	6.66	6.33
400	15	18.5	19.33	14	12.33	8	7.4
500	17	20.33	21	15.75	12.83	10.5	8.75
600	18.66	21.5	23.5	20.33	16.33	15.75	12.5
800	19.5	22.75	24.83	20.83	18.66	16.33	14.66
1000	23	25.33	28	27	24.5	19.66	19

A.1.1.1.3- 25 kV

Permeate flow rate, ml/sec							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	3.25	3.66	3.83	2.75	2.25	1.83	1.45
200	7.5	9.33	9.75	7.75	6.25	6.1	5.66
300	12.33	15	15.33	9.5	8.66	6.83	6.66
400	15.5	18.83	22.66	14.83	12.5	8.33	7.83
500	17.25	19.83	23	16.1	13	10.66	9
600	19.1	21.83	24	21	16.5	16	12.66
800	19.83	23.33	24.83	21.83	19.1	17	14.33
1000	23.25	25.83	28.83	27.5	25.33	22.5	20

A.1.1.1.4- 50 kV

Permeate flow rate, ml/sec							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	3.83	4	4.05	2.83	2.5	2	1.66
200	8	9.66	10.33	8	6.4	6.25	6
300	12.66	15.5	15.66	10	9	7	6.83
400	15.66	19.25	23.25	15.5	13	9.1	8.25
500	17.5	20.1	21.5	16.5	13.33	10.83	9.33
600	19.4	22.75	25	21.25	17.66	16.5	13
800	20.1	23.66	26	22.66	19.5	18.5	15.1
1000	24.33	26.5	29.66	28.25	30	22.75	20.75

A.1.1.1.5- 100 kV

Permeate flow rate, ml/sec							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	4.5	4.75	5.1	3.33	2.83	2.33	1.9
200	8.83	10.33	11	9.75	8.1	7.83	7.25
300	16.1	18	20.33	12	10.33	8.75	8.1
400	23	26	27.83	19.83	18.33	12.5	10.75
500	24.2	27.5	28.83	21.75	18.5	15.75	12.4
600	26.66	28.5	31.25	24	20.33	19	14
800	28	31	33	27	23	20.75	17.5
1000	29.83	32.5	38.5	35	30.66	27	24.5

A.1.1.1.6- 200 kV

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	5.66	6	6.5	4.25	3.83	2.83	2.33
200	12.1	13	14	13	10.66	9.83	9
300	21	23	25.83	14.83	12.75	10.5	10.5
400	27	31.33	33	23.75	21.33	13.66	13
500	30.5	34	36.83	27.83	22.83	18	15.33
600	34	37.83	46	35	28.83	25.75	21
800	41	46	50.5	42	37.25	33.5	25.25
1000	56	53.33	52.5	49	44.83	41	39.5

A.1.1.2- Permeate Flux Rate (L/m^2 hr)

A.1.1.2.1- No current

Permeate flux rate, J, l/m^2 hr							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	2524.7	2758.4	2945.5	1963.6	1753.3	1355.8	1192.2
200	5919	6264.9	6639	6358.4	5292.5	5049.4	4909.1
300	10594.3	11875.3	12857.1	7901.3	6639	5563.6	5292.5
400	12623.4	15194.8	15896.1	11688.3	9967.8	6545.5	6031.2
500	13792.2	15989.6	17205.2	12389.6	10285.7	8649.4	7162.6
600	14643.1	16597.4	18383.4	15428.6	12857.1	12155.8	10005.2
800	14961	17139.7	19355.8	16550.7	14493.5	12857.1	11220.8
1000	18383.4	20103.9	24311.7	21272.7	19075.3	16480.5	15054.5

A.1.1.2.2- 10 kV

Permeate flux rate, J , l/m^2 hr							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	2922.1	3272.7	3506.5	2197.4	2010.4	1402.6	1262.3
200	6919.5	8228.6	8415.6	7013	5610.4	5329.9	5142.9
300	11220.8	13090.9	14026	8415.6	7480.5	6227.5	5919
400	14026	17298.7	18074.8	13090.9	11529.4	7480.5	6919.5
500	15896.1	19009.9	19636.4	14727.3	11996.9	9818.2	8181.8
600	17448.3	20103.9	21974	19009.9	15269.6	14727.3	11688.3
800	18233.8	21272.7	23217.7	19477.4	17448.3	15269.6	13708.1
1000	21506.5	23685.2	26181.8	25246.8	22909.1	18383.4	17766.2

A.1.1.2.3- 25 kV

Permeate flux rate, J, l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	3039	3422.3	3581.3	2571.4	2103.9	1711.2	1355.8
200	7013	8724.2	9116.9	7246.8	5844.2	5703.9	5292.5
300	11529.4	14026	14334.6	8883.1	8097.7	6386.5	6227.5
400	14493.5	17607.3	21188.6	13867	11688.3	7789.1	7321.6
500	16129.9	18542.3	21506.5	15054.6	12155.9	9967.8	8415.6
600	17859.7	20412.5	22441.6	19636.4	15428.6	14961	11837.9
800	18542.3	21815.1	23217.7	20412.5	17859.7	15896.1	13399.5
1000	21740.3	24152.7	26957.9	25714.3	23685.2	21039	18701.3

A.1.1.2.4- 50 kV

Permeate flux rate, J , l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	3581.3	3740.3	3787	2646.2	2337.7	1870.1	1552.2
200	7480.5	9032.7	9659.2	7480.5	5984.4	5844.2	5610.4
300	11837.9	14493.5	14643.1	9350.7	8415.6	6545.5	6386.5
400	14643.1	18000	21740.3	14493.5	12155.9	8509.1	7714.3
500	16363.6	18794.8	20103.9	15428.6	12464.4	10126.8	8724.2
600	18140.3	21272.7	23376.6	19870.1	16513.3	15428.6	12155.9
800	18794.8	22123.6	24311.7	21188.6	18233.8	17298.7	14119.5
1000	22750.1	24779.2	27734	26415.6	28052	21272.7	19402.6

A.1.1.2.5- 100 kV

Permeate flux rate, J , l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	4207.8	4441.6	4768.8	3113.8	2646.2	2178.7	1776.6
200	8256.6	9659.2	10285.7	9116.9	7574	7321.6	6779.2
300	15054.6	16831.2	19009.9	11220.8	9659.2	8181.8	7574
400	21506.5	24311.7	26022.9	18542.3	17139.7	11688.3	10052
500	22628.6	25714.3	26957.9	20337.7	17298.7	14727.3	11594.8
600	24928.8	26649.4	29220.8	22441.6	19009.9	17766.2	13090.9
800	26181.8	28987	30857.2	25246.8	21506.5	19402.6	16363.6
1000	27893	30389.6	36000	32727.3	28669.1	25246.8	22909.1

A.1.1.2.6- 200 kV

Permeate flux rate, J, l/m^2 hr							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	5292.5	5610.4	6077.9	3974	3581.3	2646.2	2178.7
200	11314.3	12155.9	13090.9	12155.9	9967.8	9191.7	8415.6
300	19636.4	21506.5	24152.7	13867	11922.1	9818.2	9818.2
400	25246.8	29295.6	30857.2	22207.8	19944.9	12773	12155.9
500	28519.5	31792.2	34438.4	26022.9	21347.5	16831.2	14334.6
600	31792.2	35373.5	43013	32727.3	26957.9	24077.9	19636.4
800	38337.7	43013	47220.8	39272.7	34831.2	31324.7	23610.4
1000	52363.6	49867	49090.9	45818.2	41919	38337.7	36935.1

A.1.2-Emulsion EII

A.1.2.1- Permeate Flow Rate (ml/sec)

A.1.2.1.1- No current

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	2.83	3.1	3.25	2.25	2.1	1.66	1.5
200	6.5	6.83	7.25	7	6	5.5	5.5
300	11.66	13	14	9	7.5	6.25	6
400	14	16.83	18	13.5	11.5	7.83	7
500	15.1	17.83	19	14.25	12	10.33	8.5
600	16	18.5	21	18	14.83	14	11.83
800	17.25	19	22	18.5	16.83	14.5	13.33
1000	20.83	22.66	27	24	22	19.25	17

A.1.2.1.2- 10 kV

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	3.5	3.83	4	2.66	2.5	2.1	1.75
200	7.83	8.1	9.33	8.1	6.75	6.33	6
300	13.25	14.83	15.75	10.4	8.5	7.33	7.1
400	16.25	19.33	20.66	16	13.75	9.33	8.25
500	18	21	23	17.5	14.83	12.5	10.5
600	20.25	23.5	26.5	22.33	18.66	17.75	14.5
800	21.33	24.33	27.83	23.5	21	18.1	16.5
1000	25.83	27.1	32	28.33	27.1	22.75	21.25

A.1.2.1.3- 25 kV

Permeate flow rate, ml/sec							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	3.66	4.16	4.83	3.16	2.83	2.5	2
200	8	8.66	10	8.5	7.25	6.66	6.33
300	13.75	15.5	16.25	11.33	9.16	8	7.33
400	17.1	20.5	21.33	16.5	14.1	9.83	8.66
500	18.5	22.5	24.1	18.25	15.5	13.5	11.1
600	20.66	23.83	26.83	23	19	18.1	15.75
800	21.83	24.75	28.66	23.83	21.5	18.66	16.66
1000	26.5	27.5	33	29	27.66	23.5	21.75

A.1.2.1.4- 50 kV

Permeate flow rate, ml/sec							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	4.25	4.5	5.1	3.33	3	2.83	2.25
200	8.66	9	10.5	9.33	8.1	7.25	7
300	14.1	16	16.83	11.83	9.66	8.5	8
400	17.66	21.1	22.25	17.1	15	10.5	9.1
500	19	22.83	25	18.66	16.1	14.25	12
600	21.1	24.25	27.25	23.83	20	19	17.66
800	22.25	26	30	26.1	23	20	18.25
1000	27.25	28.33	34.33	29.5	28.5	24.25	22.1

A.1.2.1.5- 100 kV

Permeate flow rate, ml/sec							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	4.33	5.1	5.33	3.66	3.5	3.1	2.83
200	9.1	10	10.83	10.25	9	8.1	8
300	16	17	18.25	12.5	11	10.1	9.83
400	23.83	26	27.33	22.5	17.83	13	10.75
500	25	26.83	29.25	24.33	22.1	18	14.33
600	27.5	31.5	34.1	28.5	24	22.1	16.5
800	29.66	33	37.5	32	26.66	24	19.33
1000	32.33	34.66	41.5	36.5	33.25	28.83	24.5

A.1.2.1.6- 200 kV

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	6.1	6.5	6.83	4.75	4	3.33	2.83
200	12	13	14.33	13.66	11.83	10.5	10.33
300	22.1	24.25	26.66	17	14	11.66	10.83
400	27	33	35.66	27.1	22.5	15.5	13.66
500	32	35	36.5	28	24.5	21	20
600	35.83	40.33	43	39.25	33	29.83	24
800	42	46.5	52	46	41.75	36	32.25
1000	55.83	57.33	63	54.25	49.33	44.5	40.1

A.1.2.2- Permeate Flux Rate (L/m^2 hr)

A.1.2.2.1- No current

Permeate flux rate, J, l/m^2 hr							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	2646.2	2898.7	3039	2103.9	1963.6	1552.2	1402.6
200	6077.9	6386.5	6779.2	6545.5	5610.4	5142.9	5142.9
300	10902.9	12155.9	13090.9	8415.6	7013	5844.2	5610.4
400	13090.9	15737.1	16831.2	12623.4	10753.3	7321.6	6545.5
500	14119.5	16672.2	17766.2	13324.7	11220.8	9659.2	7948.1
600	14961	17298.7	19636.4	16831.2	13867	13090.9	11061.8
800	16129.9	17766.2	20571.4	17298.7	15737.1	13558.4	12464.4
1000	19477.4	21188.6	25246.8	22441.6	20571.4	18000	15896.1

A.1.2.2.2- 10 kV

Permeate flux rate, J, l/m^2 hr							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	3272.7	3581.3	3740.3	2487.3	2337.7	1963.6	1636.4
200	7321.6	7574	8724.2	7574	6311.7	5919	5610.4
300	12389.6	13867	14727.3	9724.7	7948.1	6854	6639
400	15194.8	18074.8	19318.4	14961	12857.1	8724.2	7714.3
500	16831.2	19636.4	21506.5	16363.6	13867	11688.3	9818.2
600	18935.1	21974	24779.2	20880	17448.3	16597.4	13558.4
800	19944.9	22750.1	26022.9	21974	19636.4	16924.7	15428.6
1000	24152.7	25340.3	29922.1	26490.4	25340.3	21272.7	19870.1

A.1.2.2.3- 25 kV

Permeate flux rate, J , l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	3422.3	3889.8	4516.4	2954.8	2646.2	2337.7	1870.1
200	7480.5	8097.7	9350.7	7948	6779.2	6227.6	5919
300	12857.1	14493.5	15194.8	10594.3	8565.2	7480.5	6854
400	15989.6	19168.8	19944.9	15428.6	13184.4	9191.7	8097.7
500	17298.7	21039	22535.1	17064.9	14493.5	12623.4	10379.2
600	19318.4	22282.6	25087.8	21506.5	17766.2	16924.7	14727.3
800	20412.5	23142.9	26799	22282.6	20103.9	17448.3	15578.2
1000	24779.2	25714.3	30857.2	27116.9	25863.9	21974	20337.7

A.1.2.2.4- 50 kV

Permeate flux rate, J , l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	3974	4207.8	4768.8	3113.8	2805.195	2646.2	2103.9
200	8097.7	8415.6	9818.2	8724.2	7574.027	6779.2	6545.5
300	13184.4	14961	15737.1	11061.8	9032.728	7948.1	7480.5
400	16513.3	19729.9	20805.2	15989.6	14026	9818.2	8509.1
500	17766.2	21347.5	23376.6	17448.3	15054.6	13324.7	11220.8
600	19729.9	22675.3	25480.5	22282.6	18701.3	17766.2	16513.3
800	20805.2	24311.7	28052	24405.2	21506.5	18701.3	17064.9
1000	25480.5	26490.4	32100.8	27584.4	26649.4	22675.3	20664.9

A.1.2.2.5- 100 kV

Permeate flux rate, J , l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	4048.8	4768.8	4983.9	3422.3	3272.7	2898.7	2646.2
200	8509.1	9350.7	10126.8	9584.4	8415.6	7574	7480.5
300	14961	15896.1	17064.9	11688.3	10285.7	9444.2	9191.7
400	22282.6	24311.7	25555.3	21039	16672.2	12155.9	10052
500	23376.6	25087.8	27350.7	22750.1	20664.9	16831.2	13399.5
600	25714.3	29454.6	31885.7	26649.4	22441.6	20664.9	15428.6
800	27734	30857.2	35064.9	29922.1	24928.8	22441.6	18074.8
1000	30230.7	32409.4	38805.2	34129.9	31090.9	26957.9	22909.1

A.1.2.2.6- 200 kV

Permeate flux rate, J , l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	5703.9	6077.9	6386.5	4441.6	3740.3	3113.8	2646.2
200	11220.8	12155.9	13399.5	12773	11061.8	9818.2	9659.2
300	20664.9	22675.3	24928.8	15896.11	13090.9	10902.9	10126.8
400	25246.8	30857.2	33344.4	25340.3	21039	14493.5	12773
500	29922.1	32727.3	34129.9	26181.8	22909.1	19636.4	18701.3
600	33503.4	37711.2	40207.8	36701.3	30857.2	27893	22441.6
800	39272.7	43480.5	48623.4	43013	39039	33662.3	30155.9
1000	52204.7	53607.3	58909.1	50727.3	46126.8	41610.4	37496.1

A.2- Membrane MII

A.2.1- Emulsion EI

A.2.1.1- Permeate Flow Rate (ml/sec)

A.2.1.1.1- No current

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	2.4	2.8	2.95	2.33	2.15	2.05	1.83
200	5.2	5.8	6.25	5.9	4.45	4.2	3.9
300	10	10.75	11.25	7.8	5.25	4.45	4.33
400	16.5	17.75	21.25	13.5	12	7.8	7.1
500	17.33	19	23.33	15.8	12.7	9.83	7.85
600	19.66	21.8	24.7	21.83	14	13.25	9.33
800	21	22.33	25.83	24	17.83	14	11.25
1000	23.1	26.5	28	27.33	22	19.33	14.75

A.2.1.1.2- 10 kV

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	2.83	3.25	3.33	2.63	2.2	2.15	2
200	6	6.66	7.33	6.33	4.8	4.66	4.4
300	11	12.4	12.66	8.5	5.6	5	4.6
400	18.5	19.5	22.66	15	12.66	8.5	7.7
500	21	26.66	27.66	17.5	13.25	10.4	8.66
600	23	28	29	26	16.83	16.83	12
800	25	28	30	27.83	18.5	17.33	14
1000	27	30	31	29	26.83	22	20

A.2.1.1.3- 25 kV

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	3	3.33	4	3	2.66	2.66	2.2
200	6.25	7.33	8.125	7.33	5.25	5	4.5
300	12.33	13.33	14	9.25	6.25	5.66	5.25
400	19	21	23.5	16.5	14.33	9.5	8.33
500	21.66	27	28	18.5	14	10.83	9.1
600	24	28.33	30	26.83	17.66	17.25	12.5
800	25	29	31	28.5	20	17.5	14.83
1000	27.75	31	32	31	27.75	23.25	20.5

A.2.1.1.4- 50 kV

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	3.5	4	4.25	3.33	3.1	3	2.5
200	6.5	8.1	8.75	7.83	5.66	5.25	4.66
300	12.66	14	14.66	9.83	6.83	6	5.66
400	19.83	21.66	24.66	17.5	14.83	10	9.5
500	22.5	27.5	29	19	14.66	11.83	9.66
600	24.75	29.83	31	28.5	18.25	17.66	13
800	26.5	30.83	33.1	31.25	24	20	18
1000	28.66	31.83	33	32	28.66	24.5	22

A.2.1.1.5- 100 kV

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	4	5	5	3.66	3.25	3	2.75
200	7	8.5	10	8.5	6.33	6	5.83
300	13.83	14.66	15.5	11.33	7.75	6.25	6
400	26.83	27.5	28	20.5	19	14	12
500	27.75	30.5	34	25	20	16.1	14
600	31.66	32	36.5	30	22	20.5	16
800	34.25	36.83	41.33	36.83	27.66	22	20.5
1000	37	41	42	40.5	32.33	27.66	23.83

A.2.1.1.6- 200 kV

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	4.83	5.83	6.25	4.83	4.33	3.75	3.6
200	9.66	11	11.83	11.5	8.5	7.33	6.25
300	18.5	19.66	20.33	14	9.66	8.1	7.83
400	28	32	34	23.75	22	14.83	13.5
500	32.5	35	38	30	23.83	18.66	14.83
600	38.33	43.66	51.5	45	34	29.5	19.66
800	51	53	54.5	53	41	33.5	26
1000	57	62	59	57.33	50.66	46.5	34

A.2.1.2- Permeate Flux Rate (L/m^2 hr)

A.2.1.2.1- No current

Permeate flux rate, J , l/m^2 hr							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	2244.2	2618.2	2758.4	2178.7	2010.4	1916.9	1711.2
200	4862.3	5423.4	5844.2	5516.9	4161	3927.3	3646.8
300	9350.7	10052	10519.5	7293.5	4909.1	4161	4048.8
400	15428.6	16597.4	19870.1	12623.4	11220.8	7293.5	6639
500	16204.7	17766.2	21815.1	14774	11875.3	9191.7	7340.3
600	18383.4	20384.4	23096.1	20412.5	13090.9	12389.6	8724.2
800	19636.4	20880	24152.7	22441.6	16672.2	13090.9	10519.5
1000	21600	24779.2	26181.8	25555.3	20571.4	18074.8	13792.2

A.2.1.2.2- 10 kV

Permeate flux rate, J , l/m^2 hr							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	2646.2	3039	3113.8	2459.2	2057.1	2010.4	1870.1
200	5610.4	6227.5	6854	5919	4488.3	4357.4	4114.3
300	10285.7	11594.8	11837.9	7948	5236.4	4675.3	4301.3
400	17298.7	18233.8	21188.6	14026	11837.9	7948.1	7200
500	19636.4	24928.8	25863.9	16363.6	12389.6	9724.7	8097.7
600	21506.5	26181.8	27116.9	24311.7	15737.1	15737.1	11220.8
800	23376.6	26181.8	28052	26022.9	17298.7	16204.7	13090.9
1000	25246.8	28052	28987	27116.9	25087.8	20571.4	18701.3

A.2.1.2.3- 25 kV

Permeate flux rate, J, l/m^2 hr							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	2805.2	3113.8	3740.3	2805.2	2487.3	2487.3	2057.1
200	5844.2	6854	7597.4	6854	4909.1	4675.3	4207.8
300	11529.4	12464.4	13090.9	8649.4	5844.2	5292.5	4909.1
400	17766.2	19636.4	21974	15428.6	13399.5	8883.1	7789.1
500	20253.5	25246.8	26181.8	17298.7	13090.9	10126.8	8509.1
600	22441.6	26490.4	28052	25087.8	16513.3	16129.9	11688.3
800	23376.6	27116.9	28987	26649.4	18701.3	16363.6	13867
1000	25948.1	28987	29922.1	28987	25948.1	21740.3	19168.8

A.2.1.2.4- 50 kV

Permeate flux rate, J , l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	3272.7	3740.3	3974	3113.8	2898.7	2805.2	2337.7
200	6077.9	7574.03	8181.8	7321.6	5292.5	4909.1	4357.4
300	11837.9	13090.9	13708.1	9191.7	6386.5	5610.4	5292.5
400	18542.3	20253.5	23058.7	16363.6	13867	9350.7	8883.1
500	21039	25714.3	27116.9	17766.2	13708.1	11061.8	9032.7
600	23142.9	27893	28987	26649.4	17064.9	16513.3	12155.9
800	24779.2	28828.1	30950.7	29220.8	22441.6	18701.3	16831.2
1000	26799	29763.1	30857.2	29922.1	26799	22909.1	20571.4

A.2.1.2.5- 100 kV

Permeate flux rate, J, l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	3740.3	4675.3	4675.3	3422.3	3039	2805.2	2571.4
200	6545.5	7948.1	9350.7	7948.1	5919	5610.4	5451.4
300	12932	13708.1	14493.5	10594.3	7246.8	5844.2	5610.4
400	25087.8	25714.3	26181.8	19168.8	17766.2	13090.9	11220.8
500	25948.1	28519.5	31792.2	23376.6	18701.3	15054.6	13090.9
600	29604.2	29922.1	34129.9	28052	20571.4	19168.8	14961
800	32026	34438.4	38646.2	34438.4	25863.9	20571.4	19168.8
1000	34597.4	38337.7	39272.7	37870.1	30230.7	25863.9	22282.6

A.2.1.2.6- 200 kV

Permeate flux rate, J, l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	4516.4	5451.4	5844.2	4516.4	4048.8	3506.5	3366.2
200	9032.7	10285.7	11061.8	10753.3	7948.1	6854	5844.2
300	17298.7	18383.4	19009.9	13090.9	9032.7	7574	7321.6
400	26181.8	29922.1	31792.2	22207.8	20571.4	13867	12623.4
500	30389.6	32727.3	35532.5	28052	22282.6	17448.3	13867
600	35841	40824.9	48155.9	42077.9	31792.2	27584.4	18383.4
800	47688.3	49558.5	50961	49558.5	38337.7	31324.7	24311.7
1000	53298.7	57974	55168.8	53607.3	47370.4	43480.5	31792.2

A.2.2- Emulsion EII

A.2.2.1- Permeate Flow Rate (ml/sec)

A.2.2.1.1- No current

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	2.5	2.8	3.1	2.5	2.33	2.25	2
200	5.33	6	6.5	6.1	5	4.33	4.25
300	10.5	11.1	11.66	8	5.66	4.66	4.5
400	17.1	18.25	21.83	14.1	12.66	8.25	8
500	18	19.66	24.5	17.5	14.1	11	8.5
600	20.83	22.75	26	23	15.66	14.5	12
800	22	23.5	27	25.25	19.1	16	12.66
1000	24.66	28	30.25	28.5	24.1	21	16.25

A.2.2.1.2- 10 kV

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	3	3.33	3.66	3	2.83	2.25	2
200	6.33	6.83	7.25	6.83	6	5.25	4.66
300	12.1	13.25	14	9.33	6.5	5.5	5.1
400	20.25	21.5	24.83	16.1	14.33	9.5	9.25
500	22.33	24.1	27.5	21	16.66	12.75	9.66
600	25.83	27.5	31	27.5	19.5	18	15.5
800	26.5	27.75	32.33	30	23	20.25	16.5
1000	29	32.5	35.1	32.75	29.66	24.75	21.5

A.2.2.1.3- 25 kV

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	3.33	3.5	4.33	3.5	3.1	3	2.83
200	6.66	7.33	8.33	7.83	6.25	5.33	5.1
300	13.5	13.83	14.66	9.66	7	6.1	5.66
400	21	22.1	25.75	17	15.1	9.75	9.33
500	23.1	25.33	29	21.75	17.25	13.5	10.33
600	26.25	29.5	32.5	29.5	20.33	19.66	16.66
800	27.66	29.1	33.5	31	23.83	20.75	17.1
1000	30.5	33.83	36.33	35.1	31.33	25.83	23

A.2.2.1.4- 50 kV

Permeate flow rate, ml/sec							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	3.83	4.25	4.66	3.75	3.5	3.33	2.83
200	6.83	7.66	8.83	8.1	6.75	6	5.33
300	13.66	14.66	15.5	10.25	7.83	6.33	6
400	21.5	23	26.66	18	15.75	10.5	9.75
500	23.66	26.33	31	22.5	18	13.83	11
600	26.83	31.5	33.66	31	21	19.83	17
800	28.5	31.75	34.5	33.83	26	23	17.5
1000	31.66	35.1	38.66	36	32	27.83	25

A.2.2.1.5- 100 kV

Permeate flow rate, ml/sec							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	4.25	5.1	5.33	4.1	3.66	3.5	3.1
200	7.33	9	10.66	9.1	7.66	6.5	6.5
300	15.1	15.5	16.5	11.83	8.5	6.75	6.5
400	28.25	29.1	31	22.5	20.66	15.5	13.25
500	29.5	32.5	37.5	28.83	23	18.5	14.5
600	34	35.25	39.1	33	26	23.5	19.66
800	37	38.83	43.5	40.5	31	26	22
1000	40.5	44	46.83	44.25	37.5	31.1	26.5

A.2.2.1.6- 200 kV

Permeate flow rate, ml/sec							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	5.5	5.83	6.66	5.33	4.83	4.5	4
200	10.1	11.5	12.5	12	9.75	8	7.25
300	20.25	21	22.25	15.5	10.75	8.83	8.33
400	31	33.5	37.25	25	23.83	16.25	14.83
500	34.5	37	42	34.83	27.25	21.5	16.83
600	41.5	46.5	55.33	49.5	39	33	26
800	54.5	57.1	58.83	58	46	39	31
1000	62	68.1	69	61.5	57.5	52.25	39.66

A.2.2.2- Permeate Flux Rate (L/m^2 hr)

A.2.2.2.1- No current

Permeate flux rate, J , l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	2337.7	2618.2	2898.7	2337.7	2178.7	2103.9	1870.1
200	4983.9	5610.4	6077.9	5703.9	4675.3	4048.8	3974
300	9818.2	10379.2	10902.9	7480.5	5292.5	4357.4	4207.8
400	15989.6	17064.9	20412.5	13184.4	11837.9	7714.3	7480.5
500	16831.2	18383.4	22909.1	16363.6	13184.4	10285.7	7948.1
600	19477.4	21272.7	24311.7	21506.5	14643.1	13558.4	11220.8
800	20571.4	21974	25246.8	23610.4	17859.7	14961	11837.9
1000	23058.7	26181.8	28285.7	26649.4	22535.1	19636.4	15194.8

A.2.2.2.2- 10 kV

Permeate flux rate, J , l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	2805.2	3113.8	3422.3	2805.2	2646.2	2103.9	1870.1
200	5919	6386.5	6779.2	6386.5	5610.4	4909.1	4357.4
300	11314.3	12389.6	13090.9	8724.2	6077.9	5142.9	4768.8
400	18935.1	20103.9	23217.7	15054.6	13399.5	8883.1	8649.4
500	20880	22535.1	25714.3	19636.4	15578.2	11922.1	9032.7
600	24152.7	25714.3	28987	25714.3	18233.8	16831.2	14493.5
800	24779.2	25948.1	30230.7	28052	21506.5	18935.1	15428.6
1000	27116.9	30389.6	32820.8	30623.4	27734	23142.9	20103.9

A.2.2.2.3- 25 kV

Permeate flux rate, J , l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	3113.8	3272.7	4048.8	3272.7	2898.7	2805.2	2646.2
200	6227.5	6854	7789.1	7321.6	5844.2	4983.9	4768.8
300	12623.4	12932	13708.1	9032.7	6545.5	5703.9	5292.5
400	19636.4	20664.9	24077.9	15896.1	14119.5	9116.9	8724.2
500	21600	23685.2	27116.9	20337.7	16129.9	12623.4	9659.2
600	24545.5	27584.4	30389.6	27584.4	19009.9	18383.4	15578.2
800	25863.9	27210.4	31324.7	28987	22282.6	19402.6	15989.6
1000	28519.5	31633.3	33970.9	32820.8	29295.6	24152.7	21506.5

A.2.2.2.4- 50 kV

Permeate flux rate, J , l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	3581.3	3974	4357.4	3506.5	3272.7	3113.8	2646.2
200	6386.5	7162.6	8256.6	7574	6311.7	5610.4	4983.9
300	12773	13708.1	14493.5	9584.4	7321.6	5919	5610.4
400	20103.9	21506.5	24928.8	16831.2	14727.3	9818.2	9116.9
500	22123.6	24620.3	28987	21039	16831.2	12932	10285.7
600	25087.8	29454.6	31474.3	28987	19636.4	18542.3	15896.1
800	26649.4	29688.3	32259.7	31633.3	24311.7	21506.5	16363.6
1000	29604.2	32820.8	36149.6	33662.3	29922.1	26022.9	23376.6

A.2.2.2.5- 100 kV

Permeate flux rate, J , l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	3974	4768.8	4983.9	3833.8	3422.3	3272.7	2898.7
200	6854	8415.6	9967.8	8509.1	7162.6	6077.9	6077.9
300	14119.5	14493.5	15428.6	11061.8	7948.1	6311.7	6077.9
400	26415.6	27210.4	28987	21039	19318.4	14493.5	12389.6
500	27584.4	30389.6	35064.9	26957.9	21506.5	17298.7	13558.4
600	31792.2	32961	36561	30857.2	24311.7	21974	18383.4
800	34597.4	36308.6	40675.3	37870.1	28987	24311.7	20571.4
1000	37870.1	41142.9	43789.1	41376.6	35064.9	29080.5	24779.2

A.2.2.2.6- 200 kV

Permeate flux rate, J, l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	5142.9	5451.4	6227.5	4983.9	4516.4	4207.8	3740.3
200	9444.2	10753.3	11688.3	11220.8	9116.9	7480.5	6779.2
300	18935.1	19636.4	20805.2	14493.5	10052	8256.6	7789.1
400	28987	31324.7	34831.2	23376.6	22282.6	15194.8	13867
500	32259.7	34597.4	39272.7	32568.3	25480.5	20103.9	15737.1
600	38805.2	43480.5	51737.2	46285.7	36467.5	30857.2	24311.7
800	50961	53392.2	55009.9	54233.8	43013	36467.5	28987
1000	57974	63677.9	64519.5	57506.5	53766.2	48857.2	37084.7

A.3- Membrane MIII

A.3.1- Emulsion EI

A.3.1.1- Permeate Flux Rate (ml/sec)

A.3.1.1.1- No current

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	2.8	3.66	3.8	3.75	2.9	2.33	1.4
200	7.25	7.5	8.8	7.33	6.8	5.33	4
300	11	12.75	13.33	8.5	7	6.25	4.8
400	17.33	18	19.5	13.83	11	7.5	6
500	18.25	19.75	21	16	12.33	10.33	7.83
600	19.33	21	23.33	18.5	16.25	12.25	9.5
800	22	23.75	26.1	21.33	18.1	16.5	13
1000	25.33	27.5	30.25	24	22.5	20.75	18.83

A.3.1.1.2- 10 kV

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	3.25	4	4.33	4	3.25	2.66	1.83
200	8	8.66	10.5	9	7.66	6.33	4.83
300	11.83	13.5	14.25	9.25	7.83	7.125	5.5
400	19.5	20	22.25	15.66	13	8.5	6.83
500	21	21.75	23	18.75	14.5	12	9.25
600	22.83	24.5	26	21	18.5	14.75	11.5
800	26	28.5	31	24.5	22.1	19.5	19
1000	30.5	32	34	28.5	26.33	24	23

A.3.1.1.3- 25 kV

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	3.5	4.33	5	4.66	3.75	2.83	2
200	8.4	9.25	11	10.25	8.33	6.83	5.5
300	12.33	14.83	14.5	9.83	8.1	7.5	5.66
400	19.5	21.25	22.83	16.5	13.66	9	7.1
500	22	22.5	24	19.5	15.5	12.66	9.83
600	23.5	25	27	21.5	19.33	15.1	12
800	26.83	29.66	31.33	25.1	22.66	20.83	20
1000	31.83	33	34.83	29	27.1	25	24

A.3.1.1.4- 50 kV

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	3.83	5	5	4.83	4	3.33	2.125
200	9.33	10.33	12.25	10.66	9	7.1	6
300	12.75	16	16.83	10.5	9	8.1	6.83
400	21	22	23.1	18	15.5	10.33	8.25
500	23	24.5	25.83	21	18.1	15.5	11
600	25	27	28	22	21	16.5	13
800	28	30.5	33	27	24.5	23	20.5
1000	33	34.33	36	31	28	26	24.5

A.3.1.1.5- 100 kV

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	4.5	5.75	6.33	5.66	4.25	3.66	2.25
200	10	11	12.83	11.5	9.83	7.83	7
300	15.25	17.83	18.66	11.33	9.75	9	7.25
400	28.25	29	31	22	18	12.25	9.5
500	30	32	34.75	25.25	19.75	17.25	12.5
600	31.83	34	36	28	25.66	18.5	13.5
800	40	40.5	42	34	27.25	24.25	21
1000	4.5	5.75	6.33	5.66	4.25	3.66	2.25

A.3.1.1.6- 200 kV

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	5.33	6	7.5	7	5.66	4.5	2.66
200	13	14.25	16	14	13	10.5	7.75
300	20	22	25	16	12.5	11.5	9
400	31	32.5	34	27.66	21	13.5	11.5
500	34.66	36.5	39	30.5	24	20	15.5
600	35.5	42.83	48	39	34	23.83	18
800	48	56	57.5	51	42	38	37
1000	65.83	69.33	68.1	52.33	48.5	43.5	41

A.3.1.2- Permeate Flux Rate (L/m^2 hr)

A.3.1.2.1- No current

Permeate flux rate, J, l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	2618.2	3422.3	3553.3	3506.5	2711.7	2178.7	1309.1
200	6779.2	7013	8228.6	6854	6358.4	4983.9	3740.3
300	10285.7	11922.1	12464.4	7948.1	6545.5	5844.2	4488.3
400	16204.7	16831.2	18233.8	12932	10285.7	7013	5610.4
500	17064.9	18467.5	19636.4	14961	11529.4	9659.2	7321.6
600	18074.8	19636.4	21815.1	17298.7	15194.8	11454.6	8883.1
800	20571.4	22207.8	24405.2	19944.9	16924.7	15428.6	12155.9
1000	23685.2	25714.3	28285.7	22441.6	21039	19402.6	17607.3

A.3.1.2.2- 10 kV

Permeate flux rate, J, l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	3039	3740.3	4048.8	3740.3	3039	2487.3	1711.2
200	7480.5	8097.7	9818.2	8415.6	7162.6	5919	4516.4
300	11061.8	12623.4	13324.7	8649.4	7321.6	6662.3	5142.9
400	18233.8	18701.3	20805.2	14643.1	12155.9	7948.1	6386.5
500	19636.4	20337.7	21506.5	17532.5	13558.4	11220.8	8649.4
600	21347.5	22909.1	24311.7	19636.4	17298.7	13792.2	10753.3
800	24311.7	26649.4	28987	22909.1	20664.9	18233.8	17766.2
1000	28519.5	29922.1	31792.2	26649.4	24620.3	22441.6	21506.5

A.3.1.2.3- 25 kV

Permeate flux rate, J , l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	3272.7	4048.8	4675.3	4357.4	3506.5	2646.2	1870.1
200	7854.6	8649.4	10285.7	9584.4	7789.1	6386.5	5142.9
300	11529.4	13867	13558.4	9191.7	7574	7013	5292.5
400	18233.8	19870.1	21347.5	15428.6	12773	8415.6	6639
500	20571.4	21039	22441.6	18233.8	14493.5	11837.9	9191.7
600	21974	23376.6	25246.8	20103.9	18074.8	14119.5	11220.8
800	25087.8	27734	29295.6	23470.1	21188.6	19477.4	18701.3
1000	29763.1	30857.2	32568.3	27116.9	25340.3	23376.6	22441.6

A.3.1.2.4- 50 kV

Permeate flux rate, J, l/m^2 hr							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	3581.3	4675.3	4675.3	4516.3	3740.3	3113.8	1987
200	8724.2	9659.2	11454.6	9967.8	8415.6	6639	5610.4
300	11922.1	14961	15737.1	9818.2	8415.6	7574	6386.5
400	19636.4	20571.4	21600	16831.2	14493.5	9659.2	7714.3
500	21506.5	22909.1	24152.7	19636.4	16924.7	14493.5	10285.7
600	23376.6	25246.8	26181.8	20571.4	19636.4	15428.6	12155.9
800	26181.8	28519.5	30857.2	25246.8	22909.1	21506.5	19168.8
1000	30857.2	32100.8	33662.3	28987	26181.8	24311.7	22909.1

A.3.1.2.5- 100 kV

Permeate flux rate, J , l/m^2 hr							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	4207.8	5376.6	5919	5292.5	3974	3422.3	2103.9
200	9350.7	10285.7	11996.9	10753.3	9191.7	7321.6	6545.5
300	14259.7	16672.2	17448.3	10594.3	9116.9	8415.6	6779.2
400	26415.6	27116.9	28987	20571.4	16831.2	11454.6	8883.1
500	28052	29922.1	32493.5	23610.4	18467.5	16129.9	11688.3
600	29763.1	31792.2	33662.3	26181.8	23993.8	17298.7	12623.4
800	37402.6	37870.1	39272.7	31792.2	25480.5	22675.3	19636.4
1000	39272.7	40207.8	41376.6	35532.5	33662.3	31090.9	27116.9

A.3.1.2.6- 200 kV

Permeate flux rate, J , l/m^2 hr							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	4983.9	5610.4	7013	6545.5	5292.5	4207.8	2487.3
200	12155.9	13324.7	14961	13090.9	12155.9	9818.2	7246.8
300	18701.3	20571.4	23376.6	14961	11688.3	10753.3	8415.6
400	28987	30389.6	31792.2	25863.9	19636.4	12623.4	10753.3
500	32409.4	34129.9	36467.5	28519.5	22441.6	18701.3	14493.5
600	33194.8	40048.8	44883.1	36467.5	31792.2	22282.6	16831.2
800	44883.1	52363.6	53766.2	47688.3	39272.7	35532.5	34597.4
1000	61555.3	64828.1	63677.9	48932	45350.7	40675.3	38337.7

A.3.2- Emulsion EII

A.3.2.1- Permeate Flow Rate (ml/sec)

A.3.2.1.1- No current

Permeate flow rate, ml/sec							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	3	4	4.25	3.83	3.1	2.5	1.66
200	7.83	8.1	9.83	8	7.33	6	4.5
300	11.66	13.5	14.5	9.5	7.66	6.83	5.66
400	18.5	19.66	22	15.1	12.5	8.33	6.83
500	19.33	20.83	22.5	17.66	13.5	11.25	9
600	20.83	22.66	25	20.33	17.83	13.83	10.83
800	23.1	25.83	28.25	24	20.25	17.83	14.66
1000	27.33	29.66	34.1	26	24.5	22.5	21

A.3.2.1.2- 10 kV

Permeate flow rate, ml/sec							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	3.66	4.5	5.25	4.66	3.83	3.25	2.1
200	9.25	9.75	12	10.5	8.66	7.25	6
300	13.66	15.5	16.33	11.33	8.83	8.25	6.75
400	21.83	23	25.5	18.1	15.5	10	8.33
500	22.83	24.83	26.5	21.66	16.5	13.66	11
600	25	27.25	30.5	24.66	21.5	16.83	13.25
800	28.25	32	34.66	28.83	26	21.75	19
1000	34	36.25	41.83	33	29.5	27.66	27

A.3.2.1.3- 25 kV

Permeate flow rate, ml/sec							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	3.83	5.1	5.83	5	4.25	3.5	2.5
200	10	10.5	12.33	10.83	9.25	7.83	6.5
300	14	16.25	17	12	9.5	8.83	7
400	22.5	25	26.5	18.5	16.25	11	8.66
500	23.5	27	28.1	23	17.5	14.66	12
600	26.25	27.83	30.83	25.1	22.5	17.5	14
800	29.5	33.1	35.66	30	27	24	20.66
1000	35.5	38	42.25	34.66	31	29	27

A.3.2.1.4- 50 kV

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	4.25	5.66	6.1	5.25	4.5	3.83	2.66
200	10.33	11.5	14	12.1	10	8.5	7.1
300	15	17	18.25	13	11	10.25	8
400	23.66	24.83	27.1	20.83	17	11.5	9
500	25.1	27	28.5	24	19.5	16.5	13
600	27.5	29.66	32	27	23.5	19.1	15
800	30.1	34	36.75	31	28.5	26	22
1000	36	38.1	42.5	35.5	31.66	29.5	28

A.3.2.1.5- 100 kV

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	4.75	6.1	6.83	6	4.83	4.1	3
200	11	12	14.66	12.1	11	9.5	8.33
300	16.5	19.25	20.33	13	11.1	10	9
400	30.5	32.5	35.25	24.5	21	14.1	11.5
500	32.5	34.5	37.1	29	23	19.5	15.66
600	35	37.66	39.83	31.66	29	22.1	17
800	42	44.25	46.66	40	33	27.66	24.5
1000	46.5	47.5	51.66	43	41	37.83	34

A.3.2.1.6- 200 kV

Permeate flow rate, ml/sec							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	6	6.83	8.66	7.33	6.25	5	3.33
200	14.5	15.83	18.5	15.66	14.5	12	9.1
300	22	24.33	26.5	18.5	14.5	13	11.25
400	32.83	36	38.5	31.5	24.5	15.83	13.5
500	37.1	39.5	42.75	34.5	26.66	22	18.1
600	39	46.5	51.5	44	37.5	27.66	21
800	50.83	61	66.83	59	49.1	44	38.5
1000	73.83	76.5	80.5	58	55.1	49.33	46.5

A.3.2.2- Permeate Flux Rate (L/m^2 hr)

A.3.2.2.1- No current

Permeate flux rate, J , l/m^2 hr							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	2805.2	3740.3	3974	3581.3	2898.7	2337.7	1552.2
200	7321.6	7574	9191.7	7480.5	6854	5610.4	4207.8
300	10902.9	12623.4	13558.4	8883.1	7162.6	6386.5	5292.5
400	17298.7	18383.4	20571.4	14119.5	11688.3	7789.1	6386.5
500	18074.8	19477.4	21039	16513.3	12623.4	10519.5	8415.6
600	19477.4	21188.6	23376.6	19009.9	16672.2	12932	10126.8
800	21600	24152.7	26415.6	22441.6	18935.1	16672.2	13708.1
1000	25555.3	27734	31885.7	24311.7	22909.1	21039	19636.4

A.3.2.2.2- 10 kV

Permeate flux rate, J, l/m^2 hr							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	3422.3	4207.8	4909.1	4357.4	3581.3	3039	1963.6
200	8649.4	9116.9	11220.8	9818.2	8097.7	6779.2	5610.4
300	12773	14493.5	15269.6	10594.3	8256.6	7714.3	6311.7
400	20412.5	21506.5	23844.2	16924.7	14493.5	9350.7	7789.1
500	21347.5	23217.7	24779.2	20253.5	15428.6	12773	10285.7
600	23376.6	25480.5	28519.5	23058.7	20103.9	15737.1	12389.6
800	26415.6	29922.1	32409.4	26957.9	24311.7	20337.7	17766.2
1000	31792.2	33896.1	39113.8	30857.2	27584.4	25863.9	25246.8

A.3.2.2.3- 25 kV

Permeate flux rate, J , l/m^2 hr							
	Filtration time, min						
Rpm	0	5	10	15	20	25	30
100	3581.3	4768.8	5451.4	4675.3	3974	3272.7	2337.7
200	9350.7	9818.2	11529.4	10126.8	8649.4	7321.6	6077.9
300	13090.9	15194.8	15896.1	11220.8	8883.1	8256.6	6545.5
400	21039	23376.6	24779.2	17298.7	15194.8	10285.7	8097.7
500	21974	25246.8	26275.3	21506.5	16363.6	13708.1	11220.8
600	24545.5	26022.9	28828.1	23470.1	21039	16363.6	13090.9
800	27584.4	30950.7	33344.4	28052	25246.8	22441.6	19318.4
1000	33194.8	35532.5	39506.5	32409.4	28987	27116.9	25246.8

A.3.2.2.4- 50 kV

Permeate flux rate, J, l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	3974	5292.5	5703.9	4909.1	4207.8	3581.3	2487.3
200	9659.2	10753.3	13090.9	11314.3	9350.7	7948.1	6639
300	14026	15896.1	17064.9	12155.9	10285.7	9584.4	7480.5
400	22123.6	23217.7	25340.3	19477.4	15896.1	10753.3	8415.6
500	23470.1	25246.8	26649.4	22441.6	18233.8	15428.6	12155.9
600	25714.3	27734	29922.1	25246.8	21974	17859.7	14026
800	28145.5	31792.2	34363.6	28987	26649.4	24311.7	20571.4
1000	33662.3	35626	39740.3	33194.8	29604.2	27584.4	26181.8

A.3.2.2.5- 100 kV

Permeate flux rate, J, l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	4441.6	5703.9	6386.5	5610.4	4516.4	3833.8	2805.2
200	10285.7	11220.8	13708.1	11314.3	10285.7	8883.1	7789.1
300	15428.6	18000	19009.9	12155.9	10379.2	9350.7	8415.6
400	28519.5	30389.6	32961	22909.1	19636.4	13184.4	10753.3
500	30389.6	32259.7	34690.9	27116.9	21506.5	18233.8	14643.1
600	32727.3	35214.6	37243.6	29604.2	27116.9	20664.9	15896.1
800	39272.7	41376.6	43630.1	37402.6	30857.2	25863.9	22909.1
1000	43480.5	44415.6	48305.5	40207.8	38337.7	35373.5	31792.2

A.3.2.2.6- 200 kV

Permeate flux rate, J , l/m^2 hr							
Rpm	Filtration time, min						
	0	5	10	15	20	25	30
100	5610.4	6386.5	8097.7	6854	5844.2	4675.3	3113.8
200	13558.4	14802.1	17298.7	14643.1	13558.4	11220.8	8509.1
300	20571.4	22750.1	24779.2	17298.7	13558.4	12155.9	10519.5
400	30698.2	33662.3	36000	29454.6	22909.1	14802.1	12623.4
500	34690.9	36935.1	39974	32259.7	24928.8	20571.4	16924.7
600	36467.5	43480.5	48155.9	41142.9	35064.9	25863.9	19636.4
800	47529.4	57039	62490.4	55168.8	45911.7	41142.9	36000
1000	69035.9	71532.5	75272.7	54233.8	51522.1	46126.8	43480.5

Appendix B

Demulsification Efficiency

B.1- Membrane MI

B.1.1- Emulsion EI

B.1.1.1- No current

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	19.6	9.5	13.25	34.9	29.4	9.3	13	11
4	23.5	24.77	26.5	42.6	39.2	23.4	22	19
6	31.4	38.1	35.3	46.5	45.7	30.4	34	36
7	54.9	55.2	58.3	58.9	62	63.1	63.3	66.8

B.1.1.2- 10 kV

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	18.5	13.6	11.8	33.8	25.7	22	16.5	18
4	29.6	31.8	15.8	40.5	34.3	38	34	31
6	44.4	40.9	31.6	50.7	45.7	52	55	27
7	55	56.4	58.5	59.5	62.9	64	64.1	68.4

B.1.1.3- 25 kV

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	17.2	35.3	26.3	25.5	39	31.6	21	20.5
4	34.5	44.2	37.5	38.3	44.4	43.4	41.5	38
6	51	57.4	45	54.3	55.6	55.3	57	60
7	55.2	57.4	59.6	60.7	63.9	64	64.5	68.8

B.1.1.4- 50 kV

Demulsification efficiency, *DE,* %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	15.1	16.7	14.6	24.2	10.7	9.6	13	13
4	45.2	29.2	32.9	39.4	26.8	21.2	22	25
6	51	33.3	43.9	48.5	42.9	34.6	38	44.5
7	55.7	58.3	58.6	61.8	64.3	64.6	66.2	68.9

B.1.1.5- 100 kV

Demulsification efficiency, *DE,* %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	13.2	27.6	33.9	37.2	36.3	23.2	26	28
4	39.5	37.9	49.4	41.9	48.4	50	48	49
6	57.9	60.7	61.7	63.3	66.6	67.9	68.6	69.4

B.1.1.6- 200 kV

Demulsification efficiency, *DE,* %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	10.7	44.4	42.9	30.8	16.3	9.5	14	14
4	32.2	52.8	61.9	48.1	35.9	22.6	26	28.5
6	60.1	63.9	64.8	64.4	66.9	67.9	69.3	69.6

B.1.2- Emulsion EII

B.1.2.1- No current

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	33.3	36.4	33.3	57.1	50	29.6	26	29.5
4	51	63.6	37.5	64.3	70.6	50.7	47	44
6	56.7	63.6	65	75	76.5	78.2	78.8	79.4

B.1.2.2- 10 kV

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	57.1	50	42.3	48.5	42.9	41.4	40.5	42.5
4	57.1	66.7	49.3	60.6	57.1	58.6	61	64
6	57.1	70.8	73.9	75.8	77.1	81	83.3	83.5

B.1.2.3- 25 kV

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	50	31.6	27.3	34.6	40.5	25.4	22	24
4	58.5	55.3	54.6	57.7	54.1	41.3	45.5	48.5
6	62.5	71.1	75	77.9	78.8	81	84	85.1

B.1.2.4- 50 kV

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	44.4	28.6	50	38.5	37.5	34	33	37.5
4	66.7	50	75	54.9	58.3	48.1	51.5	49
6	66.7	71.4	75	78	79.2	82.1	84.9	86

B.1.2.5- 100 kV

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	35.3	25	30.5	18.6	31.4	27.3	29.5	33
4	44	56.3	53.4	41.9	41.9	48.5	50	52
6	47.2	75	76.3	79.1	80.3	83.3	84.4	86.7

B.1.2.6- 200 kV

demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	26.5	29	36.9	25.6	40	27.1	29	31
4	35.3	38.7	46.2	43.9	47.5	45.8	46.5	52
6	74.2	77.4	77.6	80.5	81.3	83.3	86	86.7

B.2- Membrane MII

B.2.1- Emulsion EI

B.2.1.1- No current

Demulsification efficiency, *DE,* %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	27.3	25.6	23.1	35.2	25.5	21.4	24	28
4	41	51.3	34.6	42.2	51	37.5	38	40
6	41.5	51.3	34.6	56.3	57.3	42.9	44.5	44
7	43.7	51.3	52	59.9	60.5	62	64.4	66.1

B.2.1.2- 10 kV

Demulsification efficiency, *DE,* %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	25	22.7	21.7	26	23.1	25	26.5	26.5
4	47	34.1	27.2	45.5	34.6	37.5	41	43.5
6	50	45.5	43.5	52	46.2	58.3	60	48
7	50	56.8	59.8	61.7	63.5	65.8	67.1	68

B.2.1.3- 25 kV

Demulsification efficiency, *DE,* %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	45.5	22.2	28.6	18	27.5	24	18	26
4	46	55.6	28.6	24	33	32	29	33
6	47	57.25	38.1	48	49.5	44.5	40.5	47
7	54.5	57.8	61.9	64.8	65.9	66	67.4	68.3

B.2.1.4- 50 kV

Demulsification efficiency, *DE,* %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	40	32.2	26.5	10.5	25.9	32.7	22	21.5
4	51	32.2	53	26.3	38.8	38.5	37.5	39
6	52.5	42.9	61.8	42.1	54.3	46.2	51	54
7	56	59	63.6	65.8	67.3	67.3	68.1	69.3

B.2.1.5- 100 kV

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	36.4	17.2	25	20.8	32.1	21.9	23	28
4	54.5	42.9	33.3	33.3	42.9	53.1	42.5	44
6	63.6	64.3	66.7	66.7	67.9	68.8	69.5	70.3

B.2.1.6- 200 kV

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	27.8	16	19.2	33.3	27	25.4	23	28
4	41.7	48	44.7	44.4	43.8	43.2	49	46
6	63.9	68	70.2	70.4	70.8	71.2	71.2	71.3

B.2.2- Emulsion EII

B.2.2.1- No current

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	50	47.1	33.3	18.8	35.3	33.3	37	38.5
4	50	52.5	44.4	50	64.7	45.8	49	52
6	50	58.8	61.1	68.8	70.6	72.9	75	76.9
7								

B.2.2.2- 10 kV

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	44.5	32.2	19.6	32.4	25.9	25.8	27	30.5
4	48	42.9	49	48.7	51.8	54.8	51	55
6	50	59	63.7	70.3	72.5	74.2	75.8	77.9

B.2.2.3- 25 kV

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	53	39.2	26.5	26.8	24.2	24	26	29
4	53	49	53	48.2	58.1	39	40.5	46
6	61.8	62.7	66.3	72.3	72.6	75	76	78.3

B.2.2.4- 50 kV

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	53	37.5	25	15.4	18.2	20.6	23	22
4	55.5	65.7	66.7	51.3	40.9	47.1	49	51.5
6	61.8	65.7	70.8	74.4	75	75	77.1	79

B.2.2.5- 100 kV

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	48.4	23.1	15.4	34	20.7	12.7	19.5	22
4	64.5	46.2	38.5	49.1	37.9	35.6	40	43
6	64.5	69.2	73.1	75.5	75.9	76.3	77.3	79.2

B.2.2.6- 200 kV

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	25	34.5	30	27	20.8	15.4	24	29
4	62.5	55.2	42	33.7	35.7	42.3	40.5	44
6	68.8	72.4	75	75.9	77.2	77.9	78.2	79.4

B.3- Membrane MIII

B.3.1- Emulsion EI

B.3.1.1- No current

Demulsification efficiency, *DE,* %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	35.7	12.5	20.8	8.3	12.8	26.3	30	29
4	35.7	25	31.3	33.3	44.7	42.1	44.5	44
6	35.7	50	52.1	50	57.5	52.6	54	51.5
7	53.6	55	57.3	58.3	60.7	62.1	62.3	63.7

B.3.1.2- 10 kV

Demulsification efficiency, *DE,* %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	54.6	0	18.2	7.3	16.2	21.7	20	23
4	54.6	31.1	45.5	7.3	32.5	34.8	38	39
6	54.6	42.5	45.5	30.3	43.5	56.5	55	57.5
7	54.6	55.9	58.2	58.6	62.2	63.5	63.7	64.1

B.3.1.3- 25 kV

Demulsification efficiency, *DE,* %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	25	27.3	17.7	7	5.1	25	28	29
4	50	36.4	35.3	28.2	15.3	29.2	31.5	33
6	52	44	44.2	49.3	40.7	50	52	53
7	55	56.4	58.3	59.9	63.6	64.6	65	65.6

B.3.1.4- 50 kV

Demulsification efficiency, *DE,* %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	23.5	25	22	12.1	18.2	23.1	22	22
4	30.5	50	29.3	30.3	40.9	26.9	29	33
6	35	50	51.2	34	50	38.5	40	43.5
7	56.5	58.3	58.6	60.6	63.6	64.6	65.9	66.3

B.3.1.5- 100 kV

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	22.5	28.6	20.7	10.5	20	37	38	38.5
4	44.4	35.7	41.4	42.1	56	48.1	49.5	41
6	57.8	58.6	58.6	61.1	64	64.8	65.5	66.4

B.3.1.6- 200 kV

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	18.8	38.7	22.2	30.4	9.7	16.7	18	22
4	37.6	45.2	44.4	52.2	41.9	25	26.5	30
6	60.2	61.3	63.9	65.2	65.2	65.3	66.2	67.1

B.3.2- Emulsion EII

B.3.2.1- No current

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	22	33.3	26.5	36.6	44.4	18.5	21	21
4	40.5	55.6	53	58.6	50	46.2	47	53
6	54.2	61.1	61.8	73.2	75	76.2	78.4	78.6

B.3.2.2- 10 kV

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	47.6	16.7	22.2	12	18.2	22.6	24	24
4	52	41.7	66.7	36	45.5	64.2	51	53
6	57.1	62.5	66.7	73.2	75	77.7	78.9	79.6

B.3.2.3- 25 kV

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	60	15.4	42.9	46.2	29.2	7.1	18.5	22
4	60	46.2	50	52	41.7	32.1	38	43
6	60	65.4	67.9	75.1	77.1	78.6	79.9	80.6

B.3.2.4- 50 kV

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	37.6	28.2	37.5	22.2	26.9	26.7	29	29
4	56.4	49.3	62.5	33.3	38.5	43.3	45	47
6	65.8	70.4	71.9	77.8	78.8	80	81.8	83

B.3.2.5- 100 kV

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	33.3	24	27.8	39.1	19.2	32.4	33	27.5
4	50	36	44.4	47.8	25.5	47.1	62.5	50.5
6	66.7	72	72.2	78.3	79.8	80.9	82.7	83.1

B.3.2.6- 200 kV

Demulsification efficiency, *DE*, %								
Time, hr	Rpm							
	100	200	300	400	500	600	800	1000
0	0	0	0	0	0	0	0	0
2	45	33	17.8	11.1	16.6	23.8	27.5	29
4	60	38.5	40	44.4	38.7	52.4	54	51
6	72.1	72.5	73.3	79.6	80.1	81	83.8	84.4

Appendix C

The Experimental Rig

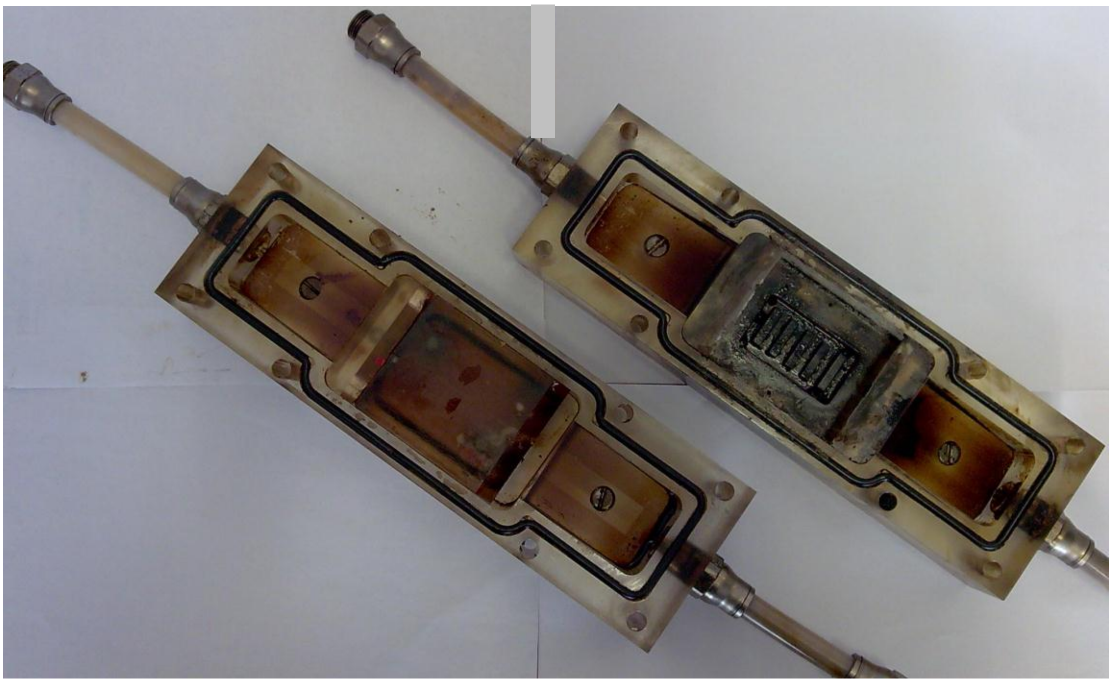


Fig. (C.1): A photograph of the inside of the electrofiltration cell.

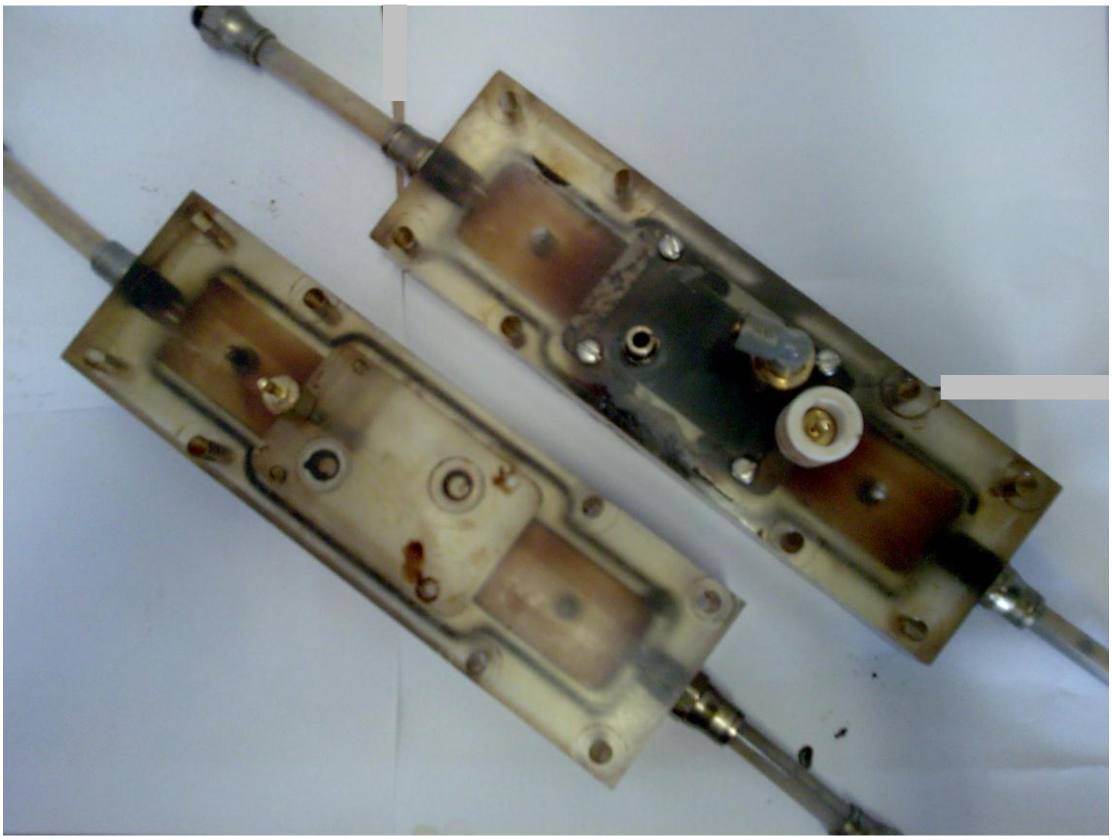


Fig. (C.2): A photograph of the outside of the electrofiltration cell.

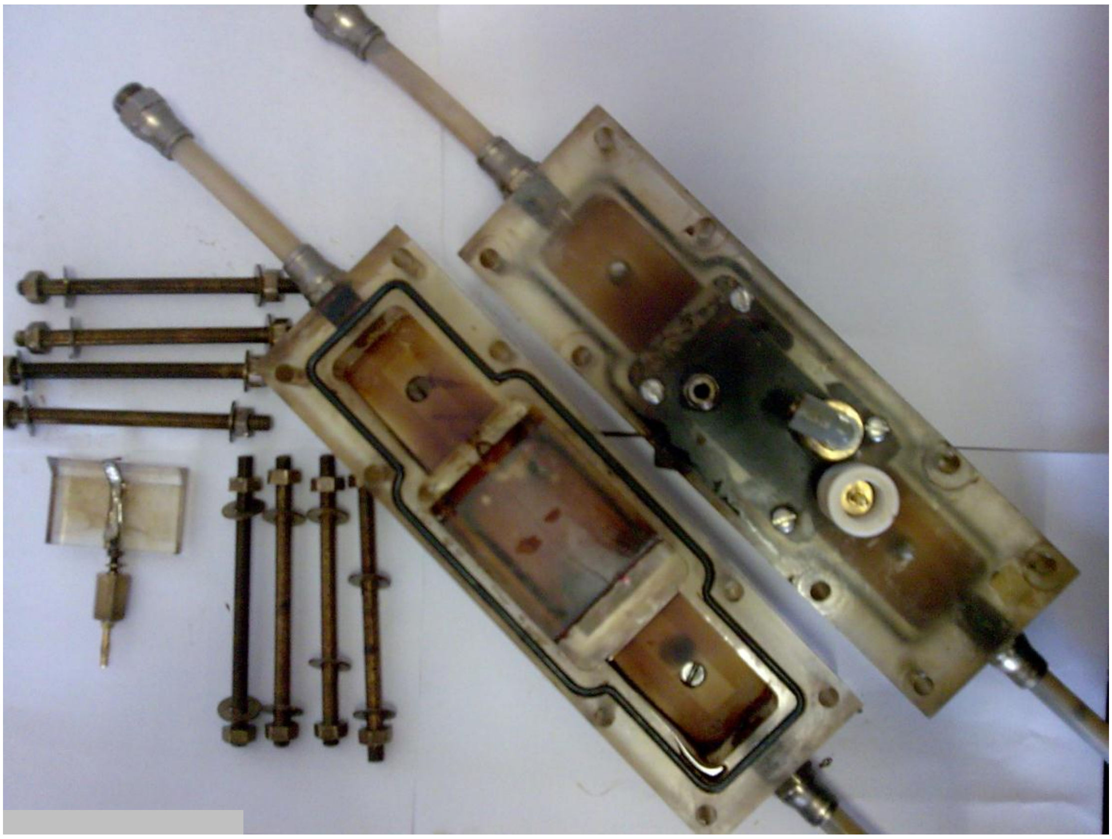


Fig. (C.3): A photograph of the inside of the electrofiltration cell along with the other components.

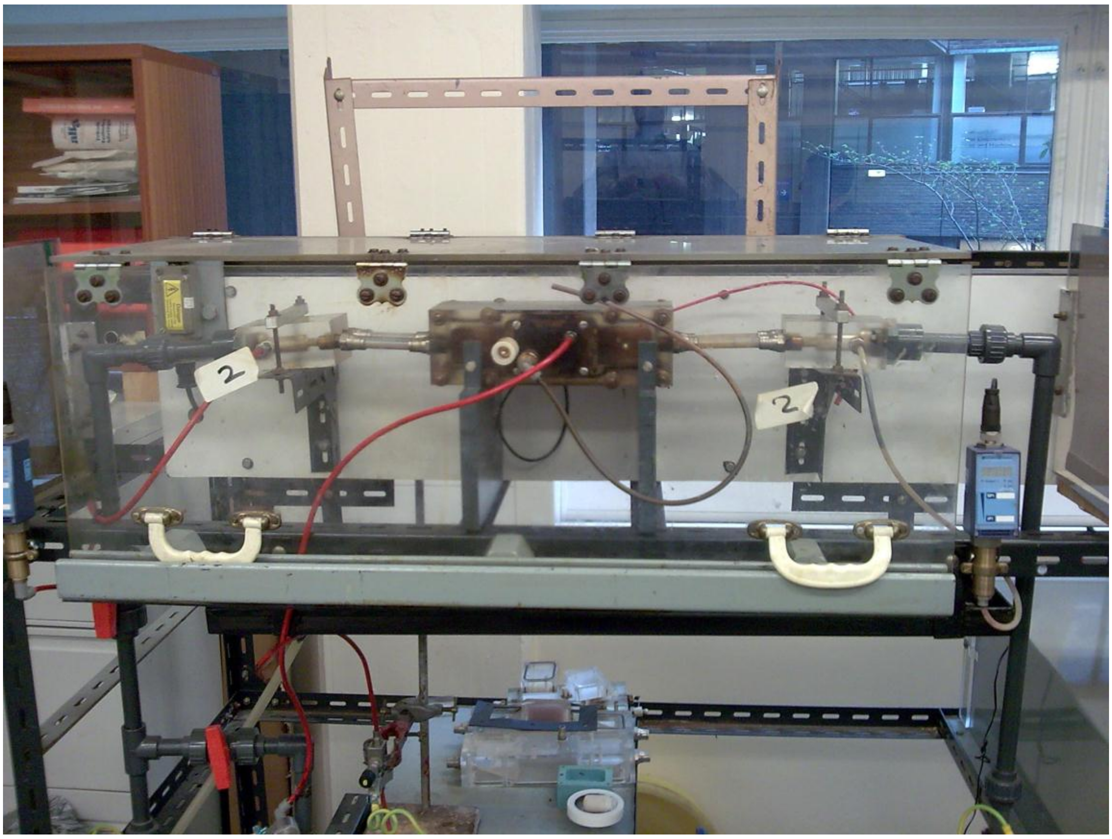
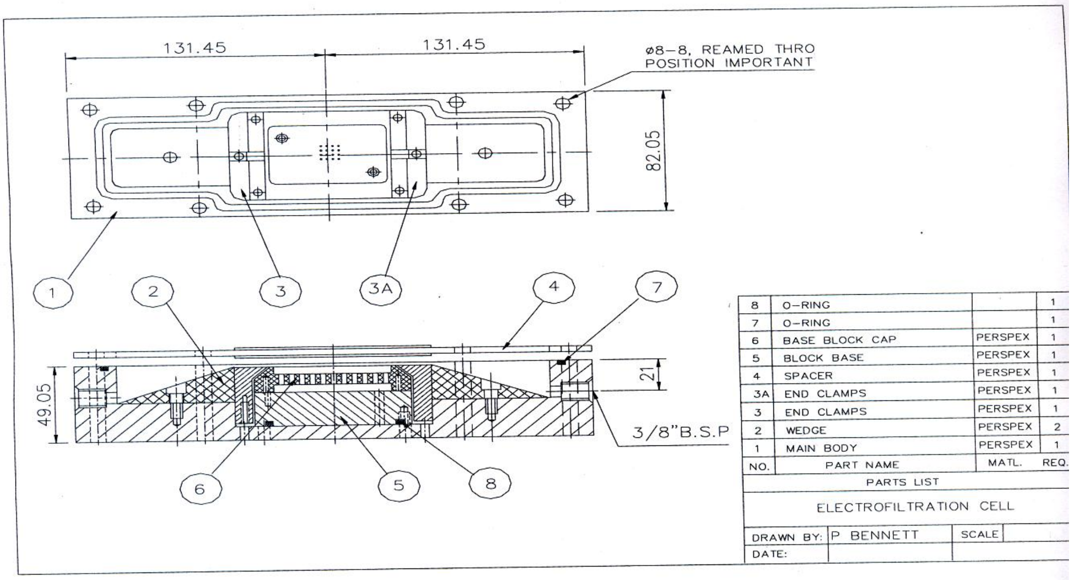


Fig.(C.4): A pictorial representation of the experimental rig.



NO.	PART NAME	MATL.	REQ.
8	O–RING		1
7	O–RING		1
6	BASE BLOCK CAP	PERSPEX	1
5	BLOCK BASE	PERSPEX	1
4	SPACER	PERSPEX	1
3A	END CLAMPS	PERSPEX	1
3	END CLAMPS	PERSPEX	1
2	WEDGE	PERSPEX	2
1	MAIN BODY	PERSPEX	1

PARTS LIST

ELECTROFILTRATION CELL

DRAWN BY: P BENNETT SCALE

DATE:

Fig. (C.5): Engineering drawing of the electrofiltration cell.

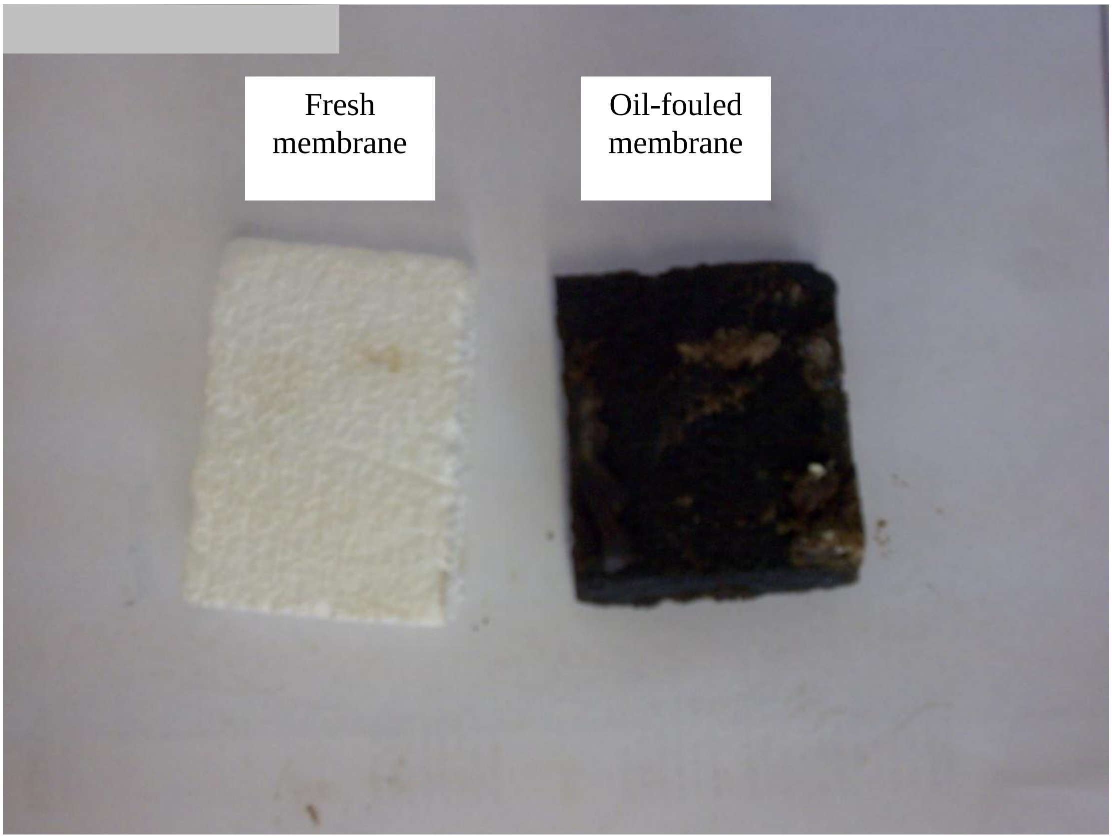


Fig. (C.6): A photograph of both fresh and oil-fouled membranes.