

The preparation and characterisation of hydrophobic
polymeric membranes for use in the separation of liquid
mixtures using pervaporation separation processes

A thesis presented for the degree of Master of Science

by

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August 1998

I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of M Sc in Chemistry is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work

Signed Susan Byrne

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Date 28th August 1998

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Acknowledgements

I would like to take this opportunity to thank my supervisor in the Dublin Institute of Technology, Kevin Street, Mr Paul Ashall for this expertise and guidance throughout the course of the project. I would also like to express my gratitude towards all the staff of the School of Chemistry, especially Dr Eilish O'Donoghue and the laboratory technicians.

Special thanks to Dr Odilla Finlayson of D C U for taking time out of her schedule to supervise this project in D C U. To Dr Aine Allen at Tallaght RTC for her patience and kindness in providing me with some great SEM images.

Finally, I would like to acknowledge the support shown to me by my family and friends. A particularly large thank you to my Mum, Dad, Maura and Ben.

Abstract

Pervaporation is a membrane separation process used to separate liquid mixtures. Separation is achieved by establishing a concentration vapour-pressure gradient across the membrane.

Polyurethane (PU) and polydimethylsiloxane (PDMS) membranes were prepared from their prepolymers by solution casting. Dilute aqueous solutions of ethyl acetate, methyl isobutyl ketone, methyl ethyl ketone and aniline were separated using these polyurethane and polydimethylsiloxane polymeric membranes at temperature ranging from 50 to 80°C. The effects of the systems operating temperature was studied.

The separations were characterised and examined by the effect of temperature on the composition of the retentate and permeate samples taken during the separation process. Gas chromatography was used to analyse the resulting retentate and permeate samples.

Extensive physical characterisation of the membranes was carried out using a number of techniques including Scanning Electron Microscopy, gravimetric sorption experiments, Differential Scanning Calorimetry.

A combination of the physical examinations and the pervaporation data was used to evaluate the membranes performances in the separation of all four solutions within the temperature range examined.

Higher selectivity values were obtained for separations carried out using the polydimethylsiloxane membrane whereas higher flux values were achieved using the polyurethane membranes.

The most successful separations, based on selectivity and flux values, was deemed to be the separation of methyl isobutyl ketone and water at 80°C using the polydimethylsiloxane membrane, PDMS1, with selectivity and flux values reaching 774 and 0.400 kg/m²hr, respectively

Some of the physical characteristics of the membranes which were examined, such as the activation energy of permeation and the glass transition temperature, were found to be unsuitable for use as prediction methods for the performance of a particular membrane/liquid mixture system. The most preferable membrane preparation conditions were also isolated during the course of this study with the aid of scanning electron microscopy images.

1. Introduction

1.1 Pervaporation - a definition

Pervaporation is a membrane separation process which may be characterised by the imposition of a barrier (in this case a membrane), between a liquid and vapour phase ^[1] Separation is achieved by applying a lower pressure to the permeate side of the membrane whilst the other side is exposed to the liquid to be separated The practical pressure of permeate vapour is thus kept lower than the saturation vapour pressure and provides the necessary driving force for separation Mass transfer occurs selectively across the membrane to the vapour side ^[2] Since different species permeate through the membrane at different rates, a substance which is at low concentration in the feed stream can be highly enriched on the vapour, or permeate, side of the membrane ^[3]

1.2 Historical Background of Pervaporation

The phenomenon of pervaporation was first observed in 1917 by Kober when he described an observation that a 'liquid in a collodian* bag, which was suspended in the air, evaporated despite the bag being tightly closed' Kober also reported that some less volatile components of the mixture permeated faster through the collodian wall than more volatile ones He concluded that this process could be used for the separation of liquid mixtures, such as azeotropes ^[4]

* Collodian - a thin film of cellulose nitrate made by dissolving the cellulose nitrate in ethanol or ethoxyethane, coating the surface and evaporating the solvent

In the 1960's, Binning et al reported the use of pervaporation for the dehydration of a ternary azeotrope of isopropanol, ethanol and water from the overhead product of a distillation column. However, despite investigating and developing several membranes for a variety of separation problems, pervaporation was relatively forgotten about for the next decade [5]

It was not until the energy crisis of the 1970's and a renewed interest in novel separation techniques, that research attention was refocused on pervaporation. Pervaporation research was aggressively pursued in Europe as the process showed an ability to dewater aqueous mixtures of alcohols with the intention of utilising the recovered alcohols as an alternative fuel source. In the mid 1970's, GFT commercialised an economical pervaporation process for dehydrating ethanol, producing high purity ethanol rivaling the azeotropic distillation process [1]. In 1982, the first commercial pervaporation plant began its operation in a small alcohol distillery in Brazil [6]

1.3 Membrane Separation Processes

A membrane is a permeable or semi-permeable phase, polymer or inorganic barrier, which restricts the motion and transport of certain species [1]. The membrane controls the relative rates of transport of various species through itself, and thus, as with all separations, gives one product depleted in certain components and another product concentrated in these components. The performance of a membrane is defined in terms of two simple factors, flux and selectivity. Flux or permeation rate is the volumetric (mass or molar) flowrate of fluid passing through the membrane per unit area of membrane per unit time. Selectivity is a measure of the relative permeation rates of

different components through the membrane ^[1] Ideally a membrane with a high selectivity and high flux is required, although typical attempts to maximise one factor are compromised by a reduction in the other ^[2]

Membranes may be used for a number of separations in industry the main examples of which are

- (i) Microfiltration - the filtration of micron and submicron size particles from liquids and gases (MF)
- (ii) Ultrafiltration - the separation and concentration of macromolecules and colloidal particles (UF)
- (iii) Pervaporation - the separation of mixtures of miscible liquids (PV)
- (iv) Gas & Vapour Permeation - the selective separation of mixtures of gases and vapour and gas mixtures (GP & VP)
- (v) Electrodialysis - the selective transport of only ionic species (ED)
- (vi) Reverse Osmosis - the virtual complete removal of all material, suspended and dissolved, from water or other solvents (RO)

The transport of selected components through a membrane is achieved by applying a driving force across the membrane This is the main feature by which membrane separation processes are characterised The flow of material across a membrane is kinetically driven by the application of either mechanical, chemical, electrical or thermal work The following table (*Table 1 3 1*) lists the main separation processes, their driving forces and some of their common applications The development of many pervaporation systems has been derived from some of these analogous membrane separation technologies which have been researched for other specific separations ^[7]

Table 1 3 1 Driving forces and applications of established membrane separation processes

Separation Process	Driving Force	Applications
Microfiltration	Hydrostatic Pressure	Clarification, sterile filtration
Ultrafiltration	Hydrostatic Pressure	Separation of macromolecular solutions
Nanofiltration	Hydrostatic Pressure	Separation of small organic compounds & selected salts from solutions
Reverse Osmosis	Hydrostatic Pressure	Separation of micro-solutes & salts from solutions
Dialysis	Concentration Gradient	Separation of micro-solutes & salts from macromolecular solutions
Pervaporation	Concentration Gradient Vapour Pressure	Separation of mixtures of volatile liquids in solution
Vapour Permeation	Concentration Gradient	Separation of volatile vapours from gases and vapours
Electrodialysis	Electrical Potential	Separation of ions from water & other solutes

As may be seen in *Figure 1 3 1*, the pore sizes in the membrane produced are instrumental in deciding the area of their use in membrane separation processes ^[7]

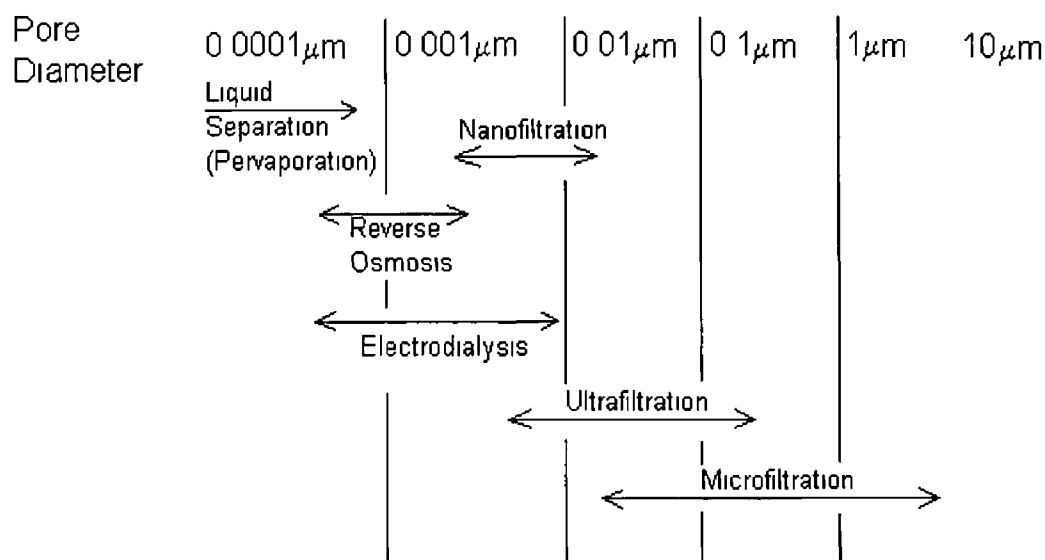


Figure 1 3 1 An overview of the pore sizes of membranes used in various separation processes

1 4 Other Applications of Pervaporation

The main use of pervaporation in recent years has been it's successful application to the separation of two component liquid mixtures containing water. In the past such mixtures, e.g. azeotropic or liquid mixtures comprising of components which have close boiling points, have either never been separated or have been separated with great effort by conventional methods such as distillation, or extraction ^[8]. However, there are a number of potential applications for pervaporation which have been highlighted in recent years, the most promising being the dehydration of organic mixtures ^{[9],[10]}, the removal of organic liquids from waste water ^[11], the separation of organic/organic liquid mixtures

[12] [8] and the introduction of pervaporation processes into production processes in an attempt to increase product yields and conversions and reduce waste [13] [14]

The use of pervaporation in the dehydration of aqueous mixtures has broadened the scope of separation techniques [15] by, in some cases, eliminating the need for azeotropic distillation because of lower investment and operating costs along with drastically reduced environmental problems as the use of entrainers such as benzene are not required. Another advantage of using pervaporation in some selected separation processes over and above its relatively lower operating and capital costs and environmental benefits is its simplicity of operation.

Pervaporation has found application in many industrial processes where conventional separation techniques, such as rectification or azeotropic distillation, would normally be used [6]. It has been integrated into many currently operating industrial systems but it is mainly incorporated into already existing processes to overcome difficult stages of a separation, i.e. azeotrope limitations in distillations. It is rarely used as an isolated method but rather as part of a hybrid separation system in conjunction with other separation processes [13].

Azeotropic distillation

An example of the application of pervaporation to such a process is in the production of anhydrous ethanol. Ethanol production is usually based on either fermentation or on synthesis methods such as the sulphuric acid process or the direct catalytic hydration of ethene.

A fermented ethanol product is typically 8 to 12% by volume, which after several stages of distillation to rectify and purify the product, is

produced as a near azeotropic mixture. Anhydrous ethanol for chemical and fuel use is obtained typically by azeotropic distillation using benzene or/and trichloroethane. The direct hydration route uses extractive distillation in a similar manner to the fermented product.

Azeotropic distillation is a relatively costly procedure and in addition there is some concern on environmental and safety and health grounds over the use of some of the dehydrating agents previously mentioned. Pervaporation is considered to be an appropriate and competitive replacement for azeotropic distillation in the production of anhydrous ethanol. A product of 99.5% by volume ethanol is produced and a permeate, containing a relatively high percentage of ethanol, which is recycled back to distillation [16].

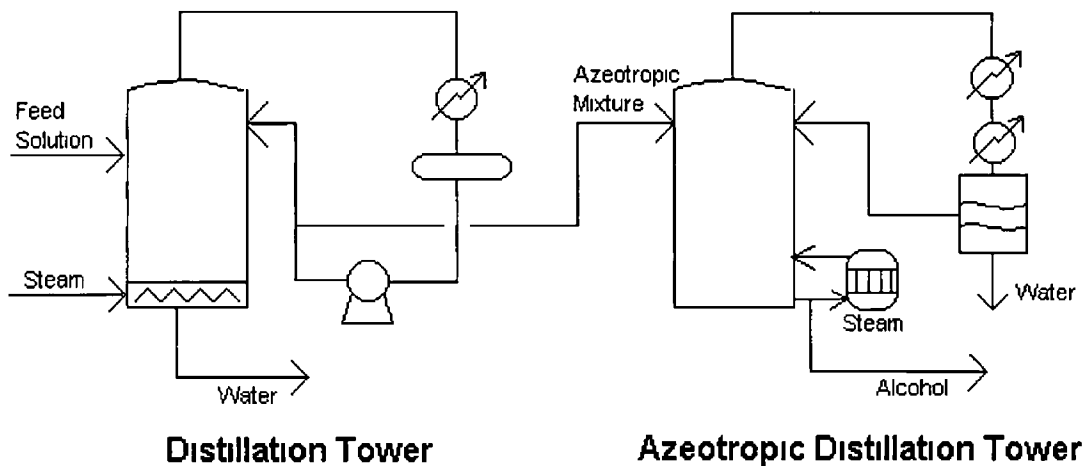


Figure 1 4 1 Schematic representation of the production of anhydrous ethanol incorporating an azeotropic distillation tower

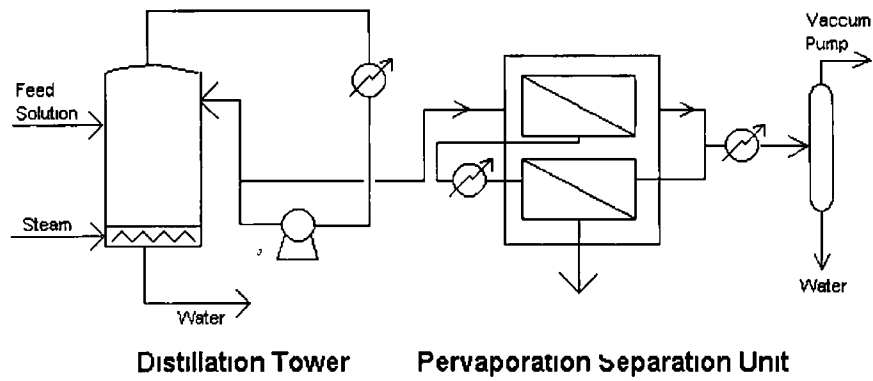


Figure 1 4 2 Schematic representation of the production of anhydrous ethanol incorporating a pervaporation separation unit

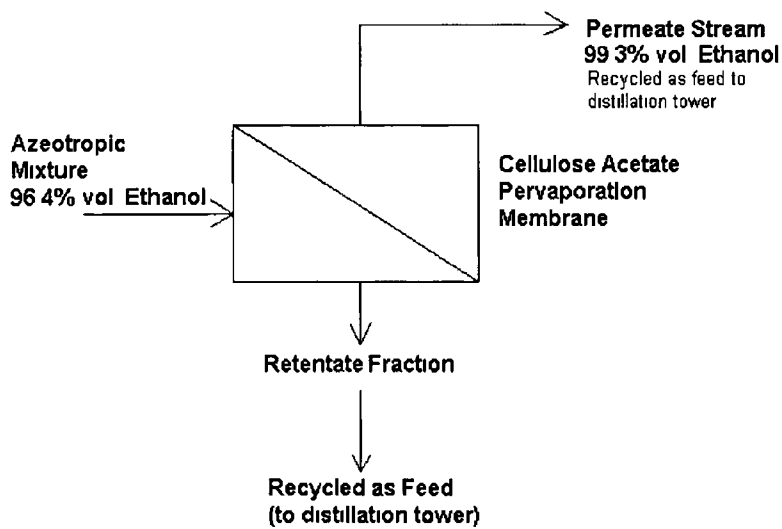


Figure 1 4 3 Detailed illustration of the pervaporation unit utilised in the process shown in Figure 1 4 2

Pervaporation in reactor processes

Pervaporation can be introduced into many processes such as its implementation at various points into pharmaceutical production for either of two reasons, the first being to increase the yield of the desired final product by removing the product as it is produced and secondly to reduce environmental problems. An example of the former being the separation of mixtures from reactors in chemical processes [11] [17]. This process can often represent the main cost of production. In this area, the classical unit operations such as rectification, adsorption and extraction are dominant. Separation by membranes as a possible alternative compared to classical unit operations, has gained interest in recent years. For example, Brandt and Adelman [18] have documented the use of pervaporation using 'Nafion[®]' perfluorinated membranes as a method of increasing the capacity of a conventional acetic acid recovery step in a vinyl acetate polymerisation process.

Separation of Miscible Liquid Organic Solutions

However, it is not just aqueous mixtures that can be separated using pervaporation. A considerable amount of research has also been carried out into the separation of organic/organic mixtures and more specifically aliphatic/aromatic mixtures. Some examples of organic/organic separations are given in *Table 1.4.2*.

Pervaporation has been applied to the area of organic/organic separation where aromatic organics are separated from aliphatic hydrocarbons an example of which being the removal of toluene from cyclohexane using polyurethane membranes [19].

Table 1 4 2 Membranes used to separate mixtures of aromatic and aliphatic organic liquids

Membranes	Mixture Separated
POUA*** [20]	Benzene/n-hexane
Polyethylene / Polypropylene [8]	Benzene/methanol
Polyurethane (PU) [12]	Cyclohexane/benzene

*** POUA - Poly(oxiethylene urethane acrylate)

Other materials have also been utilised in pervaporation membrane preparation such as ceramics and co-polymers [21], [22] Fillers have also been incorporated into membranes to enhance the permeation of one component in a mixture over another e.g cyclodextrins in PVA [23] and zeolites in PDMS [24] However, for the purpose of this study the membranes which will be examined are composed of elastomeric polymers

Combination of organic separation and reactor processes

An interesting example of pervaporation applied to organic/organic separations combined with incorporating pervaporation into reactor processes is in the production of methyltertiary butyl ether (MTBE) from methanol and isobutene (C₄)

This process produces a reactor product mixture of all three components of which both the methanol and ether and methanol and C₄ form azeotropes A process has been developed in which pervaporation is integrated into the system to separate out the methanol and recycle it back to the reactor The membrane used is made from cellulose acetate This cellulose acetate membrane has a separation factor for methanol from MTBE of over 10,000 because the

material is hydrophilic and methanol is more polar and hydrophilic in character than MTBE or the isobutene ^[16]

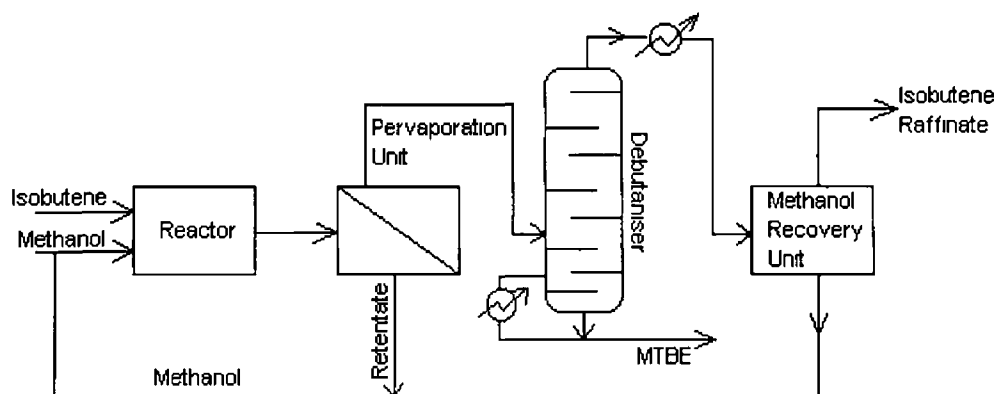
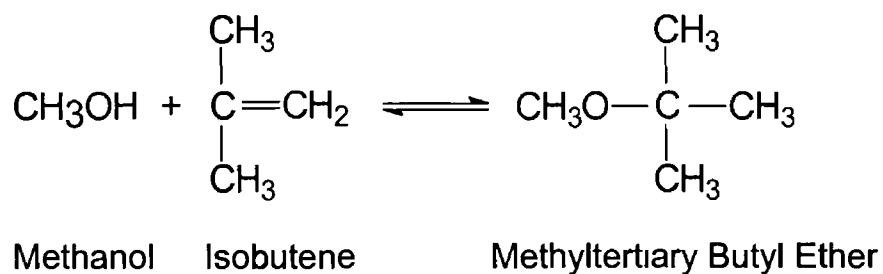


Figure 1 4 4 Schematic representation of the production of methyl tertiary butyl ether from methanol and isobutene with a pervaporation unit in place before the butaniser

Advantages & disadvantages of pervaporation

The commercial application of pervaporation processes still faces some competition from more conventional separation techniques. As already mentioned, distillation is the technology that pervaporation most frequently competes against. Despite the advantages of pervaporation over distillation, from a scale-up point of view, distillation is difficult to compete with because such systems are fully optimised and scale-up is cheaper than scale-up in membrane systems. This factor is also coupled with the fact that pervaporation is generally not as economically viable as a multi-stage separation process [2]

For large scale plant operations, one of the biggest problems is system reliability to such an extent that many plant managers may only consider a technology which has been proven in the field for at least a year [25]. Other plant design factors must also be considered such as membrane maintenance and the tendency for membrane fouling (*Section 1.6*), as well as the extensive pre-treatment which is required in order to ensure that the liquid mixture being separated is not excessively aggressive to the membrane.

The main advantage of pervaporation is that once the initial capital costs have been invested, the operation costs of the system is considerably less than other processes. The reason for this is that the energy consumed during the separation process is reduced as only the portion of the mixture which is to permeate the membrane must be vapourised.

1 5 Solvent Recovery

Solvents are an integral part of many manufacturing processes across a wide range of industries. In the past, treatment and disposal practices for most volatile waste solvents have been subject to minimal regulations. The situation is now changing due to concerns over pollution and industrial safety. With the introduction of new legislation, such as the Waste Management Act, 1996, a serious impact has been made on the way in which wastes, from car batteries to complex mixtures of hazardous chemicals, may be transported, treated and disposed of ^[26]. As a result, producers of waste are involved in a continuous search to find alternatives to their current disposal methods which are both cost-effective and which comply with the requirements of the Act and their local regulatory authorities.

With current European Commission restrictions on the transfrontier shipment of wastes already in place, of all the EC countries producing wastes, Ireland faces perhaps the greatest short-term problem. With the introduction of this legislation and the current lack of sufficient disposal and recovery facilities in this country, the development of economically viable in-house techniques will be beneficial to a large number of industries. This is even more significant when the statistics for the recovery and disposal of waste in this country are examined. From the current data available, it may be seen that the disposal of industrial waste (82.6%) still takes precedence over the recovery of waste (17.3%) in this country. EPA data suggests that current levels of disposal are high, however, little information is available regarding the extent of on-site recovery which takes place in this country ^[27].

Due to ever increasing economic and legislative restrictions on the treatment of wastes, considerations of how waste products may be

dealt with has become an integral part of the development of new industrial processes. This is particularly so when biological treatment may be involved since long residence times and therefore, large site areas may be required. Some solvents e.g. dimethyl sulphoxide, can give rise to unacceptable odour nuisances when disposed of biologically and others may have high BOD's and long lives even in the most active conditions ^[28]. As a result, the obvious environmental benefits associated with the removal of solvent from waste water is not always counter-balanced by an economic benefit to the re-processor.

Regardless of the type of recovery or disposal a waste producer may decide to employ, it is almost impossible to isolate a general purity level which is applicable to all discharges. This is due to the variety of volumes of disposed materials, disposal destinations and the requirements of the various regulatory authorities. For example, despite the fact that offenders may be prosecuted or fined according to the Waste Management Act, the main function of the Act is to ensure that waste producers keep up-to-date, accurate records of waste produced and of its disposal for inspection by the relevant local authority. Due to the requirements of these authorities differing from county to county, a national overview of the acceptable levels of hazardous discharge permitted is not easily attainable.

1 6 Alternative Methods of Recovering Organic Liquids from Water

Some of the most commonly used processes leading to possible recovery of solvents from dilute solutions are ^[16]

- 1 Decanting or Phase Separation
- 2 Solvent Extraction
- 3 Membrane Separation
- 4 Adsorption
- 5 Air Stripping
- 6 Steam Stripping

Phase Separation

One method of separating organics that are only sparingly soluble in water is decanting. To minimise the contamination of the water, it is vital that uncontaminated water is not exposed to the organic and so phase separation of the organic from the water is carried out as near to the source as possible. However, this particular method is only suitable in cases where the organic is present in quantities in excess of its solubility limit in water e.g. the solubility of ethyl acetate at 25°C in water is 7.7%w/w ^[16] so a mixture of composition 20%w/w ethyl acetate in water will exist as two phases and so decanting may be suitable as a possible method of separation and decanting also does nothing to remove materials in solution. Decanting may also be considered appropriate in a hybrid process e.g. where a membrane separation process is used to produce a permeate sample rich in organic, the organic phase being decanted off and the aqueous layer being recycled for further treatment through the membrane.

Extraction

There are a large number of common organics that can be extracted from their aqueous solutions to a level that would allow discharge to biological treatment on site or into municipal sewers

An example of the use of solvent extraction for cleaning up contaminated water occurs in the recovery of ethyl acetate vapour from air with an activated carbon bed. When the bed is steam heated for regeneration, the ethyl acetate is recovered along with the hydrolysis products produced by the heating of the ethyl acetate i.e. acetic acid and ethanol

After the removal of the acetic acid and the majority of the ethanol by contacting the water phase with a hydrocarbon such as C₁₀ n-isoalkane. The acetic acid and the alcohol from the aqueous phase remain in the hydrocarbon phase. However, aqueous streams containing appreciable concentrations of organic contaminants present problems when using solvent extraction as a clean-up technique. Once the organic content of the aqueous phase has been removed, contaminants which are insoluble in water build up in the extraction solvent [16]

Adsorption with Activated Carbon

Activated carbon is very widely used, often in a final polishing step, to reach the high purities demanded of effluents for discharge. It is a flexible technique capable of being applied to one-off situations such as spillages, which cannot be satisfactorily dealt with by biodegradation [29]

Treatment on a fairly small scale can be carried out batchwise using powdered activated carbon stirred in contact with the effluent which is

removed by filtration when spent. Used activated carbon of this sort is seldom regenerated on site and usually has to be disposed of by landfill dumping along with its associated filter aids. This technique is also used as a final stage in solvent recovery as a means of removing unacceptable colour from the recovered solvent.

Activated carbon is more effective at removing high-boiling non-polar solvents from water. It is noticeable in practice that whereas regenerated activated carbon maintains its overall adsorption capacity it is poor at adsorbing low-boiling solvents such as 1,1,1-trichloroethane [25]

Air Stripping

Many organics can be removed from waste water by air-stripping, to a level at which the water is fit to discharge according to the relevant by-laws. This applies particularly to solvents that have a low solubility in water or a high volatility with respect to water. In extreme cases, a comparatively short residence in a shallow lagoon can result in the evaporation of a large proportion of the solvent present. Many biological treatment plants rely on the evaporation of volatile solvents for an appreciable part of their effect.

Solvents in low concentrations have no effect on each other as far as air-stripping is concerned and can be treated individually in calculating their rate of air-stripping [25]

Steam Stripping

The disadvantage of air-stripping as a means of solvent recovery has been shown to be the low concentration of solvent in the effluent air, which poses a problem in recapturing the solvent. Steam stripping, although requiring a more elaborate plant for stripping the solvent from

waste water, needs much simpler equipment for trapping the stripped solvent

The steam costs are modest provided that good heat exchange can be maintained between the hot stripped water being discharged and the feed to the stripper. However, steam stripping is not suitable for the water-miscible high-boiling solvents [30]

1 7 Economics of the Recovery of Organic Liquids from Water

Three factors contribute to the economics of removing solvent from waste water. The water itself may have a positive value that can vary widely depending on how plentiful it is and how pure the cleaned up aqueous effluent needs to be for use as a substitute for purchased water for recycling. If the recovered water is to be used as cooling tower make-up, its passage through the cooling tower may form part of its treatment. On the other hand, the presence of dissolved chloride salts may prevent water that has been thoroughly cleaned of its organic impurities from being used industrially.

The solvents to be removed from the waste water may represent an economic asset or liability. It is unlikely that the solvents arising from water clean-up will be fit for reuse. Further purification is usually necessary unless the treatment is close to the point of source and therefore as free as possible from further contamination. In the worst case, such as the cleaning of ground water contaminated with a variety of solvents, it may be necessary to dispose of the removed solvents by land-filling of the spent activated carbon or by incineration of the solvents.

Some relatively cheap solvents such as hydrocarbons and chlorinated solvents form such dilute aqueous solutions that unless they can be recovered by decantation, their recovered value, even if fit for immediate use is trivial ^[16]

An example of an organic liquid which is attractive to remove from water is benzene due to its high solubility in water. However, benzene is generally only used when extremely pure and therefore extra costs will probably be incurred in working up for reuse ^[31]

Organic solvents that are soluble in water can have large recycled values when stripped out, but because of the subsequent purification costs and the large range of possible concentrations in the waste water, no helpful indication of the possible economics can be made. It will be clear when considering the costs of stripping that it is possible for the value of the recovered solvent to cover the expense incurred in the removal of the pollutant from the effluent

It is a well established fact that air-stripping is the cheapest removal technique with costs, depending on the concentration of solvent left in the water, of US\$0.1-0.3 per cubic metre of water treated ^[16]. The capital cost is low but there is little possibility of credit for recaptured solvent and the air contamination, in many cases, may be unacceptable

Supplementing air-stripping with an activated carbon unit for removing solvent from the air emission results in an increase in cost of about \$0.4 per cubic metre but a credit for recovered solvent may offset that ^[31]

The use of disposable powdered activated carbon to remove non-volatile solvents (and other high-boiling organic contaminants) from the air-stripped water is likely to raise the water to reusable quality but yields no further recovered solvent. In addition, cost is incurred for disposal of spent carbon. Costs will be affected by the value of the pollutant removed by the activated carbon but a further outlay of \$0.4-0.5 per cubic metre would be realistic. Thus the cost of a combination of air-stripping, liquid-phase polishing with activated carbon and recapture of solvent from the air with activated carbon will total \$1.0-1.2 per cubic metre less any credit for solvent and water [5]

Pervaporation is more expensive than any of these techniques at about US\$2 per cubic metre before allowing for solvent credits, however, it is a comparatively new method. It has been proposed since the first development of pervaporation as a method of removing organic liquids from water, that with developments in membrane materials, its cost will decrease, whereas air-stripping and activated carbon treatment, are by comparison well tried and mature. Steam stripping is also long established and its cost is very dependent on the relative volatility of the solvent being stripped from the water. Solvent extraction, since it involves a stripping stage, albeit under very favourable conditions, is likely to cost between the best and worst air-stripping figures [16]

1.8 Liquid mixtures to be separated

The liquid mixtures selected for examination were not chosen randomly. The organic components of these mixtures are three commonly used solvents and the fourth being a raw material in many industrial processes. Another reason for the choice of these organic liquids is that they exhibit relatively high biological oxygen demands (BOD's) at low concentrations which result in an increased environmental impact on a discharge watercourse if they are expelled out of a process facility and if reprocessed, tend to place an increased load on the effluent treatment plant being employed ^[16]

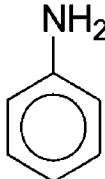
These liquids were also chosen as the main objectives of this study was to examine the separation of basic two component liquid mixtures of substances which are commonly expelled as waste or by-products from industrial processes. All the of the organic liquids, as 1% w/w aqueous solutions, examined in this study may be classed as Category II, Hazardous Wastes according to the Waste Management Act, 1996 and the Hazard Waste List, 1994.

Some relevant physical and chemical data is given in *Table 1 8 1* and a brief description of their industrial uses, chemical structure and physical appearance are given in *Table 1 8 2*.

Table 1 8 1

Compound X	Sol of X in H ₂ O (%w/w at 25°C)	Sol of H ₂ O in X (%w/w at 25°C)	Azeotrope of X with H ₂ O		BOD of pure liquids (mg/dm ³)
			Temp (°C)	%w/w X	
Ethyl Acetate	7.7	3.3	70°C	92	1.2
Methyl Isobutyl Ketone	1.7	1.9	88°C	76	2.06
Methyl Ethyl Ketone	26.0	12.0	73°C	89	2.14
Aniline	3.5	5.0	-	-	2.54

Table 1 8 2

Compound	Common Uses	Structure	Physical Description
Ethyl Acetate [32]	Solvent for varnishes, nitrocellulose & lacquers Pharmaceutic acid & artificial fruit essence	$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{C}_2\text{H}_5$	Clear, volatile, flammable liquid Boiling Pt 77°C
Methyl Isobutyl Ketone (MIBK) ^[28]	Solvent for nitrocellulose & resins Dewaxing mineral oils & cleaning metal Solvent for chemical synthesis	$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_4\text{H}_9$	Colourless liquid Faint ketonic & camphor odour Boiling Pt 117-118°C
Methyl Ethyl Ketone (MEK) ^[28]	Solvent for nitrocellulose & other resins Dewaxing solvent for lubricating oils	$\text{H}_5\text{C}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	Flammable, clear liquid Acetone-like odour Boiling Pt 79.6°C
Aniline ^[28]	Manufacture of polymers, rubbers, isocyanates, dyes, & photographic chemicals		Oily colourless liquid when freshly distilled Darkens on exposure to air Boiling Pt 184-186°C

1 9 Transport through the Membrane

Mass transfer in pervaporation may be considered to occur by a solution-diffusion model so the permeation characteristics of the membrane are therefore highly dependent on the solubility and diffusivity characteristics of the system. The transport mechanism through the membrane is a three step process ^[1]

Absorption	The liquid is brought into contact with one side of the membrane, a chemical potential vapour-pressure gradient is established between the liquid and the permeate side of the membrane and one component is preferentially absorbed into the membrane
Diffusion	The liquid components migrate, by diffusion, through the membrane along the vapour pressure gradient
Desorption	The component leaves the membrane in the vapour phase and is condensed using a cold trap

The driving force for transport across the membrane is generally recognised as a chemical potential gradient across the membrane. The chemical potential is expressed as

$$\mu_i = \mu_i^{\circ} + RT \ln a_i$$

μ_i = chemical potential of component i

μ_i° = standard chemical potential

a_i = activity of the permeating component

R = universal Gas Constant

T = absolute temperature

The component activity is expressed as

$$a_i = P_i/P_i^\circ$$

P_i° = component saturation vapour pressure of component i

P_i = vapour pressure of component i

To describe the performance of pervaporation for separating multicomponent mixtures, the transport of pure components must first be understood

Consider the diffusion step in the vacuum permeation of a pure component. The permeation may be described by a Fick's Law relationship

$$J_i = -D_i dc_i/dl$$

J_i = Flux

D_i = Diffusivity

c_i = Concentration of component i in the membrane

l = Transmembrane distance

Much attention has been paid to the relationship between the diffusion co-efficient and the concentration. Preliminary work carried out by Fujita^[33] and further adapted by Fels and Huang^[34] was based on the free-volume theory but this proved too difficult to apply to pervaporation due to its complexity.

It was work in this area conducted by Long^[35] which led to diffusivity being expressed as an exponential function of concentration

$$D_i = D_{i0} \exp(A_i c_i)$$

D_{i0} = Diffusion co-efficient at infinite dilution

A_i = Plasticisation co-efficient to account for interaction of the particular polymer & permeant. It represents the magnitude of the effect of solvent concentration on solvent mobility in the membrane

However Greenlaw et al ^[36] proposed another relationship between diffusivity and concentration

$$D_i = D_{i0} (1 + A_i c_i^n)$$

n = number of components in the liquid mixture

They also found that the simplified expression

$$D_i = K c_i$$

followed the data from Roger, Stannett and Szwarc ^[37] for modelling the case of hexane in polyethylene membranes. Rautenbach and Albrecht ^{[38], [39]} also found this form to be sufficient for basic design. They used a modified form of Greenlaw and co-workers with the exponent equal to unity in their analysis of single component transport

$$D_i = D_{i0} (1 + A_i c_i)$$

Substituting the exponential relationship for diffusivity into Fick's Law for diffusion and integrating over the membrane thickness, l , the permeation equation becomes

$$J_i = D_{i0}/A_i l [\exp(A_i c_{if}) - \exp(A_i c_{ip})]$$

c_{if} , c_{ip} = component concentrations in the membrane at the feed (upstream) and permeate (downstream) sides respectively

When the permeate side is kept at sufficiently low pressure, c_{ip} goes to zero, giving

$$J_i = D_{io}/A_i l [\exp (A_i c_{if}) - 1]$$

For a given liquid-polymer system, the diffusion co-efficient D_{io} , plasticisation co-efficient A_i and the membrane thickness, l , are constant

Therefore, the variable affecting the transport is the concentration of the permeant in the feed side of the membrane. The interaction which takes place between the permeating component and the membrane on the feed side produces a swelling phenomenon which increases the membrane thickness. As the concentration in this region increases, so does the flux.

The solubility aspects of transport in the pervaporation process are analysed by looking at the basic sorption thermodynamics. Assuming equilibrium conditions at both the feed and the permeate sides of the membrane, a relationship for equilibrium at the membrane /solution interfaces can be included. Using a solubility parameter, a simple expression can be used to relate concentration to activity^{[36], [37]}

$$c_i = Ks_i a_i$$

Ks_i = sorption co-efficient

An overall permeation equation can be obtained for the pure component case taking into account the feed and permeate streams. Taking the activity of the feed solution to be unity and the permeate activity is expressed by the ratio of downstream pressure to saturation pressure, the relationship for the feed and permeate side conditions

can be substituted into Fick's Law to obtain an overall permeation equation for the pure component case ^[1]

$$J_i = D_{i0}/A_i \{ \exp(A_i K_{s_i}) - \exp[(A_i K_{s_i})(P_p/P_i^0)] \}$$

P_p = permeate (downstream) side vapour pressure

P_i^0 = saturation vapour pressure for component i

The permeation rate for the separation of a binary mixture is therefore, composed of the fluxes of the desired and undesired permeating species. As in the case of pure component permeation, the transport of binary components i & j is dependent on solubility and diffusivity. The prediction of the separation performance of a system based on the pure component results is made difficult due to interactions which occur between the two components of the mixture. Some of these interactions have been recognised as flux coupling and thermodynamic interactions.

Greenlaw, Sheldon and Thompson ^[40] presented expressions to quantify the permeation behaviour of binary systems through pervaporation membranes in which the diffusion co-efficients for components i & j are interdependent on both component concentrations

$$D_i = K_{d_i} (c_i + B_{ij}c_j)$$

$$D_j = K_{d_j} (c_j + B_{ji}c_i)$$

K_{d_i} & K_{d_j} are the diffusion constants relating diffusivity to concentration for pure i & j

B_{ij} & B_{ji} are the coupling parameters for multicomponent transport

However, it was subsequently found that this relationship holds for some ideal mixtures such as heptane-hexane but not for nominal mixtures such as ethanol-water. On reanalysis of these results, a numerical method was developed that solved the model equations for thermodynamically non-ideal solutions [41] [42] [43]. It also allowed the use of a more general relationship for the dependence of component diffusivities and activities on the composition.

$$a_i = f(c_i, c_j)$$

$$a_j = f(c_i, c_j)$$

$$D_i = f(c_i, c_j)$$

$$D_j = f(c_i, c_j)$$

As a result of this work, the following expressions for the diffusion of the components of a binary mixture in a pervaporation separation process were obtained:

$$D_i = D_{i0} + K_{di} (c_i + B_{ij}c_j)^{k_i}$$

$$D_j = D_{j0} + K_{dj} (c_j + B_{ji}c_i)^{k_j}$$

Where the constants D_{i0} , D_{j0} , K_{di} , K_{dj} , k_i and k_j depend on individual components and the constants B_{ij} and B_{ji} represent the coupling effect of the interaction of the two components.

k_i & k_j are exponents in the multicomponent transport relationship.

1 10 Membranes and Membrane Module Selection

Rubbery, elastomeric polymers which may be used in the preparation of pervaporation membranes are classed in two categories: hydrophobic and hydrophilic. Hydrophilic membranes, also known as organophobic, allow the preferential permeation of water molecules.

over organic molecules. Hydrophobic, or organophilic, allow the preferential permeation of organic molecules over water molecules^[44]. The liquid mixtures to be separated in this study comprise of large bulks of water containing up to 1%w/w organics. As a result, a membrane is required which will allow the preferential permeation of these organics over water i.e. hydrophobic. The hydrophobic polymeric membranes chosen for this study were polydimethylsiloxane (PDMS) and polyurethane (PU).

The first step in the mechanism for transport of molecules through the pervaporation membrane is the sorption of components in the liquid phase at the membrane surface (see *Section 1.9*) and so the solubility of the components in the membrane material plays an important role in the separation, as previously described in the sorption-diffusion-desorption model. The success of the pervaporation process is mainly controlled by the intrinsic properties of the polymer used in the membrane preparation^[45]. Therefore, selection of the polymer for use in a system is a key element in the development of a pervaporation system.

Membrane materials should ideally possess many of the following properties to be effective for separation^[46]

- 1 chemical resistance
- 2 mechanical stability
- 3 thermal stability
- 4 high permeability
- 5 high selectivity
- 6 stable operation and low cost

Within the boundaries of membrane separation technology there is a wide range of membrane modules i.e. the physical form and housing of

the membrane, ranging from tubular to hollow fibre to plate and frame set-ups. Some of the characteristics of the modules which must be considered in system design include investment cost, fouling tendency, cleaning, operating costs and membrane replacements ^[47]. For example, tubular modules are the most expensive per installed membrane area and are suited to applications where high membrane fouling is expected because of its ease of operation and of membrane cleaning. However, smaller diameter hollow fibre modules are very susceptible to fouling and are often difficult to clean.

The mode of operation of the system must also be considered in the design of a membrane separation system. The two modes of operation to choose from are dead-end operation and cross-flow operation. Separation techniques such as microfiltration operate on a dead-end system. In such a system the concentration of the rejected components in the feed region above the membrane increases with time and consequently there is a risk to the quality of the permeate with time.

However, due to the nature of the pervaporation separation process, i.e. the separation of liquid and the absence of all solid particulates, the cross-flow mode of operation is employed. In this mode of operation, the feed flows across the membrane surface and the feed composition inside the membrane module varies with distance in the module. The feed stream is separated into two streams: a permeate stream and a retentate stream. Various cross-flow operations are available but in the case of the plate and frame pervaporation membrane module used in this study, the following system was employed (*Figure 1.11.1*) ^[2]

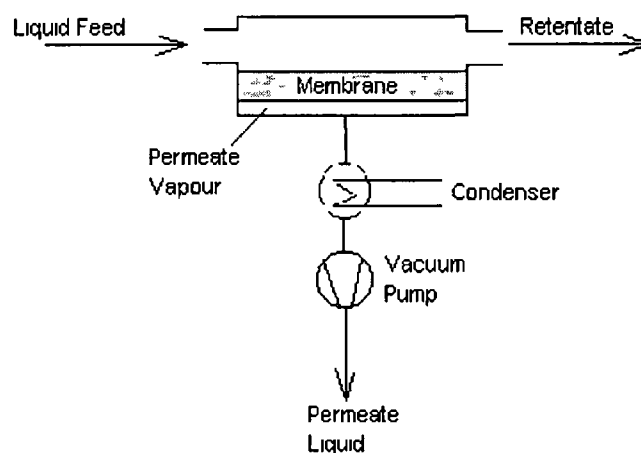


Figure 1 11 1 Schematic representation of crossflow operation in a pervaporation separation process

A typical system, such as the one employed in this study, operates with a recycle of the feed through the module and the concentration of the feed thus gradually decreases with time while the permeate is drawn off

1 10 1 Types of Membranes

There are two basic membrane structures which are currently used in membrane separation processes

- 1 Symmetric
- 2 Asymmetric

Symmetric membranes are of three general types, those with approximate cylindrical pores, porous and non-porous (homogeneous) Asymmetric membranes are characterised by non-uniform structure comprising of an active top layer, or skin, supported by a porous support or sub-layer Again there are three general types, porous, non-porous and composites Composites differ from those other symmetric

membrane which are produced by phase inversion in that the skin and support layer are of different materials ^[2]

A membrane's function depends on its structure as this essentially determines the mechanism for separation and thus the possible applications of the membrane. Pervaporation membranes may be produced from polymer solutions involving the dissolution of a polymer in a solvent medium. It is the method by which the polymer is cured into membrane form that distinguishes between membrane preparation techniques and therefore its application. *Figure 1.3.1* outlines some of the applications of membranes with varying pore sizes ^[2]

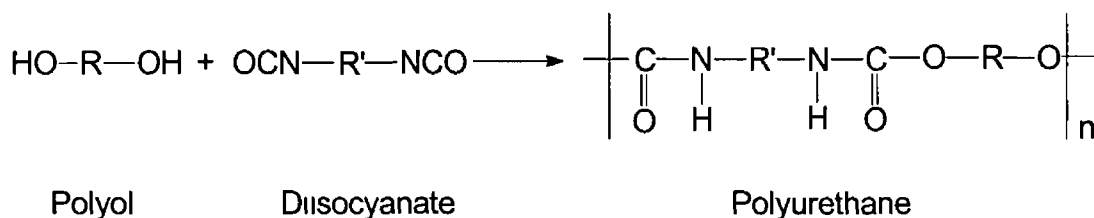
Phase inversion is a membrane preparation technique which involves precipitating a swollen three-dimensional macromolecular complex or gel from a polymer solution. The two most common methods of pervaporation membrane preparation are immersion precipitation in a gelation medium and total solvent evaporation ^[48]. The process of phase inversion by immersion precipitation involves the phase separation of a moderately concentrated polymer solution to form a gel in which the polymer becomes the continuous phase and the solvent molecules coalesce to form pockets within the forming membrane. The subsequent removal of the solvent from these pockets results in voids which constitute the macroporous structure of the membrane. The phase inversion process is induced by the action of a non-solvent which in many cases is water. When water is used as the non-solvent, the process is termed wet phase inversion ^[49]. The production of such a membrane will be discussed further in *Section 1.10.2*

Phase inversion by total solvent evaporation is more simplistic in its operation. It is the simple precipitation of a solid film from a single-phase, homogeneous polymer solution by the action of evaporating the

solvent from the polymer solution. The process generally requires the addition of a crosslinking agent to the polymer solution to aid polymer formation. After the polymer/solvent system has been cast onto a suitable substrate i.e. a glass plate, the curing of the polymer and the evaporation of the solvent occurs at elevated temperatures ^[3]. An example of the preparation of such a membrane may be seen in *Section 1 10 3*.

1 10 2 Polyurethane Membranes

Polyurethane elastomers are block copolymers consisting of alternating 'soft' and 'hard' segments which are respectively polymer chains above and below their glass transition temperatures ^[49]. They are addition polymers formed by the reaction of di- or poly-isocyanates with polyols ^[50].



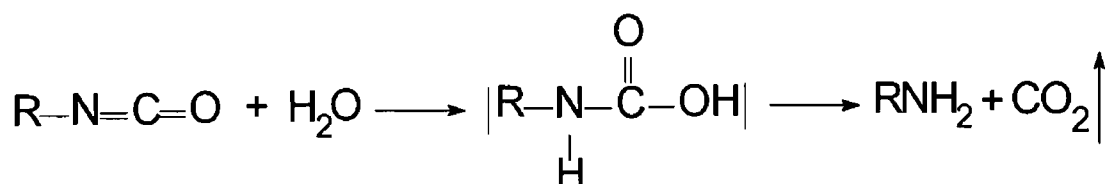
R = alkyl or aromatic group

Reaction 1 10 1 (a)

Little information regarding the composition of the polyurethane prepolymer used in this study is available from the manufacturer but it is known ^[51] that the prepolymer contains terminal isocyanate groups and that the polyol which is reacted with the diisocyanate to produce the polyurethane was a tri-functional polyol in order to achieve satisfactory crosslinking. Within the scope of this study and due to the fact that the physical, and not the chemical properties of the

membranes were used in the process evaluations, the chemical composition of the prepolymers was not investigated further. With this in mind, the proposed mechanism for the formation of the polyurethane membrane is thought to be similar to that used by Cipriano, Diogo and de Pinho ^[52] in which a two step reaction takes place as outlined below

Taking the remaining portion of the macromolecular structure of the polymer chain to be group R, the initial reaction which takes place on the exposure of the cast membrane to atmospheric moisture involves the reaction of the prepolymer terminal isocyanate groups with water to produce an amine group, RNH₂

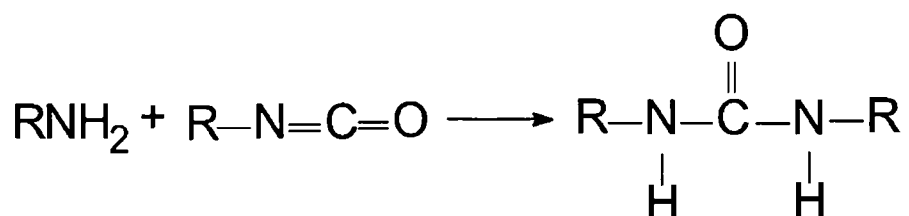


Reaction 1 10 1 (b)

This reaction of the terminal isocyanate groups with water is vital to the structural integrity of the membrane. The gradual, as opposed to rapid, production of the carbon dioxide ensures that the appearance of pinholes in the membranes surface due to the carbon dioxide molecules breaking the surface are kept to a minimum. On the partial solidification of the membrane in the atmosphere, it is then placed into the gelation bath ^{[52] [53]}

The second step in the membrane formation process is the reaction of the amine groups produced in the first step. Amines are frequently used as chain extenders in polyurethane elastomer production and so the reaction of the amine with the terminal isocyanate groups yields a

rubbery, dense polymer with urea linkages which are insoluble in most common solvents^[54]

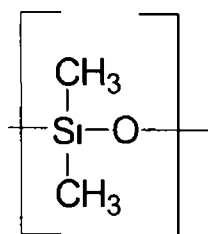


Reaction 1 10 1 (c)

A number of researchers have studied the effects of varying some of the synthesis conditions such as concentration of the casting solution^[55], temperature of the gelation medium and the presence of additives in the gelation medium^[56]. The main result of these variations have been different pore sizes leading to a range of membrane technology applications^[57] as seen in *Figure 1 3 1*

1.10 3 Polydimethylsiloxane Membranes

Polydimethylsiloxane is a rubbery polymer comprising of an inorganic backbone and of the general structure^[50]



The PDMS membranes used in this study were prepared using a silicone polymer RTV 615 A & B supplied by General Electric. Room temperature vulcanising (RTV) silicone elastomers are supplied as

uncured rubbers with liquid or pastelike consistencies. The curing process is based on chemical reactions which increase molecular weights and which provide crosslinking. The action of catalysts ensure the curing is controlled.

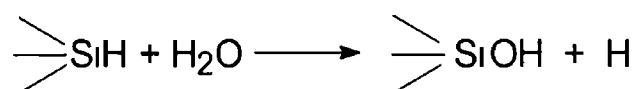
RTV polymers may be supplied as one or two-component systems. In a one-component system, the curing process is triggered by exposure to atmospheric moisture. However, with a two-component system, in which the components are supplied separately, the polymer formation process does not require atmospheric moisture to trigger onset. The two components are mixed and the presence of a catalyst in one of the components triggers the curing reaction under the action of elevated temperatures. It is this type of rubber which is used in the preparation of PDMS membranes for this study^[58]. Once again, rigorous chemical composition identification was not carried out as only the physical characteristics of the membranes were used in the separation process evaluation.

There are a number of curing systems which may be employed but in the case of the membranes used in this study, it is thought that the curing process involves a hydrosilation reaction at elevated temperatures (80°C).

Hydrosilation curing gives RTV rubbers without liberating a by-product which is the case in some of the other curing processes. The curing system proposed to occur in the synthesis of the membranes used involves the creation of ethylene bridges between polymer chains to form repeating units.

The curing of this polymer requires several days when carried out at room temperature, however, it is usually achieved at higher

temperatures (80°C) thus reducing the curing time considerably (24 hours) The strict control of the polymerisation environment is vital due to the ease of catalyst poisoning, i.e. water and alcohols react with Si-H groups in the presence of the catalyst ^[59]



Reaction 1 10 2 (a)

1 11 Membrane Characterisation

In addition to evaluating the potential for the separation of a liquid mixture using pervaporation, from the flux and selectivity data, other characteristic parameters may also be determined so as to characterise the membrane/mixture system A number of different techniques may be used to examine the membrane and several parameters may be defined, all of which may be combined in characterising the pervaporation membranes

1 11 1 Flux through the Membrane

The flux or permeation rate is the volumetric (mass or molar) flow rate of fluid passing through the membrane per unit area of membrane per unit time ^[2] The flux of a liquid through a pervaporation membrane is given by the expression ^{[60] [61]}

$$J = W_p / A \ t$$

J = Flux through the membrane (kg/m²hr)

W_p = Weight of the permeate (kg)

A = Membrane Area (m²)

t = Time period of pervaporation experiment (hr)

The general trend one encounters when examining this parameter is that the value for flux decreases as the concentration of the component to be preferentially permeated in the feed decreases [62] [63],[64]. The partial flux through the membrane of one component of the mixture may also be calculated. This is a simple matter of multiplying the total flux by the fraction of the component in question contained in the permeate [65], [66].

1.11 2 Membrane Selectivity

The performance of a membrane in a pervaporation process may be described by the permeation flux, as described in the previous section, and by the selectivity factor [57]. The selectivity is a measure of the relative permeation rates of different components of a liquid mixture through the pervaporation membrane [2]. It is given by the following expression

$$\alpha = \frac{y_i / y_j}{x_i / x_j}$$

α = membrane selectivity

y_i = %w/w of component i in the permeate sample

y_j = %w/w of component j in the permeate sample

x_i = % w/w of component i in the feed sample

x_j = % w/w of component j in the feed sample

This selectivity calculated in this way is with respect to component i , the preferentially permeating component.

1.11.3 Swelling Factors

Simple gravimetric measurements may be carried out to evaluate the capacity of the pervaporation membranes to absorb a liquid. Using the data from these measurements, a parameter known as the swelling factor is calculated for a membrane/liquid system using the following expression ^{[53], [67]}.

$$S = (W_1 - W_0) / W_0$$

S = Swelling Factor

W_1 = Weight of the swollen membrane, g.

W_2 = Weight of the dry membrane, g.

A comparison of the calculated swelling factors for a given membrane using a number of liquids may be used to help predict the separation potential of a membrane/liquid mixture system ^{[53], [67]}.

1.11.4 Activation Energy of Permeation

In pervaporation, mass transport through a membrane is induced by maintaining the permeate (or downstream) pressure lower than the saturated vapour pressure of the feed liquid. The driving force for permeation may be expressed in terms of chemical potential, fugacity or partial pressure across the membrane. The phase change of the

permeating species from the liquid to vapour phase is one of the distinguishing features of pervaporation and as a result, sufficient energy must be supplied to prevent a temperature drop during the process

Experimental data concerning the dependence of both total and partial flux on temperature has been seen to exhibit an Arrhenius relationship thus producing a linear trend between the natural log of flux and the reciprocal of the operating temperature according to

$$J = J_0 \exp(-E_J/RT)$$

E_J = Activation Energy of Permeation

J = Flux

J_0 = Flux at infinite dilution

R = Universal Gas Constant

T = Temperature (K)

This expression has been extensively used in pervaporation studies to evaluate the activation energy of permeation from a plot of $\ln J v 1/T$. However, it has been shown by Feng & Huang^[68] that the value of E_J calculated for a specific separation is, in fact, the energy barrier which must be overcome by the permeating molecules if transport through the membrane is to be achieved

2. Experimental

2.1 Materials/Equipment

<u>PU Prepolymer</u>	Resicork UPU9731, (Hoechst)
<u>PDMS Prepolymer</u>	RTV 615 A & B, (General Electric)
<u>Solvents for</u>	
<u>Membrane Preparation</u>	Methyl Isobutyl Ketone, (Riedel de Haen) N,N-Dimethylformamide, (Riedel de Haen) p-Xylene, (Merck)
<u>Organic Liquids used</u>	
<u>in Separation Processes</u>	Methyl Isobutyl Ketone, (Riedel de Haen) Methyl Ethyl Ketone, (Riedel de Haen) Ethyl Acetate, (BDH) Aniline, (Riedel de Haen)
<u>GC Stationary Phases</u>	Carbowax 10% C1500 FFAP 10%100-120 Mesh
<u>Gas Chromatograph</u>	Shimadzu GC-8A Chromatograph using a Flame Ionisation Detector equipped with a Shimadzu C-RSA Chromatopac Integrator
<u>Differential</u>	
<u>Scanning Calorimeter</u>	Rheometric Scientific DSC-QC
<u>Scanning</u>	
<u>Electron Microscope</u>	Hitachi S-2400 SEM

2 2 Membrane Preparation

2 2 1 Polyurethane Membrane Preparation

Prepolymer Casting Solution Preparation

To a 100cm³ volumetric flask was added the PU prepolymer (Resicork UPU9731, Hoechst) [18.9g], dimethylformamide (Riedel de Haen) [6.0g] and p-xylene (Merck) [5.1g]. The flask was set aside to mix overnight using a mechanical shaker.

Membrane Casting

The prepolymer solution was cast onto a clean, dry glass plate (24cm x 30cm) using a brass 'Gardener' knife (2.5cm x 2.5cm x 20cm), the front face of the knife being raised by 250µm thus providing a uniform deposition of the film on the plate.

Membrane Curing

In the case of the polyurethane membrane, PU1, the cast membrane was allowed to stand, exposed to the atmosphere, for ten minutes. The plate was then immersed in an ice-cold water bath for two days. In the cases of the polyurethane membrane PU2, the membrane was immersed in the water bath immediately after casting. After two days, a rubbery, translucent membrane formed in both cases and was easily removed from the plate. The membranes were allowed to dry in air.

Membrane Cutting & Installation

Using the inner plate of the test-cell, the membrane was cut to size. A filter paper (Grade 1 Qualitative, Whatman) of the same size was used as a mechanical support for the membrane inside the test-cell.

2 2 2 Polydimethylsiloxane Membrane Preparation

Prepolymer Casting Solution Preparation

The two component prepolymer system RTV 615 A & B (General Electric) [31.5g] was added to a beaker in the ratio of nine parts prepolymer to one part crosslinker. To this mixture was added p-xylene (Riedel de Haen) [18.5g]. In the preparation of the polydimethylsiloxane membrane, PDMS1, the mixture was stirred using a magnetic stirring bar for twenty minutes, until a homogeneous solution was obtained. In the case of the polydimethylsiloxane membrane, PDMS2, the mixture was stirred for three minutes. The mixture was gently heated to 60°C until the viscosity of the mixture increased sufficiently so as to allow the casting of the membrane.

Membrane Casting

The prepolymer solution was cast onto a glass plate (24cm x 30cm) using a brass 'Gardener' knife (2.5cm x 2.5cm x 20cm), depositing a film of nominal thickness of 250µm in a similar way to the PU membrane.

Membrane Curing

The membrane was placed in a convection oven preheated to 80°C for 24 hours to ensure curing and crosslinking.

Membrane Cutting & Installation

This process was identical to that described for the cutting and installation of the PU membrane.

2.3 Laboratory Scale Pervaporation Unit

The laboratory scale test cell unit allows for an easy and fast first evaluation of the feasibility of pervaporation processes. Liquid mixtures of different compositions can be permeated with different membranes at preset temperatures. Correlation between feed compositions and feed temperatures on one side (retentate) and permeate compositions and flux can be measured in a short time, giving sufficient information on the applicability and feasibility of pervaporation processes.

The test-cell itself, a schematic layout of which may be seen in *Figure 2.3.1*, comprises of a number of components the basic material for which being stainless steel

- Pressure tight feed reservoir with liquid capacity of 3dm³
- Filling valve
- Heating bath/circulator with temperature control unit (Haake D8-L)
- Feed pump with electronic drive (Verder V 096 07) 1850rev min⁻¹
- Feed sampling point
- Test-cell for membrane (membrane area 0.0198m²)
- Condenser (round bottomed flask, 100cm³) immersed in liquid N₂
- Vacuum system (pressure ~5mbar), consisting of vacuum pump (Edwards E2M2) and an additional liquid N₂ finger cold trap
- Support frame
- Pipe Connections

The operation of the test-unit is described in detail in *Section 2.4*

Laboratory Scale Pervaporation Test-Unit

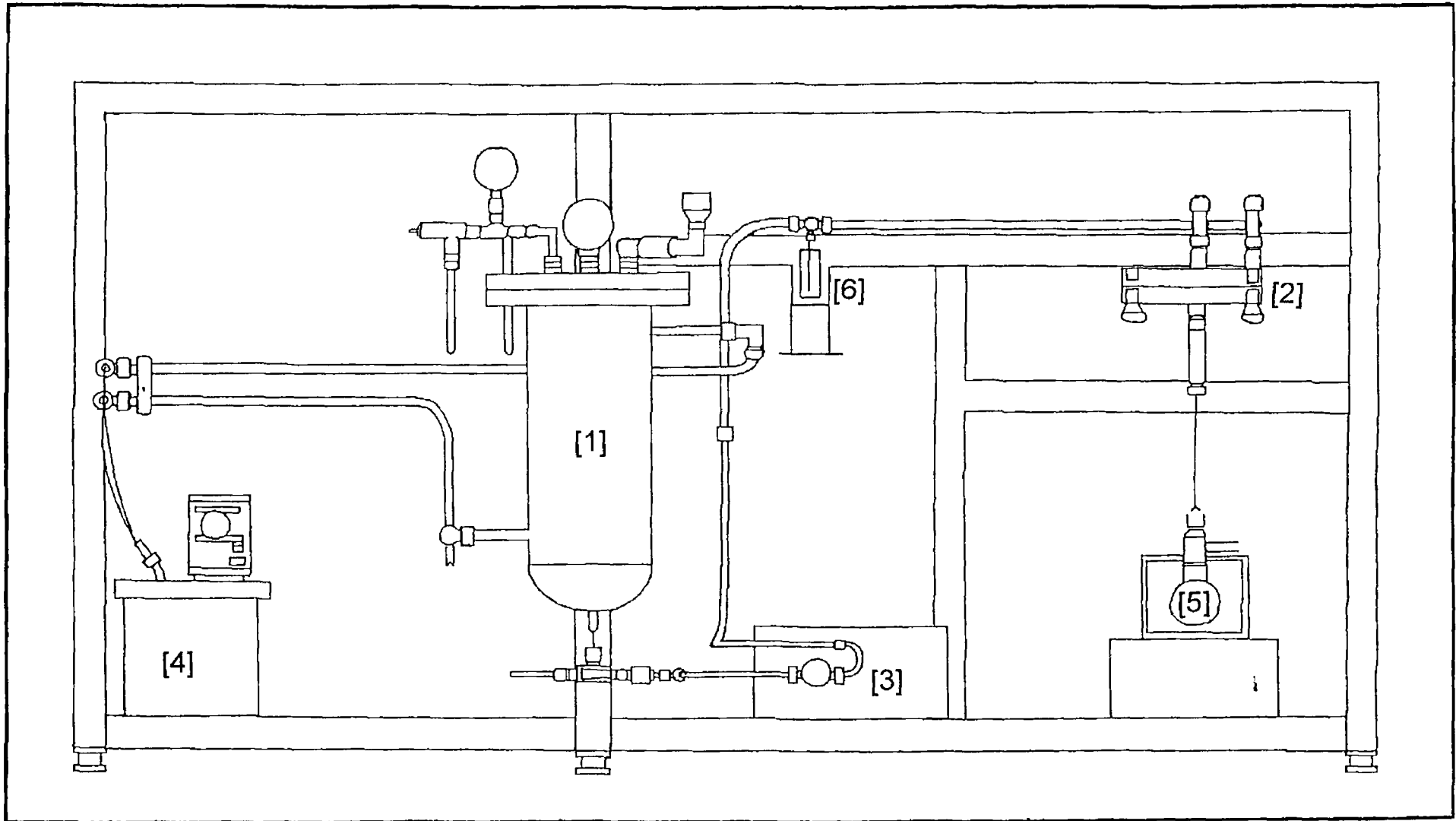


Figure 2 4

Key to the components of the pervaporation test-cell

- [1] Feed reservoir
- [2] Membrane test-cell
- [3] Feed pump
- [4] Circulating heating bath
- [5] Permeate collection vessel
- [6] Feed sampling point

2 4 Pervaporation Test-Cell Operation

After installation of the membrane into the test-cell, the reservoir was charged with $\sim 2.7 \text{ dm}^3$ of the liquid mixture to be pervaporated. The temperature controller on the heating bath was set to just below the atmospheric boiling point of the most volatile component of the mixture and the feed pump was started. With the filling valve of the reservoir still open, the liquid was heated. When the preset temperature was achieved, the valve was closed, any air in the system now having been displaced, and the temperature controller was set to the required operating temperature. During the heating process, the permeate side of the membrane was maintained at a pressure of $\sim 5 \text{ mbar}$. The contents of the permeate collection vessel were collected and cooled using a liquid nitrogen cold trap in series with a liquid nitrogen finger cold trap.

When the operating temperature was reached the membrane was allowed to condition for approximately thirty minutes. At this stage, the permeate collection vessel was exchanged for an empty one and a sample of the feed solution in the reservoir was taken. This sampling

process was repeated at the end of each test period, which ranged from one to three hours depending on the separation requirements. These pervaporation experiments were carried out using a selection of aqueous/organic liquid solutions (see Table 2.4.1) over a range of temperatures (50 - 80°C).

Table 2.4.1

Aqueous Solutions (~1% w/w in water)
Methyl Isobutyl Ketone
Methyl Ethyl Ketone
Ethyl Acetate
Aniline

2.5 Sample Analysis

The permeate and feed samples were analysed using a Shimadzu GC-8A Chromatograph with a flame ionisation detector equipped with a Shimadzu C-RSA Chromatopac Integrator.

The feed samples were analysed without pre-treatment (*Appendix 1*). The permeate samples produced were in two phases, organic and aqueous. Before analysis, the two-phase samples were diluted using water until a single phase was obtained. The new weight of the permeate samples was noted in each case and after analysis, the amount of organic in the original sample was calculated (*Appendix 2*).

The following parameters were employed during sample analysis

	MIBK/H ₂ O	MEK/H ₂ O	Ethyl Acetate/H ₂ O	Aniline/H ₂ O
Stationary Phase	Carbowax	Carbowax	Carbowax	FFAP
Sample Size	1µl	1µl	1µl	1µl
Nitrogen	1.9kg/cm ³	1.8kg/cm ³	1.8kg/cm ³	1.9kg/cm ³
Hydrogen	0.6kg/cm ³	0.6kg/cm ³	0.7kg/cm ³	0.6kg/cm ³
Air	0.5kg/cm ³	0.5kg/cm ³	0.5kg/cm ³	0.5kg/cm ³
Slope	2500	2500	2500	750
Min Area	3000	1000	1000	1000
Attenuation	4	3	3	3

2.6 Sorption Experiments

Each membrane was cut into sections with the dimensions 3cm x 3cm. Each section was immersed in the liquid to be examined for a predetermined time period ranging from two to thirty minutes. On removal from the liquid, any surface moisture was removed by gently wiping with sterile tissue and each membrane section was weighed. The immersion, wiping and weighing process was repeated until the allotted time had elapsed. The weight of the membrane after each weighing was noted (Tables 3.4.1 & 3.4.2). This sorption data was normalised for 1g of membrane (dry weight). From the data obtained, a plot of weight of liquid absorbed versus time was made (Figures 3.4.1 & 3.4.2).

In addition to these tests being carried out, tests were also carried out in the same way for an ongoing period of twenty-four hours to determine the weight of liquid the membrane absorbed on reaching equilibrium

2.7 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) was used to determine the glass transition of the polymeric membranes used. A small, weighed portion of the membrane to be examined was sealed in the appropriate aluminium pans and the DSC experiment was run between -50 and 240°C on a Rheometric Scientific DSC-QC. The glass transition temperatures recorded may be seen in (*Appendix 8*)

2.8 Scanning Electron Microscopy

All the images obtained were produced using an Hitachi S-2400 SEM set at an operating voltage of 10kV. All images are secondary electron (SE) images and the magnification is displayed on each individual image. These images may be seen in *Chapter 4*

3 Results

3.1 Pervaporation Data

Table 3.1.1 1%w/w MIBK/Water mixture at 70°C using PU1 membrane

Sample	Feed Conc (%w/w organic)	Permeate Conc (%w/w organic)	Total Flux (kg/m ² hr)	Partial Organic Flux (kg/m ² hr)
1	0.995	36.544	0.744	0.272
2	0.914	36.124	0.729	0.263
3	0.833	35.952	0.707	0.254
4	0.787	33.573	0.695	0.233
5	0.704	33.507	0.657	0.220
6	0.643	33.413	0.599	0.200
7	0.572	32.012	0.594	0.190
8	0.531	31.970	0.599	0.191
9	0.489	30.234	0.615	0.186
10	0.439	29.954	0.579	0.174
11	0.396	26.428	0.613	0.162
12	0.332	25.416	0.570	0.145
13	0.323	25.277	0.519	0.131
14	0.185	15.070	0.447	0.067
15	0.129	12.015	0.468	0.056
16	0.097	14.931	0.345	0.052

See Appendices 1 & 2 for sample feed and permeate concentration calculations, respectively

See Appendix 3 for plots of feed concentration v partial organic flux

See Appendix 4 for plots of feed concentration v permeate concentration

Table 3 1 2 1%w/w MIBK/Water mixture at 80°C using PU1
membrane

Sample	Feed conc (%w/w organic)	Permeate Conc (%w/w organic)	Total Flux (kg/m²hr)	Partial Organic Flux (kg/m²hr)
1	0 993	58 34	1 011	0 589
2	0 970	57 56	1 010	0 581
3	0 919	59 82	1 003	0 599
4	0 882	54 77	0 998	0 547
5	0 835	53 49	0 987	0 528
6	0 747	55 01	0 942	0 518
7	0 676	45 68	0 878	0 401
8	0 629	44 01	0 813	0 358
9	0 588	43 55	0 775	0 338
10	0 550	39 98	0 744	0 298
11	0 493	37 37	0 692	0 259
12	0 412	31 52	0 613	0 193
13	0 357	28 15	0 452	0 127
14	0 279	19 50	0 431	0 084
15	0 250	19 05	0 406	0 077
16	0 193	12 83	0 389	0 050
17	0 175	9 67	0 352	0 034
18	0 121	8 67	0 348	0 030
19	0 104	7 93	0 329	0 026

Table 3 1 3 1%w/w MEK/Water mixture at 70°C using PU1 membrane

Sample	Feed Conc (%w/w organic)	Permeate Conc (%w/w organic)	Total Flux (kg/m²hr)	Partial Organic Flux (kg/m²hr)
1	0 946	10 348	0 400	0 041
2	0 825	10 189	0 329	0 034
3	0 613	9 871	0 359	0 035
4	0 580	9 376	0 279	0 026
5	0 458	8 684	0 266	0 023
6	0 454	7 465	0 274	0 021
7	0 438	7 021	0 271	0 019
8	0 367	6 221	0 276	0 017
10	0 352	5 945	0 254	0 015
11	0 323	5 055	0 266	0 014
12	0 281	4 872	0 263	0 013
13	0 267	4 495	0 261	0 012
14	0 222	4 325	0 255	0 011
15	0 145	4 233	0 264	0 011
16	0 139	3 319	0 278	0 010
17	0 129	3 298	0 275	0 009
18	0 101	3 284	0 271	0 008

Table 3 1 4 1% w/w MEK/Water mixture at 80°C using PU1
membrane

Sample	Feed Conc (%w/w organic)	Permeate Conc (%w/w organic)	Total Flux (kg/m²hr)	Partial Organic Flux (kg/m²hr)
1	0 928	12 313	0 519	0 064
2	0 737	10 875	0 502	0 055
3	0 602	10 188	0 414	0 042
4	0 568	8 813	0 471	0 041
5	0 570	8 500	0 401	0 034
6	0 456	6 813	0 444	0 030
7	0 450	7 563	0 413	0 031
8	0 429	6 813	0 399	0 027
9	0 339	5 579	0 351	0 019
10	0 332	5 375	0 323	0 017
11	0 284	5 054	0 286	0 014
12	0 106	4 750	0 258	0 012
13	0 094	2 500	0 204	0 005

Table 3 1 5 1% w/w Ethyl Acetate/Water mixture at 70°C using
PU1 membrane

Sample	Feed Conc (%w/w organic)	Permeate Conc (%w/w organic)	Total Flux (kg/m²hr)	Partial Organic Flux (kg/m²hr)
1	0 952	32 607	0 258	0 084
2	0 853	24 176	0 187	0 063
3	0 722	18 986	0 251	0 055
4	0 591	11 699	0 411	0 048
5	0 484	11 186	0 211	0 024
6	0 333	8 061	0 268	0 022
7	0 282	5 812	0 313	0 011
8	0 265	4 022	0 271	0 007
9	0 249	3 001	0 244	0 008
10	0 228	2 791	0 206	0 006
11	0 225	2 104	0 266	0 005
12	0 198	1 145	0 190	0 002
13	0 177	0 944	0 284	0 002
14	0 164	0 919	0 153	0 001

Table 3 1 6 1% w/w Ethyl Acetate/Water mixture at 80°C using a PU1 membrane

Sample	Feed Conc (%w/w organic)	Permeate Conc (%w/w organic)	Total Flux (kg/m²hr)	Partial Organic Flux (kg/m²hr)
1	0 979	33 867	0 484	0 164
2	0 664	12 323	0 492	0 061
3	0 608	12 395	0 411	0 051
4	0 568	9 958	0 364	0 036
5	0 491	5 497	0 384	0 021
6	0 433	4 226	0 418	0 018
7	0 414	2 909	0 417	0 012
8	0 391	2 936	0 405	0 012
9	0 381	2 539	0 373	0 010
10	0 380	2 238	0 348	0 008
11	0 360	2 044	0 301	0 006
12	0 326	1 716	0 338	0 006
13	0 201	1 287	0 423	0 005
14	0 114	0 419	0 305	0 001
15	0 111	0 529	0 171	0 0009
16	0 107	0 521	0 170	0 0008

Table 3 1 7 1% w/w Aniline/Water mixture at 70°C using PU1 membrane

Sample	Feed Conc (%w/w organic)	Permeate Conc (%w/w organic)	Total Flux (kg/m²hr)	Partial Organic Flux (kg/m²hr)
1	0 981	8 252	0 458	0 038
2	0 910	8 002	0 462	0 037
3	0 854	7 876	0 461	0 036
4	0 746	7 394	0 450	0 035
5	0 688	6 117	0 490	0 030
6	0 612	5 865	0 488	0 029
7	0 543	4 840	0 523	0 025
8	0 492	3 901	0 538	0 021
9	0 431	3 154	0 539	0 019
10	0 373	2 859	0 463	0 013
11	0 273	2 352	0 455	0 011
12	0 166	1 851	0 449	0 008
13	0 113	1 734	0 456	0 007
14	0 102	1 520	0 480	0 007

Table 3 1 8 1% w/w Aniline/Water mixture at 80°C using PU1 membrane

Sample	Feed Conc (%w/w organic)	Permeate Conc (%w/w organic)	Total Flux (kg/m²hr)	Partial Organic Flux (kg/m²hr)
1	0 971	9 184	0 801	0 074
2	0 922	9 002	0 802	0 072
3	0 864	8 779	0 796	0 070
4	0 807	8 542	0 797	0 068
5	0 535	8 190	0 803	0 066
6	0 439	7 535	0 798	0 060
7	0 330	6 052	0 792	0 052
8	0 292	6 500	0 685	0 045
9	0 199	5 445	0 710	0 039
10	0 138	4 321	0 613	0 027
11	0 105	3 812	0 600	0 023

Table 3 1 9 1% w/w MIBK/Water mixture at 70°C using PDMS1 membrane

Sample	Feed Conc (%w/w organic)	Permeate Conc (%w/w organic)	Total Flux (kg/m²hr)	Partial Organic Flux (kg/m²hr)
1	0 935	87 727	0 356	0 312
2	0 879	85 901	0 349	0 300
3	0 831	85 013	0 263	0 224
4	0 773	83 988	0 240	0 202
5	0 764	75 888	0 284	0 215
6	0 340	73 228	0 208	0 152
7	0 328	58 925	0 195	0 115
8	0 148	38 050	0 090	0 034
9	0 081	26 168	0 088	0 024
10	0 041	17 376	0 078	0 019

Table 3 1 10 1% w/w MIBK/Water mixture at 80°C using a PDMS1 membrane

Sample	Feed Conc (%w/w organic)	Permeate Conc (%w/w organic)	Total Flux (kg/m²hr)	Partial Organic Flux (kg/m²hr)
1	0 939	88 012	0 400	0 352
2	0 928	80 937	0 329	0 266
3	0 793	80 247	0 321	0 260
4	0 737	78 683	0 319	0 251
5	0 602	65 175	0 310	0 202
6	0 570	59 033	0 279	0 165
7	0 568	53 574	0 266	0 143
8	0 456	45 882	0 274	0 126
9	0 450	38 346	0 271	0 104
10	0 429	32 903	0 276	0 091
11	0 339	27 988	0 254	0 071
12	0 332	19 995	0 260	0 052
13	0 284	11 516	0 231	0 027
14	0 106	9 747	0 244	0 024
15	0 094	8 101	0 239	0 019

Table 3 1 11 1% w/w MEK/Water mixture at 70°C using PDMS1 membrane

Sample	Feed Conc (%w/w organic)	Permeate Conc (%w/w organic)	Total Flux (kg/m²hr)	Partial Organic Flux (kg/m²hr)
1	1 059	45 925	0 181	0 083
2	0 952	42 102	0 167	0 070
3	0 791	37 274	0 173	0 064
4	0 649	37 534	0 151	0 057
5	0 584	34 472	0 148	0 051
6	0 548	38 829	0 120	0 047
7	0 479	34 624	0 091	0 032
8	0 419	29 975	0 097	0 029
9	0 366	25 014	0 172	0 024
10	0 330	20 709	0 121	0 021
11	0 281	20 431	0 144	0 023
12	0 243	20 061	0 106	0 021
13	0 203	17 446	0 068	0 012
14	0 157	16 557	0 061	0 010
15	0 103	16 491	0 057	0 009

Table 3 1 12 1% w/w MEK/Water mixture at 80°C using PDMS1 membrane

Sample	Feed Conc (%w/w organic)	Permeate Conc (%w/w organic)	Total Flux (kg/m²hr)	Partial Organic Flux (kg/m²hr)
1	0 830	42 482	0 193	0 082
2	0 658	37 012	0 208	0 076
3	0 611	36 560	0 175	0 064
4	0 510	34 652	0 134	0 046
5	0 464	26 807	0 140	0 038
6	0 373	22 698	0 122	0 028
7	0 355	21 461	0 139	0 030
8	0 297	21 223	0 152	0 032
9	0 254	17 306	0 150	0 026
10	0 214	14 479	0 138	0 020
11	0 135	6 770	0 125	0 008
12	0 110	5 727	0 108	0 006
13	0 090	5 793	0 105	0 006

Table 3 1 13 1% w/w Ethyl Acetate/Water at 70°C using PDMS1 membrane

Sample	Feed Conc (%w/w organic)	Permeate Conc (%w/w organic)	Total Flux (kg/m²hr)	Partial Organic Flux (kg/m²hr)
1	1 048	57 013	0 253	0 144
2	0 809	56 793	0 242	0 137
3	0 785	55 309	0 240	0 133
4	0 703	54 987	0 231	0 127
5	0 543	53 041	0 187	0 099
6	0 499	51 805	0 167	0 087
7	0 301	42 989	0 161	0 069
8	0 205	33 286	0 142	0 047
9	0 162	19 337	0 110	0 021
10	0 115	6 217	0 082	0 005
11	0 110	3 479	0 079	0 003
12	0 105	2 814	0 082	0 002

Table 3 1 14 1% w/w Ethyl Acetate/Water at 80°C using PDMS1
membrane

Sample	Feed Conc (%w/w organic)	Permeate Conc (%w/w organic)	Total Flux (kg/m²hr)	Partial Organic Flux (kg/m²hr)
1	0 893	53 897	0 233	0 126
2	0 701	53 451	0 213	0 144
3	0 574	52 987	0 191	0 101
4	0 497	51 372	0 173	0 089
5	0 340	49 401	0 161	0 080
6	0 241	25 613	0 193	0 050
7	0 190	25 512	0 155	0 035
8	0 134	11 839	0 128	0 015
9	0 101	7 202	0 114	0 00

Table 3 1 15 1% w/w Aniline/Water mixture at 70°C using PDMS1 membrane

Sample	Feed Conc (%w/w organic)	Permeate Conc (%w/w organic)	Total Flux (kg/m²hr)	Partial Organic Flux (kg/m²hr)
1	0 911	30 248	0 139	0 042
2	0 874	29 073	0 126	0 037
3	0 689	28 333	0 128	0 036
4	0 681	28 120	0 123	0 035
5	0 672	27 711	0 116	0 032
6	0 567	23 636	0 103	0 024
7	0 557	23 795	0 098	0 023
8	0 456	21 756	0 096	0 021
9	0 449	17 531	0 91	0 016
10	0 332	16 363	0 086	0 014
11	0 317	14 975	0 089	0 013
12	0 244	14 266	0 085	0 012
13	0 157	13 160	0 082	0 011
14	0 101	12 855	0 079	0 010

Table 3 1 16 1% w/w Aniline/Water mixture at 80°C using PDMS1 membrane

Sample	Feed Conc (%w/w organic)	Permeate Conc (%w/w organic)	Total Flux (kg/m²hr)	Partial Organic Flux (kg/m²hr)
1	0 933	30 877	0 156	0 047
2	0 850	29 783	0 148	0 044
3	0 773	27 012	0 142	0 039
4	0 714	26 990	0 132	0 036
5	0 665	24 126	0 126	0 030
6	0 597	21 791	0 140	0 030
7	0 529	19 021	0 141	0 025
8	0 463	18 631	0 107	0 020
9	0 398	17 291	0 117	0 020
10	0 352	16 262	0 124	0 020
11	0 287	15 109	0 119	0 018
12	0 204	14 555	0 118	0 017
13	0 164	14 219	0 120	0 017
14	0 110	13 901	0 120	0 016
15	0 097	13 882	0 122	0 017

3.2 Flux and Selectivity Data

Table 3.2.1. Data produced using a polyurethane membrane, PU1, with a feed concentration of 1% w/w organic in water

Liquid Mixture	Temperature (°C)	Flux (kg/m ² hr)	Selectivity
MIBK / H ₂ O	50	0.384	25
	60	0.593	36
	70	0.773	50
	80	1.011	62
MEK / H ₂ O	50	0.223	7
	60	0.307	8
	70	0.400	11
	80	0.519	15
Ethyl Acetate/H ₂ O	50	0.098	48
	60	0.153	49
	70	0.258	50
	80	0.484	51
Aniline / H ₂ O	50	0.213	6
	60	0.296	7
	70	0.458	9
	80	0.801	10

See Appendices 5 & 6 for sample flux and selectivity calculations, respectively

Table 3 2 2

Data produced using a polydimethylsiloxane membrane, PDMS1, with a feed concentration of 1%w/w organic in water

Liquid Mixture	Temperature (°C)	Flux (kg/m ² hr)	Selectivity
MIBK / H ₂ O	50	0 273	378
	60	0 318	585
	70	0 356	757
	80	0 400	774
MEK / H ₂ O	50	0 130	53
	60	0 143	61
	70	0 181	79
	80	0 193	88
Ethyl Acetate/H ₂ O	50	0 129	148
	60	0 169	159
	70	0 242	161
	80	0 344	172
Aniline / H ₂ O	50	0 088	39
	60	0 103	44
	70	0 139	47
	80	0 156	49

3.3 Activation Energies of Permeation

Table 3.3.1 Data produced using polyurethane membrane, PU1

Liquid Mixture	E_a (kJ mol ⁻¹)
MIBK / Water	60.06
MEK / Water	46.10
Ethyl Acetate / Water	55.36
Aniline / Water	135.54

Table 3.3.2 Data produced using polydimethylsiloxane membrane, PDMS1

Liquid Mixture	E_a (kJ mol ⁻¹)
MIBK / Water	10.25
MEK / Water	2.83
Ethyl Acetate / Water	12.29
Aniline / Water	25.72

See Appendix 7 for plots of $\ln J v 1/T$

See Appendix 8 for data used in E_a calculations

See Appendix 9 for sample activation energy of permeation calculation

3 4 Swelling Factors

Table 3 4 1 Weight of liquid absorbed per gram of polyurethane membrane, PU1

Time (mins)	MEK (g)	MIBK (g)	Ethyl Acetate (g)	Aniline (g)	Water (g)
0	0 411	0 411	0 409	0 407	0 411
2	1 057	0 664	1 063	0 413	0 412
4	1 159	0 713	1 239	0 416	0 412
6	1 164	0 788	1 244	0 418	0 413
8	1 166	0 827	1 257	0 419	0 414
10	1 167	0 841	1 265	0 420	0 414
15	1 169	0 863	1 272	0 422	0 415
20	1 171	0 899	1 275	0 424	0 416
25	1 174	0 915	1 278	0 429	0 416
30	1 175	0 922	1 280	0 435	0 417
40	1 178	0 927	1 284	0 439	0 418
50	1 179	0 931	1 287	0 441	0 419
60	1 181	0 935	1 289	0 442	0 419
90	1 181	0 935	1 289	0 442	0 419

See Appendix for graphical representation of sorption data normalised for one gram of membrane

Table 3 4 2 Weight of liquids absorbed per 3cm x 3cm sample of polydimethylsiloxane membrane, PDMS1

Time (mins)	MEK (g)	MIBK (g)	Ethyl Acetate (g)	Aniline (g)	Water (g)
0	0 330	0 327	0 319	0 309	0 313
2	0 373	0 399	0 354	0 314	0 314
4	0 398	0 485	0 379	0 314	0 314
6	0 425	0 522	0 402	0 315	0 314
8	0 449	0 527	0 421	0 316	0 315
10	0 457	0 531	0 426	0 316	0 315
15	0 462	0 534	0 428	0 317	0 315
20	0 469	0 535	0 431	0 317	0 315
25	0 475	0 536	0 434	0 317	0 315
30	0 482	0 537	0 436	0 318	0 315
40	0 490	0 538	0 448	0 318	0 315
50	0 496	0 540	0 452	0 319	0 315
60	0 499	0 542	0 459	0 319	0 315
90	0 499	0 542	0 459	0 319	0 315

See Appendix 10 (ii) for graphical representation of sorption data normalised for one gram of membrane

Table 3 4 3 Data produced using a polyurethane membrane, PU1, at ambient temperatures

Liquid	Swelling Factor, S
MIBK	1 27
MEK	1 87
Ethyl Acetate	2 15
Aniline	0 09
Water	0 019

Table 3 4 4 Data produced using polydimethylsiloxane membrane, PDMS1, at ambient temperatures

Liquid	Swelling Factor, S
MIBK	0 66
MEK	0 51
Ethyl Acetate	0 44
Aniline	0 03
Water	0 006

See Appendix 11 for sample swelling factor calculation

4 Discussion

4.1 Scanning Electron Microscopy

To illustrate the importance of correct membrane preparation procedure in generating a polymeric membrane suitable for use in a pervaporation process, a number of membranes were prepared according to the description in *Section 2.2*. These membranes were analysed using SEM in order to determine their structural integrity on a microscopic level.

As previously discussed in *Section 1.12.1*, the partial evaporation of the solvent system from the polyurethane prepolymer solution is a vital step if a homogeneous, defect-free membrane is to be prepared. This partial evaporation allows the terminal isocyanate groups of the polyurethane prepolymer to slowly react with atmospheric moisture. This reaction results in the generation of small quantities of carbon dioxide; however, these small amounts of carbon dioxide are sufficient to cause defects in the membrane if generated too quickly. The slow reaction of isocyanate groups with atmospheric moisture allows some control over the membrane synthesis to be introduced.

Figure 4.1.1 shows the top surface of membrane PU1, the polyurethane membrane which was prepared strictly according to the method described in *Section 2.2.1* with an allowed evaporation time of ten minutes before the cast membrane was immersed in the water bath.



Figure 4 1 1 **Top surface of polyurethane membrane, PU1 , at 800 times magnification**

This image shows how the carbon dioxide generated during the curing reaction has broken the surface of the membrane resulting in what has previously described by Pessoa, Nobrega and Habert ^[57] as an 'orange-peel' effect. However, the defects on the surface of the membrane due to the release of the carbon dioxide are thought not to penetrate the main body of the membrane, a fact which is confirmed by the image shown in *Figure 4 1 2* which shows a corner view and the top surface of the membrane.

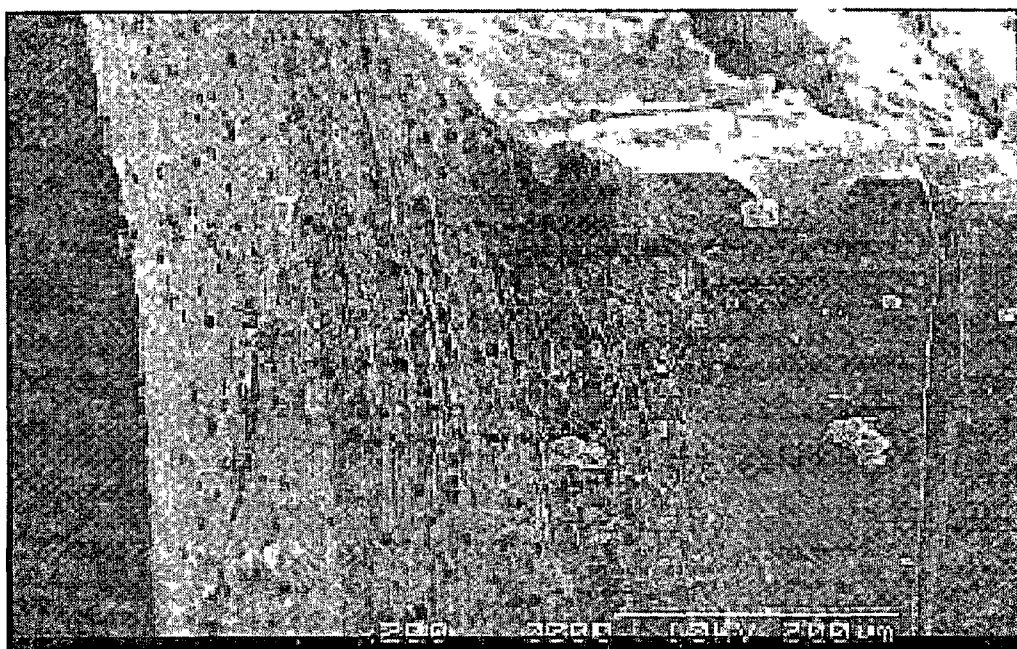


Figure 4 1 2: Corner cross-sectional view and top surface of polyurethane membrane, PU1, at 200 times magnification

It is clear from this image that there are pores present through the membrane. A cross-sectional view of the membrane PU1 shows how the density of pores is greatest at the top surface of the membrane and gradually decreases towards the bottom surface (*Figure 4 1 3*)

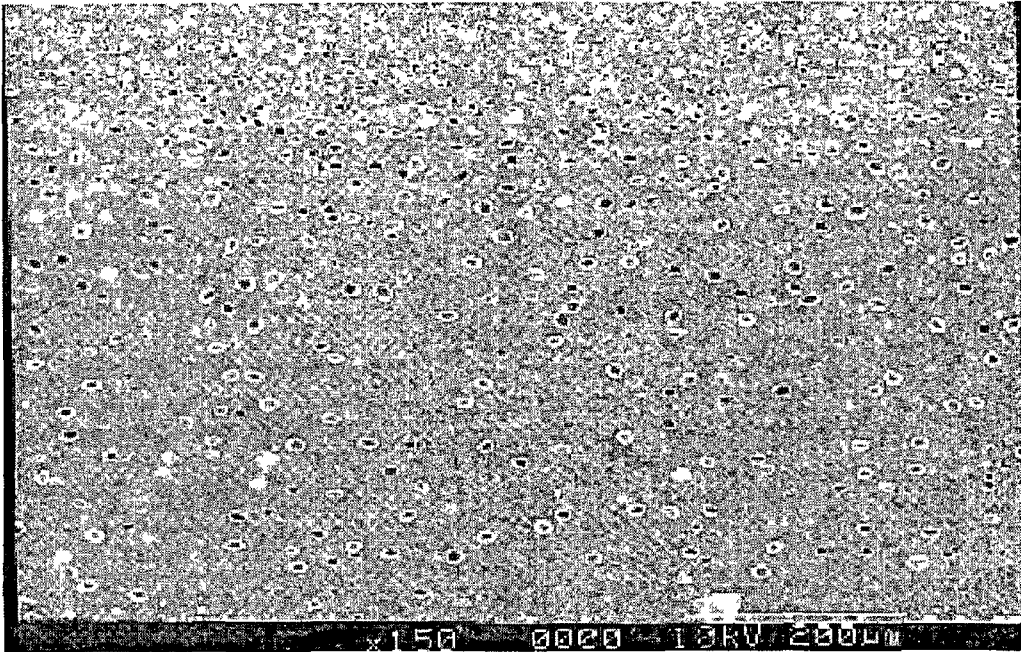


Figure 4 1 3 **Cross-sectional view of the main body of the polyurethane membrane, PU1, at 150 times magnification**

A possible reason for the greater density of pores at the top surface of the membrane is that it is at this surface that the carbon dioxide produced escapes from the body of the cast membrane. Because the bottom surface is in contact with the glass casting plate and not with the water of the coagulation bath, the carbon dioxide is not evolved at this surface to the same extent as at the top surface resulting in a lower density of pores in this area.

The polyurethane membrane PU2 was produced, again, according to the procedure described in *Section 2 2 1*, i.e., the membrane was immersed in the water bath immediately after casting, not allowing the isocyanate groups of the polyurethane prepolymer to react gradually with atmospheric moisture.



Figure 4 1 4 **Bottom surface of polyurethane membrane, PU2,
at 1000 times magnification**

Figure 4 1 4 shows the bottom surface of the PU2 membrane. Immediately, it is clear from this image that the defects on this surface of the membrane are, in fact, holes. The SEM image of the top of this membrane, shown in *Figure 4 1 5*, shows that these holes have penetrated through the membrane and also appear on the top surface.

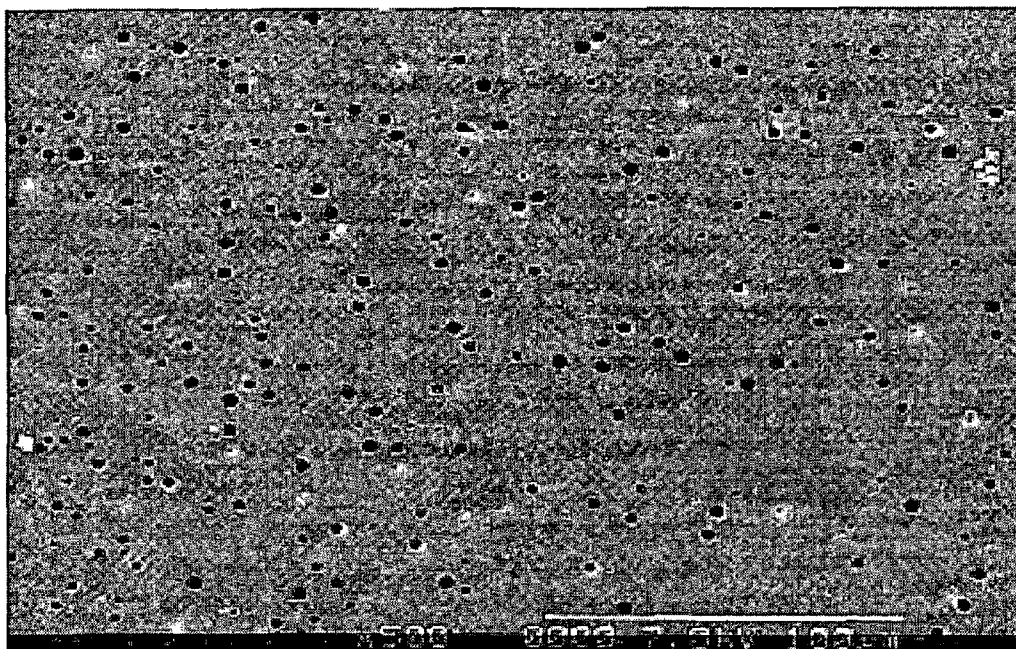


Figure 4 1 5 Top surface of polyurethane membrane, PU2, at 500 times magnification

It is clear, on comparing the images of the two polyurethane membranes, that the duration of the evaporation time prior to immersing the cast membranes into the coagulation bath is a vital step in the successful production of a pervaporation membrane

Because there was no evaporation time allowed before the PU2 membrane was immersed in the coagulation bath, the evolution of the carbon dioxide during the curing reaction was far more rapid than in the case of membrane PU2 where a pre-immersion evaporation time was allowed. It was the absence of this opportunity for the prepolymers terminal isocyanate groups to gradually react with atmospheric moisture, that was responsible for producing flaws in the membrane and thus rendering it unsuitable for use in a pervaporation process.

The synthesis of the polydimethylsiloxane membrane did not include the immersion of the cast membrane in a coagulation medium but the

simple evaporation of the solvent system. As a result, the presence of defects in the membrane is not expected for the same reasons as in the preparation of the polyurethane membrane.

However, a preparation step which was expected to determine the structural integrity of the membrane was the mixing step. As described in *Section 2.2.2*, two polydimethylsiloxane membranes were produced. The first, PDMS1, was produced from a prepolymer solution which was mixed with its solvent system for the manufacturer's recommended twenty minutes whereas the second, PDMS2, was mixed for only three minutes.

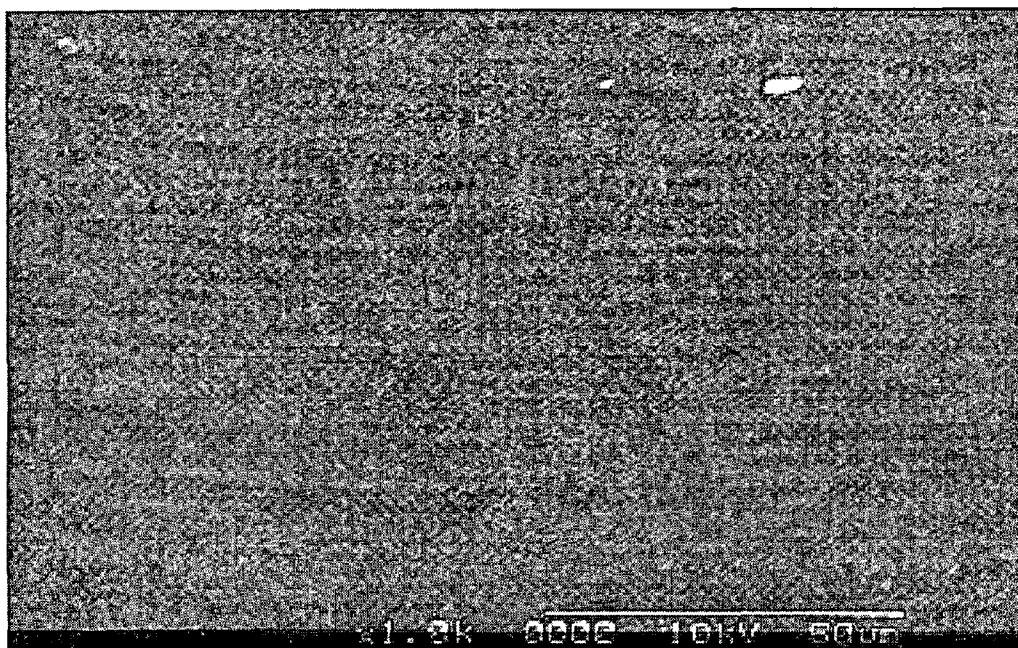


Figure 4 1 6 Top surface pf the polydimethylsiloxane membrane, PDMS 1, at 1000 times magnification

Figure 4 1 6 shows the top surface of membrane PDMS1, the production procedure of which has been described in Section 2 2 2. No defects are present on this surface and this image suggests that a dense polymeric membrane has been produced.

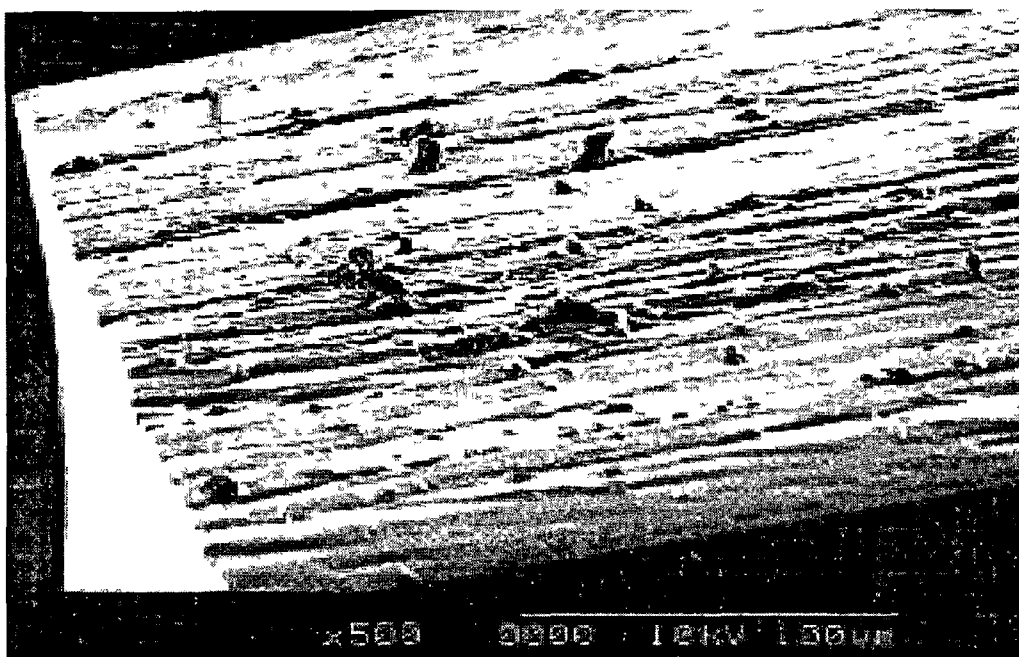


Figure 4 1 7 Cross-sectional corner view of the polydimethylsiloxane membrane, PDMS1, at 500 times magnification

Figure 4 1 7 shows a cross-sectional corner view of the same membrane. This image shows that no pores are present in the body of the membrane. Some ridges are unavoidably present which may be attributed to the cutting process during sample preparation. Another cross-sectional view of the same PDMS1 membrane may be seen in *Figure 4 1 8*. This image again confirmed that PDMS1 was a dense, defect-free membrane.

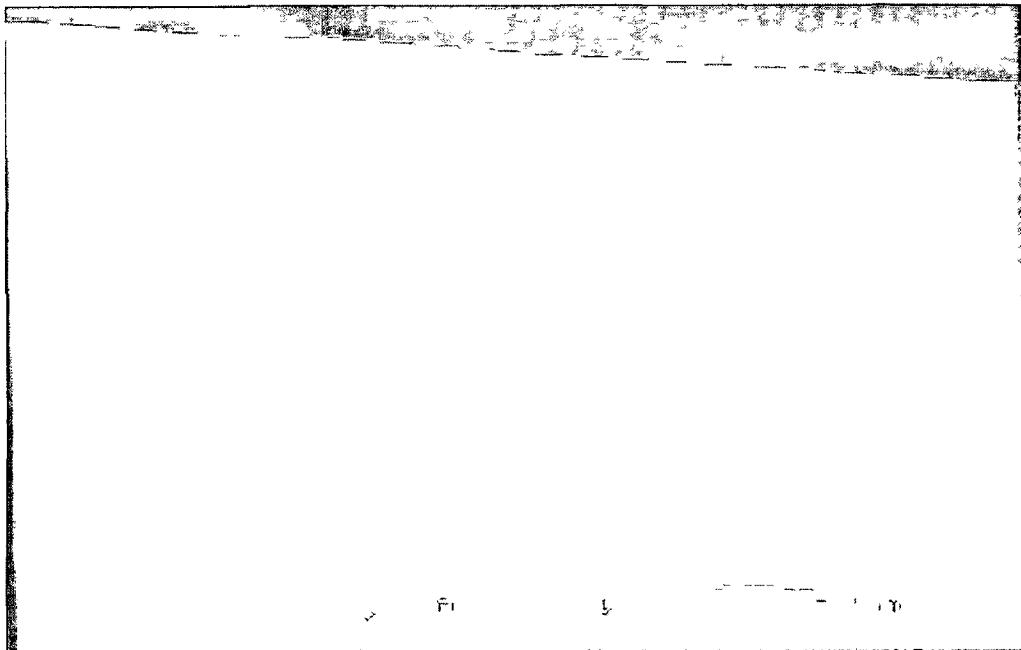


Figure 4 1 8 **Cross-sectional view of the main body of the polydimethylsiloxane membrane, PDMS1, at 1000 times magnification**

As previously mentioned in this section, the polydimethylsiloxane membrane, PDMS2, was prepared from a prepolymer solution which was mixed with its solvent system for three minutes, not the manufacturers recommended twenty minutes. The result of this inadequate mixing resulted in the production of an inhomogeneous prepolymer mixture. *Figure 4 1 9* shows the image of the top surface of this membrane.



Figure 4 1 9 **Top surface of the polydimethylsiloxane membrane, PDMS2, at 100 times magnification**

From this image, it may be seen that there are sections of the membrane which contain a higher concentration of the prepolymer. The sections are surrounded by, what appears to be, veins of a lower concentration and more homogeneous mixture of the prepolymer. On magnifying this image (*Figure 4 1 10*) it may be seen that these aggregates of polymer contain, themselves, defects.

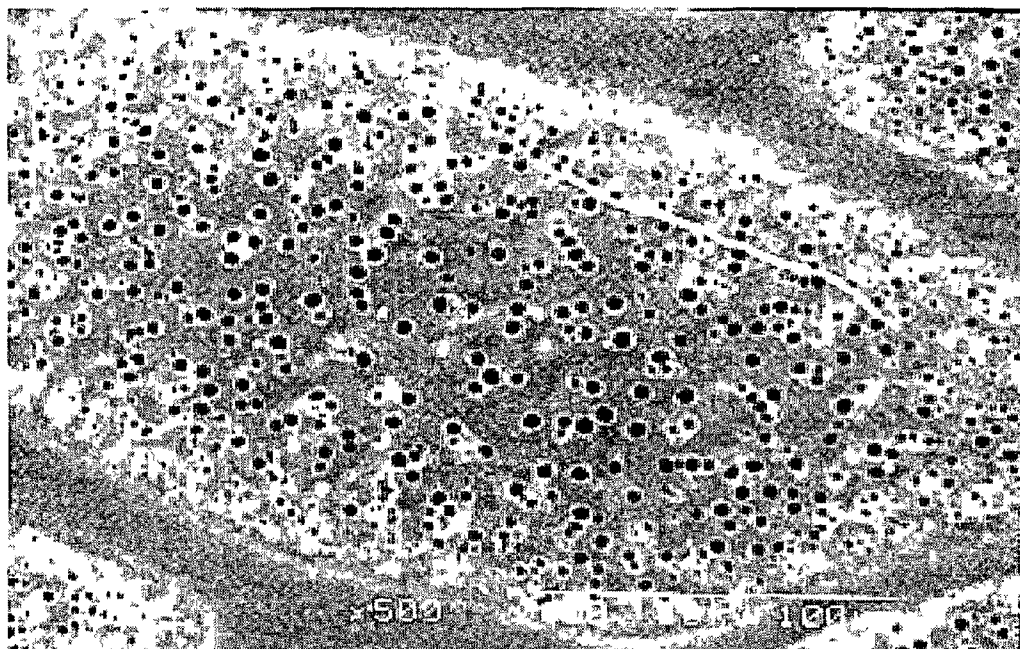


Figure 4 1 10 Top surface of the polydimethylsiloxane membrane, PDMS2, at 500 times magnification

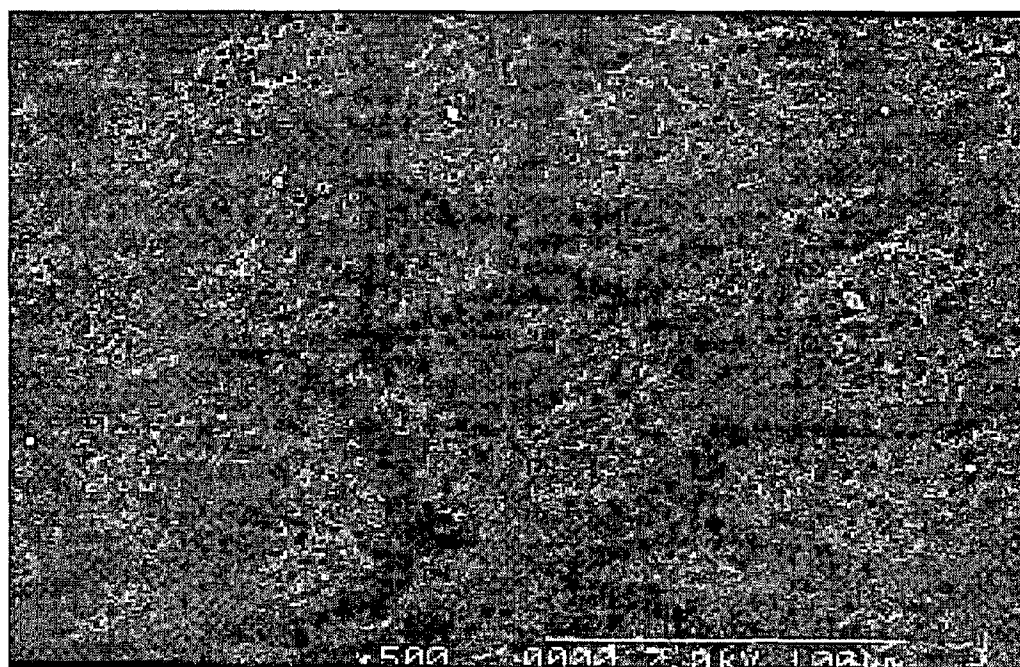


Figure 4 1 11 Bottom surface of the polydimethylsiloxane membrane, PDMS2, at 500 times magnification

The bottom surface of the membrane is shown in *Figure 4 1 11* and illustrates how these aggregates may also be seen on the bottom surface of the membrane although the defects present on the top surface are not as apparent on the bottom

The presence of these aggregates of polymer throughout the membrane renders it useless in pervaporation processes. Under the conditions of reduced pressure which a pervaporation membrane must be capable of withstanding, a membrane such as PDMS2 would buckle. The main effects of a pervaporation buckling would be seen in exaggerated flux through the membrane and a decrease in the selectivity of the membrane.

The SEM images of the membranes PU1 and PDMS1 also provided information regarding the possible densities of these membranes. Because it was not possible within the scope of this study to analytically determine the densities of the synthesised membranes, a visual examination of the SEM images was carried out to identify the more dense membrane relative to the other. The images of the PU1 membrane seen in *Figures 4 1 4, 4 1 2* and *4 1 3* have all shown the presence of pores in the body of the membrane PU1. However, no pores have been seen in the PDMS1 membrane.

As a result, it may be deduced that purely on a visual basis, the polyurethane membrane, PU1, is less dense than the polydimethylsiloxane membrane, PDMS1.

4.2 Glass Transition Temperatures

As described in *Section 2.7*, the glass transition temperatures, T_g , of the polyurethane and the polydimethylsiloxane membranes were measured using differential scanning calorimetry (DSC). The T_g is exhibited by amorphous polymers or the amorphous regions of partially crystalline polymers when a viscous or rubbery state is transformed into a hard, brittle, glass-like state. The T_g of a polymer is observed by DSC as a stepped increase in the heat capacity of the sample during heating due to an enhancement of molecular motion in the polymer. As a result, the magnitude of the T_g gives an indication as to the degree of motion which may take place within a polymer chain.^[69]

The glass transition temperatures measured for the polyurethane and the polydimethylsiloxane membranes were found to be -22.8°C and -24.37°C respectively. It should be noted at this point that the aforementioned measured T_g values shall be used solely as an indicator as to the degree of 'glassiness' of the two polymers. Because, in all cases, the operating temperature of the pervaporation processes were greatly in excess of the glass transition temperatures of the two membranes, these values may not be validly related to the separation performance and characteristics of the membranes.

Bearing this in mind, relating these T_g values to the physical characteristics which are expected to influence the membranes performance in a separation process, the fact that the T_g of the polydimethylsiloxane membrane is less than that of the polyurethane membrane, suggests that the polydimethylsiloxane membrane is 'less glassy' than the polyurethane membrane.

This is supported by the structural characteristics of the two polymers which have previously been discussed in *Section 1 10*. The presence of the hard-soft-hard segment sequences throughout the polyurethane polymeric chains suggests that the polyurethane is less flexible and has the potential for a more restricted chain mobility compared to the polydimethylsiloxane.

However, before any observation and comparisons may be made regarding the structural characteristics of the two membranes based on the evidence originating from the measured glass transition temperatures, it should be noted that the differences between the T_g values of the two membranes is very small. Ideally this analytical techniques would be more successfully used when dealing with polymers with greatly varying degrees of crystallinity but the values do appear to substantiate the other physical evidence previously discussed.

4 3 Swelling Factors

As previously stated (*Section 1 6*), the separation process in pervaporation is dependent on the different permeabilities of the components to be separated by the membrane. Because these permeabilities depend, to some extent, on the sorption properties of the individual components, the solubilities of the mixture components have been investigated as they describe the affinity of a component for a given membrane.

The amount of pure liquid absorbed into the membrane was measured and because the liquid mixtures separated in this study were aqueous

solutions of the organic liquids mentioned in *Table 2 4 1*, the sorption data will be discussed in terms of a comparison of the extent of swelling of a given membrane in the organic component with respect to that in water

The solubility differences between the components of a mixture in the polymeric membranes constitute some of the principle factors considered in the choice of a suitable polymer for a separation ^[8] because of this, any differences observed in the measured solubilities may be used in predicting a membranes performance in a given separation

4 3 1 Polyurethane Membrane

As can be seen from the table of swelling data (*Table 3 4 3*), the liquid with the greatest affinity for the polyurethane membrane was ethyl acetate, with a swelling factor of 2 25, and that with the lowest affinity for polyurethane was water, its swelling factor being measured as 0 019 Between these limits lie the other three liquids tested MEK, MIBK and aniline with values of 1 87, 1 27, and 0 09 respectively

Due to the fact that polyurethane is a hydrophobic polymer it is expected that water would be preferentially excluded from the polymer matrix compared to organic liquids This fact was confirmed by the low swelling factor calculated from the sorption tests carried out on the polyurethane membrane

The presence of a bulky benzene ring, and as a result its relatively higher molecular volume (*Figure 4 3 1*), which makes up part of the

aniline molecule and the proposed lack of flexibility of the polyurethane polymer matrix (Section 4.2) both contribute to the low sorption of the aniline into the polyurethane membrane

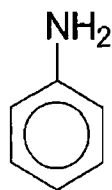
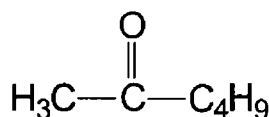


Figure 4.2.1

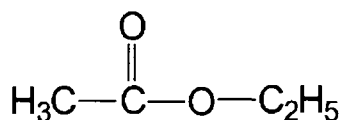
Of all the organic liquids tested, it exhibited the lowest affinity for the polyurethane membrane (0.09) and was only marginally greater than water (0.019) which was almost completely excluded from the hydrophobic polymer

Other pervaporation studies have shown that the uptake of bulkier molecules decreases as $C_1 \rightarrow C_n$. Also, the same research showed that branched molecules show slower uptake than their linear homologues due to their restricted movements [46]

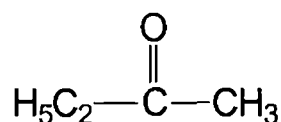
However in this study, the molecular size of the other organic liquids examined contributed very little to their relative affinities for the membrane



Methyl Isobutyl Ketone



Ethyl Acetate



Methyl Ethyl Ketone

Figure 4 2 2

This was due to the fact that all three liquids have a similar degree of branching (*Figure 4 2 2*), in that, the differences in their molecular sizes and structures are not significant enough to influence their relative sorption into a polymer matrix and to predict their sorption abilities

4 3 2 Polydimethylsiloxane Membrane

As for the polydimethylsiloxane membrane, again water was excluded from the membrane, it producing a swelling of 0 006, and even to a greater extent than in the polyurethane membrane. A possible explanation for the greater sorption of water into the polyurethane polymer matrix is that water has a tendency to bind to the urethane sites present throughout the polyurethane polymer (*Section 1 12 1*). The absence of these urethane sites from the polydimethylsiloxane membrane (*Section 1 12 2*), results in water being, for the most part, excluded from this polymer to a greater extent than seen in the polyurethane polymer. As with the polyurethane membrane, the aniline affinity for the PDMS membrane was the lowest of all the organic liquids tested with a swelling factor of 0 03. However, a difference in the swelling factor trend may be seen compared to the polyurethane membrane. In this case, MIBK had the greatest degree of sorption in the membrane (0 95) with ethyl acetate (0 66) and MEK (0 49) following

Comparing the overall values of swelling factors calculated for all five liquids in both membranes, it may be seen that the magnitude of those values in the polyurethane membrane for all the liquids was considerably larger than those calculated in the PDMS. However, once again the lack of significant difference between the extent of branching in seen the three linear organic liquids is apparent from these sorption experiments as the extent of the sorption into the PDMS membrane of these liquids showed no obvious correlation with their molecular size.

Having shown that the sorption experiments are, alone, relatively inconclusive in the prediction of a membranes performance in the pervaporation processes studied, they may be used in conjunction with the pervaporation data to ascertain some additional information regarding the potential separations. However, it should be noted at this point that all sorption experiments were carried out at ambient temperatures whereas the pervaporation experiments were run at temperatures ranging from 50 to 80°C. As a result, the sorption data presented in this report may only be used as an evaluation of suggested trends in the sorption of different molecules into the polymer membranes during the course of the pervaporation processes, as has been the case for other researchers presenting similar material [53].

A number of examples of the correlation of sorption and pervaporation data may be seen. The first of these being in the case of the separation of aniline and water at 80°C through a polyurethane membrane. This experiment produced the second highest of all the permeate flux values at that temperature i.e. 0.801 kg/m²hr suggesting that the presence of aniline in the polymer matrix tends to enhance the flux of water through the membrane at elevated temperatures. This observation may be made due to the fact that the high flux was coupled

with low selectivity, which was predicted from the low swelling factor for aniline (0.09) in the membrane. To deduce that the presence of aniline in the membrane enhances that flux of water through the membrane may not be entirely accurate but the fact that the boiling point of water is less than that of aniline indicates that the diffusion coefficient of water through this membrane and in the presence of aniline and at a temperature of 80°C is sufficient to increase its flux relative to aniline.

However, there are also some examples of limited correlation between the sorption data and the pervaporation data in the cases of the separation of a number of other liquid mixtures studied. From the swelling factors calculated (*Table 3.4.3*), it may be seen that aniline showed the lowest affinity for polyurethane. It is also observed that the lowest selectivity values are obtained in the pervaporation of aniline and water using the polyurethane membrane.

Other similarities are also apparent e.g. sorption experiments show that ethyl acetate has a greater affinity for polyurethane than MEK. The trend is also seen in the pervaporation experiments as the selectivity values are higher for the separation of ethyl acetate and water than for the separation of MEK and water, at all the temperatures examined.

In the case of the PDMS membrane, the sorption experiments show that MIBK had the greatest affinity for the PDMS membrane (*Table 3.4.4*) and in the separation of MIBK and water using PDMS, the largest values of selectivity are observed over the whole temperature range examined. This correlation between the two sets of data continues for all the mixtures separated using the PDMS membrane.

4.4 Activation Energy of Permeation

The calculated activation energies of permeation are shown in *Tables 3.3.1 & 3.3.2* for polyurethane and polydimethylsiloxane, respectively. For all four aqueous solutions separated, the activation energy values were seen to be higher in all cases using the polyurethane membrane PU1 compared to the polydimethylsiloxane membrane PDMS1. This indicates that the energy barrier which must be overcome by the molecules to permeate through the polyurethane membrane is significantly greater than that which must be overcome in order to permeate the polydimethylsiloxane membrane.

The differences in activation energy for the organic liquids examined arise from the differences in the molecular sizes of the organic molecules and the affinity the permeating molecule has for the membrane through which it is passing.

This is clearly shown in the case of the permeation of aniline through both membranes. As discussed in an earlier section (*Section 4.3*), the main structural differences between the organic liquids are due to the presence of a benzene ring in aniline and no such ring in any of the other molecules. In the case of the activation energy of permeation of aniline through the polyurethane membrane compared to the other liquids i.e. MEK, MIBK and ethyl acetate, the calculated value was significantly higher for aniline (46.90, 60.06, 55.36 & 135.54 kJmol⁻¹, respectively).

A possible explanation for this may be due to the greater molecular volume of the aniline molecule compared to that of the organic components of the other liquid mixtures which were separated. The

same trend is observed in the case of the polydimethylsiloxane membrane with an almost twofold difference in activation energy between aniline and the highest value for any other liquid (aniline 25.72 and ethyl acetate 12.29 kJmol⁻¹)

However, differences in the values of activation energy calculated for the two membranes relate to differences in the polymer matrix, pore size and the extent of the polymers hydrophobic/hydrophilic nature. The fact that the activation energies for the polyurethane membrane are significantly higher than those for the polydimethylsiloxane membrane, indicates the greater hydrophobic nature of the polydimethylsiloxane as compared to that of the polyurethane membrane. This reasoning is also supported by the calculated swelling factors of water in the two membranes. As previously discussed in *Section 4.3*, the ability of water to sorb into the polyurethane polymeric matrix is twice that in the polydimethylsiloxane membrane. These figures show that a greater energy barrier must be overcome in order for organic molecules to penetrate the polyurethane membrane but this is coupled with higher total flux values than are seen with the polydimethylsiloxane membrane indicating that there is a greater tendency for water to permeate the polyurethane membrane.

The relatively low values of activation energy seen with the polydimethylsiloxane membrane indicates that, energetically, it is more favourable for organic liquids to permeate this type of membrane. This may be combined with the fact that higher selectivity values are produced when using the polydimethylsiloxane membrane compared to those for the polyurethane membrane, a subject which will be discussed further in *Section 4.5*.

4 5 Flux & Selectivity

4 5 1 General trends in flux & selectivity

Pervaporation measurements were carried out on aqueous solutions of the four organic liquids listed in *Table 2 4 1* at temperatures of 50, 60, 70 and 80°C in order to investigate the influence of the operating temperature on the permeate flux and the selectivity of the mixture/membrane system. A starting feed concentration of 1% w/w organic in water was chosen in all cases and as a result, the characteristic pervaporation parameters obtained for these separations may be compared.

In all separations carried out in this study, the membranes used both permeated the organic components of the mixtures preferentially, which was to be expected due to the hydrophobic nature of the membranes used. However, the extent to which this occurred varied greatly depending on the membrane used, the mixtures separated and the system operating temperature.

The flux through the membrane and the selectivity of the membrane towards the organic component of the mixtures were both seen to increase with increasing temperature. As previously mentioned in *Section 1 9*, the driving force for the separation and the way in which the separation is achieved in a pervaporation process relies on the establishing of a concentration-vapour pressure gradient across the membrane which, in turn, is dependent on the diffusion coefficient of the permeating molecules in the membrane. Because the diffusion coefficient of the permeating molecules, and therefore the concentration of these molecules in the membrane, is temperature dependent (*Section 1 9*), an increase in temperature will result in an increase in

the flux through the membrane and selectivity of the membrane towards the organic component of the mixture with increasing temperature, trends also found in the work of Meckl & Lichtenhaler ^[13] and Slater et al ^[63], respectively

As mentioned earlier, in all cases the permeate flux through the membrane was also seen to increase with increasing temperature. This was due to the increased thermal motion of the polymer chains in the membranes on increasing the operating temperature of the system. Increasing the operating temperature serves to create more free volume in the polymer matrix through which the molecules may diffuse at a faster rate. As a result the transport through the membrane is enhanced resulting in a total increase in flux.

4.5.2 Flux & selectivity in the PU and PDMS membranes

Even though the flux values were seen to increase with elevated temperatures, the flux through the polyurethane membrane was, in all separations, greater than the corresponding fluxes through the polydimethylsiloxane membrane. These high flux values were, however, accompanied by disappointing selectivity values, whereas the selectivity of the polydimethylsiloxane membrane towards the organic component of the liquid mixtures separated was significantly larger in all cases.

It may be suggested that the high flux values and the corresponding low selectivity values fully substantiate the fact that, as previously discussed in *Sections 4.3 & 4.4*, it is more favourable for water to permeate the polymer matrix of the polyurethane membrane compared

to the polydimethylsiloxane membrane. The greater quantities of water passing through the polyurethane membrane correlates with the data produced by the sorption experiments which showed that the levels of water absorbed into the polydimethylsiloxane membrane was three times less than that absorbed in the polyurethane membrane.

Conversely, it would appear that the low flux and high selectivity values obtained using the polydimethylsiloxane membrane would agree with the activation energy of permeation data and the sorption experiment results. Both sets of results indicate that water is preferentially excluded from the polydimethylsiloxane polymer matrix, when separated from the organic liquids chosen, to a greater extent than in the case of the polyurethane membrane. The reason for this may lie with the fact that water binds to the urethane sites found in the polyurethane polymer and so enhances the amount of water which is absorbed into the membrane and so permeates through it. Polydimethylsiloxane has no such sites onto which the water molecules may bind and so the permeation of water through the polymer is less than that seen in the polyurethane membrane.

The ideal criteria for a pervaporation membrane as laid down in *Section 1.10* state that the membrane should exhibit high permeability and high selectivity. It would appear that neither of the membranes used in this study exhibit these ideal requirements. However, it is quite rare to isolate a membrane which exhibits both of these criteria and so the membranes performance in the separation must be evaluated with the required stipulations for the separation in mind. In the case of the liquids mixtures examined in this study, the production of a organic rich, two-phase permeate which may be further separated by decanting will

suffice. As a result, both membranes fulfilled this criteria as two-phase permeate samples were produced in each case (Tables 3.1.1 - 3.1.16)

4.5.3 Flux & selectivity of individual separation

Having previously highlighted the differences in flux and selectivity values obtained using the two membranes, it must be stressed that the differences in these parameters for different separation also vary significantly.

Taking first the case of the polyurethane separations, very low selectivity and flux values were obtained for the separation of aniline/water. These results were expected from the sorption experiments and the activation energies of permeation which were calculated for this system. The swelling factors indicated that aniline was absorbed into the polyurethane membrane to a level only marginally greater than water. The activation energy of permeation for aniline through the polyurethane membrane was found to be 135.54 kJ mol⁻¹, greater than twice that which was measured for the other systems. This indicated, that of all the systems examined, a greater energy barrier must be overcome if aniline is to permeate the membrane.

However, some of the data obtained for the separations carried out do not correlate with the corresponding swelling factors and activation energies of permeation. An example of this was the separation of MEK/water using the same polyurethane membrane. Both the swelling values and the activation energies indicate that this separation should exhibit this membrane's best performance in that it produced a swelling

factor of 1.87 and the lowest activation energy was calculated for this separation. In fact, this separation produced a very disappointing set of data, with flux values lower and selectivity values only marginally higher than those seen in the aniline/water separation.

A possible reason for this may be that the solvent/polymer interactions which take place at ambient temperatures are very different from those which take place under the conditions of the pervaporation process. This occurrence indicates why it is merely as an estimation tool that parameters such as swelling factors and activation energies are used throughout this study.

Like the aniline/water separation, the ethyl acetate/water separation seems to fulfil expectations based on the other experimental data. With a swelling factor of 2.15 and an activation energy of 46.10 kJ mol⁻¹, the polyurethane membrane showed good selectivity towards the ethyl acetate at all the temperatures studied. Similar to the MEK/water separation, the separation of MIBK/water using polyurethane also produced unexpected data. The swelling factor (1.27) and activation energy (60.06 kJ mol⁻¹) for this separation both suggested little potential for a successful pervaporation separation. However, it was this separation which produced, perhaps, the best combination of selectivity and flux values of all the systems studied.

The separations carried out using the polydimethylsiloxane membrane also showed varying degrees of separation success. Once again, the separation of aniline/water showed the least success. The flux values were almost four times smaller compared to the same separation carried out using the polyurethane membrane, however, the selectivity towards aniline was almost four times greater over the whole

temperature range examined. This higher selectivity was expected due to the swelling factor (0.006) and activation energy (25.72 kJ mol⁻¹) calculated both of which were the smallest for any separation carried out using this membrane. A decrease in flux was also expected due to the higher levels of hydrophobicity which have been displayed by polydimethylsiloxane throughout the course of this study.

Once again, as in the case of the polyurethane membrane, the ancillary data produced predicted that the separation of MEK/water would produce a highly successful separation with a small activation energy (2.83 kJ mol⁻¹) and a high swelling factor (0.51). However, the separation yielded flux and selectivity values which were higher than only aniline. The occurrence of this trend in the two membranes suggests that, under the conditions of the pervaporation process, the success of an MEK separation may not be predicted from its ability to absorb the pure liquid.

A convention has evolved amongst pervaporation researchers which has resulted in pervaporation data being presented in the form of scatter plots^{[10] [58] [60] [67]}. There are two types of curves which allow the operator to examine the performance of the separation processes. Scatter plots of the feed concentration versus the partial organic flux through the membrane may be seen in Appendix 3 and the plots of feed concentration versus the corresponding permeate concentrations may be seen in Appendix 4.

Beginning first with the plots of feed organic concentration (%w/w) versus the permeate organic concentration (%w/w) it was observed that as the feed organic as the feed concentration decreased, the permeate organic concentration was seen to fall off as the amount of organic

remaining in the retentate was reduced. The first example of this may be seen from Appendix 4 (i) for the separation of MEK/water at 70°C and 80°C using a polyurethane membrane. It is clear from this graph that, at both temperatures, as the concentration of MEK decreased in the feed, the concentration of MEK in the permeate samples also decreased.

However, it is interesting to note that while using the polyurethane membrane, there was little or no influence of temperature on the separation characteristics of the process. This conclusion was drawn from the fact that the two curves overlap significantly. The same trend was observed for the separation of ethyl acetate/water using polyurethane as seen in Appendix 4 (ii). Again there is little separation between the two curves which would also suggest that the operating temperature of the system has little bearing on the separation potential of this particular membrane/mixture system.

The same separation carried out using the polydimethylsiloxane (Appendix 4 (iii) & 4 (iv), respectively) showed that the operating temperature of the system, again, had little influence on the composition of the permeate sample and hence the selectivity of the membrane towards the two organic liquids. However, there was a difference in the shape of the plots for the polyurethane separations and the polydimethylsiloxane membranes. In both the separation of MEK/water and ethyl acetate/water, the polydimethylsiloxane membrane produced a series of permeate samples which were richer in the organic component of the mixture compared to the polyurethane membrane. This may simply be interpreted as a graphical representation of the higher selectivity values produced for the

polydimethylsiloxane separations and for the same reason as stated during the discussion of that data

Considering the case of the separation of aniline/water using the polyurethane membrane, it is clear from the plot shown in Appendix 4 (v) that the operation of the system at the higher temperature of 80°C produced permeate samples with a higher aniline content than those produced at 70°C. As mentioned previously, a possible explanation for this lies in the fact that as the temperature increased the diffusion coefficient for the permeation of the aniline also increased, thus producing an aniline rich permeate at the higher temperature.

In contrast to this the plots produced for the aniline/water separation using the polydimethylsiloxane membrane (Appendix 4 (vi)) showed once again that the operation of the system at the higher temperature of 80°C did not produce this increased selectivity. The molecular volume of the molecule combined with the possible solvent/polymer interactions at this temperature may explain this lack of selectivity.

It is only the MIBK/water separation which clearly exhibits the difference in selectivity possible at the two temperatures. Using both the polyurethane and the polydimethylsiloxane membranes (Appendix 4 (vii) & 4 (viii), respectively), the operation at 80°C produced greater selectivity than at 70°C, however, the use of the polydimethylsiloxane membrane showed greater levels of MIBK in the permeate 87.73% w/w compared to a maximum of 58.34% w/w produced by the polyurethane membrane.

The plots of the feed concentration versus the partial organic flux through the membrane all show a general decrease in flux through the

membrane with a decrease in organic liquid in the feed. Whereas the plots produced for the separation of MEK/water and ethyl acetate/water were similar when plotting feed concentration versus permeate concentration, the plots versus partial organic flux are different.

Once again the influence of temperature on the total flux through the polyurethane and the polydimethylsiloxane membranes for the separation of ethyl acetate/water was minimal (Appendix 4(ix) & 4 (x), respectively). Although the total flux through the polyurethane membrane was significant, 0.258 kg/m²hr at 70°C and 0.484 kg/m²hr at 80°C, there is very little difference between the partial organic flux through the polyurethane membrane at 70°C and 80°C (0.084 kg/m²hr and 0.089 kg/m²hr, respectively). This suggests that the operation of the system at the higher temperature promotes the further permeation of water through the membrane and that the levels of organic component which have been permeated reaches a maximum. This too seems to be the case for the ethyl acetate/water separation using the polydimethylsiloxane membrane, however, in this case the levels of organic permeated were higher than that using the polyurethane membrane (Appendix 4 (x)).

In the separation of MIBK/water the influence of temperature on the partial flux through the polyurethane membrane (Appendix 4 (xi)) showed an interesting pattern. At the higher concentration i.e. 0.5 – 1.0% w/w organic in water, the partial flux through the membrane was considerably higher when operating the system at 80°C. This difference tended to decrease when the feed concentration became lower than 0.5% w/w organic in water. This was not the case using the polydimethylsiloxane membrane as the difference in the partial flux values at both temperatures were minimal. This was seen at all

concentrations and a levelling-off effect did not occur at any one concentration limit

A similar trend was noted in the instance of the separation of aniline/water using the polyurethane membrane (Appendix 4 (xiii)) Once again the influence of the operating temperature was quite marked with the permeation of the organic through the membrane at 80°C being almost four times that at 70°C Comparing these to the total flux through the membrane for this separation, it may be seen that the higher operating temperature also promoted the passage of water through the membrane to almost the same extent However, the situation was very different when the same separation was carried out using the polydimethylsiloxane membrane (Appendix (xiv)) The partial flux values were similar at both temperatures as were the total flux values indicating that even at the higher temperatures the polydimethylsiloxane membrane remained more hydrophobic than the polyurethane membrane

The errors which were encountered during the course of the pervaporation measurements were random From the sorption experiments it was clear that the time taken for the membrane/liquid mixture system to reach equilibrium was no more than ninety minutes at ambient temperature So at the elevated operating temperatures, an equilibration time of thirty minutes was allowed on each occasion of starting the test-cell so as to ensure that the feed reaching the membrane was at the required operating temperature However, there were some irregularities which appeared on the plots previously mentioned which have been attributed to the difficulty encountered in regulating the operating temperature of the system This problem arose at certain times of the day and season at which the experiments

were carried out. Due to fluctuating room temperatures, the control of the feed temperature proved very difficult and may have resulted in the momentary abnormal flux of some liquids through the relevant membranes.

5. Conclusions

The dilute aqueous solutions of methyl ethyl ketone, methyl isobutyl ketone, ethyl acetate and aniline were all separated, within the limits of 1% w/w - 0.1% w/w organic in water, using polyurethane and polydimethylsiloxane membranes in pervaporation processes.

The two types of membranes synthesised in this study were both deemed to be dense polymeric membranes. However, the SEM images showed that the presence of pores throughout the body of the polyurethane rendered it less dense than its polydimethylsiloxane counterpart, based solely on the SEM images. Within the membrane synthesis procedure, the pre-immersion evaporation time was found to be a significant step in the synthesis of a polyurethane membrane suitable for use in a pervaporation process. The smaller the pre-immersion period, the greater the extent of the critical defects on the surface and throughout the body of the polyurethane membrane. The critical step in the synthesis of the polydimethylsiloxane membrane was found to be the mixing, of the prepolymer and the solvent system used. On casting a non-homogeneous prepolymer solution, the resultant membrane also proved unsuitable for use in pervaporation processes due to the presence of surface defects which may act as a potential point of collapse under the reduced pressure conditions experienced during a pervaporation process.

The polydimethylsiloxane membrane proved to be more hydrophobic than the polyurethane membrane which was illustrated by the pervaporation and sorption data obtained using both the membranes. However, despite the greater tendency of the polydimethylsiloxane to permeate organics, the total flux through the polyurethane was greater

in all cases, over the range of temperatures and feed concentrations studied. However, the partial organic flux through the polydimethylsiloxane membrane was greater than that through the polyurethane membrane. It was this fact which resulted in the selectivity of the polydimethylsiloxane membrane being greater, for all separation and all temperatures, than the organic selectivity of the polyurethane membrane. The direct cause for the higher levels of selectivity exhibited by the polydimethylsiloxane membrane lies in its higher degree of hydrophobicity as the aqueous component of the liquid mixture was, for the most part, excluded from the polydimethylsiloxane polymer matrix, thus reducing the flux of the water through the membrane.

The influence of the operating temperature of the system on the flux through the membrane and the organic concentration of the permeate varied significantly. The separation which was affected to the greatest extent by the operating temperature of the system was that of aniline and water using both membranes in that the flux through the membrane and the permeate concentration were significantly different at the different temperatures used.

Despite the sorption data and the SEM images both substantiated the evidence produced from the flux and selectivity measurements, other physical data proved unreliable as a prediction tool for the separation performance of the system. However, during the course of this study it was also found that other sets of data showed some correlation with the final pervaporation data produced, but for the most part, these experiments may solely be used as a guideline for the possible outcomes of the separation experiments. The use of the glass transition temperatures must be considered in the same light as,

despite providing insight into the 'glassiness' of the polymer being used, this data can not be related directly to the performance of a membrane in a given separation as the operating temperatures of the systems were considerably higher than the T_g values of the polymers

If any one separation is to be isolated as the most successful of all those studied, the criteria for membrane selection mentioned in Section 1.10 must be taken into account. On the basis of these criteria, the separation of MIBK/water appeared to be the most successful using the polyurethane membrane as it produced good selectivity and partial flux values combined with the highest total flux values for that particular membrane. In the case of the polydimethylsiloxane membrane, the separation of MIBK/water seemed, once again, to be the most successful. Again, a combination of reasonable selectivity and flux values were obtained thus concluding that over the range of feed concentration and operating temperatures studied, the separation of MIBK/water produced the most acceptable data.

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Appendix 2

Sample calibration curves for permeate concentration determination

1 Separation of MIBK/H₂O using PDMS membrane at 70°C

Standard Solution %w/w MIBK/H ₂ O	Peak Area (1)	Peak Area (2)	Average Peak Area
1.7	151581	150680	151130.5
1.2	112373	110764	111568.5
0.8	76324	76764	76544
0.4	38853	39350	39101.5
0.2	18663	18071	18367
0.1	92073.5	92004.5	92039

Slope = 88438.42

$R^2 = 0.997904$

Error on slope = 2.65%

2 Separation of Ethyl Acetate/H₂O using polyurethane membrane at 70°C

Standard Solution %w/w Et Ac /H ₂ O	Peak Area (1)	Peak Area (2)	Average Peak Area
1.0	54871	55590	55230.5
0.8	44061	44325	44193
0.6	33516	34061	33788.5
0.4	22973	22272	22622.5
0.2	11300	11192	11246
0.1	5683.5	5562.5	5699.5

Slope = 54769.75

$R^2 = 0.999772$

Error on slope = 1.68%

Appendix 2 (continued)

Sample permeate concentration calculations

1 Separation of MIBK/H₂O using PDMS membrane at 70°C

Original weight of sample	= 4 837g
Weight of sample diluted to single phase	= 410 218g
Slope of calibration curve (Appendix 2)	= 88438 42
Average Peak Area	= 62513 5
% w/w MIBK in diluted sample	= 62513 5 / 88438 42 = 0 695% MIBK
Weight of MIBK in original sample	= 0 695% x 410 218g = 2 851g MIBK
% w/w MIBK in original sample	= <u>2 851</u> x 100 4 837 = 58 92% w/w MIBK

2 Separation of Ethyl Acetate/H₂O using PU membrane at 70°C

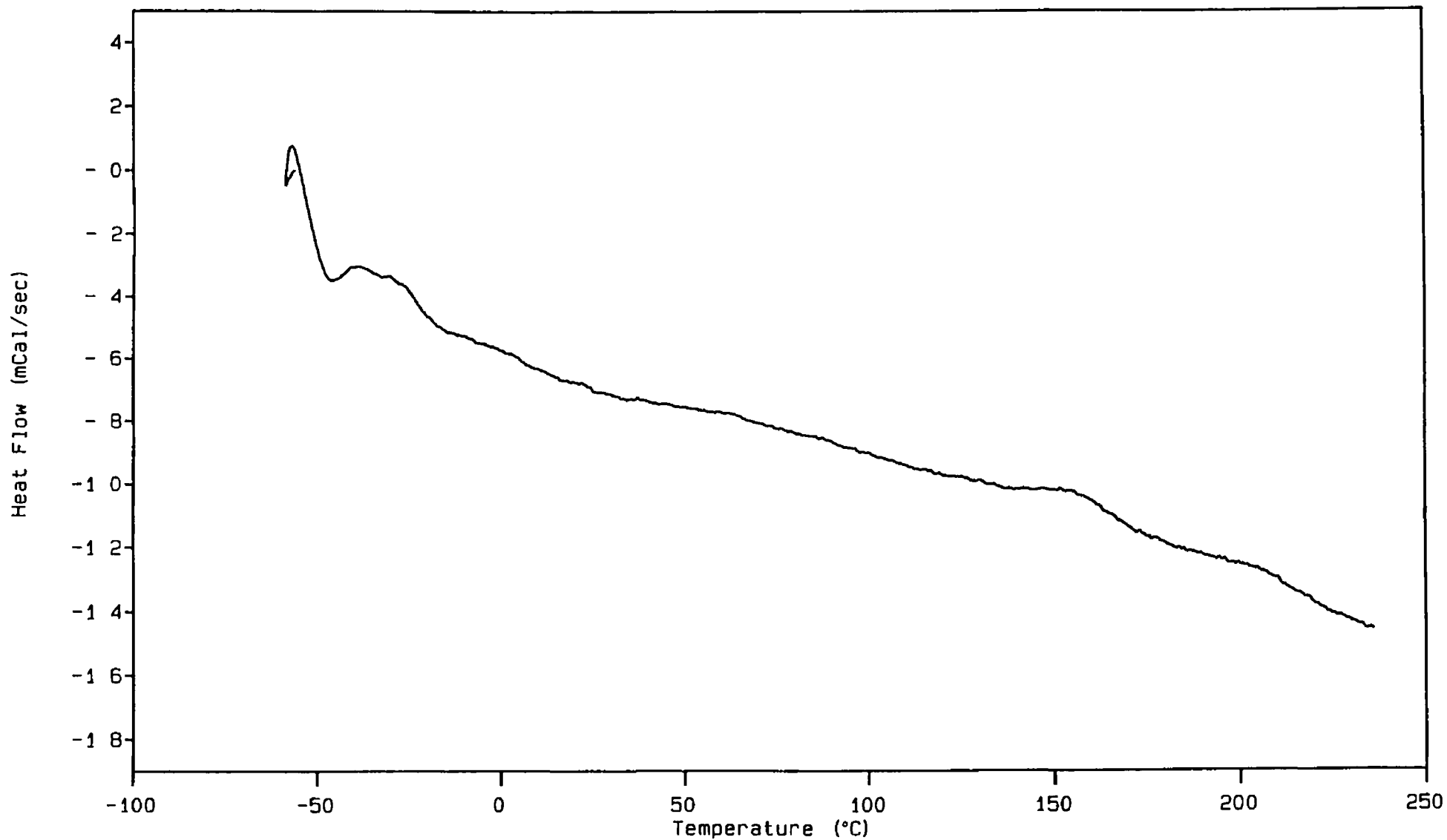
Original weight of sample	= 13 290g
Weight of sample diluted to single phase	= 100 118g
Slope of calibration curve (Appendix 2)	= 54769 75
Average peak area	= 58604 5
% w/w Ethyl Acetate in diluted sample	= 58604 5 / 54769 75 = 1 070 %w/w Et Ac
Weight of Ethyl Acetate in original sample	= 1 070% x 100 118g = 1 071g Et Ac
% w/w Ethyl Acetate in original sample	= <u>1 071</u> x 100 13 290 = 8 061%w/w Et Ac

DSC (QC)

SMPL ID PU-1
RUN ID
SIZE 1 810 mg
OPERATOR

DATE RUN
GAS 1 N2
GAS 2
COMMENT Crimp Pan

RheometricScientific

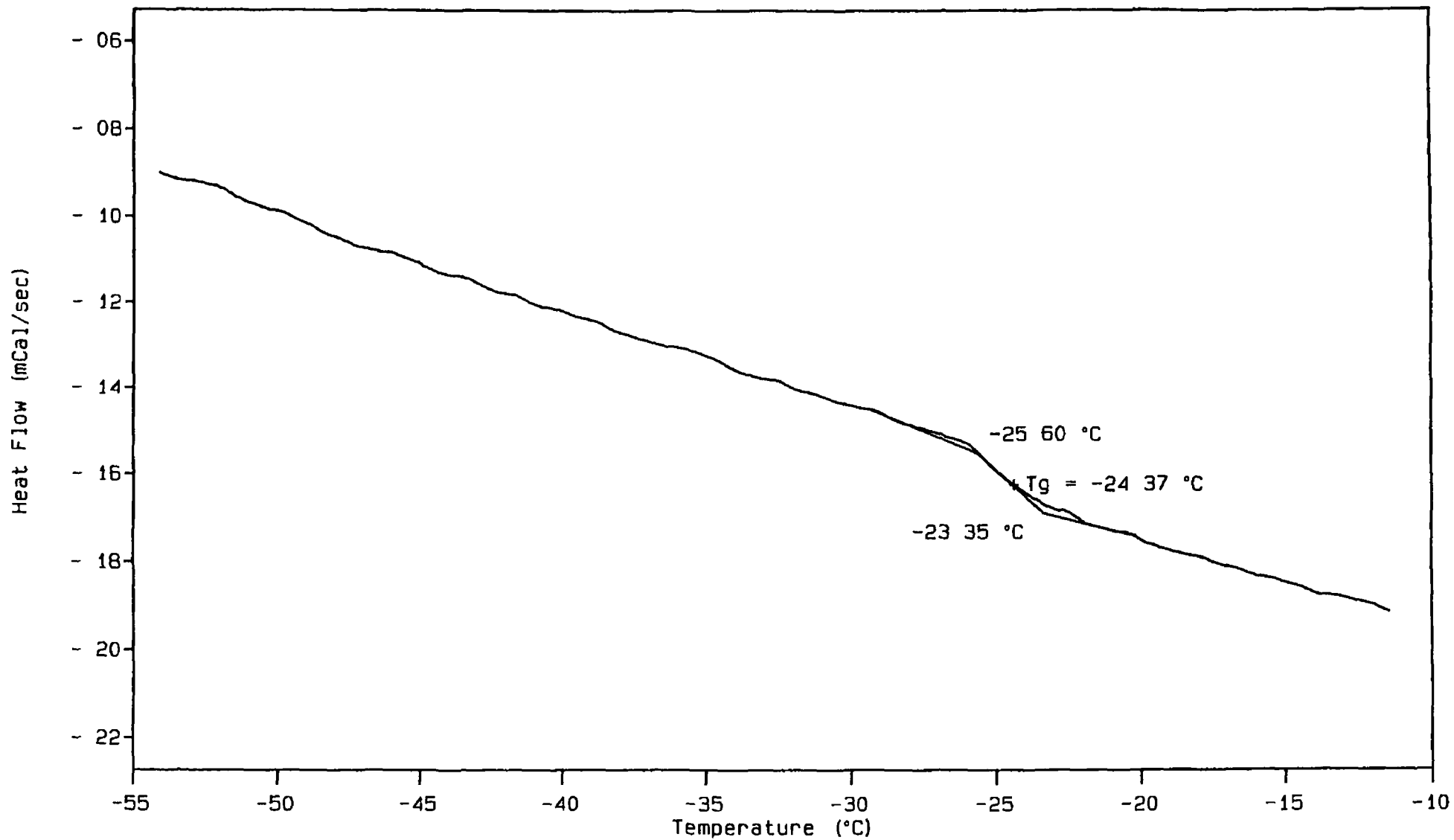


Appendix 3. Glass transition temperature of membrane, PU1

DSC (QC)

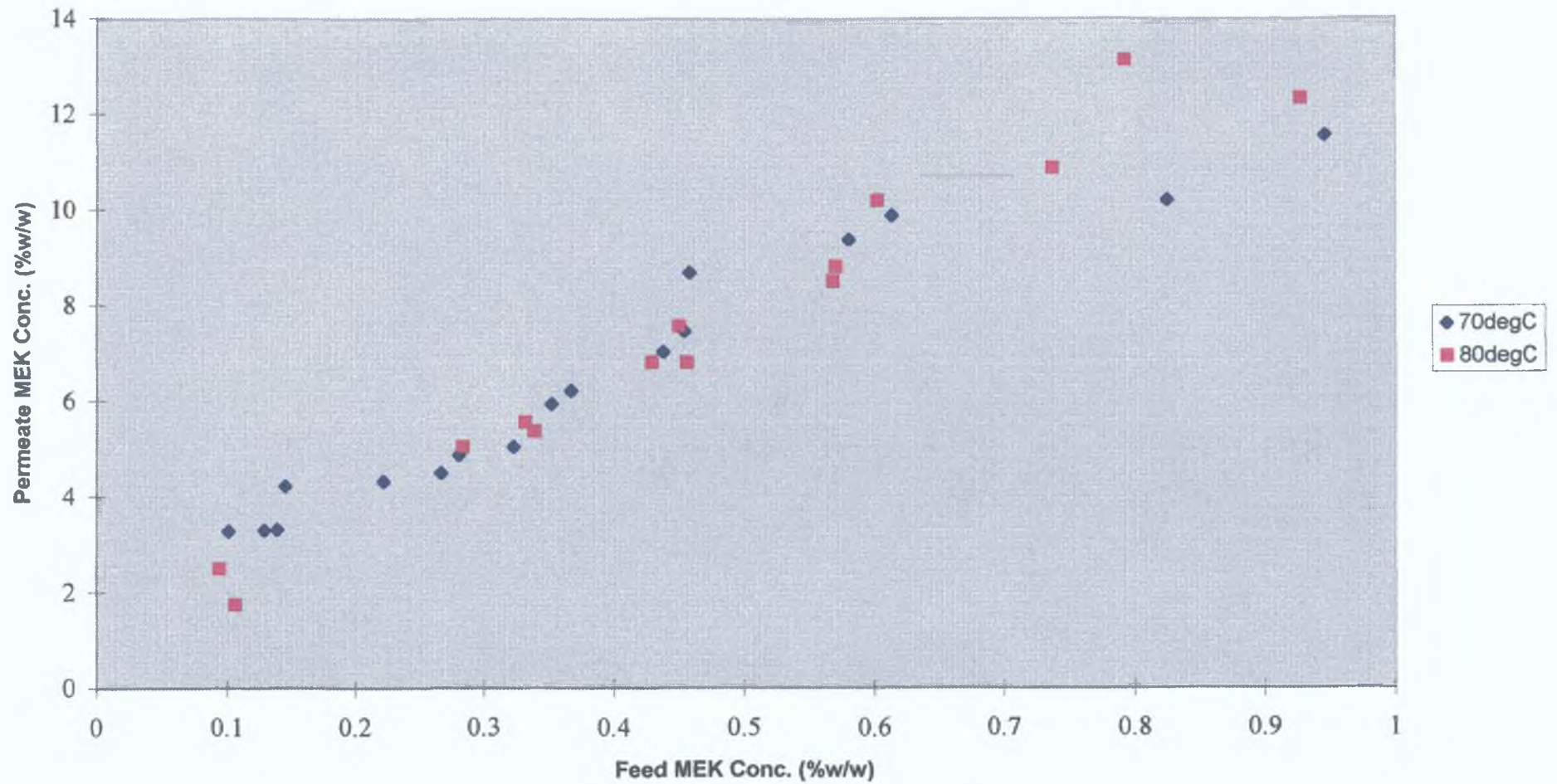
SMPL ID pdms
RUN ID
SIZE 2 330 mg
OPERATOR

DATE RUN
GAS 1 N2@10ml/min
GAS 2
COMMENT

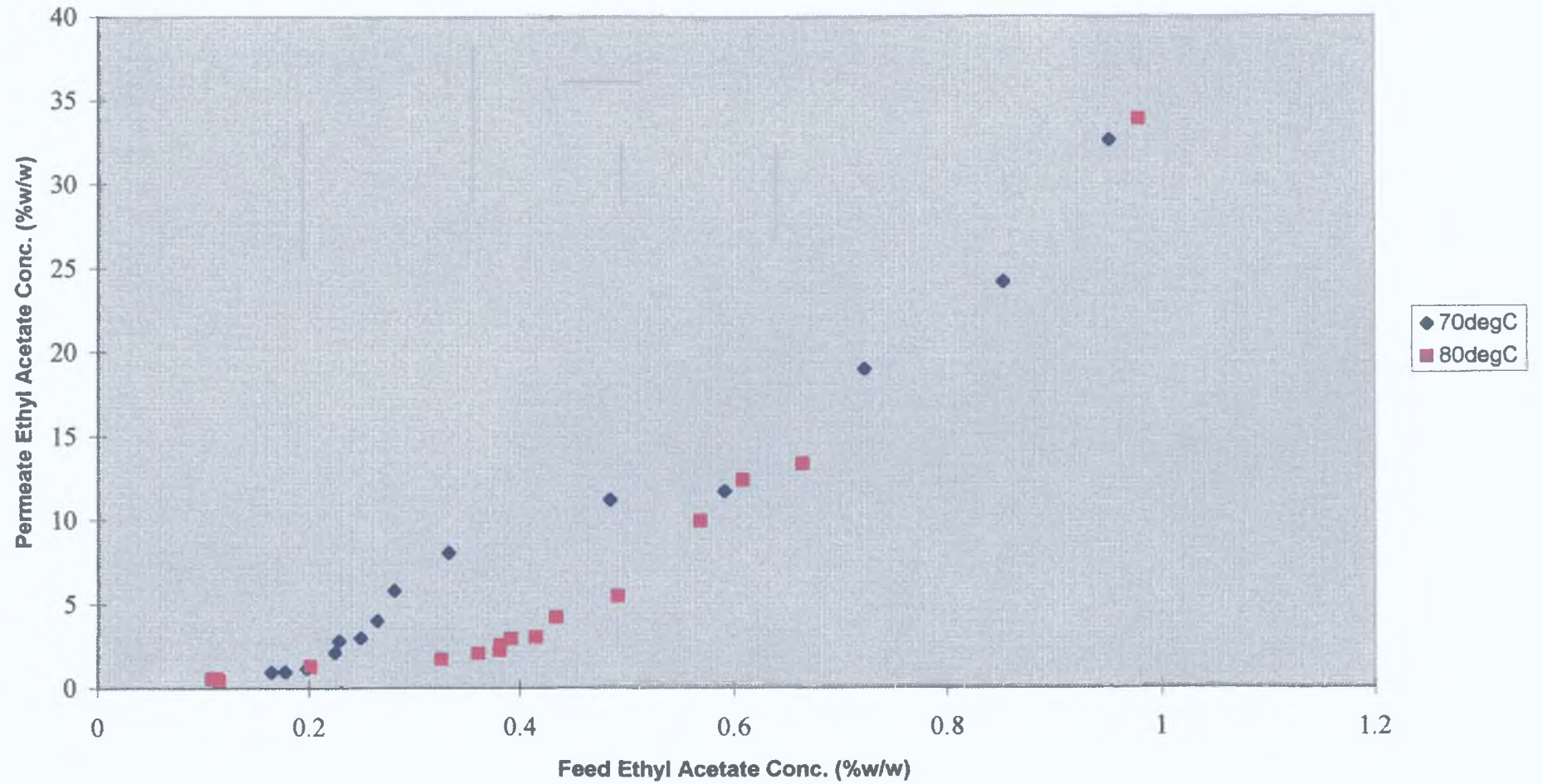


Appendix 3: Glass transition temperature of membrane, PDMS1

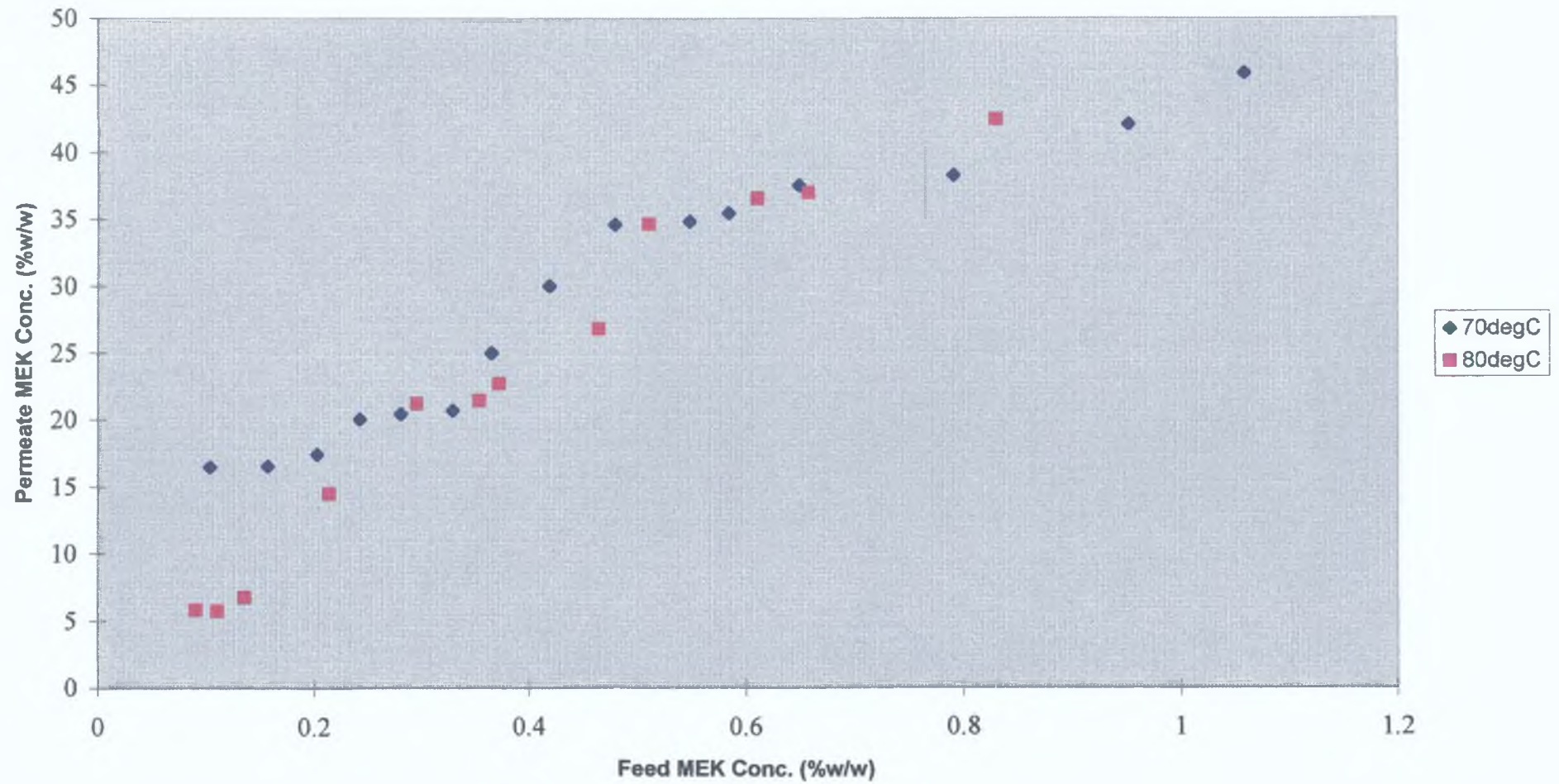
Feed MEK Conc. (%w/w) v. Permeate MEK Conc. (%w/w)
Polyurethane Membrane



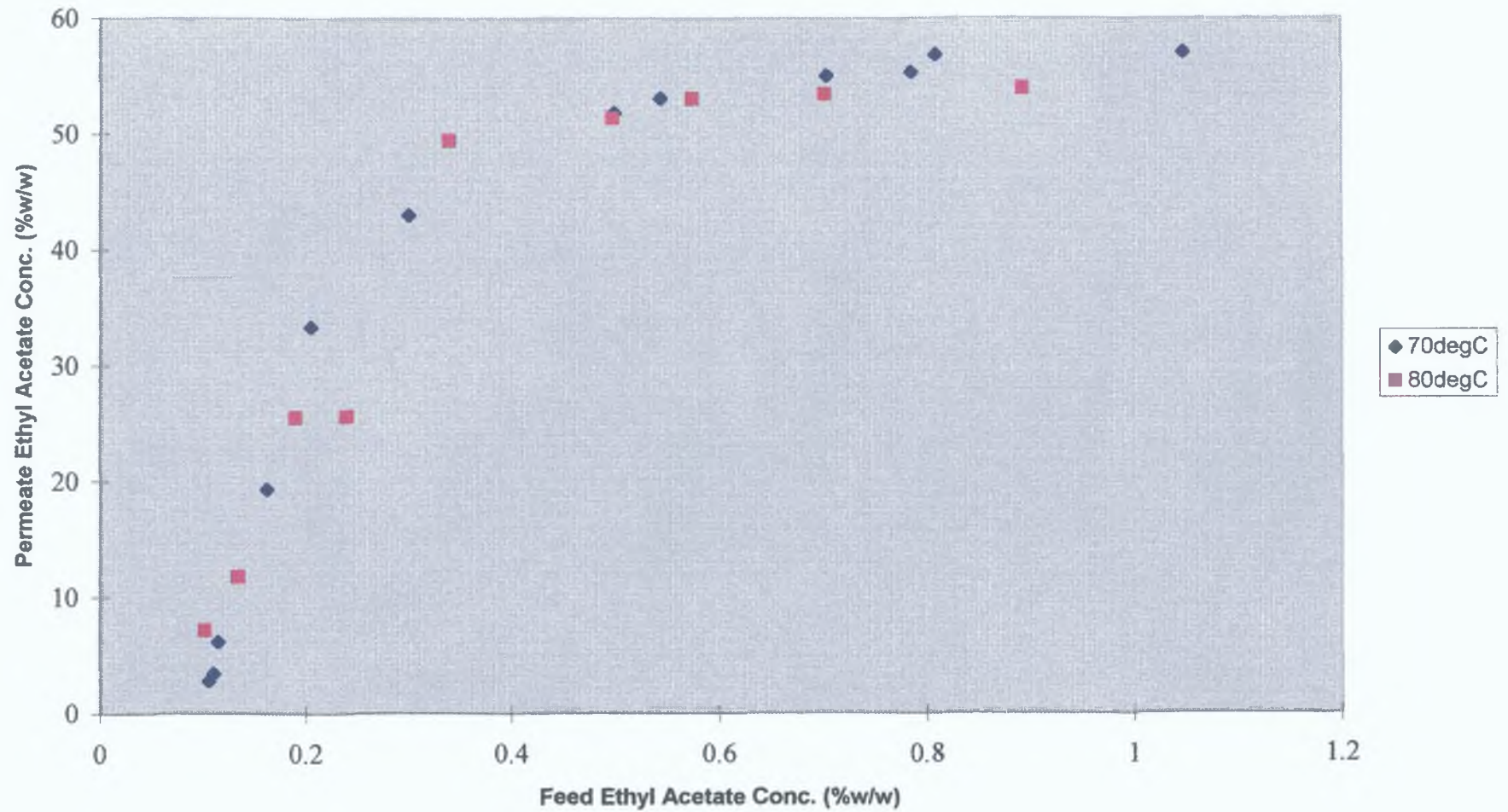
Feed Ethyl Acetate Conc. (%w/w) v. Permeate Ethyl Acetate Conc. (%w/w)
Polyurethane Membrane



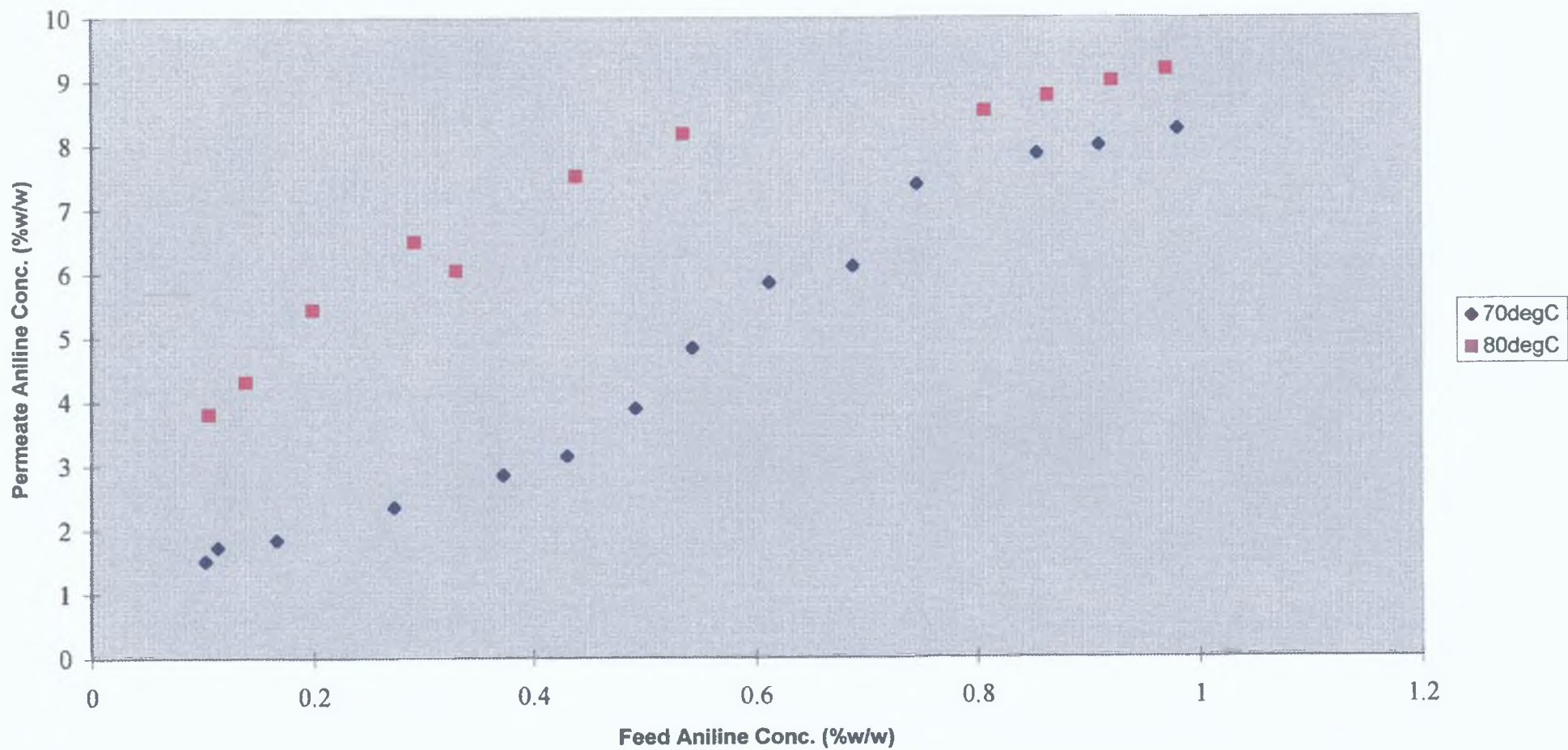
Feed MEK Conc. (%w.w) v. Permeate MEK Conc. (%w/w)
Polydimethylsiloxane Membrane



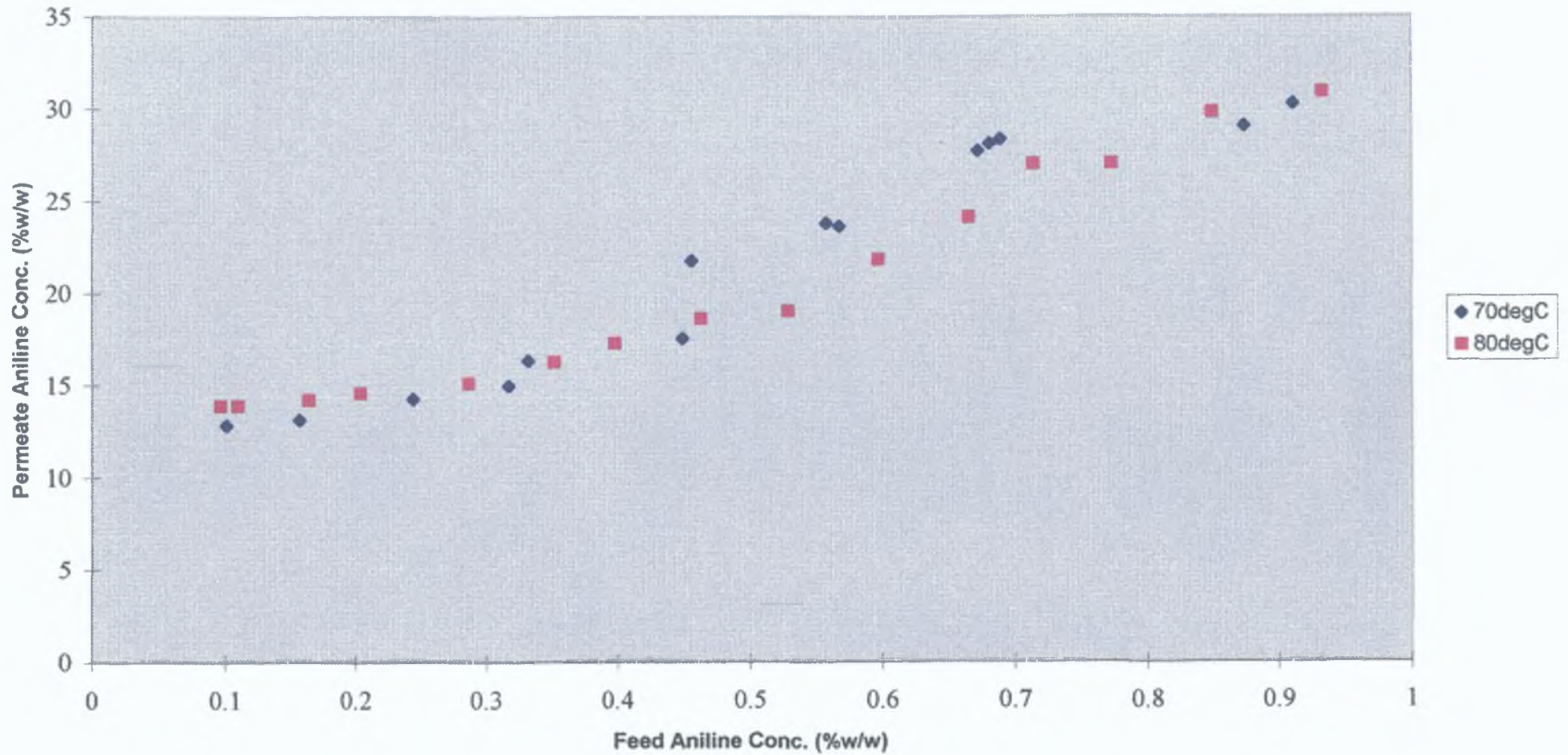
Feed Ethyl Acetate Conc. (%w/w) v. Permeate Ethyl Acetate Conc. (%w/w)
Polydimethylsiloxane Membrane



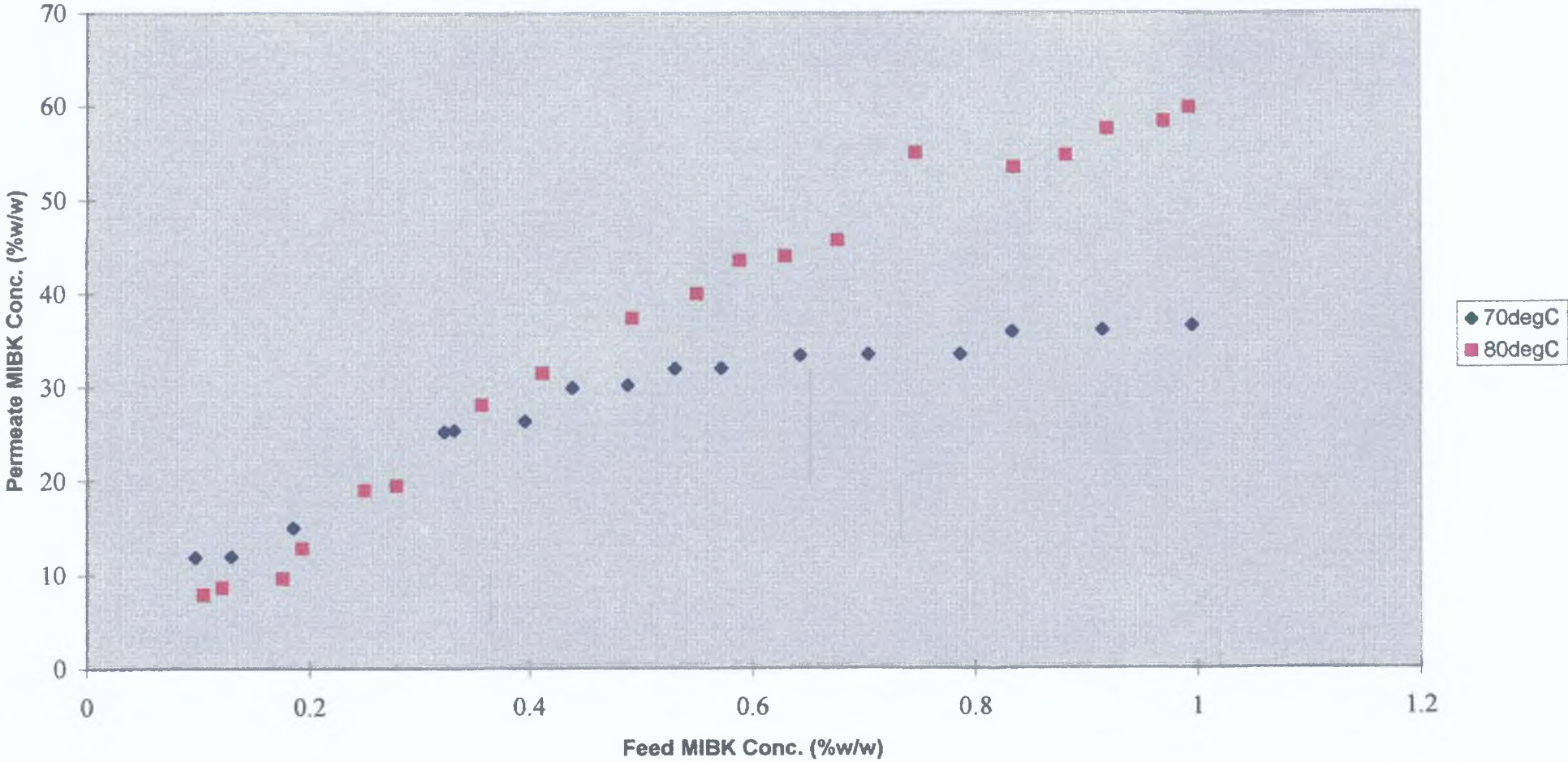
Feed Aniline Conc. (%w/w) v. Permeate Aniline Conc. (%w/w)
Polyurethane Membrane



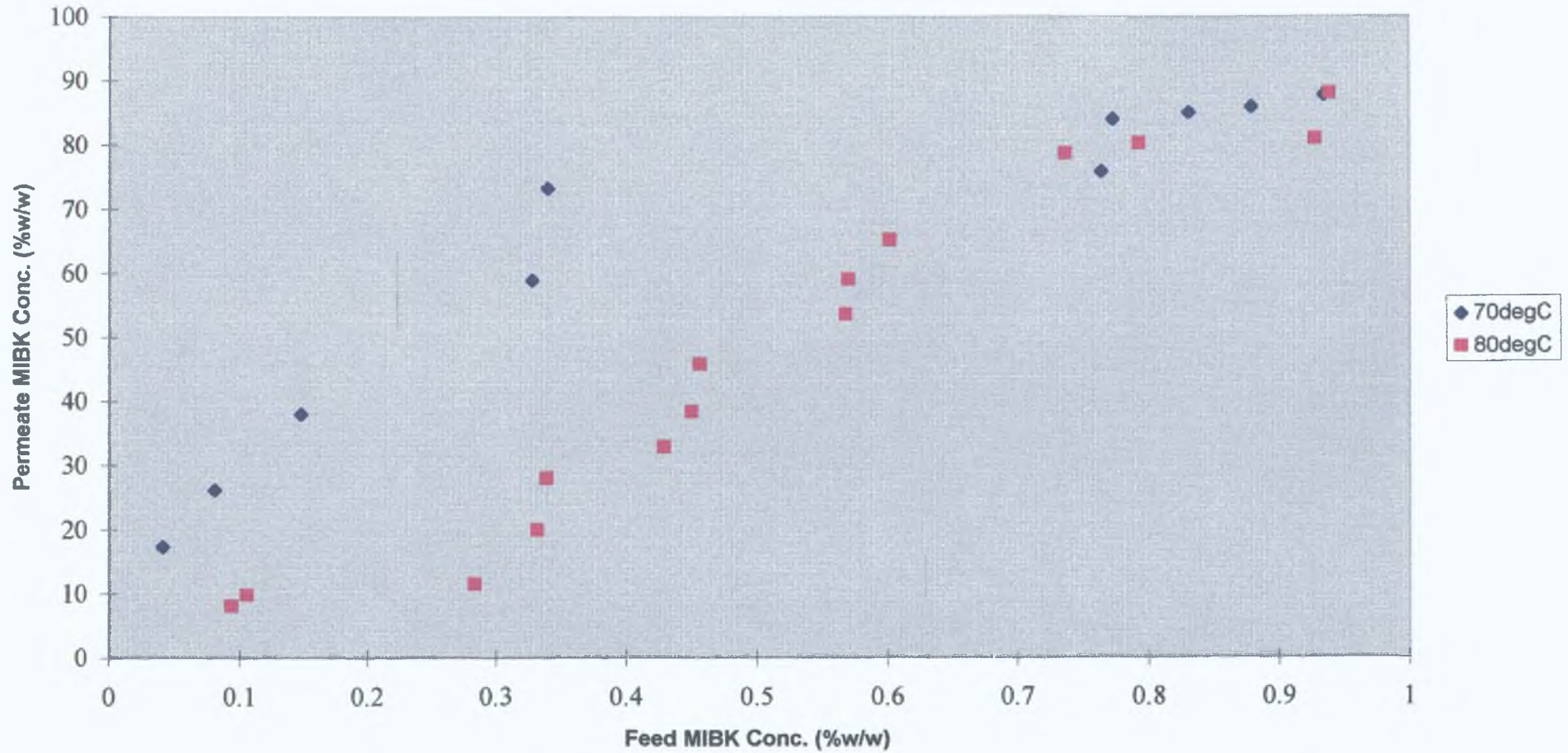
Feed Aniline Conc. (%w/w) v. Permeate Aniline Conc. (%w/w)
Polydimethylsiloxane Membrane



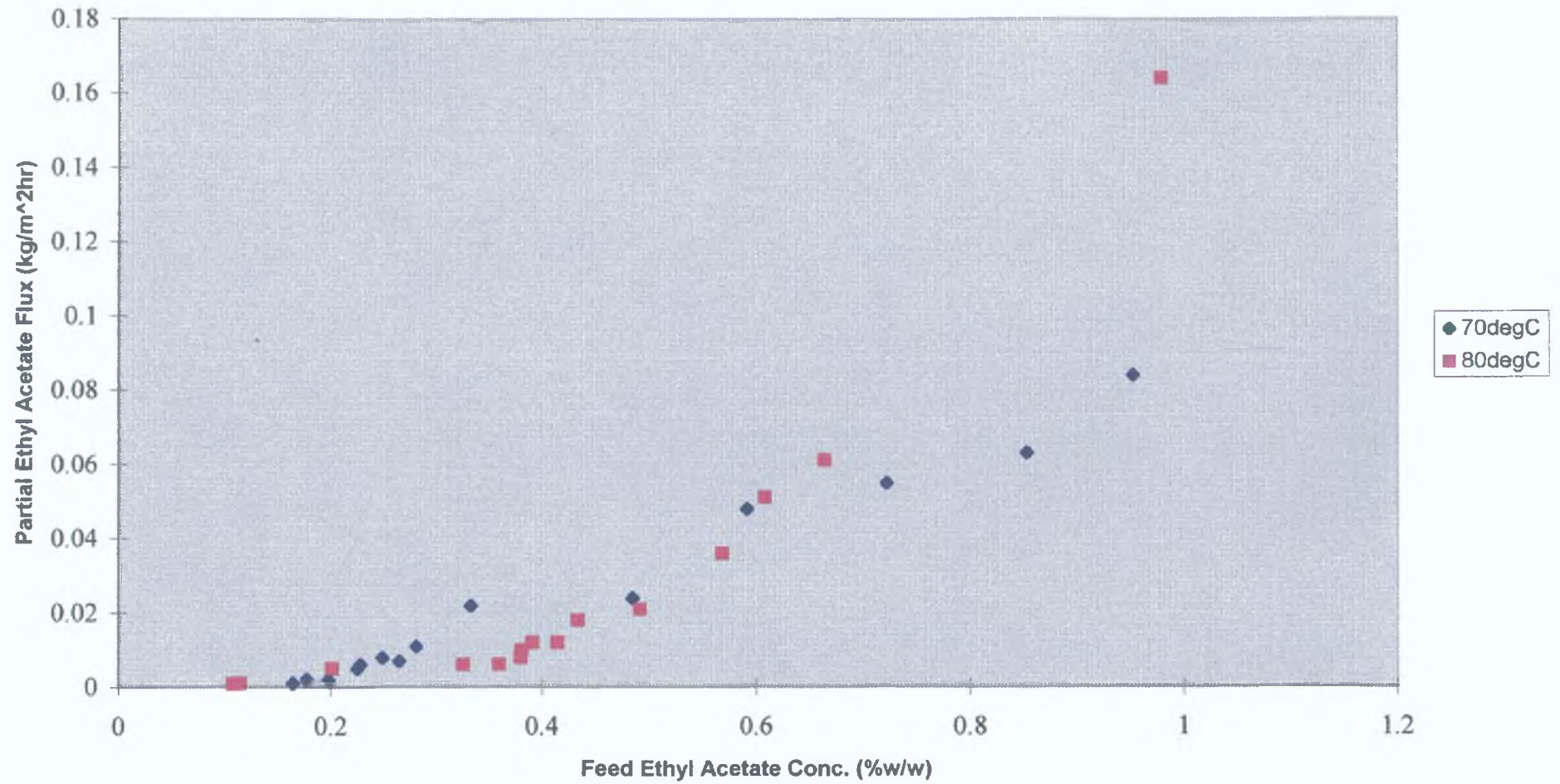
Feed MIBK Conc. (%w/w) v. Permeate MIBK Conc. (%w/w)
Polyurethane Membrane



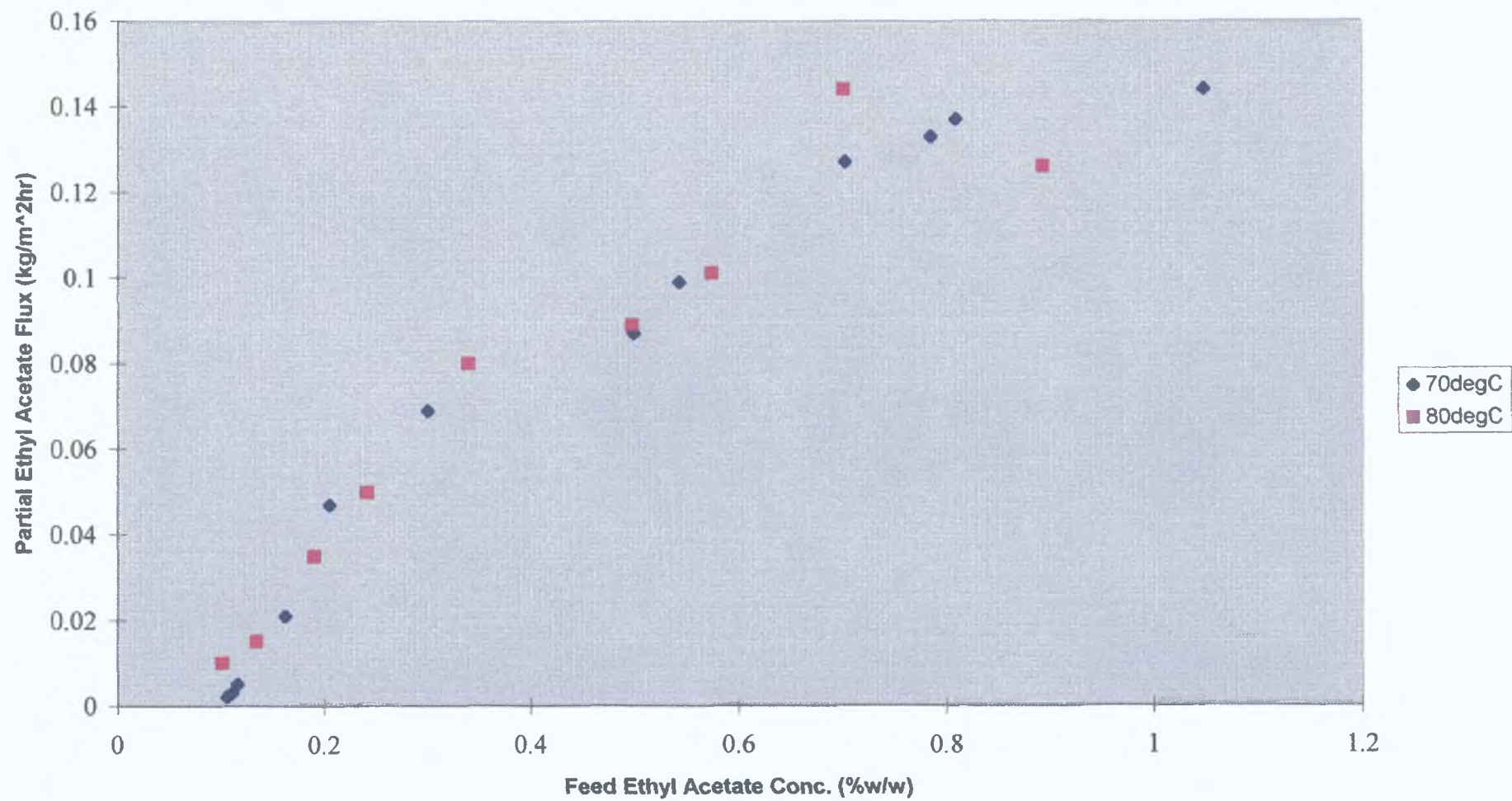
Feed MIBK Conc. (%w/w) v. Permeate MIBK Conc. (%w/w)
Polydimethylsiloxane Membrane



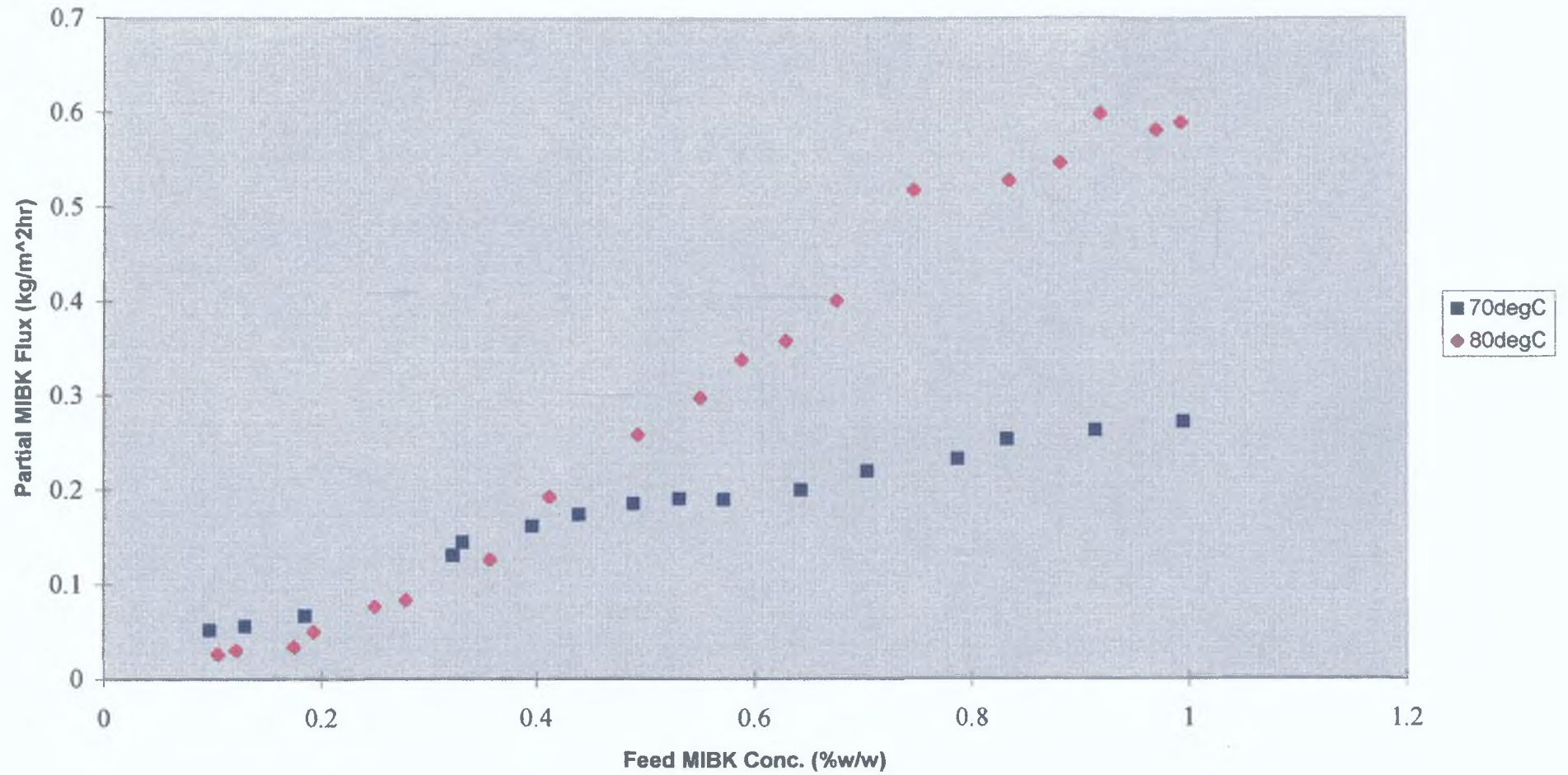
Feed Ethyl Acetate Conc. (%w/w) v. Partial Ethyl Acetate Flux (kg/m²hr)
Polyurethane Membrane



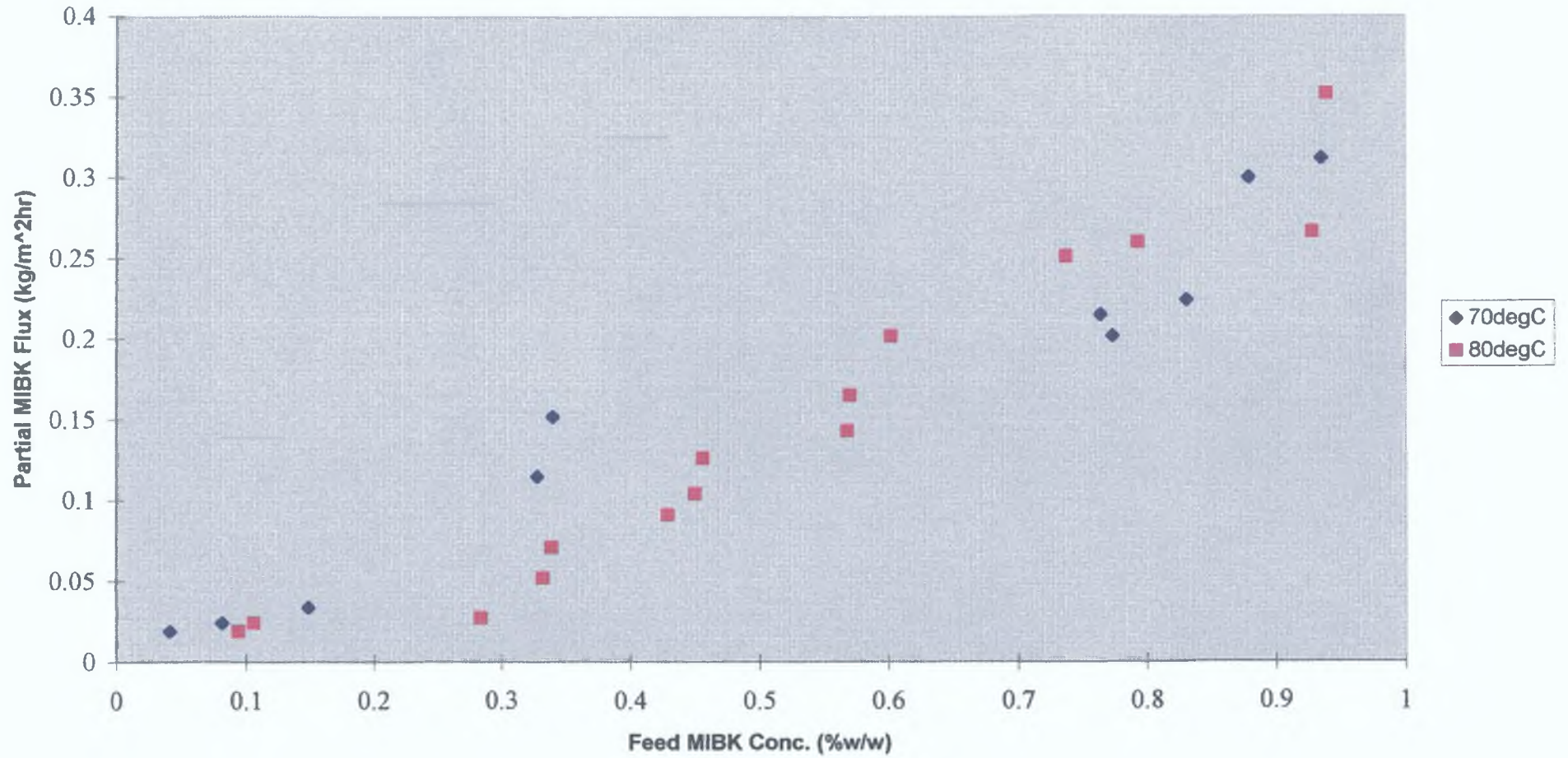
Feed Ethyl Acetate Conc. (%w/w) v. Partial Ethyl Acetate Flux (kg/m²hr)
Polydimethylsiloxane Membrane



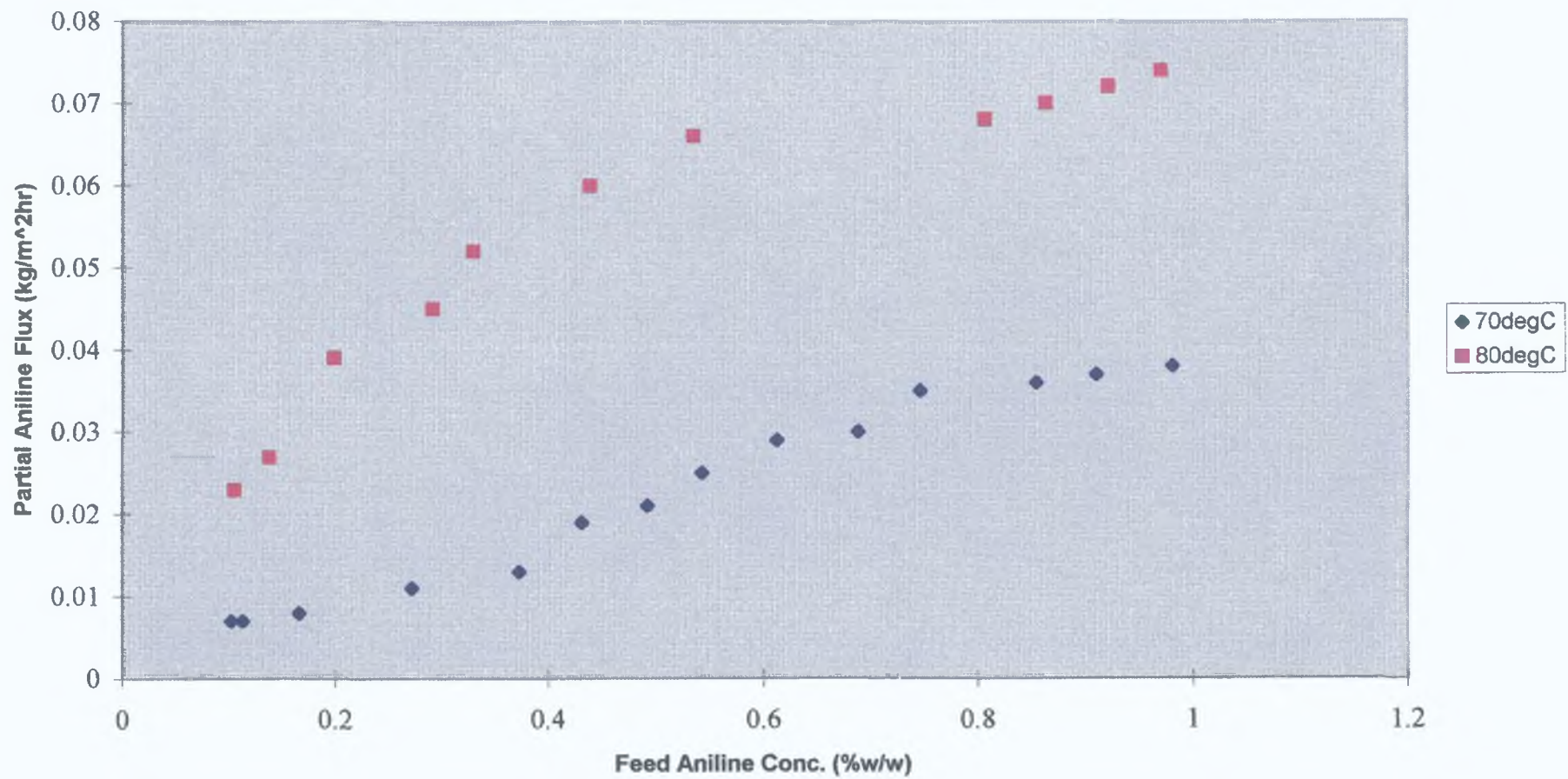
Feed MIBK Conc. (%w/w) v. Partial MIBK Flux (kg/m²hr)
Polyurethane Membrane



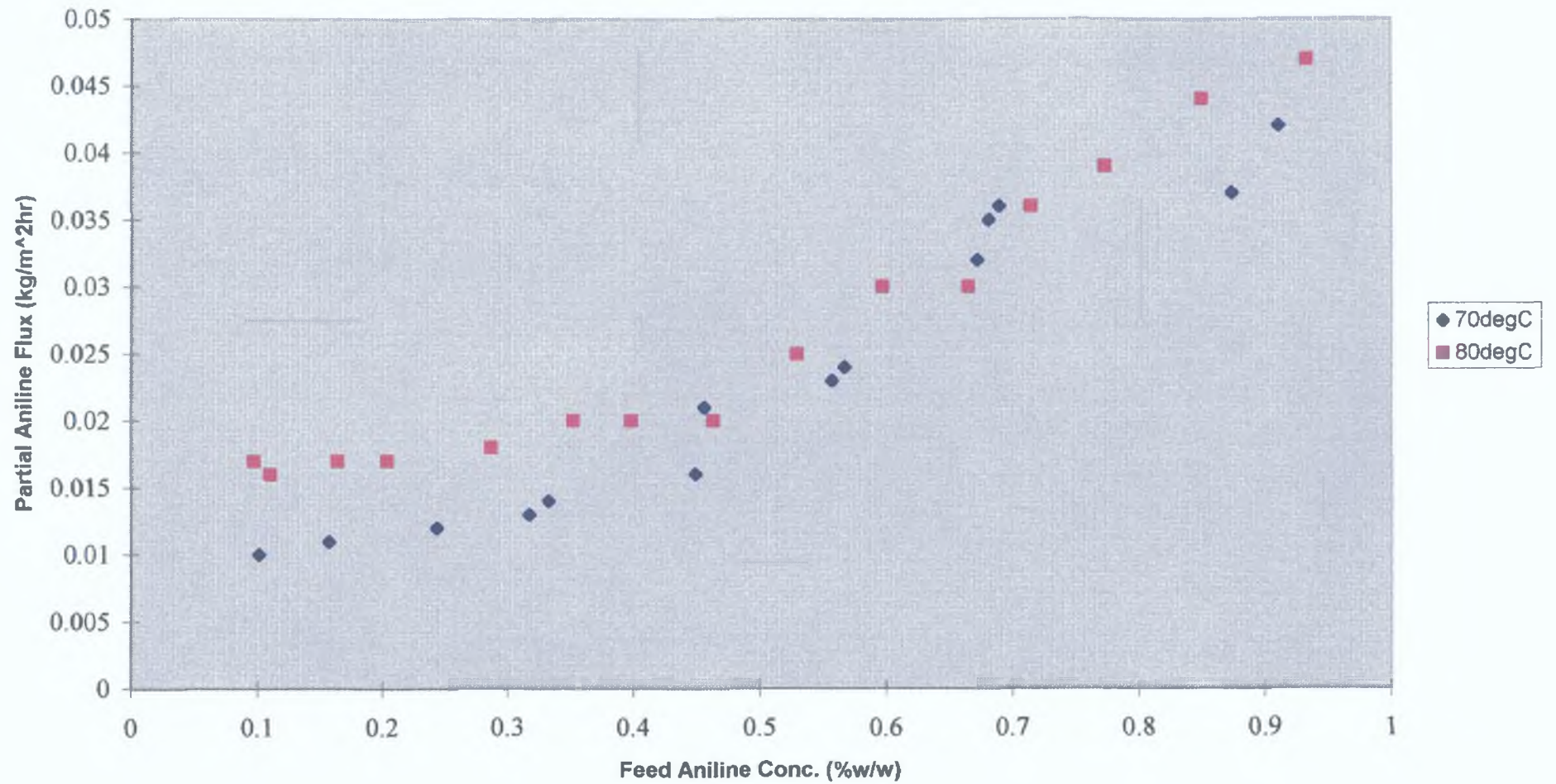
Feed MIBK Conc. (%w/w) v. Partial MIBK Flux (kg/m²hr)
Polydimethylsiloxane Membrane



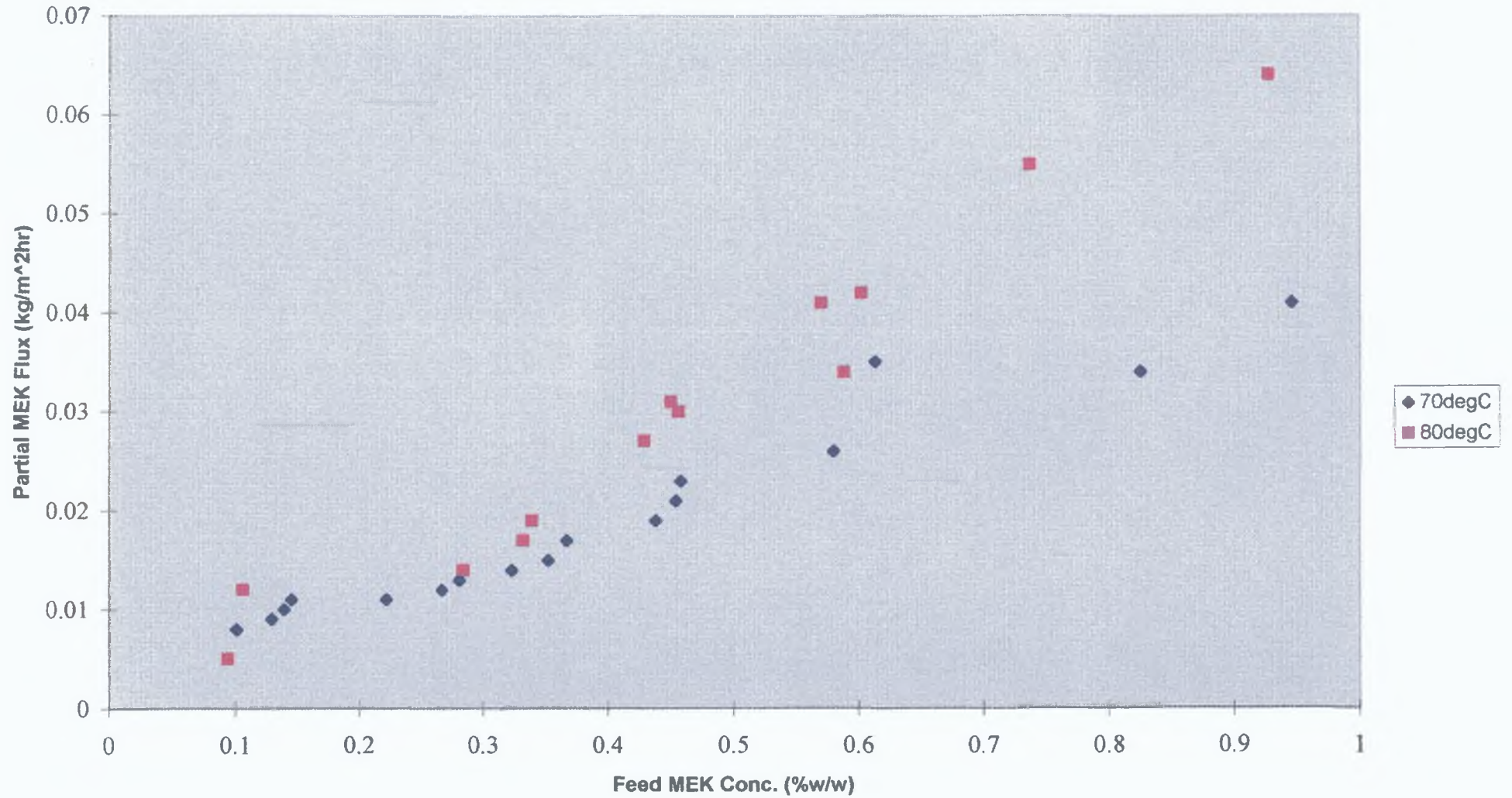
Feed Aniline Conc. (%w/w) v. Partial Aniline Flux (kg/m²hr)
Polyurethane Membrane



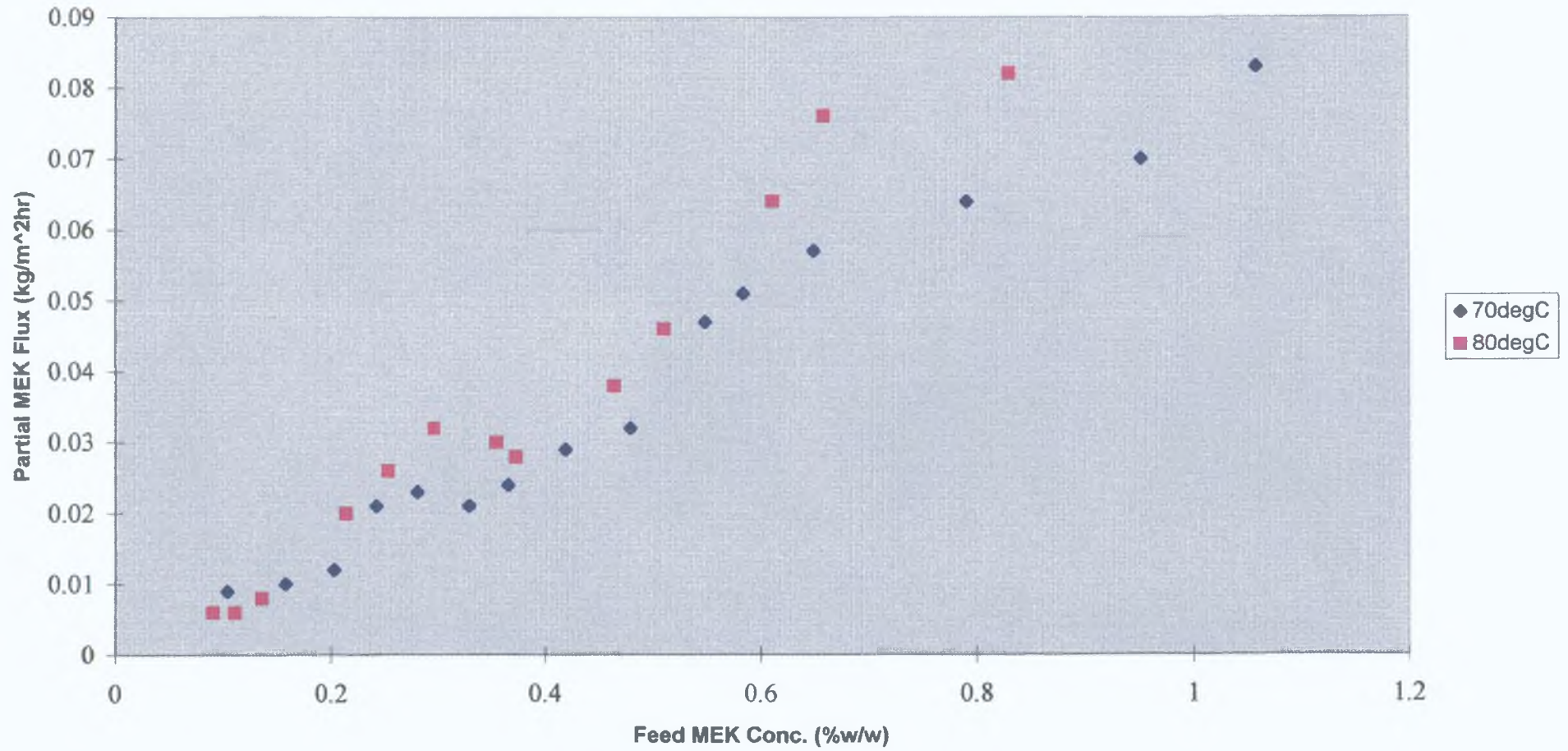
Feed Aniline Conc. (%w/w) v. Partial Aniline Flux (kg/m²hr)
Polydimethylsiloxane Membrane



Feed MEK Conc. (%w/w) v. Partial MEK Flux . (kg/m²hr)
Polyurethane Membrane



Feed MEK Conc. (%w/w) v. Partial MEK Flux (kg/m²hr)
Polydimethylsiloxane Membrane



Appendix 5

Sample permeate flux calculation

$$J = \frac{W_p}{A t}$$

J = Flux (kg/m²hr)

A = membrane area (m²)

t = duration of experiment (hr)

W_p = weight of permeate sample (kg)

1 Separation of aniline/H₂O using PU membrane at 50°C

Initial feed concentration in all cases = 1.0% w/w organic in water

$$W_p = 1.729\text{g}$$

$$A = 0.0198\text{m}^2$$

$$t = 2.75\text{hr}$$

$$\begin{aligned} J &= \frac{1.729/1000}{(0.0198)(2.75)} \\ &= \mathbf{0.213 \text{ kg/m}^2\text{hr}} \end{aligned}$$

Appendix 6

Sample selectivity calculation

$$\alpha = \frac{y_i/y_j}{x_i/x_j}$$

α = selectivity

x_i = %w/w of component i (MIBK) in feed sample

x_j = %w/w of component j (Water) in feed sample

y_i = %w/w of component i (MIBK) in permeate sample

y_j = %w/w of component j (Water) in permeate sample

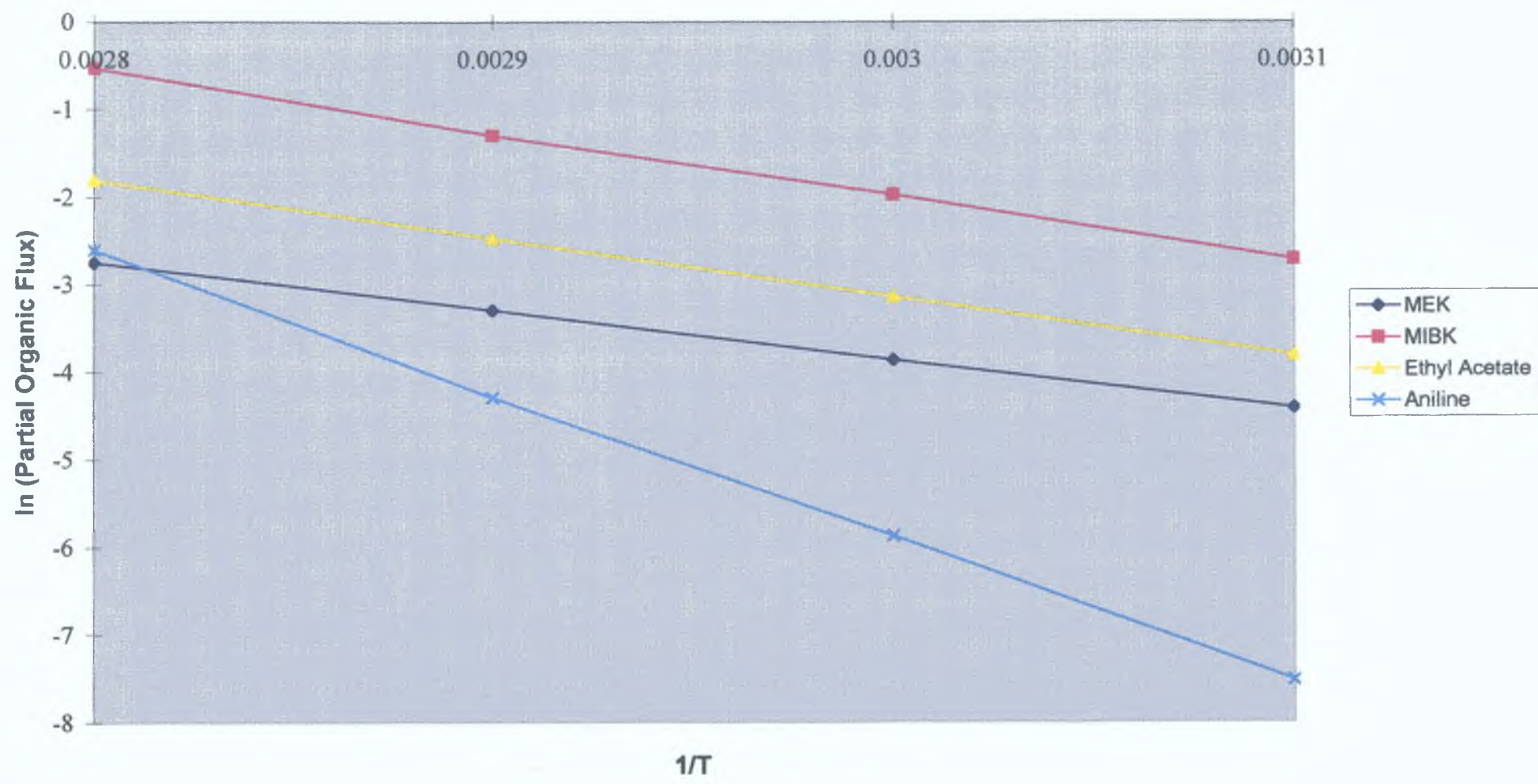
1 Separation of MIBK/H₂O using PDMS membrane at 60°C

Initial feed concentration in all cases = 1.0% w/w organic in water

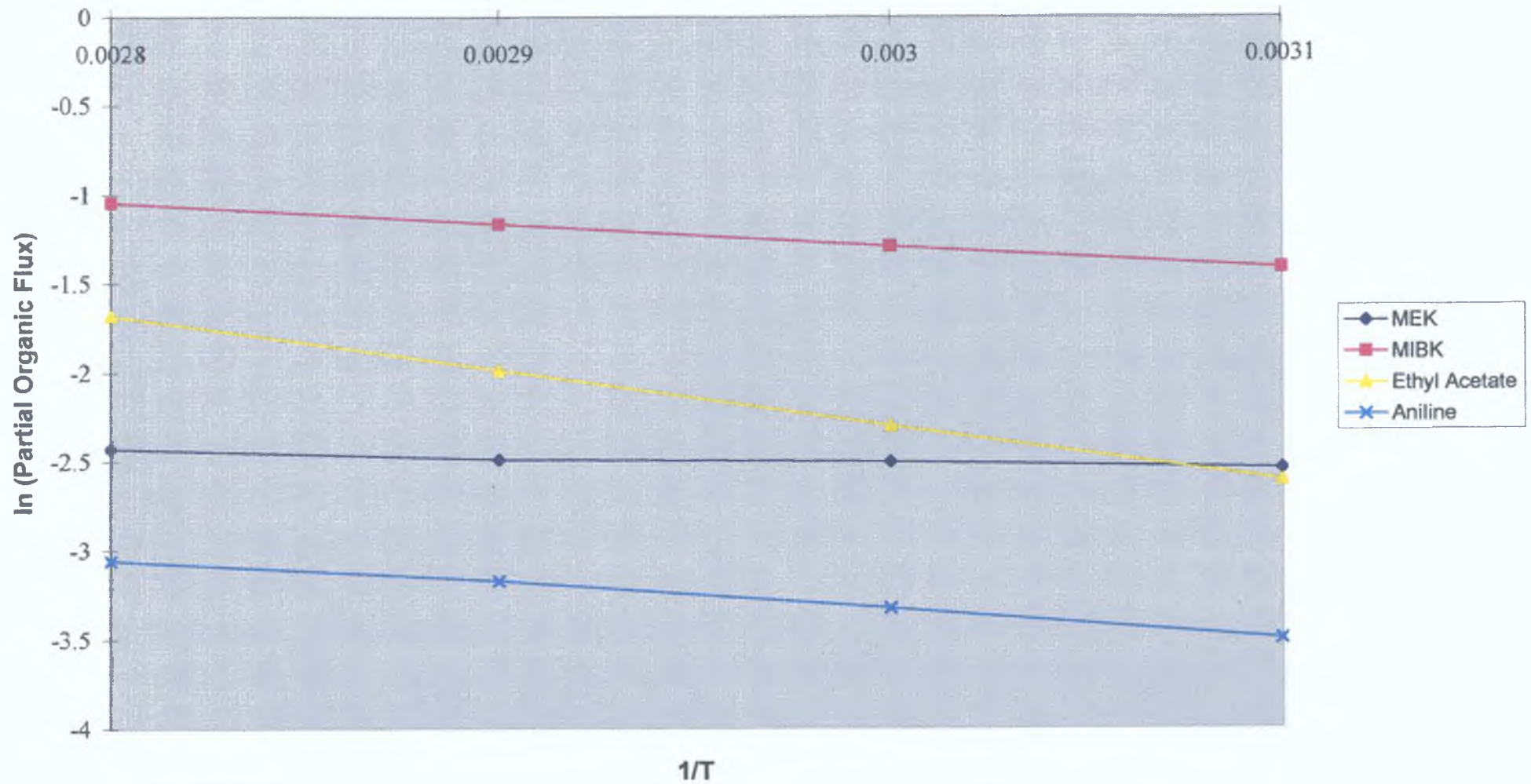
$$\alpha = \frac{82.932 / 17.068}{0.826 / 99.174}$$

$$= 585$$

1/T v. ln (Partial Organic Flux)
Polyurethane Membrane



**1/T v. ln (Partial Organic Flux)
Polydimethylsiloxane Membrane**



Appendix 8

Activation Energy of Permeation

Data used to calculate Activation Energy of Permeation values shown in Table 3.3.1 for the polyurethane membrane with an initial feed concentration of 1% w/w organic in water

Mixture	Temperature (K)	1/T (K ⁻¹)	Flux (kg/m ² hr)	Partial Flux (kg/m ² hr)	ln (Partial Flux)
MEK/H ₂ O	323	0.0031	0.223	0.012	-4.410
	333	0.0030	0.307	0.021	-3.859
	343	0.0029	0.400	0.037	-3.297
	353	0.0028	0.519	0.064	-2.749
MIBK/H ₂ O	323	0.0031	0.384	0.066	-2.713
	333	0.0030	0.593	0.139	-1.974
	343	0.0029	0.744	0.272	-1.302
	353	0.0028	1.011	0.589	-0.529
Ethyl Acetate/H ₂ O	323	0.0031	0.098	0.022	-3.808
	333	0.0030	0.153	0.043	-3.136
	343	0.0029	0.258	0.084	-2.477
	353	0.0028	0.484	0.164	-1.808
Aniline/H ₂ O	323	0.0031	0.213	0.0005	-7.515
	333	0.0030	0.296	0.003	-5.866
	343	0.0029	0.458	0.038	-4.296
	353	0.0028	0.801	0.074	-2.604

Graphs of ln Partial Flux v 1/T

Mixture	Slope (K ⁻¹)	Activation Energy (kJ mol ⁻¹)	Error on Calculation (%)
MEK/H ₂ O	-5545	46.10	0.33
MIBK/H ₂ O	-7224	60.06	0.27
Ethyl Acetate/H ₂ O	-6659	55.36	0.25
Aniline/H ₂ O	-16303	135.54	0.26

For sample calculation of Activation Energy of Permeation, see Appendix 9

Appendix 8 (continued)

Data used to calculate Activation Energy of Permeation values shown in Table 3 3 2 for the polydimethylsiloxane membrane, PDMS1

Mixture	Temperature (K)	1/T (K ⁻¹)	Flux (kg/m ² hr)	Partial Flux (kg/m ² hr)	ln (Partial Flux)
MEK/H ₂ O	323	0 0031	0 130	0 079	-2 539
	333	0 0030	0 143	0 082	-2 502
	343	0 0029	0 181	0 083	-2 489
	353	0 0028	0 193	0 088	-2 430
MIBK/H ₂ O	323	0 0031	0 273	0 243	-1 413
	333	0 0030	0 318	0 275	-1 291
	343	0 0029	0 256	0 312	-1 165
	353	0 0028	0 400	0 352	-1 044
Ethyl Acetate/H ₂ O	323	0 0031	0 129	0 074	-2 609
	333	0 0030	0 169	0 100	-2 300
	343	0 0029	0 242	0 137	-1 988
	353	0 0028	0 344	0 186	-1 682
Aniline/H ₂ O	323	0 0031	0 088	0 030	-3 499
	333	0 0030	0 103	0 036	-3 325
	343	0 0029	0 139	0 042	-3 170
	353	0 0028	0 156	0 047	-3 058

Graphs of ln Partial Flux v 1/T

Mixture	Slope (K ⁻¹)	Activation Energy (kJ mol ⁻¹)	Error on Calculation (%)
MEK/H ₂ O	-340	2 83	0 78
MIBK/H ₂ O	-1233	10 25	0 53
Ethyl Acetate/H ₂ O	-1478	12 29	0 67
Aniline/H ₂ O	-3093	25 72	0 25

For sample calculation of Activation Energy of Permeation, see Appendix 9

Appendix 9

Sample Activation Energy of Permeation calculation

$$\ln J = \ln J_0 - E/RT$$

J = Flux (kg/m²hr)

E = Activation Energy of Permeation (J mol⁻¹)

R = Universal Gas Constant (8 314 J K⁻¹ mol⁻¹)

T = Temperature (K)

A plot of $\ln J$ v $1/T$ gives a straight line of slope $-E/R$

1 Permeation of MIBK through PDMS1 membrane

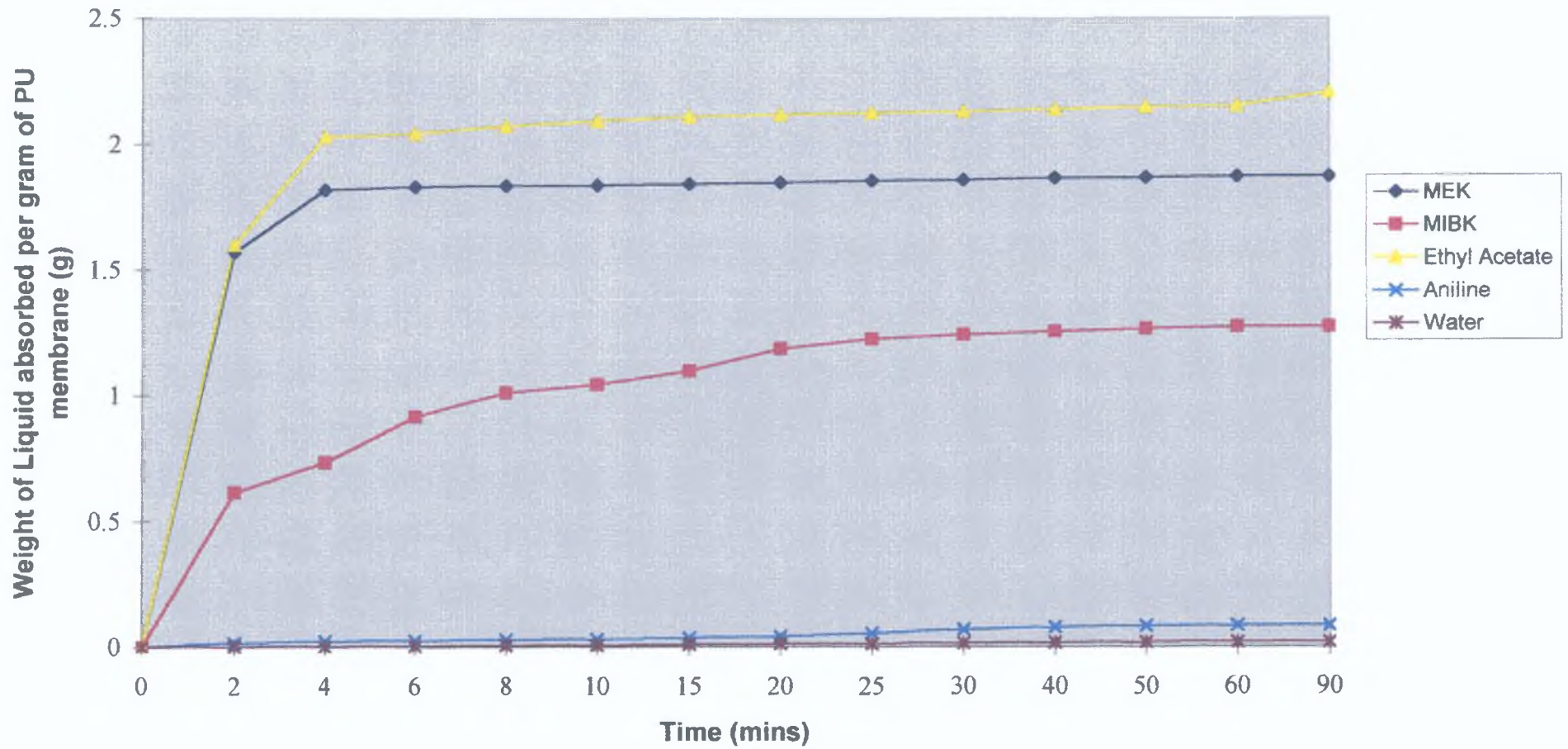
Temperature (K)	1/T (K ⁻¹)	Partial Ethyl Acetate Flux (kg/m ² hr)	ln (Partial Ethyl Acetate Flux) (kg/m ² hr)
323	0 0031	0 243	-1 413
333	0 0030	0 275	-1 291
343	0 0029	0 312	-1 165
353	0 0028	0 352	-1 044

Slope of curve = - 1233 K

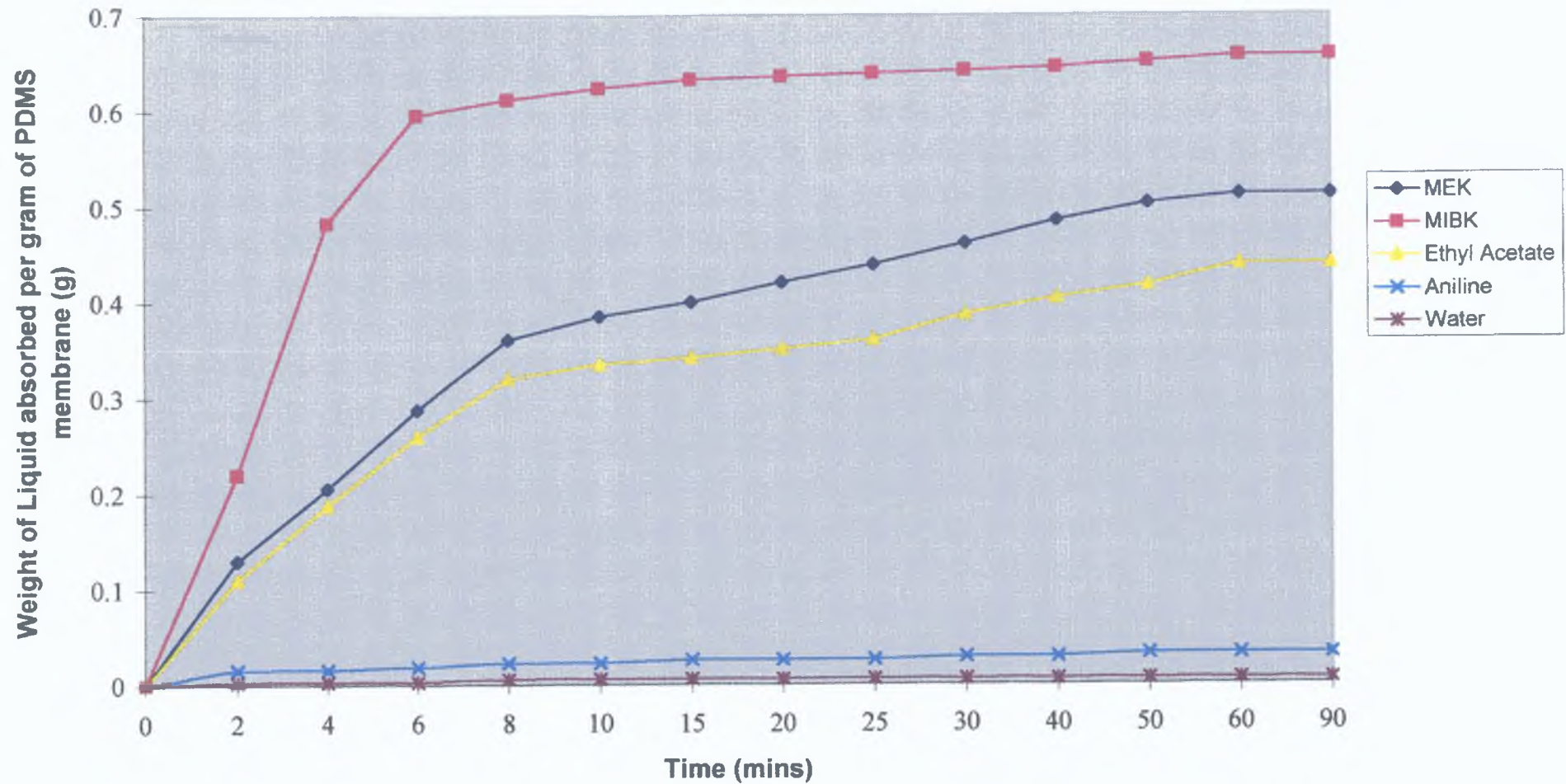
Activation Energy = - (-1233 K) x 8 314 J K⁻¹ mol⁻¹

= 10 25 kJ mol⁻¹

Weight of Organic Liquids absorbed per gram of Polyurethane Membrane (PU1) v. Time at ambient temperature



Weight of Organic Liquids absorbed per gram of Polydimethylsiloxane Membrane (PDMS1) v. Time at ambient temperature



Appendix 11

Sample swelling factor calculation

$$S = \frac{W_1 - W_0}{W_0}$$

S = Swelling Factor

W_0 = weight of dry membrane

W_1 = weight of swollen membrane

- 1 Sorption of ethyl acetate into the PU1 membrane at ambient temperature

Weight of dry membrane , W_0 = 0 409g

Weight of swollen membrane, W_1 = 1 289g

$$\begin{aligned} S &= \frac{1\ 289 - 0\ 409}{0\ 409} \\ &= 2\ 15 \end{aligned}$$