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Demulsifiers for Simulated Basrah Crude Oil

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Abstract

Water in oil emulsion occurs at many stages in the production and treatment of crude oil. In the present work three demulsifiers were used (RP6000, Chimec2439 and PAA) for dehydration (desalting) of Al-Basrah water in oil emulsion. The experimental work was performed under constant temperature 65°C and water content 30%vol. (3%wt.NaCl). The parameters studied: demulsifier dose (10, 20, 30, 40,50,60,70 and 80) ppm, separation time (5, 10, 15, 30, 60, 90 and 120) min and types of demulsifiers (RP6000 Chimec2439 and PAA). The dehydration efficiency with prepared demulsifier (PAA) was (75%). Two types of commercial demulifiers were also used (RP6000 and Chimec2439), which gave water separation efficiency (87.5% and 72.2%), respectively. pH, Salt content, remains of water content and density were estimated. The least density of the desalted crude obtained was (0.874 gm/cm^3) at (80) ppm of RP6000.

كواسر الاستحلاب المقلدة لنفط خام البصرة

الخلاصة

يكمن تواجد الماء والنفط كمستحلب في عدة مراحل من انتاج ومعالجة النفط الخام .في هذه الدراسة استخدمت ثلاثه انواع من كواسر الاستحلاب وهي (بولي اكريل امايد ,RP6000,Chimec2439) لمعالجة مستحلب نفط خام البصرة. انجزت العملية تحت درجة حرارة 65م° و محتوى مائي(30%) .تم دراسة العوامل المؤثرة على عملية فصل الماء وهي: جرعة كاسر الاستحلاب (80,70,60,50,40,30,20,10) ppm , زمن الفصل (120,90,60,30,15,10,5) دقيقة ونوع كاسر الاستحلاب(بولي اكريل امايد,,RP6000,Chimec2439) .النتائج المستحصلة لكفاءة فصل كاسر الاستحلاب المصنع (بولي اكريل امايد) هي (75%) اما كواسر الاستحلاب التجارية (RP6000,Chimec2439) اعطت كفاءة فصل (87.5%, 72.2%) . تم حساب محتوى الملح والدالة الحامضية (pH) ومحتوى الماء المتبقي و كثافة المستحلب بعد عملية فصل الماء و لجميع انواع كواسرالاستحلاب وكانت اقل كثافة تم الحصول عليها هي0.874 غم/سم^3.

1. Introduction

During petroleum production, crude oil passes through the earth's pores causing formation of stable water in oil emulsions [1,2,3], and then may create severe problems such as expensive pumping due to increase of crude oil viscosity, corrosion of pipes and pumps, poisoning catalysts, et al. Therefore, demulsification/ desalting process of petroleum emulsion is necessary to remove as much water and salt as economically possible.

Thermal treatment is often used as acceleration means in any method of demulsification [4,5,6]. Heating crude oil

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emulsion has several advantages such as; increasing the rate of water droplet's flocculation, increases the solubility of emulsifying agents then destabilizing the emulsion, decreasing emulsion viscosity which increases the probability of coalescence according to Stoke's law.

Demulsification by chemical demulsifies is the most widely used method for treating crude oil emulsion. This method based on the addition of reagents (demulsifiers) which destroy the protective action of hydrophobic emulsifying agents and allow water droplets to coalesce. Table (1) lists briefly the chemicals used as demulsifiers since the beginning of the century [7].

The formulation of commercial demulsifiers is largely based on empirical approaches in an attempt to get the effective agent, which can work in shorter separation times and smaller dosages [8]. The role of the demulsifier is the suppression of the interfacial tension gradient in addition to the lowering of interfacial viscosity, thus causing accelerated film drainage and coalescence [9].

The kinetics of chemical demulsification process is caused by three main effects: the displacement of the asphaltenic film from the (water/oil) interface by the demulsifier, flocculation and coalescence of water droplets.

Success of chemical demulsifying method depends upon the following [10]: An adequate quantity of a properly selected chemical must enter the emulsion, thorough mixing of chemicals in the emulsion, sufficient heat may be required to facilitate or fully resolve an emulsion. Sufficient residence time must exist in treating vessels to permit settling of demulsified water droplets.

The aim of the present work is to study breaking (W/O) emulsion from Basrah crude oil using prepared polyacryamide PAA demulsifier by polymerization method and the comparison with two commercial demulsifiers supplied by foreign companies with trade name RP6000 and Chimec2439. The parameters investigated include the effect of demulsifier type (RP6000, Chimec2439 and PAA), dose (10-80) ppm, separation time (5,10,15,30,60,90 and120) min, and study their effect on oil viscosity, density, salt content, remained water content and pH.

2. Experimental Work

2.1 Materials:

2.1.1 Crude Oil

Experimental work was carried out on Basrah crude oil. The physical properties of crude oil are given in Table (2), analyzed in Doura refinery.

2.1.2 Chemical Demulsifiers

The effect of introducing chemical additives into the emulsion has been investigated. In the present work the effect of three demulsifier blends on breakdown of w/o emulsion have been studied. The demulsifiers used in the present work are:

1. Commercial demulsifier supplied by foreign company with trade name RP6000 without explaining their chemical composition. The Petrolite Company has adopted this demulsifier

in desalting process in East Baghdad oil field.

2. Commercial demulsifier supplied by CHIMEC S.P. Company, Italy of trade name Chimec2439, which is a blend of non-ionic oil soluble surfactants. The physical properties are given in Table (3).

3. Polymer nonionic polyacrylamide PAA prepared by polymerization method.

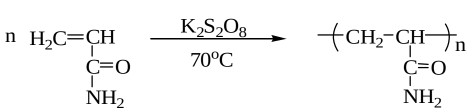
2.2 Experimental Procedure

2.2.1 Emulsion Preparation

The water in crude oil emulsion was emulsified with crude oil at ambient temperature by adding 30% vol water phase prepared from water and salt in concentration of 3% wt NaCl. The emulsified crude was prepared by using a mixer at a speed of (5000) rpm for (60) min which gave a good stable emulsion without showing any signs of flocculation. The rate of water separation was monitored for a period of up to 24 hr.

2.2.2 Polyacrylamide Preparation

Polymerization of acrylamide takes place in distilled water according to following chemical reaction:



A.A P.A.A

The reaction of acrylamide monomer and the initiator (persulfate Potassium) was carried out at 70 ^oC and 15 min to produce the polymer [11]**.** The physical properties of materials are shown in Table (4).

Gravimetric technique is used to determin the rate polymerization and viscometry is used for determination of average of polymerization. The UV-visible spectrophotometer is used to determine the rate of initiator decomposition and IR spectrophotometer is used to identify the initiators structures, the end group in the polymer and the tacticity of the polymer chain. In addition atomic absorption and conductivity molar were used to identify the stricture.

2.2.3 Screening of Demulsifiers (Bottle test)

The selected demulsifiers were screened by bottle test [12]. Tests have been performed on emulsion based blend of Basrah crude oil, which was a good representative of a crude oil giving rise to stable emulsion at room temperature since it has high asphaltene content (2.22 wt%).

The demulsification tests were undertaken in 100 ml beakers. All w/o emulsion contained 30% dispersed water. In each beaker the demulsifier was injected and mixed for one minute. The separation of water phase takes place from crude oil under gravity and at constant temperature 65 ^oC using controlled water bath. Figure (1) shows the laboratory equipment used in the separation of water process.

2.2.4 Effect of RP6000, Chimec2439 and PPA Demulsifiers on Water Separation Efficiency

In this set of experiments, the effect of RP6000, Chimec2439 and PPA was investigated. The (W/O) emulsion has been prepared at the following conditions temperature (65)^oC, water content 30% vol. (3% wt. NaCl). The doses of these compounds were (10, 20, 30, 40, 50, 60, 70 and 80) ppm.

2.3 Measuring Devices

2.3.1 Salt Content Measurements:

The salt content in the crude oil has been measured using calibrated conductivity meter.

2.3.2 pH Measurements:

The acid function of water separated from (W/O) emulsion has been measured using pH meter and calibrated with buffer solution having pH (4, 7 and 9).

2.3.3 Evaluating the Residual Water Content

The residual water content in the (W/O) emulsion after breaking emulsion has been evaluated using Dean-Stark method. The apparatus consists of a round –bottom flask of capacity (500) ml connected to a Liebig condenser by a receiving tube of capacity.

2.3.4 Evaluating Density

The emulsion density has been evaluated using picnometer.

3. Results and Discussion

3.1 Effect of Demulsifier Types on Water Separation Efficiency

The effect of RP6000 and Chimec2439 on water separation efficiency with time intervals is shown in Figures (2) and (3). Figure (2) shows an increase in water separation efficiency for RP6000 until it reaches 60 min, after that the increasing becomes slight; where the highest separation efficiency obtained at 120 min and (80) ppm RP6000 was 87.5%. These results are in agreement with the results obtained by Aamir [13].

Figure (3) shows the separation efficiency of water for Chimec2439 which was increased with time until it reaches 60 min then the increasing becomes slightly, where 72.2% was obtained at 120 min.

The Slight increase after 60 min for RP6000 and PAA has been observed, because the active chemical groups (OH, COOH, C=O, OSO_2, SO_2OH) in hydrocarbons chains for crude oil begin to be less effective. So the separation becomes slower and hence the increase in separation efficiency becomes slight. These results are in agreement with the results obtained by Dodd [14], Nimat [15], Aamir [13] and Hanapi [16], who used different demulisfiers types.

The change of water separation efficiency with time for PAA is shown in Figure (4). It can be observed that separation efficiency increases with increasing time. Where separation of water was sharp with time until it reaches 30 min, after that the increase becomes slight. The highest separation efficiency obtained was 75% for PAA at 120min.

3.2 Effect Water Separation Efficiency on pH

The effect of water separation efficiency on pH value of the aqueous phase is shown in Figure (5). Highest water separation is reached to 87.5% at pH = 7.5 for pure RP6000, 75% at pH = 7.46 for PAA and 72.2% was obtained at pH= 7.43 for Chimec2439. This behavior is similar to the are obtained by Aamir[13]. It can be seen from this figure that the increasing of water separation causes an increase in the pH value of the aqueous phase. This is due to removal of water which increased the amount of salt removed.

3.3 Effect of Water Separation on Salt content

Figure (6) shows the effect of water separation efficiency on salt content. It can be observed that salt content increases with the decreasing of water separation efficiency for types of demulsifiers (RP6000, PAA and Chimec2439), where highest separation for water reaches 87.5%, 75% and 72.2% for RP6000, PAA and Chimec2439. The reason of decreasing salt content in the oil phase with increasing of water separation efficiency, attributed to the chemical activity of hydrophilic and hydrophobic group present in the demulsifier molecular. Hence, the quality of oil will be improved.

3.4 Effect of Demulsifier Dose on Remainder of Water Content

The dose of demulsifier has a greating effect on remainder water content. Figure (7) shows the remainding water content decreases with increasing dose for types of demulsifiers (RP6000, Chimec2439 and PAA). It can be observed that RP6000 has less remainding water content than PAA or Chimec2439. This attributed to the fact that ability to remove water is greater for high dose. Lowest value of remaindering water content was obtained at (80) ppm.

3.5 Effect of Dose on Density

Figure (8) shows the effect of doses for different types of demulsifiers (RP6000, Chimec2439 and PAA) on the density of the emulsion after water separation. It can be observed that the dose of demulsifier increases, the density of emulsion after water separation decreases. Generally it can be seen that the lowest density was at dose (80 ppm), but RP6000 had the biggest effect on reducing density of emulsion. Where the density of emulsion at (80 ppm) was $0.874 gm/cm^3$ where RP6000 was used. This is because RP6000 has a great ability to remove water from emulsion. At this dose RP6000 can reaches 87.5% separation water efficiency.

4. Conclusions

The following conclusions could be summarized:

1. Water separation efficiency increases with increasing separation time for all types of demulsifiers, where highest separation obtained at (120min).
2. Water separation efficiency increases with increasing dose of demulsifiers where highest separation for water obtained at (80 ppm) for all types of demulsifiers.
3. Two types of commercial demulsifiers has been used (RP6000 and Chimec2439), which gave (87.5%) and (72.2%) water separation efficiency respectively. The prepared demulsifier (PAA) gave water separation efficiency of (75%).
4. Density of emulsion after water separation has an inverse proportionality to demulsifier dose where lowest emulsion density was ($0.874 gm/cm^3$) when RP6000 was used.

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Table (1) Demulsifier History

Period	Rate Required (ppm)	Chemistry
1920 's	1000	Soap, naphtenic acid salts and alkylaryl sulphonate, sulphated caster oil
1930 's	1000	Petroleum sulphonates, derivatives of sulpho-acid oxidized caster oil and sulphosucinic acid ester
Since 1935	100 to 500	Fatty acids, fatty alcohols, alkylphenols
Since 1950	100	Ethylene oxide/propylene oxide copolymer, Alkoxylated cyclic p-alkylphenol formaldehyde resins
Since 1965	30 to 50	Amine alkoxylate
Since 1976	10 to 30	Alkoxylated cyclic p-alkylphenol formaldehyde resins
Since 1980	5 to 20	Polyester amine and blends

Table (2) Physical Properties of the Basrah crude oil

Property	
Sp.Gr. at 15.6°C	0.8849
API	28.4
Salt content (%wt.)	0.0006
Water and Sediment content (%vol.)	0.05
Asphaltene (%wt.)	2.22
Ash content (%wt.)	0.0151
Sulfur content (%wt.)	2.1
Viscosity (cp) at 20°C	50
Conductivity (mS)	0

Table (3) Physical Properties of Chimec2439.

Appearance	Brown liquid
Sp.Gr.at 20 °C	0.94±0.02
Viscosity at 20 °C (cp)	<50
Pour point °C	<-30 °C
Flash Point °C	>62 °C

Table (4) Properties of Chemical Materials

Substance	Formula	M.Wt	Sp. Gr.	M. Pt °C
Acryl-amide	$CH_2:CHCONH_2$	71.08	1.122	84-5
Persulfate Potassium	$K_2S_2O_8$	270.32	2.477	<100
Polyacryl-amide	$-(CH_2-CH)_n-$ C=O NH_2	10^4-10^7	1.302	-----

Figure (1) The laboratory equipment used in separation of water process.

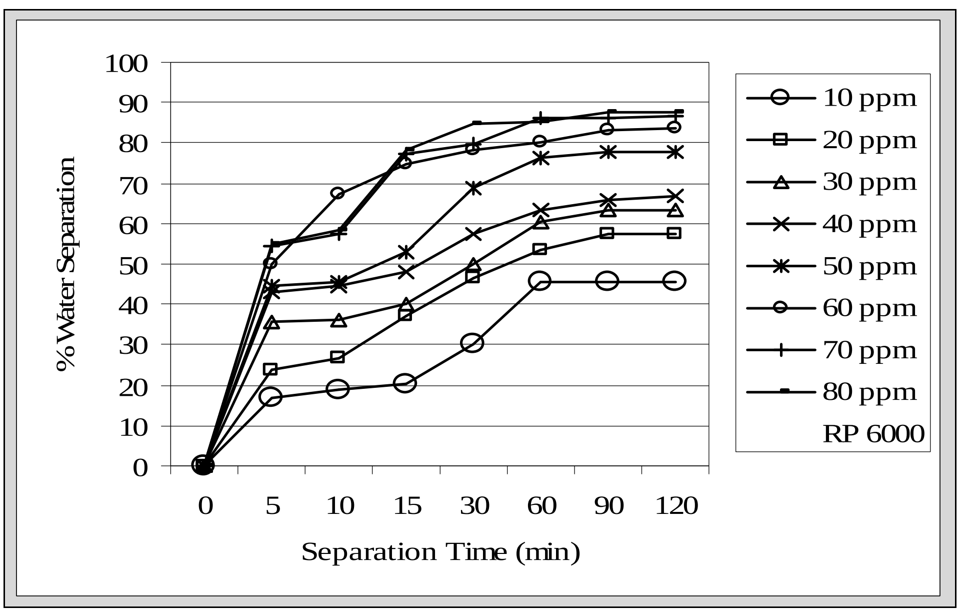

Figure (2) The influence of various concentrations of RP6000 on the separation of water. The water phase and the separation temp. were 30% vol and 65°C respectively.

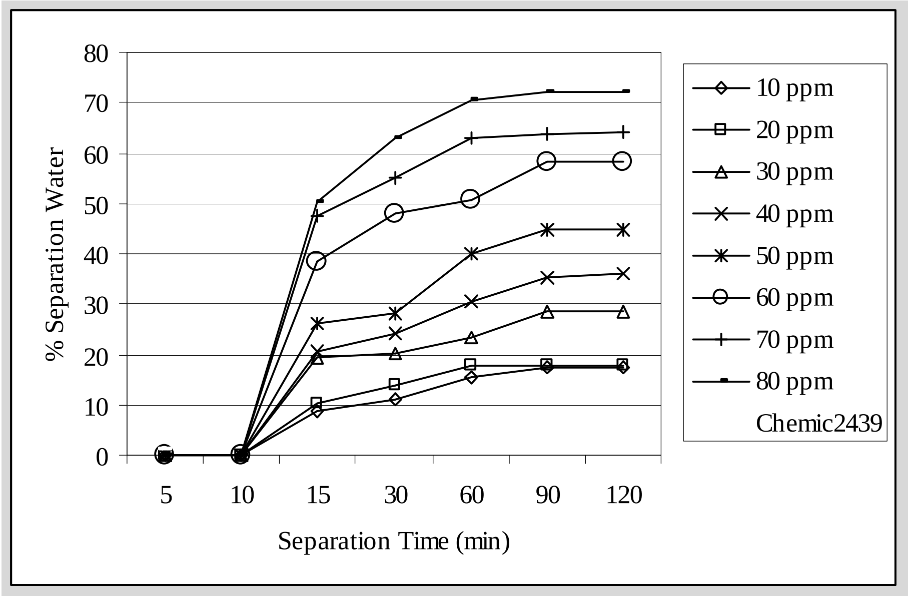

Figure (3) The influence of various concentrations of Chemic2439 on the separation of water. The water phase and the separation temp. were 30% vol and 65^{o}C respectively.

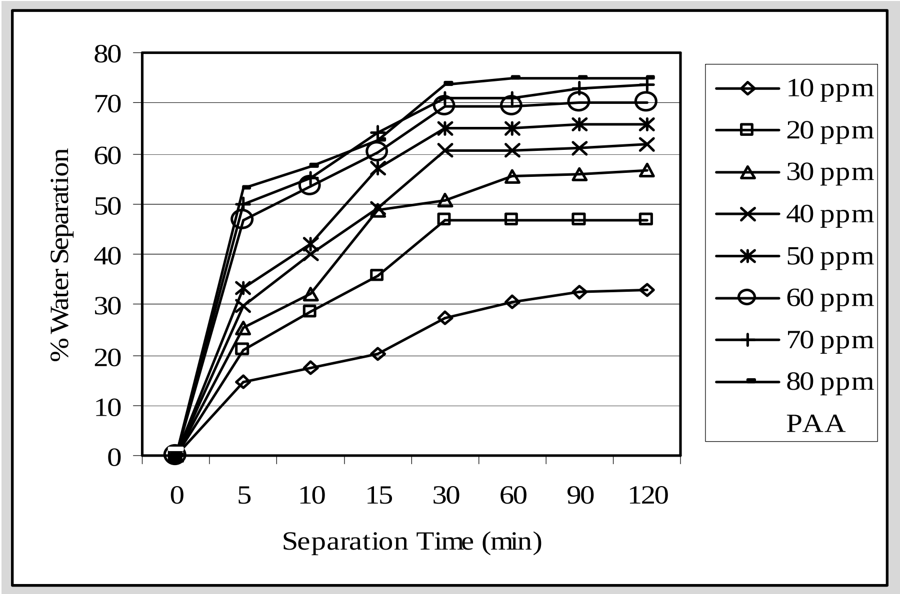

Figure (4) The influence of various concentrations of PAA on the separation of water. The water phase and the separation temp. were 30% vol and 65^{o}C respectively.

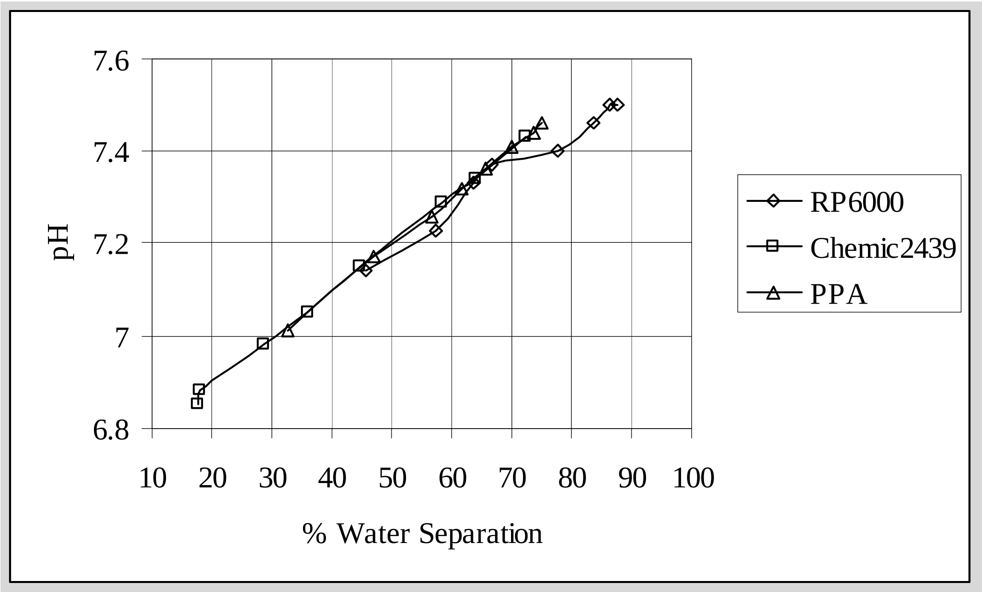

Figure (5) Effect of Water Separation Efficiency on pH Using RP6000, Chimec2439 and PAA

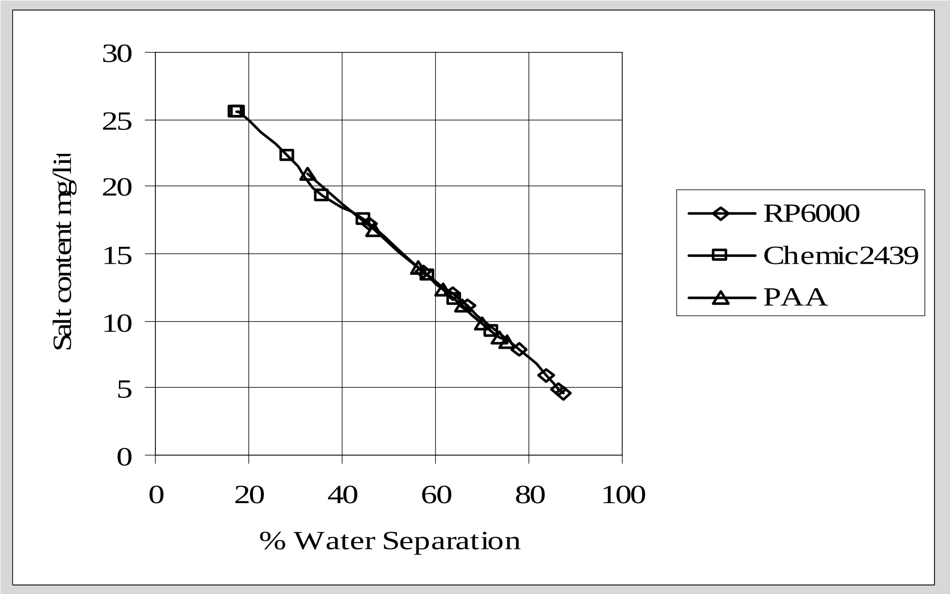

Figure (6) Effect of Salt Content on Water Separation Efficiency Using RP600, Chimec2439 and PAA

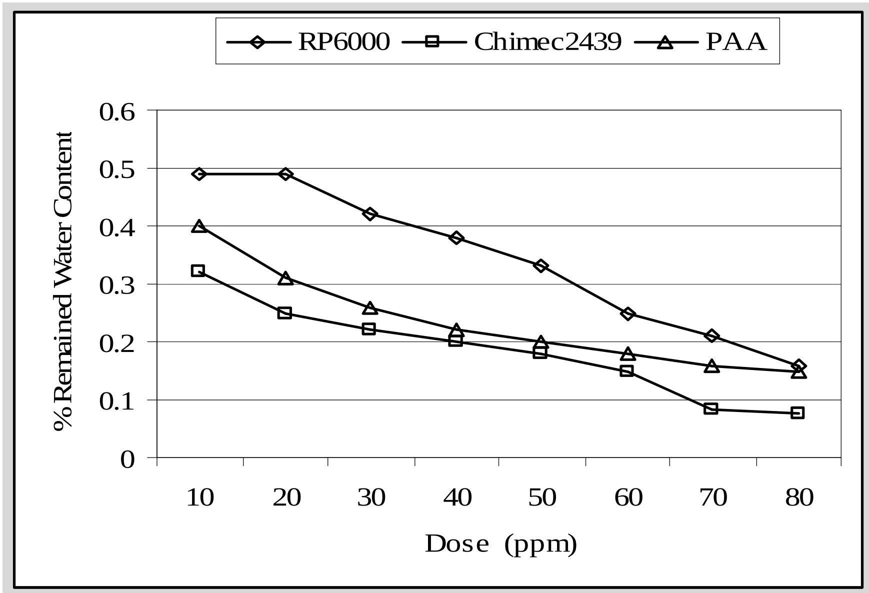

Figure (7) Effect of Dose on Remainding Water Content Using RP6000, Chimec2439 and PAA

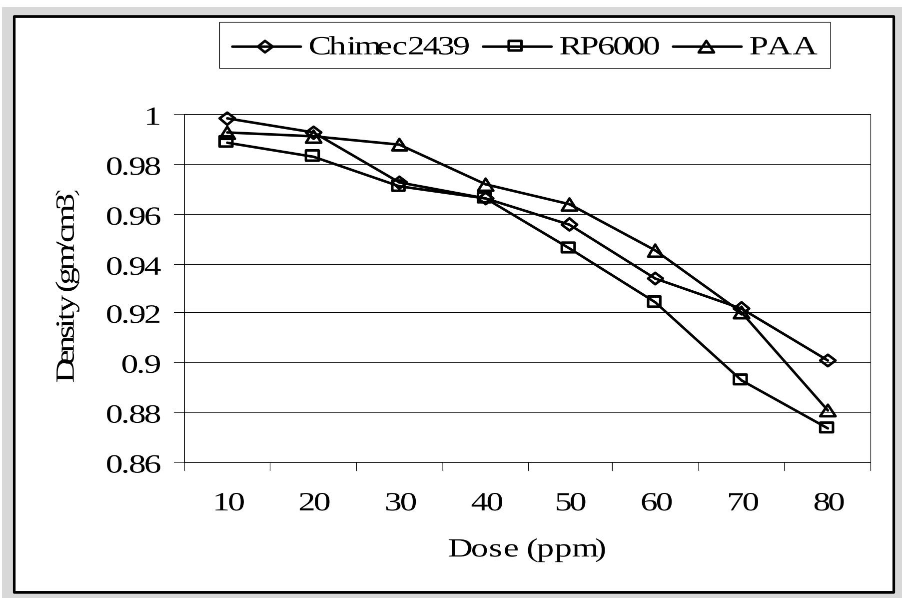

Figure (8) Effect of Dose Demulsifier on Emulsion Density after Water Separation