

## **STUDY THE EFFECT OF GLYCOLS BASE COSOLVENT ADDITIVES ON BREAKING OF CRUDE OIL EMULSION**

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**ABSTRACT** - Emulsion breaking is one of complex process used in many practical applications such as the petroleum industry, painting and waste-water treatment in environmental technology. Chemical demulsification is the most widely resolved method of treating water-in-crude oil emulsions and involves the addition of chemical reagents to destroy the protective action of emulsifying agents and allow accelerating the emulsion breaking process. Our experimental results showed that, the addition of glycols chemicals as a cosolvents like ethylene glycol methyl ether (EGME), monoethylene glycol (MEG), polyethylene glycol (PEG-1500), in combination with commercial demulsifier RP-6000 will enhancing the process of emulsion demulsification. The demulsification experiments were carried out at controlled temperature 65°C and screened by bottle test using about 100 ppm demulsifier doses. The maximum amount of water separated after 120 min found to be 87.7% for (75/25) (RP6000/PEG1500) .Where, the water separations for (75/25) (RP6000/MEG) and (75/25) (RP6000/EGME) for demulsifier were 71% and 65.2% respectively.

**Keywords:-** Demulsification efficiency, w/o emulsion breaking, glycol base surfactants.

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### **1. INTRODUCTION**

Most of the world's crude oil is produced in the form of an emulsion <sup>(1)</sup>. These emulsions are droplets of water or brine dispersed in a continuum of crude oil and, hence, is known as water-in-oil (w/o) emulsions. The emulsion stability results from the presence of interfacial barrier preventing coalescence of the dispersed water droplets. This is due to the to present of

emulsifying agents of polar components such as asphaltenes, resins, wax and naphthenic acids in the crude oil.

There are many factors affects on stability of emulsion, and thereby stability ranging from a few minutes to years depending on the nature of the crude oil and to some extent the nature of water <sup>(2)</sup>.

In the oil industry, emulsions have long been create of a severe problems such as expensive pumping due to increase of crude oil viscosity, poisoning catalysts, provoke corrosions, increase heat capacity and reduce the handling capacity of refining equipments and pipelines <sup>(3)</sup>. Therefore, the breaking of emulsions is necessary in many applications such as environmental technology, painting, coating and petroleum industry.

Emulsion breaking is one of the most complex processes in the oil industry. Breaking of water in crude oil emulsions involves chemical, thermal, electrical or a combination of these processes depending on the characteristics and properties of the emulsion <sup>(4)</sup>. Various methods of demulsification, like centrifugation, sedimentation, heating, use of dispersants and emulsion breakers have been examined <sup>(5)</sup>. Amongst these techniques, heating and centrifugation did not gain much acceptance due to the high maintenance cost and large energy requirements. The realization that dispersants cannot deal with higher viscosity emulsions, encouraged the investigation of the possible application of emulsion breakers <sup>(6)</sup>. The addition of chemical demulsifier in small quantities can greatly facilitate oil - water separation <sup>(7, 8)</sup>. The main advantages of using emulsion breakers are rapid and cost effective, reduction in the viscosity of crude oil emulsions, improve pump-ability, reduce final disposal cost by a factor of 10. <sup>(9)</sup>.

Demulsification by chemical demulsifies is the most effective method to overcome the problem. This method based on the addition of demulsifier which can destroy of the protective action of hydrophobic emulsifying agents and allow water droplets to coalesce. It has been reported that the combination of oil-soluble and water-soluble demulsifiers produced great result in water separation.

Success of chemical demulsifying method depends upon: 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 timemust exist in treating vessels to permit settling of demulsified water droplets<sup>(10)</sup> .

There are several factors affecting the demulsification process <sup>(11, 12, 13, 14, 15)</sup>, some of them depend on the characteristics of the crude oil continuous phase, such as viscosity and asphaltenes content. Others depend on the modifications of the demulsifiers composition <sup>(16)</sup>.

Commercial demulsifiers are generally polymeric surfactants such as copolymers of polyoxyethylene and polypropylene or alkyl phenol-formaldehyde resins or blends of various surface active substances. Table (1) lists briefly the chemicals used as demulsifiers since the beginning of the century <sup>(17)</sup>.

The selection of a demulsifier in a commercial application is based on the process of trial and error. However, it is an important target to elucidate the influence of the composition of the demulsifiers on their demulsification efficiency.

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<sup>(3)</sup>.

Obviously, any chemicals that give fast and complete separation of water within lower resistance time would be regarded as effective demulsifier for particular application. It is important to realize that the criteria for chemical selection depend on the condition of emulsion production system. If the residence time in the system is 24 hours, it would be pointless to use a chemical which will separate i.e. 90% of the water in the first hour and only another 5% in the remaining 23 hours. In this case speed is not required whereas complete dehydration is. However for the other extreme, the residence time may be as short as 2 to 3 minutes. Obviously, speed of dehydration becomes a major factor in product selection in this case.

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 <sup>(18, 19)</sup>.

The amount of demulsifier required to totally dehydrate the oil can vary from field to field. Some oilfields produce emulsion which can be treated with little as 2-4 ppm of chemical, on the other hand emulsion will required 100-200 ppm of demulsifier to attain pipeline specification <sup>(20)</sup>.

In general a lighter crude oil is easier to treat than a heavier one. This is function to the viscosity of the crude oil, and due to fact that for a given amount of agitation the chemical will disperse in the light oil more easily than the heavier oil. Because of the many factors affecting

emulsion stability, the treating system and specification defined by operator, the dosage rate of demulsifier can vary from 2 ppm for light crude oil to more than 100 ppm for heavier one.

Many kinds of commercial demulsifiers such as that supplied by Petrolite Company with trade name RP6000 used in oilfield are available today on the oil market, relatively high-price. The raw material of such demulsifiers, are extremely varied and come from diverse origins, with transformation ranging from simple hydrolysis to multistep high pressure synthesis process. A literature survey turns up between 2000 and 3000 patents referring directly to this subject <sup>(21)</sup>.

Recently, polyethylene glycols or polyglycols become useful in manufacturing surfactants in a verity of different field, due to their chemical stability, and water solubility. The lower molecular weight liquids are useful solvent; and the higher molecular weights solids, having a waxy appearance and various melting range are ideally suited to many applications in the surfactants industry <sup>(23)</sup>.

In the present study, different composition variations have been undertaken of some types of glycols that have similar chemical formula of  $\text{HO}[\text{CH}_2\text{CH}_2\text{O}]_n\text{H}$  in combination with commercial demulsifier RP6000 for breaking (w/o) emulsion prepared experimentally from Kirkuk crude oil. Experimental results showed that, addition of ethylene glycol methyl ether (EGME), monoethylene glycol (MEG), polyethylene glycol (PEG-1500), in combination with commercial RP-6000 demulsifier will accelerate the process of demulsification, and give feasibility of reducing the consumption amount of commercial demulsifier RP6000 for obtaining effective demulsifying reagents.

## **2. MATERIALS AND METHODS**

Experimental work was carried out on Kirkuk crude oil. Respective physical properties of crude oil are given in Table (2).

The viscosity of oil make the oil phase in a dual role, for a given amount of agitation will lead to not break up the water droplets as much, as would be case with lower viscosity oil. However, high viscosity oil is able to maintain larger water droplets in suspension and smaller droplets will have a greater resistance to settling, and then more difficult to dehydrated.

In this study, solution brine was prepared by dissolving (3) gm NaCl in (100) gm water in order to obtain the required salinity similar to crude oil field. The emulsion was prepared by adding water 30% vol. (3% wt. NaCl) to the crude oil at room temperature. The emulsification

was carried out by using a mixer at a speed of 5000 rpm for 60 min to get a stable emulsion without showing any signs of flocculation. The more serve the agitation the more shearing action, and consequently smaller water droplet are produced, and a more stable emulsion results. A typical microstructure photograph of water in oil emulsion was shown in Figure (1).

The rate of water separation was monitored for a period of up to 24 hr. since, as time progress more emulsifying agents will migrate to the water/oil interface forming a thicker film and thereby stabilizing the emulsion and making it more difficult to break.

The demulsification experiments were screened by comparative bottle test <sup>(21)</sup>. That is, it will select the most effective chemical from a series of test under carefully controlled conditions. It will not give the actual dosage rate required, although the system dosage rate is normally less than the dosage required in the bottle.

The bottle test, give the selected chemical the best chance of working in the system. The following procedure was adopted:

1. An untreated emulsion sample is taken.
2. The sample is poured in a 100 ml demulsification tube and heated to 65°C.
3. The selected chemical is injected into each tube leaving one untreated.
4. The tubes are shaken to disperse the chemical and placed pack in water bath controlled at 65°C.
5. The separated water is noted periodically.
6. After 120 min, the tubes are removed and sample from the BS&W determined.

In set of experiments, the effect of three chemical cosolvents of glycol types was used in combination with commercial demulsifier RP6000 to accelerate of demulsification process.

Cosolvents are chemical agents that can be used in order to enhancement the performance of surfactants. These selected chemicals were; ethylene glycol methyl ether (EGME), monoethylene glycol (MEG), polyethylene glycol (PEG-1500). The physical properties of chemical used were listed in Table (4).

### **3. RESULTS AND DISCUSSION**

Figure (2) shows some typical results of experiments conducted to test the influence of the EGME dose in combination with RP-6000 demulsifier. The stability of the emulsions was

determined by measuring the water separation at constant temperature (65°C) as a function of separation time at different intervals (5, 10, 15, 30, 60, 90 and 120 min).

As shown from the Fig.(2), after interval time of 20 min, the amount of water separated from emulsion for following dose; (100 ppm RP6000), (75/25) (RP6000/EGME), (50/50) (RP6000/ EGME), (25/75) (RP6000/ EGME) were found as 22.6, 44, 15 and 3.6% respectively. After a duration 120 min, (75/25) (RP6000/ EGME) separated highest percentage of water separation (65.2%), followed by (100 ppm RP6000) (56.5%), (50/50) (RP6000/ EGME) (46.3%), (25/75) (RP6000/ EGME) (35.2%), respectively.

The observed enhancement of (75/25) (RP6000/EGME) demulsifier efficiency was due to physical properties of EGME, and interaction activities of cosolvent EGME in combination with RP6000 demulsifier, which acts as flocculants in adsorption of the naturally occurring constituents in the interfacial film, and due to their ability to dissolve a variety of different types of chemical compounds and for their miscibility with water and other solvents.

The influence of MEG and PEG-1500 in combination with RP6000 demulsifier on crude oil emulsion stability has been studied. Figures (3) and (4) show the water separation from crude oil emulsions as a function of separation time. Both of MEG and PEG-1500 are aliphatic alcohol compounds which contain two hydroxyl groups as their functional groups.

As illustrated in Fig.(3), the (75/25) and (50/50) (RP6000/MEG) are better to separate water than (100 ppm RP6000) In this regards, their water separation after 120 min found as (75/25) (RP6000/MEG) (71 %) and (50/50) (RP6000/MEG) (66.4%), respectively. While for (75/25) (RP6000/PEG1500) was found better than (75/25) (RP6000/MEG) in separation of water.

The percentage of water separation is shown in Fig.(4). As shown in the Fig.(4) after 120 min the percentage of water separated for each addition of PEG1500 on RP6000 can be arranged as follows: (75/25) (RP6000/PEG1500) has the highest separation (87.7%), followed by (100 ppm RP6000) (83.1), (50/50) (RP6000/PEG1500) (75.7%), (25/75) (RP6000/PEG1500) (61%), respectively.

The observed enhancement in demulsifier efficiency is due to on the water solubility of MEG and PEG. The properties are arising from the interactions originating from the hydroxyl-hydrogen bonding. The Hydroxyl group makes the alkane soluble in water, raises the boiling point and makes the compound more viscous. The presence of two hydroxy groups as in glycol

will therefore make the boiling point even higher; the compound will be thicker or more viscous and highly soluble in water.

The influence and effectiveness of emulsion breaking between the EGME, MEG and PEG-1500 in combination with RP6000 demulsifier can be compared in their ability in separating the water from emulsions. From experimental results, it was found that PEG-1500 was more effective in emulsion breaking than MEG, and EGME. Figure (5) shows the best performance in terms of total amount of separated water achieved. The maximum amount of water separated after 120 min from PEG-1500 found to be 87.7% for (75/25) (RP6000/PEG1500). In contrast, the water separations in (75/25) (RP6000/MEG), (75/25) (RP6000/EGME) demulsifier were 71%, 65.2% respectively.

Considering the amount of separated water after 120 min of test, the classification of the demulsifiers in terms of decreasing efficiency is therefore the following: (75/25) (RP6000/PEG1500) > (75/25) (RP6000/MEG) > (75/25) (RP6000/EGME)

These phenomena results due to the demulsifier ability to modify the properties of demulsifying liquid, lower oil-water interfacial tension, and solubilize individual contaminant molecules in the surfactant <sup>(22)</sup>.

#### **4. CONCLUSIONS**

1. Chemical agents as ethylene glycol methyl ether (EGME), monoethylene glycol (MEG), polyethylene glycol (PEG-1500) can be used as cosolvents in order to enhancement the performance of commercial demulsifier RP6000.
2. Addition of ethylene glycol methyl ether (EGME), monoethylene glycol (MEG), and polyethylene glycol (PEG-1500), in combination with commercial RP-6000 demulsifier accelerated demulsification of Kirkuk crude oil.
3. The maximum amount of water separated after 120 min found to be 87.7% and 71% for (75/25) (RP6000/PEG1500) and (75/25) (RP6000/MEG), respectively. Where, the water separations in (75/25) (RP6000/EGME) demulsifier were 65.2%.
4. The amount RP6000 related to used cosolvents can be classified to decreasing their efficiency as following: (75/25) (RP6000/PEG1500) > (75/25) (RP6000/MEG) > (75/25) (RP6000/EGME).

5. Further works are nevertheless required to provide deeper understanding of the mechanisms involved to facilitate the development of an optimum system applicable to the industry.

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**Table (1):** Demulsifier History.

Period	Rate Required (ppm)	Chemistry
1920 's	1000	Soap, naphthenic acid salts and alkylaryl sulphonate, sulphated castor oil
1930 's	1000	Petroleum sulphonates, derivatives of sulpho-acid oxidized castor oil and sulphosuccinic 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 alkoxyate
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 Kirkuk Crude Oil.

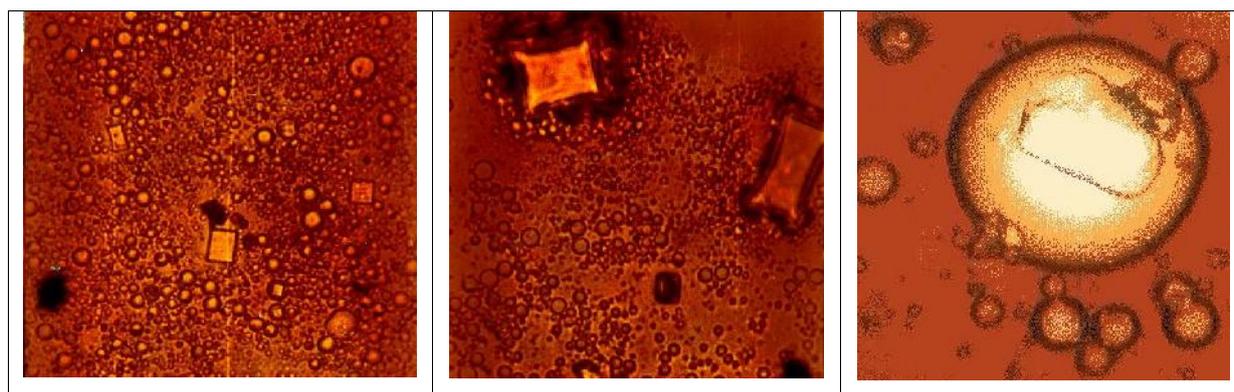
Property	value
API	35
Salt content (%wt.)	0.001
Water and Sediment content (%vol.)	0.05
Ash content (%wt.)	0.01
Sulfur content (%wt.)	2.0
Viscosity (cSt) at 15°C	10
Conductivity (mS)	0

**Table (3):** Physical Properties of Demulsifier RP6000.

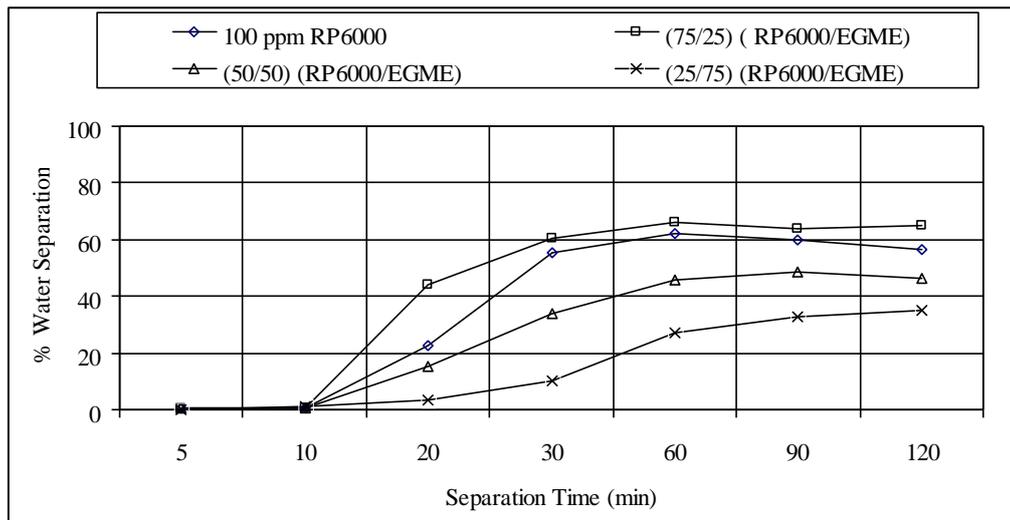
Appearance	Brown liquid
Sp.Gr. at 20 °C	0.94
Viscosity at 20 °C (cp)	<50
Pour point °C	<-30 °C
Flash Point °C	>70 °C

**Table (4):** Properties of Chemical Materials.

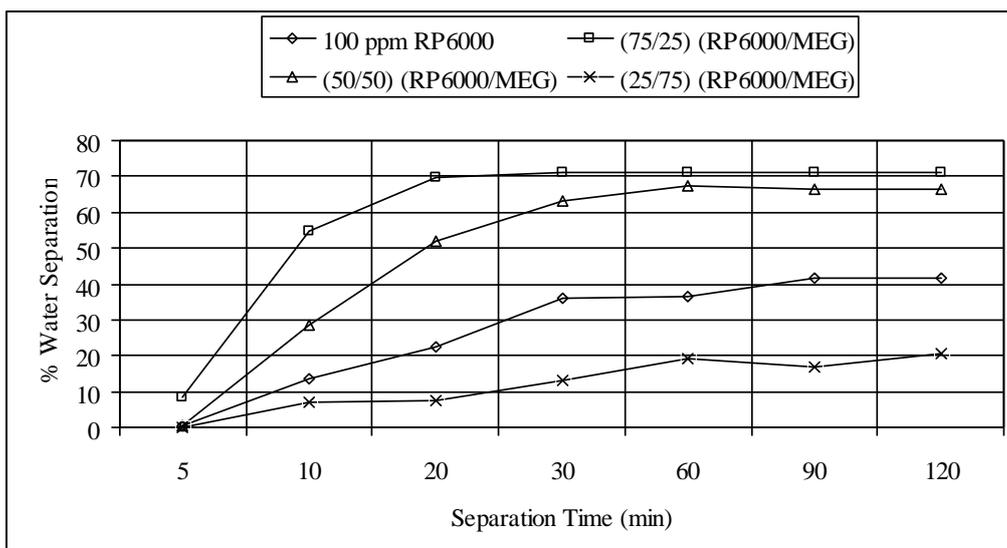
Substance	Ethylene Glycol Methyl Ether (EGME)	Mono Ethylene Glycol (MEG)	Poly Ethylene Glycol (PEG-1500)
Chemical Formula	$C_3H_8O_2$	$C_2H_6O_2$	$(C_2-H_4-O)_n-H_2-O$
Molecular Weight, g/mol	76.1	62	1350 - 1650
Density, (g/cc) @ 20°C	0.965	1.115	1.15-1.21
Viscosity, cP @ 25°C	1.6	16.9	8522-13333
Boiling Point@ 760 mm Hg, °C	124	197	>200
Freezing Point, °C	-85	-13.4	43-46
Flash Point, °C	42	116	> 177
Solubility	Soluble in water and ethanol; slightly soluble in ether. Insoluble in benzene and petroleum ether	Soluble in water	Soluble in water



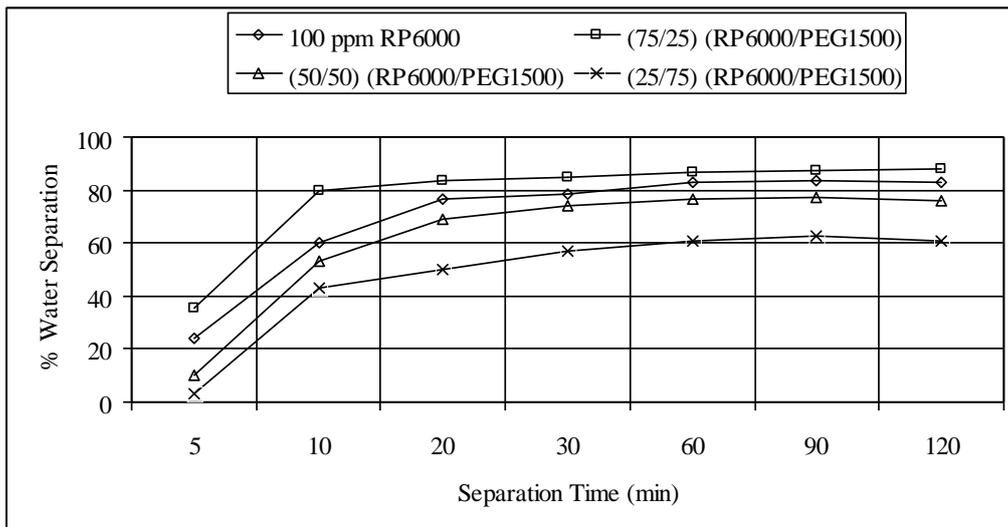
**Fig. (1):** A Typical Photograph of Water in Oil Emulsion Microstructure.



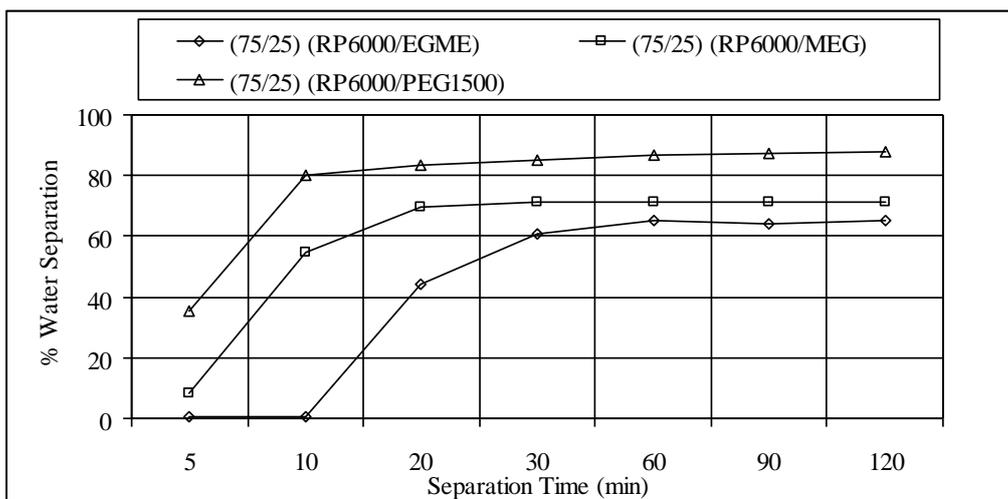
**Fig. (2):** The Influence of Various Concentrations of Ethylene Glycol Methyl Ether (EGME) and RP6000 on Crude Oil Emulsion Stability (Percentage of Water Separation %).



**Fig. (3):** The Influence of Various Concentrations of Monoethylene glycol (MEG) and RP6000 on Crude Oil Emulsion Stability (Percentage of Water Separation %).



**Fig.(4):** The Influence of Various Concentrations of Polyethylene glycol (PEG-1500) and RP6000 on Crude Oil Emulsion Stability (Percentage of Water Separation %).



**Fig. (5):** Change of Emulsion Stability for Crude Oil Emulsions, as Function of Processing Time and Demulsifier Applied

## دراسة تأثير اضافات الكلايكولات كمذيبات مشاركة في تفكيك المستحلبات النفطية

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مدرس

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### الخلاصة

تعتبر عملية تفكيك المستحلبات النفطية من العمليات المعقدة و تستخدم في العديد من التطبيقات الصناعية مثلا في الصناعة النفطية ، صناعة الاصباغ و في وحدات معالجة المياه المستخدمة لغرض حماية البيئة من التلوث. و تستخدم عملية ازالة الاستحلاب بالطريقة الكيماوية بشكل واسع في اغلب عمليات معالجة المستحلبات النفطية نوع (ماء في الزيت) والتي تتضمن اضافات عوامل كيماوية معينة لغرض تحطيم فعالية عوامل الاستحلاب وبالتالي تسهل عملية تفكيك المستحلبات. لقد بينت النتائج المختبرية بان اضافة مركبات كيماوية اساسها الكلايكول مثل اثلين كلايكول مثل ايثر ،مونو اثلين الكلايكول ، و بولمر الاثلين كلايكول ذو الوزن الجزيئي ١٥٠٠ الى كاسر الاستحلاب التجاري RP6000 بشكل مواد مذيبيبة مشتركة ستؤدي الى تحسين عملية تفكيك المستحلبات. لقد تم استخدام طريقة القنينة في جميع التجارب المختبرية عند درجة حرارة ثابتة ٦٥ سيليزية وكانت جرعة عامل مفكك الاستحلاب حوالي ١٠٠ ppm. ان اقصى كمية من الماء المفصول بعد فترة (١٢٠) دقيقة من زمن عملية الفصل ، قد كانت (٨٧.٧%) لمزيج المتكون من (75/25) (RP6000/PEG1500) بينما كان للمزيج المتكون من (75/25) (RP6000/MEG) و (75/25) (RP6000/EGME) مساوي الى و (٧١%) و (٦٥.٢%) و على التوالي.