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CHEMICAL DE-EMULSIFICATION OF SOME IRAQI WET CRUDE OILS

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ABSTRACT

Production of Wet crude oil has been a growing field problem worldwide. Applications of the right methods and technologies to treat wet crude oil are needed to solve this problem and remove as much water as is economically possible. This paper deals with laboratory test to evaluate the relative efficiency of different emulsion breakers (de-emulsifiers) under different conditions.

Five de-emulsifiers were used to treat wet crude oil from East Baghdad and Kirkuk oilfields. On the basis of a laboratory study, it is shown that using RP6000 (commercial) and NIPD de-emulsifiers achieved the best results; the latter was introduced in the present work. The de-emulsification rate is influenced to a great extent by the de-emulsifier concentration.

Finally, it is shown that water –in-oil emulsions formed from kirkuk crude oil (low viscosity 's and asphaltenes content) are less stable and more easily broken than those from the more viscous and highly asphaltenes, East Baghdad crude oil.

الخلاصة

عمليات أنتاج النفط الرطب بدأت تشكل مشكلة متفاقمة في الحقول النفطية في أرجاء كثيرة في العالم . لذلك تعتبر عمليات معالجة النفط الرطب باستخدام الطرق والتقنيات المناسبة ذات أهمية كبيرة في الصناعة النفطية في الوقت الحاضر.، وذلك لأزالة أكبر كمية ممكنة من الماء والحصول على نفط ضمن المواصفات التسويقية . الدراسة الحالية تتضمن أجراء تجارب مختبرية لتقيم كفاءة بعض المواد الكيماوية المستخدمة ككاسرات استحلاب لمعالجة بعض النفوط الرطبة العراقية وتحت ظروف مختلفة .

خمسة أنواع مختلفة من المضافات الكمياوية المستخدمة ككاسرات استحلاب تم تقيمها في هدا العمل على مستحلبات خام شرقي بغداد وكركوك . وبينت النتائج المختبرية بأن كاسر الاستحلاب المعروف تجارياً بأسم RP6000 والنموذج المقترح في هذا العمل والمعروف NIPD قد أعطيت افضل النتائج فيما يخص معالجة النفط الرطب للخامات أنفة الذكر. وإن تركيز المستحلبات المستخدمة وجد بأنه ذات تأثير كبير على كفاءة وسرعة الفصل

وأخيراً ، بينت الدراسة بأن مستحلبات نفط خام كركوك ذات اللزوجة الواطئة والمحتوى الاسفلتيني القليل هي أقل استقرارية وسهلة المعالجة من تلك المتكونة من خام شرقي بغداد ذات اللزوجة العالية والمحتوى الاسفلتيني العالي.

KEYWORDS

Wet crude, de-emulsifier, water-in-oil emulsion, chemical de-emulsification.

INTRODUCTION

The formation of water –in – oil emulsion is frequently observed in primary production of oil and in secondary recovery by water flooding .The removal of this water is then necessary for several reasons. The quality of the crude oil is highly dependent on residual contents of water and water–soluble contaminates. Even small amounts of these components can cause problems in the case of multiphase transport in pipes and refinery processes. A portion of the water, called free water, is easily separated from the crude by the action of gravity as long as the velocity of the fluid is sufficiently low. But the associated water, emulsified, water droplet 0.1-20 microns in diameter, are so small that gravity settling becomes impractical due to presence of naturally occurring emulsifying agents like asphaltenes, resins, waxes, sediments, etc. in the crude oils. These materials concentrate around the water drop and form a stable elastic film. This reduces interfacial tension at the oil – water interface, which does not permit the coalescence of the water droplet. Therefore, different methods to solve the emulsion problem have emerged.

The most widely used method of treating crude – oil emulsions are by chemical de-emulsification. Much has been written on this subject. A search of the patent literature will turn up between 2000 and 3000 patents directly referring to this subject, Lissant (1983). Extensive and excellent reviews in this area include those by Sumner (1954), Carroll (1954), Lissant (1983), and Menon and Wasan (1985). **Table (1)** is a brief listing of the chemicals used to de-emulsify crude oil emulsion since the beginning of century, Stals (1991).

The objective of this paper is to study the destabilization process of some Iraqi water-in-crude oil emulsion by chemical de-emulsifiers.

THEORETICAL BACKGROUND

Chemical methods of resolving crude –oil emulsion are based on the addition of reagents (de-emulsifiers), which destroy the protective action of hydrophobic emulsifying agents and allow the water droplets to coalesce.

De-emulsifiers chemistry

De-emulsifiers are all relatively high molecular weight polymers capable of adsorbing at an oil/water interface and displacing the surfactant film that stabilizes the emulsions.

Dow (1983), lists six classes of chemicals that can break emulsions:

1- Compounds that can take up water and react with it, (Calcium, Chloride, Quicklime and Portland cement).
2- Compounds that cause flocculation of the substance making up the protective film (Sodium Chloride, Ferrous Sulfide and Sodium Sulfide).
3- Compounds that react with salts in the water or any Organic acid that may be present (Lye, Sodium Bicarbonate and Calcium Oxide).
4- Compounds that tend to form emulsion of the opposite kind. (Iron Oxide, Finely divided Silica Sand, Clays, Sodium Soaps, Resin and Resin Soaps, Gums, Starch and organic Suffocate.
5- Electrolytes that can neutralize charges (Sulfuric acid, Acetic acid, Ferric Chloride and Ferric Nitrate).
6- Solvents for the protective film (Carbon disulfide, Benzene Acetone, Alcohol, Ether and Carbon Tetrachloride).

Jones et al. (1978), list some of the chemical structures of de-emulsifiers that are used for breaking crude –oil emulsions. They are:

1- Polymerized alkoxylated polyglycols.
2- Ethylene oxide /Propylene oxide block co-polymer.

3- Polyglycol esters.
4- Polymerized oils (Sulphonate).
5- Alkanolamine condensates (Oxyalkylated Phenols and Polyamine).

With the creation of Ethylene Oxide/Propylene Oxide (EO/PO) block copolymers, the first "genuine" demulsifiers were available. Addition of EO /and /or PO to linear or cyclic P-alkyl Phenol Formaldehyde resins and to Diamines or higher functional Amine Yield classes of modified polymers that perform quite well at relatively low concentration. Furthermore, these demulsifier bases were converted to high- molecular- weight products by reaction of one or more with difunctional compound such as di-acids, diepoxides, di-isocyanate and aldehydes, delivering a host of potential emulsion breakers, Stals (1991).

Action of de-emulsifiers

The mechanism of de-emulsifier action is breaking up, peptizing, and displacing the colloidal components of the interfacial films from the drop surface, replacing these components by an adsorbed layer of surfactant molecules or ion that do not have any structural mechanical properties. The drops, when they are freed of the interfacial films, can coalesce as a result of subsequent collision, DeGroote (1926).

The mechanisms of emulsion destabilization differ for treatment with water-soluble and oil-soluble de-emulsifiers. With water-soluble de-emulsifies, the first step is breakdown of the protective shells on the formation water globules, and only after that the adsorption activity of colloidal surfactant present in the oil is suppressed. With oil-soluble de-emulsifiers, the first step is suppression of the adsorption activity of the natural emulsifier; the protective shells are broken later, or in parallel with the first process, Petrov et.al. (1985).

After the de-emulsifier has been brought up to each globule, it is necessary to provide additional time for aging of the emulsion, and only then to carry out the coalescence of the drops, separation of the layers in the stream, and settling of the water from oil.

Little (1981), suggests that the following sequence of steps leading to de-emulsification of water-in-crude oil emulsion:

1- Displacement of asphaltinic material and solids from the interface by the de-emulsifier.
2- Neutralization of any weakly acidic material and lowering of surfactant micelle concentration by using an alkaline salt such as Potassium Carbonate.
3- Formation of surfactant micelles, which solubilize and/ or stabilize the asphaltic compounds in the oil and/ or water.
4- Addition of suitable agent, which prevent re-emulsification.
5- Coalescence of water droplets.
6- Coalescence of the large droplets with the bulk separated water phase.

The de-emulsifiers must contact each stabilized water droplet in order to destabilize it. Therefore, the de-emulsifiers should be applied so that they are thoroughly mixed with all of the emulsion.

EXPERIMENTAL WORK AND PROCEDURE

Materials

The two crude oils used in this study were: East Baghdad crude oil and Kirkuk crude oil, properties of these crude oils are given in **Table (2).**

The aqueous phase used in the emulsification was synthetic formation water prepared from distilled water and Analar salt. Salts may vary widely in ratio of metal ions and in brine concentration. The mixed salts concentrations used in the present work are 70% Sodium Chloride, 20% Magnesium chloride and 10% Calcium Chloride. These concentrations were based on an average analysis of brine, Becher (1966).

Five de-emulsifier blends were used to destabilize the water –in-crude oil emulsions. These de-emulsifiers are given in **Table (3)**. The first two are commercially available from a service company. The third and fourth were obtained from the Petroleum Research and Development Center/ Ministry of Oil, Iraq. The last was introduced by the present work. It comprises a flocculent material like polymers (non-ionic dry Polyacrylamide), in combination with non-iconic surfactant (NID) .The physical properties of the polymer are as follows:

Molecular Weight	5.5 10
Density at 20C, gm/cc	1.12
Viscosity, mPa.s	
0.5% polymer	60
1.0% polymer	110
Refractive Index at20C	1.3352

Emulsification Methods

The emulsion was prepared in approximately one-liter batches. A variable speed model IKA-RE 166 stirring motor was used to mix the water-oil emulsion. In all cases, the emulsions were mixed at low speed for 8 minutes. The mixer was then stopped for 4 minutes to allow the trapped air to rise out of the emulsion. The emulsion was then mixed at high speed for 7 minutes and allowed to stand for 20-30 minutes before being treated further.

The water in-crude oil emulsions were prepared by first preheating the oil to about 60^0C, and then gradually adding water to the crude oil, while mixing at low speed.

De-emulsification Method

The recommended method for testing de-mulsifying chemicals involves adding the various chemicals to samples of the emulsion and observing the results. This is commonly called "bottle test", Lissant (1983). It is not a foolproof approach; however, it is the most standard universal screening method for evaluating the de-emulsifiers.

The de-emulsification tests were made in 100(ml) graduated test tubes. All water-in crude oil emulsions contained 25% dispersed water and were prepared as described above. Into each of test tubes the de-emulsifier under investigation was injected into the emulsified phase and shaken by hand for about 200 shakes. The separation of the aqueous phase from the emulsion took place under normal gravity conditions and at 40 and 50^0C for Kirkuk and E. Baghdad crude oil, respectively. Each de-emulsification was repeated twice and the average value was reported.

RESULTS AND DISCUSSIONS:

The de-emulsifiers given in **Table (3)** were screened using the "bottle test" method as explained above. **Fig. (1) and (2)** give the separation of water from 25% W/O emulsions of E-Baghdad and Kirkuk crude oils, respectively, as a function of time and for various de-emulsifier types and concentrations.

Emulsions based on E-Baghdad crude oil cannot be resolved using Sodium Sulfonate as de-emulsifier even at high doses (up to 10,000 ppm). The NIPD and RP6000 were found to be the most promising de-emulsifiers for maximum resolution of both water- in- E-Baghdad and Water-in-Kirkuk emulsions Prodeco was the next best.

Concentration effects of different de-emulsifiers on the separation of synthetic formation water from W/O emulsion are shown in **Fig. (3) and (4)** for E-Baghdad and Kirkuk crude oil, respectively. The volume of the aqueous phase is measured after 30 and 15 minutes for E-Baghdad and Kirkuk crude oils, respectively. Emulsions based on Kirkuk crude oil were easier to break at 40 ^{0}C and required less agent concentrations and less retention time. While E-Baghdad crude oil emulsions offer more resistance to de-emulsification at 50 ^{0}C and required higher de-emulsifier concentration and retention time. It is therefore concluded that the less viscous and lower asphaltenes content emulsions (Kirkuk crude) require minimal amounts of de-emulsifier and retention time than the highly viscous crude emulsions. However, the de-emulsification characteristics of both crudes are quite similar with respect to de- emulsifier type used. For both crude oil emulsions, the highest efficiency as de-stabilizer is achieved for RP6000 and NIPD de-emulsifiers. With Prodeco the results are good but the settling of water is relatively slow as compared to the other.

The structures of commercial chemical de-emulsifiers are unknown. Therefore it is difficult to explain the mechanisms of emulsion destabilization by these de-emulsifiers. For the de-emulsifier introduced in the present work (NIPD), it is possible to explain the basic m lyacrylamide neutralizes the repelling charges on the colloidal particulate matter encapsulating the water droplets producing floc, thus removing the particulate barrier. Under this condition the NID can easily diffuse through the phase boundaries rupturing the interfacial film and resulting in lowering of IFT, thus causing resolution of the emulsion. The idea behind the combination of a hydrophilic polymer (Polyacrylamide) and a hydrophobic surfactant (NID) is that the de-emulsification process can take place from the aqueous side as well as from the crude oil side when attacking the oil-water interface. The results from **Fig. (3) and (4)** clearly show that the NIPD is more effective than the surfactant (NID) alone.

CONCLUSIONS

The conclusions drawn from this work are:

1- Emulsions generated from Kirkuk crude oil (low viscosity) are less stable and more easily broken than those from the more viscous, E-Baghdad crude oil.

2- RP6000 and NIPD are effective de-emulsifiers for water-in crude oil emulsions under study, when used within the appropriate concentration range.

3- De-emulsifier concentration in the range of (20-30) ppm are used for less viscous Kirkuk crude oil emulsions, while concentration of (30-40) ppm are needed for the highly viscous E.Baghdad crude emulsions with higher retention time.

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Table (1): De-emulsifier History

Period	Rates Required (ppm)	Chemistry
1920's	1000	Soaps, salts of nephthenic acids; "aromatic and alkylaromatic sulfonates;"; "Turkish red oil"; and sulfated castor oil.
1930's	1000	Petroleum sulfonates, "mahogany soaps", oxidized caster oil, and sulfosuccinic acid esters.
Since 1935	100 to 500	Ethoxylates of fatty acids, fatty alcohols, and alkylphenols.
Since 1950	100	EO/PO copolymers, P-alkylphenol formaldehyde resins + EO/PO and modifications.
Since 1965	30 to 50	Amine oxalkylate.
Since 1976	10 to 30	Oxalkylated, cyclic P-alkylphenol formaldehyde resins, and complex modifications.
Since 1986	5 to 20	Polyesteramines and blends

Table (2) Properties of East Baghdad and Kirkuk Crude Oils

Properties	East Baghdad	Kirkuk
Sp. Gr. @ 15.6°C/15.6°C	0.92	0.844
Gravity (API)	22.3	36.1
Pour Point (°C)	-	-
Flash Point (°C)	-	-
Sulphur Content (%wt)	5.04	1.88
Hydrogen Sulphide Content (ppm)	-	20.0
Wax Content (%)	1.1	2.8
Carbon Residue (Conradson) (% wt)	10.0	3.7
Asphaltenes (%wt)	6.2	1.3
Acidity (mg KOH/gm)	-	0.17
Ash Content	0.06	0.007
Water Content (% vol)	Trace	Trace
Water and Sediment (% vol)	0.2	< 0.2
Salt Content (lb/1000 bbl)	9.0	3.0
Reid Vapour Pressure (psi)	-	4.8
Heat of Combustion (gross) (Kcal/gm)	-	10.7
Characterization Factor	11.9	11.8
Cetane Number	-	54.3
Kinematic Viscosity (Cst) @ ( ) °C		
10.0	-	12.6
21.1	58.20	7.5
37.8	38.68	4.8
48.9	26.65	-

Table (3) De-emulsifiers used in the Present Work

Designation	Solubility	
	In Water	**In Hydrocarbons**
RP6000	Insoluble	Soluble
Prodeco	Insoluble	Soluble
NID (non-ionic S.)	Insoluble	Soluble
Sodium Sulfonate	Soluble	Disperses
NIPD	Polyacrylamide, Soluble	NID, Soluble

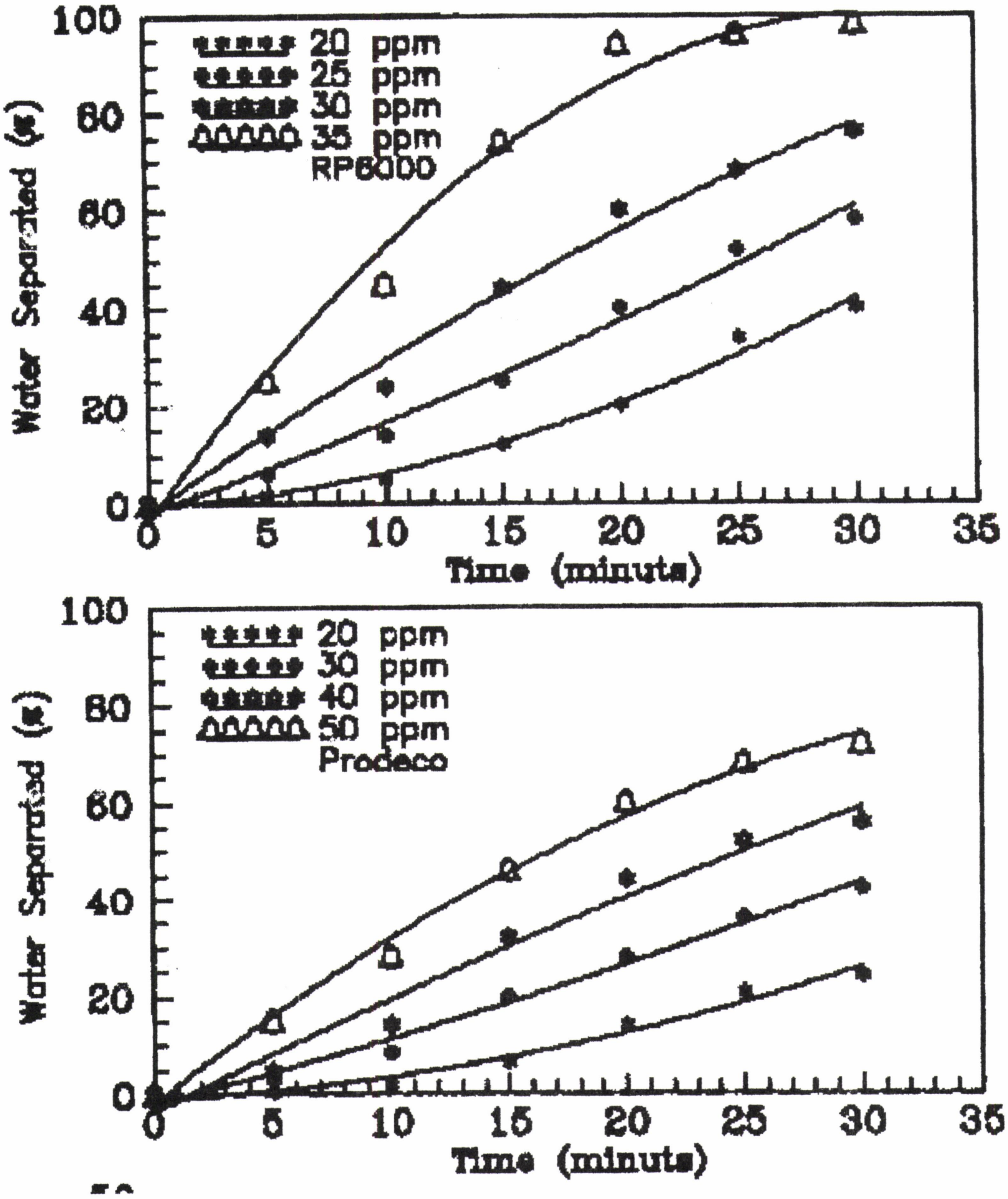
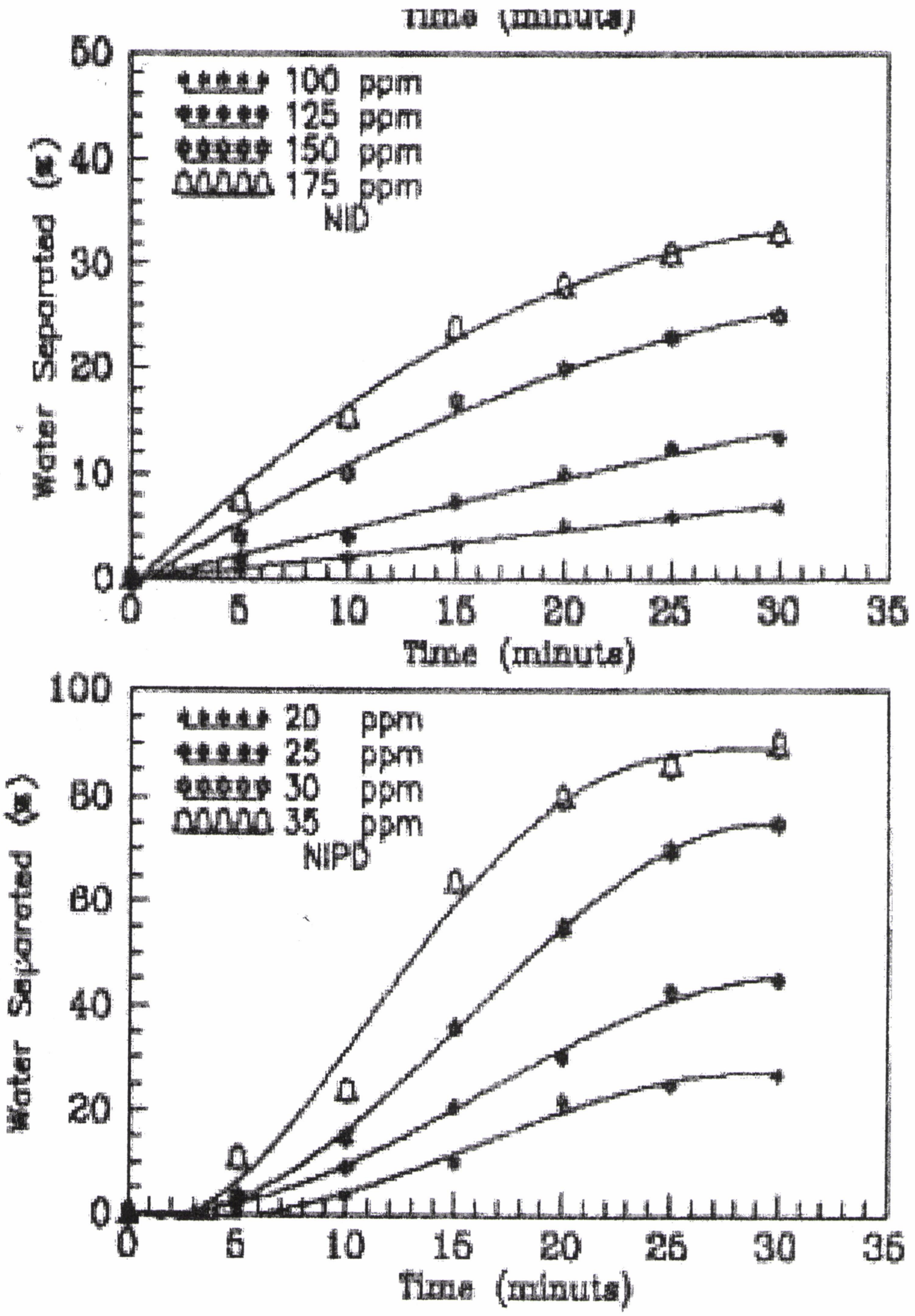


Fig.(1): The influence of various concentrations of de-emulsifiers on the separation of synthetic formation water from water-in E. Baghdad crude oil emulsions. The aqueous phase and the separation temperature were 25% (v/v) and 50°C respectively.



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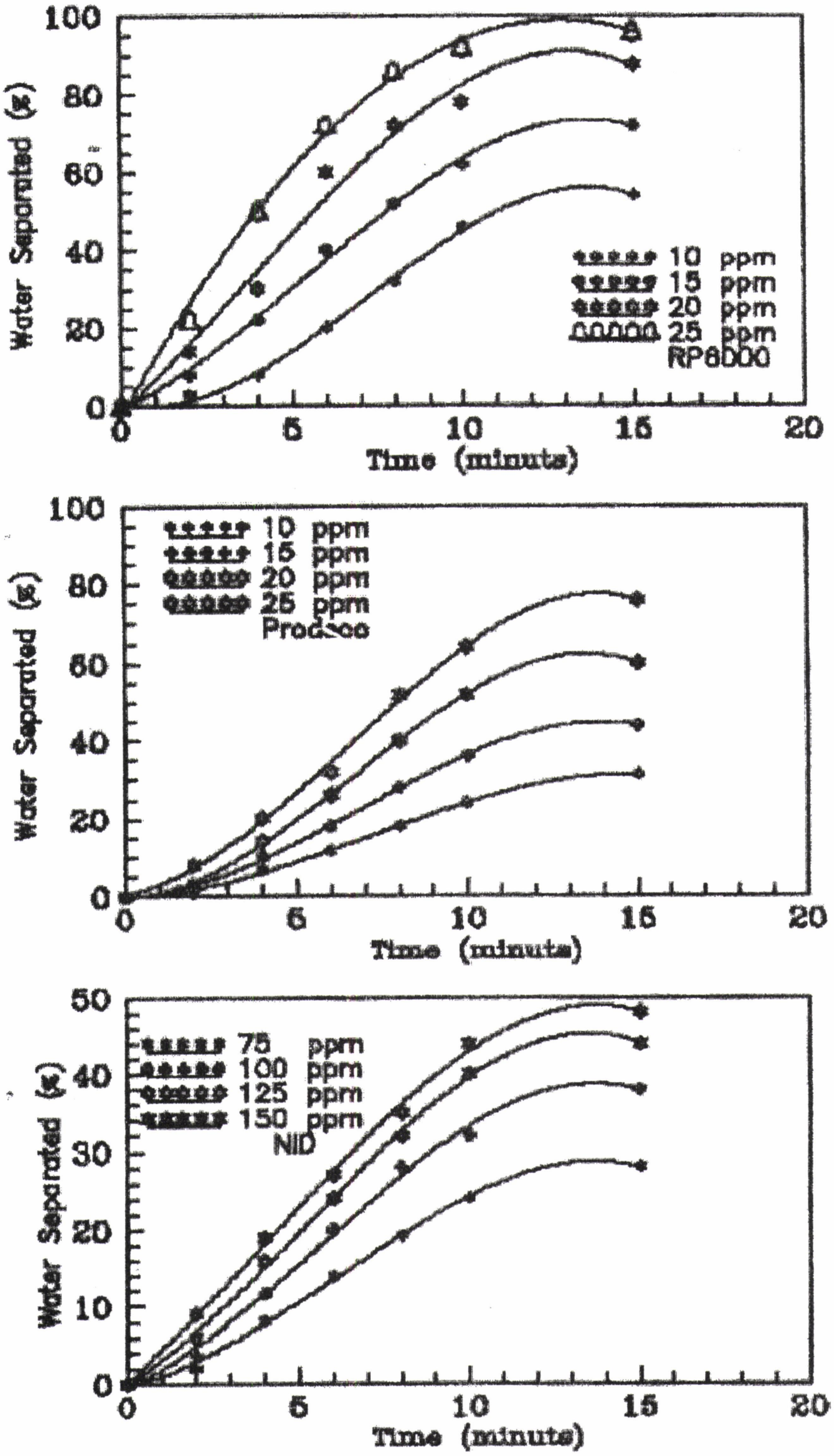
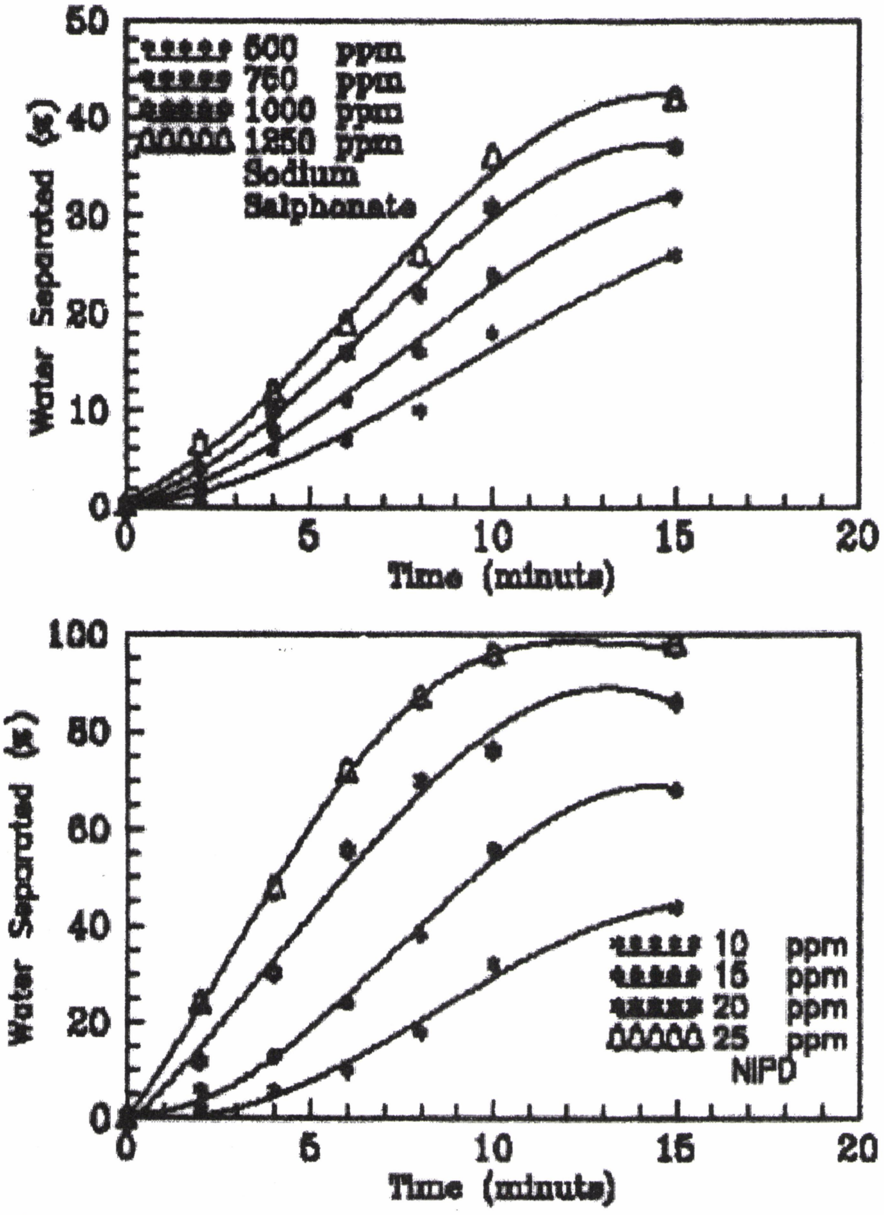


Fig.(2): The influence of various concentrations of de-emulsifiers on the separation of synthetic formation water from water-in Kirkuk crude oil emulsions. The aqueous phase and the separation temperature were 25% (v/v) and 40°C respectively.



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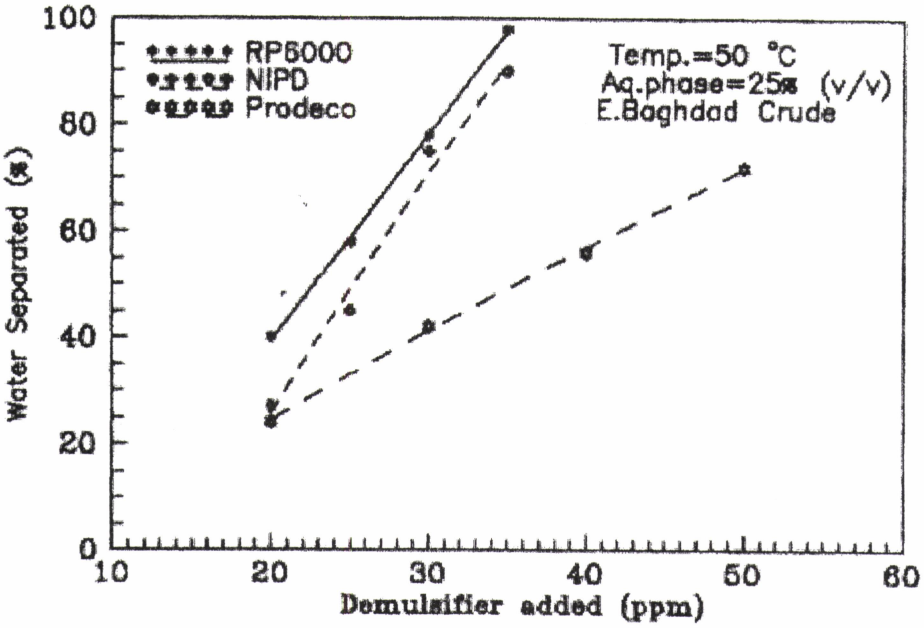

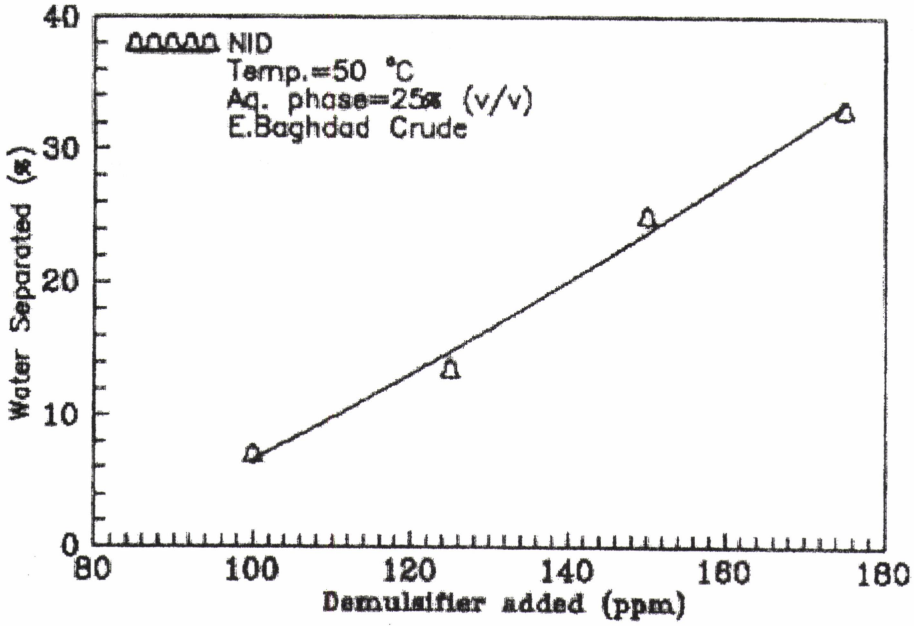

Fig.(3): The influence of various concentrations of de-emulsifiers on the separation of synthetic formation water from water-in E. Baghdad crude oil emulsions. Separation time (30 Minute).

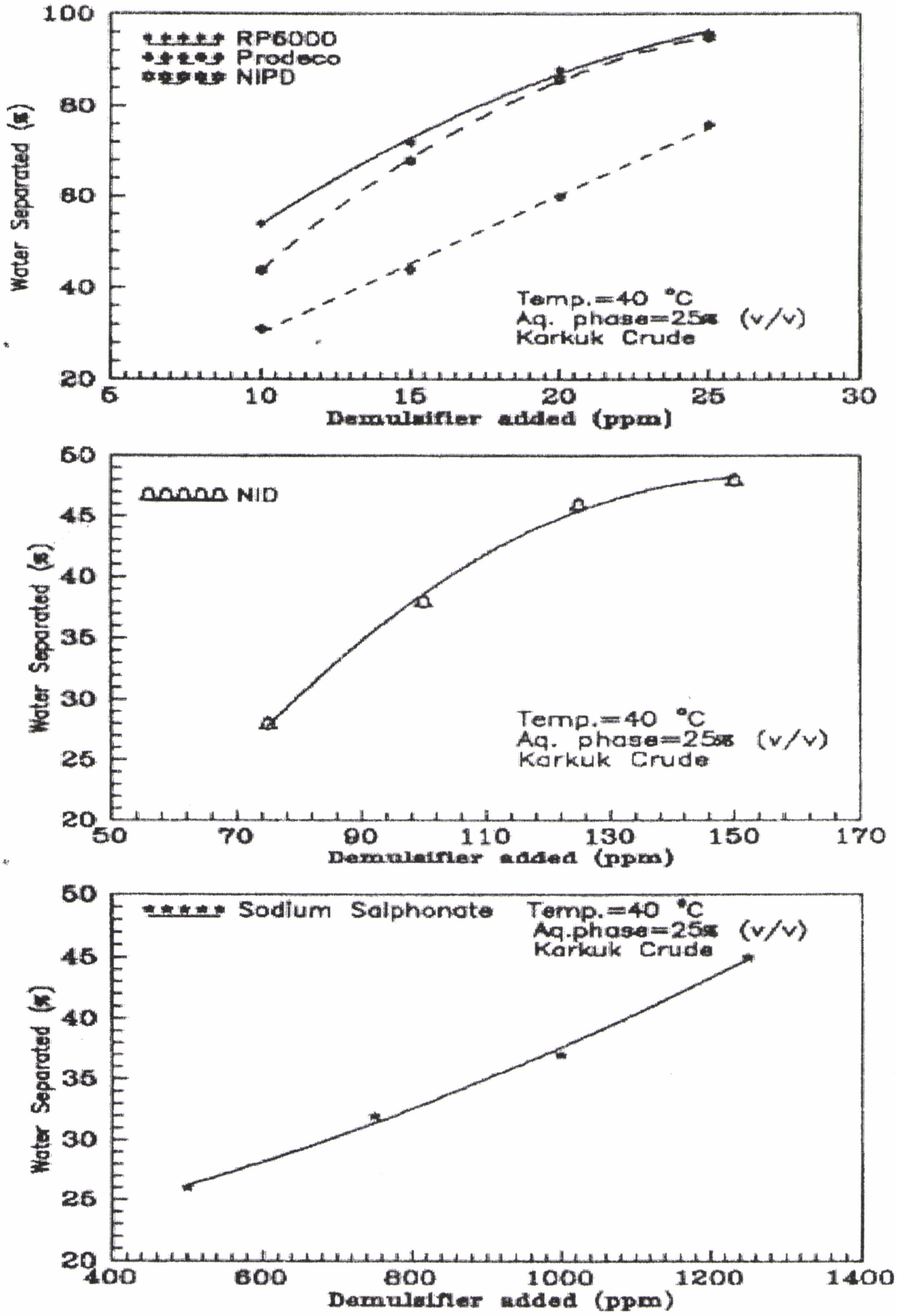

Fig.(4): The influence of various concentrations of de-emulsifiers on the separation of synthetic formation water from water-in Kirkuk crude oil emulsions. Separation time (15 Minute).