Optimization of (RP6000 and MAKS-9150) demulsifiers for separation of water from (Kirkuk / baba, Khbbaz) crude oil emulsion

دراسة الظروف المثلى لفصل الماء عن النفط الخام لحقل كركوك (بابا) وخباز مختبريا باستخدام مفكك الاستحلاب (RP6000 and MAKS-9150)

Dr. Mueyyed Akram Arslan[1*], Dr. Ghassan Burhan Yaqoob[2]

[1]Ministry of Construction and Housing

[2]Ministry of Oil, North Oil Company- Kirkuk

[*]Corresponding Author E-mail: Alparsalan1961.ma@gmail.com, ghassan7jul@yahoo.com

Abstract:

In this study oil-soluble (RP6000 and MAKS-9150) emulsion breakers have been selected for separation of water from Kirkuk / baba (50°C), Khbbaz (40°C) crude oil emulsions and their activity measured using the Bottle test method at different concentration and found the activity of RP6000 demulsified best than MAKS-9150 emulsion breakers. RP6000 separated water (100%) in (15)min., (40)ppm and in (60)min., (20)ppm of demulsified for Kirkuk/ baba Crude oil and for khbbaz Crude oil the (100%) water separation was in (15)min., (80)ppm and in (30)min., (60)ppm and PH effect, salinity, temperature and density of emulsion stability depending on literature were explained for Optimization.

Introduction:

During production of crude oil water-in-oil emulsions are forming which is often accompanied by water. The water in oil emulsion is normally difficult because of immiscibility between these two liquid phases. However, the mixing of the fluids during production and the existence of natural surfactants in the petrole's composition contribute to formation of such emulsions [1, 2] natural emulsifiers are concentrated in the higher polar fraction of the crude oil [3-8] like asphaltenes, resins, and oil-soluble organic acids and bases, which are the main constituents of the interfacial films surrounding the water droplets and make emulsion stability. Asphaltenes are solids with no definite melting point. The aromatic sheets with alkyl and cyclic side chains and heteroatoms (nitrogen, sulfur, oxyge,) and small amount of metals like vanadium and nickel [9]. Asphaltenes exist in the petrole as a colloidal suspension and stabilizing by resins on their surface [10]. In this regard, the resins and asphaltenes make together clusters form called micelles. These micelles or colloids in most of the polar material in the crude oil plays as surface-active agents (interfacial active material). It is an important to know that the asphaltene-resin ratio in crude oil is responsible for the type of film formed and, therefore, is in charge of to the stability of the emulsion [3, 4]. There are many other facters that acts as to strong the stability of the interfacial film and as a result to emulsion stability, such as PH of water and the additive compounds [11-13].

But these effects are different from crude oil to others [14-16]. For example, the pH effect on Algerian crude oil emulsions and found that a (PH=7) is more efficient than an acidic or basic environment for stabilizing the emulsions [13]. the effects of salinity, temperature,PH and water content on the stability of crude oil emulsions based on microwave treatment studied by Fortuny et al. and showed that, in emulsions containing high water contents, the rate of emulsion breaking is high, except when high salt content and base medium were simultaneously involved. Additionally, the emulsions are more stable at lower ionic strength of the aqueous phase. Proved by Moradi et al. When thay studied the salinity on crude oil/water emulsions by measuring the droplet size using an optical microscopy method [17].

The effect of pH values, temperature, salinity on the stability of (Kirkuk / baba, Khbbaz) crude oil emulsion have been studied in the present investigation. In addition, the influence of demulsifies ingredients on stability of the emulsion is studied in order to understand the water-in-oil emulsion behavior an experimental data designed and software, used to state an optimized formulation *for water* separation These experiments were done by bottle test method, which is the most common method for evaluating the amount of water separated from water- in-oil emulsion [18].

Method:

Characterization of crude oil:

Crude oils used for these types of methods are from two fields, (Kirkuk / baba , Khbbaz) crude oil. Their physical properties are shown in Table 1. Chemical properties act important roles in the crude oil emulsion stability.and shows the Khbbaz field is more stable than the other as a result of making more interfacial active agents in the crude oil.

Table (1) Physical properties of wet crude oils .at room temperature

characteristics	Khbbaz	Kirkuk / baba
specific gravity	0.8595	0.8524
Water %	10	10
Salt %	15	2
specific gravity for emulsified water	1.1061	1.0098
Asphaltene (%w/w)	1.86	1.60
Wax (%w/w)	4.28	3.00

Equipment and Materials:

The chemicals, tools and demulsifiers used in this investigation are chosen based on suitability shown in Tables (2, 3) and physical characteristics of demulsifiers are shows in Table (4).

Table (2) Types of chemicals

No.	Name	Supplier
1	NaCl	Fisher/USA
2	$CaCl_2$	Fisher/USA
3	$MgCl_2$	Fisher/USA
4	Xylene	Scharlau/ spanish
5	toluene	Fisher/USA
6	Acetone	Fisher/USA

Table (3) Used apparatuses and tools

No.	Name	Supplier
1	Spectrum one FTIR spectrometer	Perkin Elmer U.S.A
2	Distillation of Crude	Koehler instrument comp U.S.A
3	Digital Density Meter	Japan
4	Hydrometer	Perkin Elmer U.S.A
5	Hamilton Beach Mixer	Perkin Elmer U.S.A
6	Oven	Perkin Elmer U.S.A
7	water Bath	Perkin Elmer U.S.A

Table (4) Physical characteristics of demulsifiers

Physical characteristics	RP-6000	Maks 9150
specific gravity at (R T)	0.9195	1.0296
colour	dark brown	white
PH	6	5
Viscosity (Cst)	35.39	437.68
(distillation) I.B.P. ^{o}C	80	116
(distillation) Residue %	40	70

Methods:

This study was achieved using two types of demulsifier the bottle-test method was used in both demulsifiers screening in order to find out the most effective demulsifiers.

Emulsion Preparation:

Water-in-oil emulsions were prepared by mixing crude oil and water to obtain 10% (v/v) water content. The emulsification was carried out using a homogenizer at a rate of 16000 rpm for (5-10) minutes to get a stable emulsion About 100 mL of emulsion sample was prepared.

Bottle-Test:

The test was carried out using series of tubes or bottles each containing the (100) ml of an emulsion to be broken in water Bath at a constant temperature (50 ^{o}C for Kirkuk /baba crude oil and 40 ^{o}C Khbbaz crude oil) demulsifier was injected into 100 mL of the emulsion system to obtain (0, 20, 40.60, 80, 100) ppm of each demulsifier in the emulsion,Then, the bottles were shaken for 2 min. to thoroughly mix the demulsifier and the emulsion. The bottles were then returned to the water Bath. Separation of phases was monitored by the position of the water/emulsion interface and recorded as a function of time to verify the volume of water separated in (5, 15, 30, 60) min. A bottle containing an emulsion without any additive was employed as a reference (blank). The volume of water separation from the emulsion system was observed. Water separation versus time and demulsifier concentration was plotted [18].

Results and Discussions:

Optimization of the Demulsifier Formulation

The results from experimental runs were used as a factor in optimizing formulations in order to produce the best results in breaking the water-in-oil emulsion system. The two types of demulsifier and the concentration were used as the variables in the experimental design.

Effect of pH Values:

According to the literature [19, 20] adjusting the pH of emulsions seems indeed to be effective in resolution of water-in- oil emulsions. Figure1 summarizes the results of pH adjustments on the ability of the demulsifier to separate water from water-in-oil emulsions under various pH values.

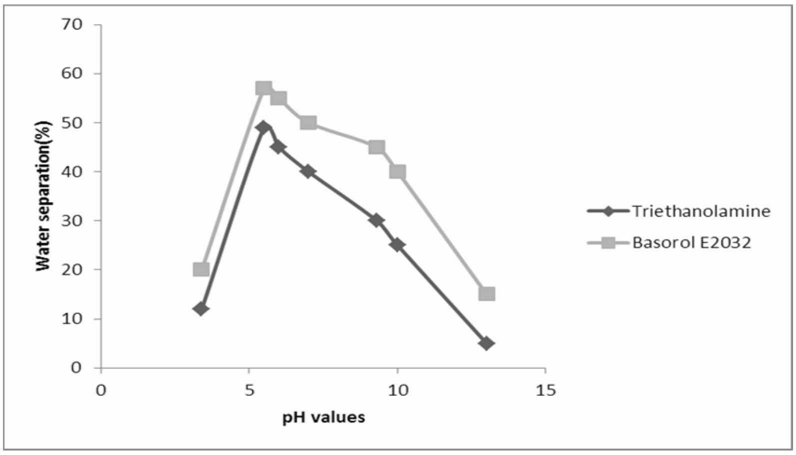

Fig. (1) Effects of water separation using various pH values. Experimental conditions: T = 70 °C, demulsifier concentration = 10^{-5} volume fraction

Table (4) shows the PH of demulsifiers RP-6000 and Maks 9150 (PH=6) (PH=5) respectively and PH of used formation water was (PH= 6.35),Therefore, we can conclude that, at very high and very low pH values, the emulsions seem to be stable, while intermediate pH values cause instability. The range and degree of emulsion stability are very dependent on the crude oil from which the emulsion was prepared. The optimal pH for treating crude oil emulsions seem vary from 5 to 9 [21]. A main reason for this is that a low permittivity medium causes the cancellation of electrostatic repulsion and of any importance of multivalent counter-ions as destabilizers. In addition the pH has a strong influence on the interfacial properties of asphaltenes at high or low pH. This is because, at these pH values, asphaltene functional groups become charged, leading to enhancing surface activity [11].

Effect of Temperature, Salinity and Density (water contents):

Despite of the temperature and salinity is very important in emulsion study where increasing the temperature increase the water separation dramatically and this destabilization effects attribute to increase Brownian motion and mass transfer across the interface, which is mainly due to the fact that the interfacial viscosity of the internal phase decreases as the temperature increases and according to Binks, O/W droplets increase in size upon increasing salt concentration, while W/O droplets decrease in size; hence, the presence of salt seems to have an adverse effect on emulsion stability [22] , demulsification process achieves with high efficiency for emulsions containing high water contents, salt contents were simultaneously involved. The emulsions are more stable at lower ionic strength of the aqueous phase [17]. but, in this study the temperature fixed on (50)^{o}C for Kirkuk / baba crude oil and on (40)^{o}C for Khbbaz crude oil because of the dehydrator and desalter in the field designed on these temperature and the salinity in emulsified formation water was 2% for Kirkuk / baba crude oil and 15% for Khbbaz crude oil. Figures (6, 7) show specific gravity for wet oil and formation water percentage in kirkuk/baba and khbbaz crude oil.

Demulsifiers Effect:

The emulsion destabilization, an essential step for the efficient separation of water from petroleum, can be carried out by the addition of chemical substances, named demulsifiers [23].These substances include block copolymers based on ethylene oxide and propylene oxide (PEO-b-PPO). In the present study, Rp600 and Maks 9150 demulsifiers were used to separate water from Kirkuk / baba, Khbbaz crude oil. The results are shown in Tables (5-8) and Figures (2-5).

Table (5) Water separation using RP6000 on Kirkuk/ baba Crude oil in different time and conc.

Conc. ppm	5min	15 min	30min	1hr
Blank	0	0	0	0
20	6.0	8.0	9.0	10.0
40	7.0	10.0	10.0	10.0
60	8.0	10.0	10.0	10.0
80	8.5	10.0	10.0	10.0
100	9.0	10.0	10.0	10.0

Table (6) Water separation using RP6000 on khbbaz Crude oil in different time and conc.

Conc. ppm	5min	15 min	30min	1hr
Blank	0	0	0	0
20	0.5	1.0	2.5	7.0
40	1.0	4.0	6.0	9.0
60	5.0	8.0	10.0	10.0
80	8.0	10.0	10.0	10.0
100	9.0	10.0	10.0	10.0

Table (7) Water separation using Maks9150 on Kirkuk/ baba Crude oil in different time and conc.

Conc. ppm	5min	15 min	30min	1hr
Blank	0	0	0	0
20	0.5	2.0	3.0	4.0
40	1.5	5.5	6.0	6.5
60	2.0	6.0	6.5	7.0
80	3.0	6.0	7.0	8.0
100	4.0	6.0	7.0	8.0

Table (8) Water separation using Maks9150 on khbbaz Crude oil in different time and conc.

Conc. ppm	5min	15 min	30min	1hr
Blank	0	0	0	0
20	0.7	1.3	1.5	2.0
40	3.0	4.0	5.5	6.0
60	5.0	5.5	6.0	8.0
80	5.5	6.0	7.0	8.0
100	5.5	6.0	7.0	8.0

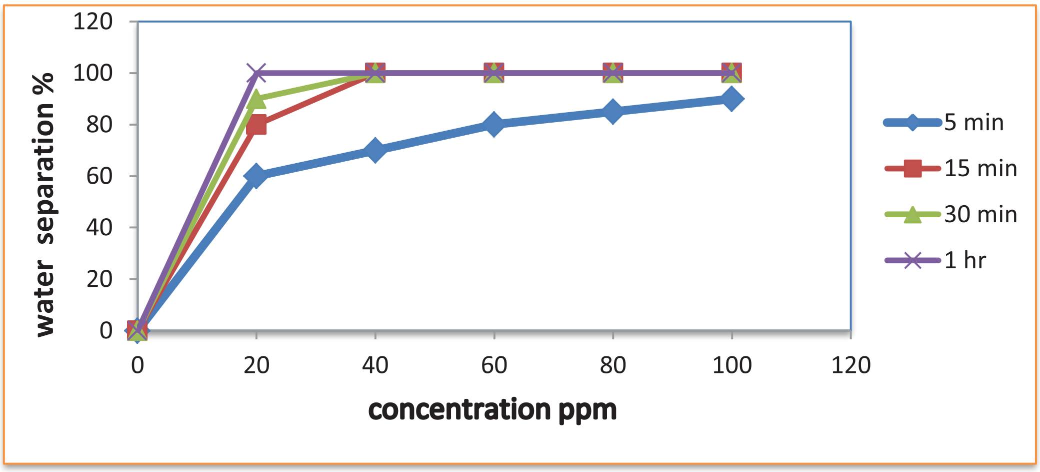

Fig. (2) Water separation using RP6000 on Kirkuk/ baba Crude oil in different time and concentration

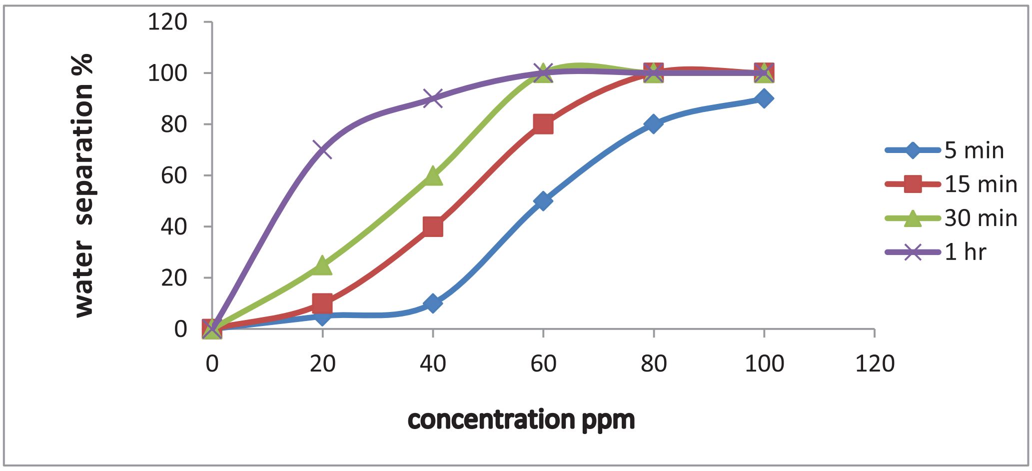

Fig. (3) Water separation using RP6000 on khbbaz Crude oil in different time and concentration

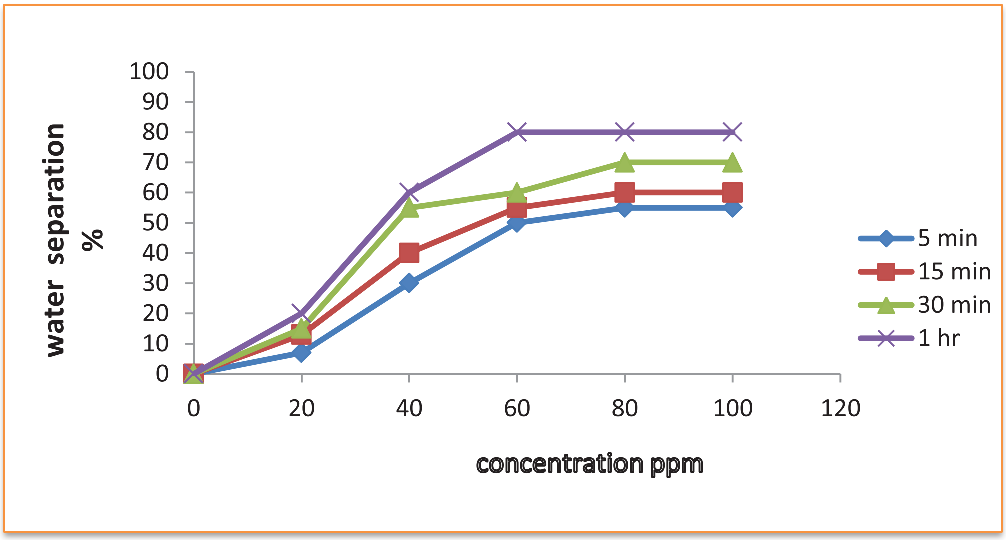

Fig. (4) Water separation using Maks9150 on Kirkuk/ baba Crude oil in different time and concentration

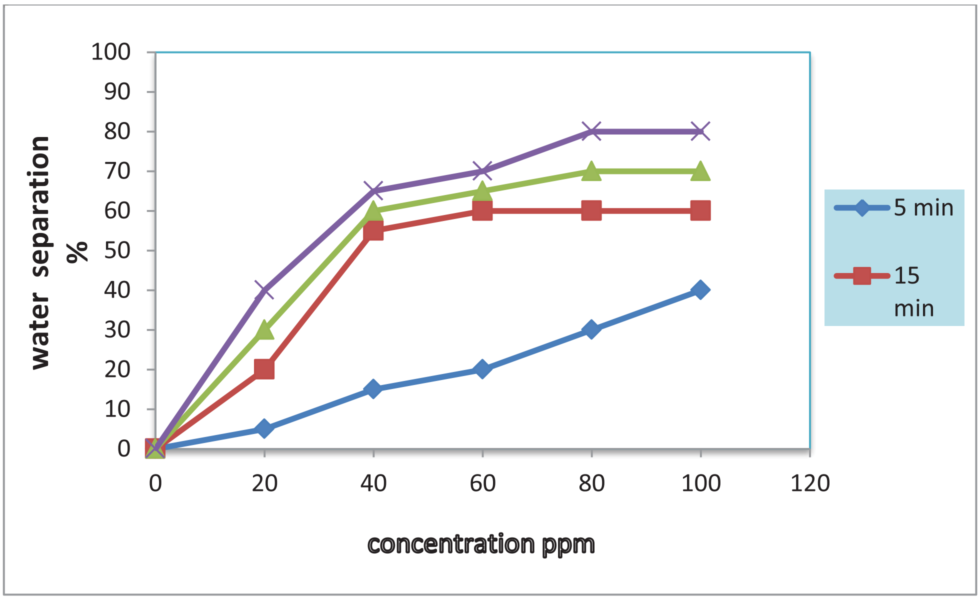

Fig. (5) Water separation using Maks9150 on khbbaz Crude oil in different time and concentration

It was found that the effective demulsifier for water separation is RP6000 for separation (100%) in (15)min., (40) ppm and in (60) min., (20) ppm of demulsifier for Kirkuk/ baba Crude oil and for khbbaz Crude oil the (100%) water separation was in (15) min., (80) ppm and in (30) min., (60) ppm, but Maks9150 didn't reach (100%) separation even in one hour and (100) ppm of demulsifier.

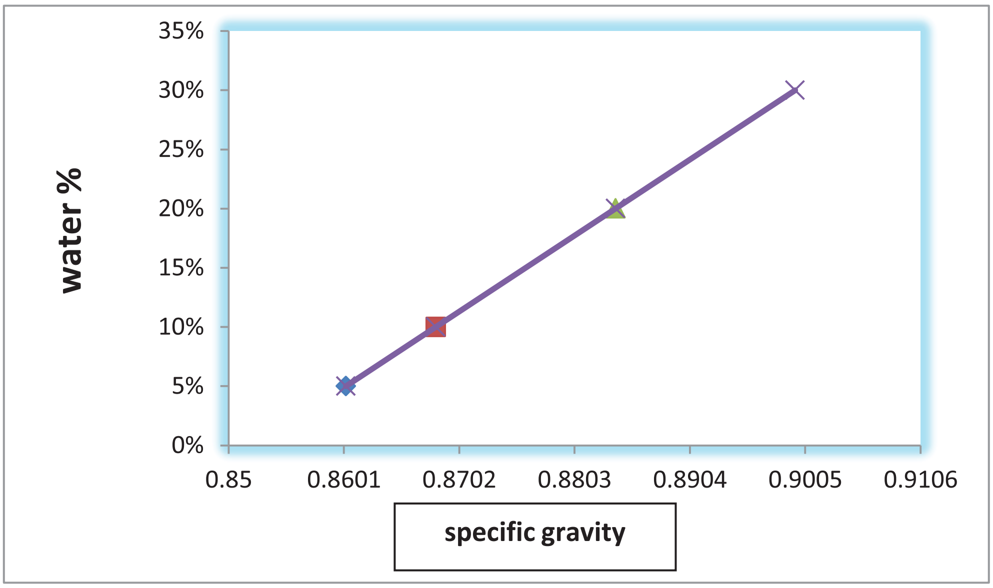

Fig. (6) Specific gravity for kirkuk/baba wet oil and formation water percentage at salinity (2%)

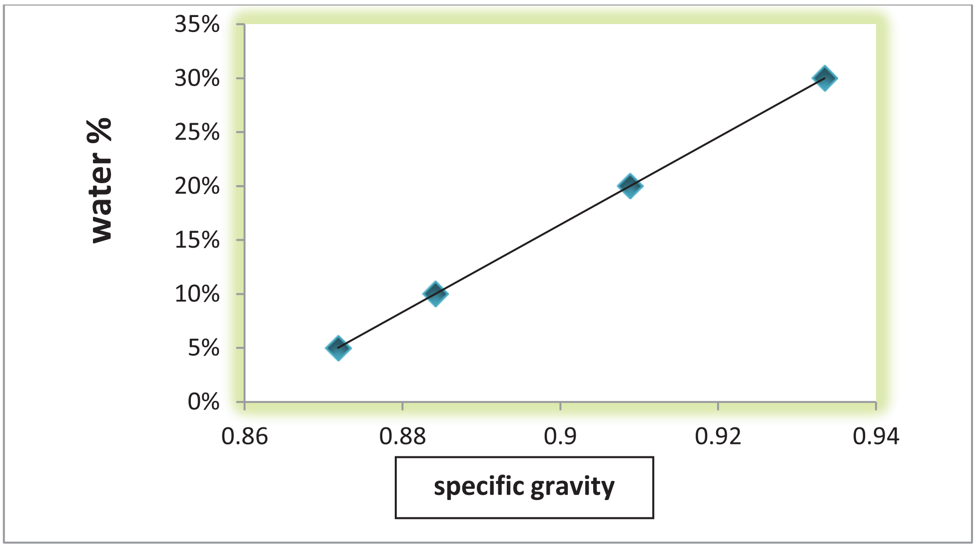

Fig. (7) Specific gravity for khbbaz wet oil and formation water percentage at salinity (15%)

Mechanism of demulsifier action:

Chemically emulsion breaking is very complex there are several hypotheses and theories regarding the physicochemical mechanism for the action of chemical demulsifier [24]; however, there are a few general rules for chemical demulsifiers and their ability in breaking emulsions [25].The demulsifiers displace the natural stabilizers present in the interfacial film around the water droplets this displacement is brought about by the adsorption of the demulsifier at the interface and influences the coalescence of water droplets through enhanced film drainage [26]. Table (4) shows the specific gravity of demulsifier Maks 9159 (1.0296) is heavier than RP6000 (0.9195) and from crude oil too, so it get down faster and it hasn't enough time to diffuse inside oil phase to reach every water droplets and viscosity of Maks 9156 is (437.68 Cst) and its residue (70 %) while viscosity of RP6000 is (35.39 Cst) and the residue (40%) for that Maks 9156 demulsifier cannot displace the natural stabilizers (asphaitenes) film that adsorbed on water droplets easily because the interfacial viscosity among water droplets is very high, there is competition for adsorption when surface active species are present [26] Figure (8) shows the film drainage process schematically.

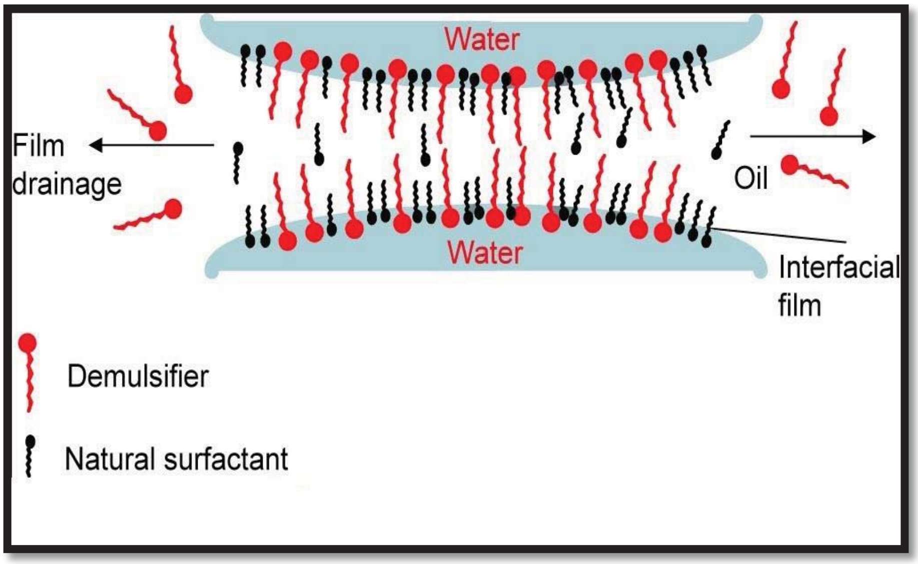

Fig. (8) The film drainage process schematically

An increase in emulsion breaking rate is generally with increasing demulsifier concentration up to critical aggregation concentration for monolayer adsorption of demulsifier at the interface. But injecting the demulsifier higher than critical concentration (over dosage) to separate all water from crude oil in short time make two different types of behavior: [27]

1- Leveling of the emulsion breaking rate with increased demulsifier concetration, this type of behavior is attributed to the formation of a liquid crystalline phase.

2- Reduction in emulsion breaking rate with increased demulsifier concentration this type of behavior is attributed to steric stabilization of grown water droplets and detrimental to emulsion breaking because it retards the separation rate during overdosing.

Identification of demulsifiers:

The active material after distillation of demulsifiers have been identified by FTIR spectrometer RP6000 showed peaks at ($3033_{str.}$ cm^{-1})for aromatic(C-H) ($2919_{str.}$ cm^{-1}) for aliphatic (C-H) and strong Broad peak at ($3428_{str.}$ cm^{-1}) this peak is attributed to hydrogen bond for (O-H) group (hydrophilic groups) and showed ($1606_{str.}$ cm^{-1}) peak for aromatic (C=C) as it's proved by flame test [28] Figure (9) shows FTIR chart for RP6000 demulsifier .

While MAKS-9150 demulsifier showed ($2970_{str.}$ cm^{-1}) and ($2980_{str.}$ cm^{-1}) peaks for aliphatic (C-H) and ($1108_{str.}$ cm^{-1}) for ethers and without strong hydrophilic groups like (O-H) to compete natural surfactants. Figure (10) shows FTIR chart for MAKS-9150 demulsifier, to displace natural surfactant by demulsifier need 4000 calorie. getting by hydrophilic groups for each hydrogen bond [24].

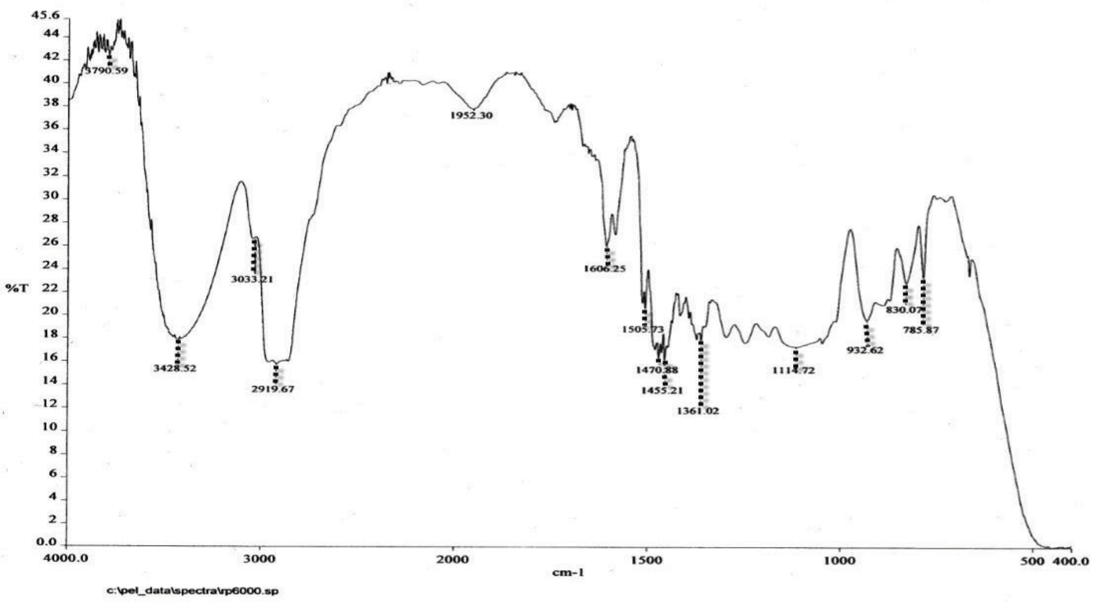

Fig. (9) FTIR chart for RP6000 demulsifier.

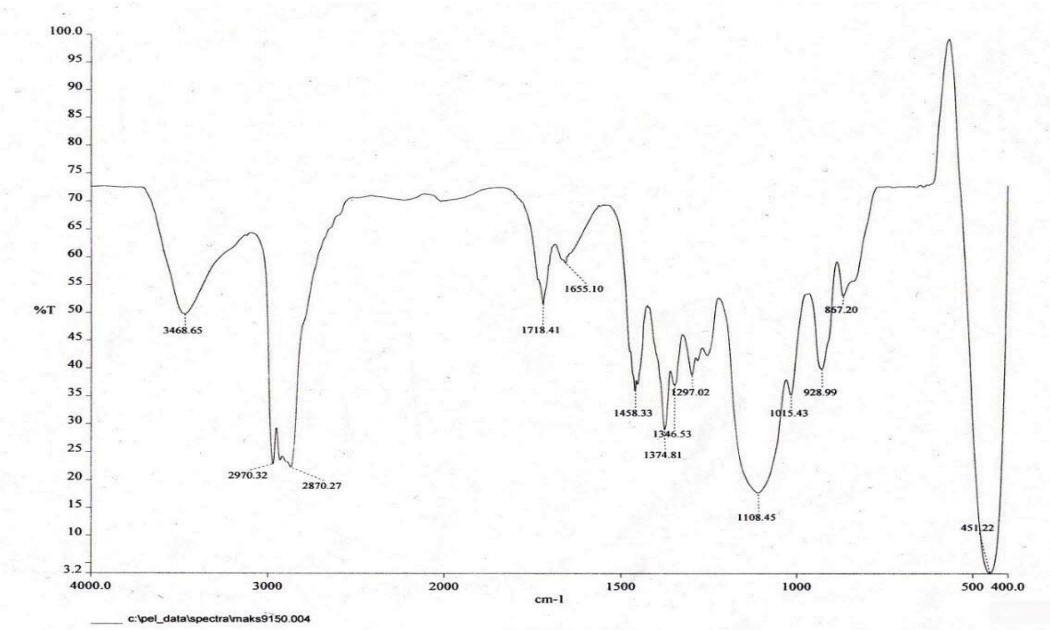

Fig. (10) FTIR chart for MAKS-9150 demulsifier

Conclusions:

The activity of RP6000 demulsifier best than MAKS-9150, demulsifier RP6000 separated water (100%) in (15) min., (40) ppm and in (60) min., (20) ppm of demulsifier for Kirkuk/ baba Crude oil and for khbbaz Crude oil the (100%) water separation was in (15)min., (80) ppm and in (30) min., (60) ppm, but Maks9150 didn't reach (100%) separation even in one hour and (100) ppm of demulsifier.

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