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INFLUENCE OF WATER IONS AND ALUMINUM SILICATE PARTICLES ON EMULSION RESOLUTION OF CRUDE OIL

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Abstract

The price of exporting oil is defined by its qualitative properties. These properties are in a direct relation to emulsion stability of desalter feed. The present study was undertaken to experimentally investigate the effects of water ions, and solid particles on emulsions stability. These studies have also confirmed the effects of several process variables such as temperature and contact time between two phases. The selected waters used in this work were distillated water and Persian Gulf water and the fine aluminum silicate solids used include bentonite and kaolinite particles. The emulsion was prepared using 10 ml Maroon crude oil / Iran with 10 ml of each kinds of water, where the bentonite and kaolinite particles were added to the mixture. The results showed that at 30°C and after two days contact time between oil and distillated water, the emulsion became stable and its volume was nearly constant, although no emulsion was observed at 70°C. The use of Persian Gulf water instead of distillated water leaded to unstable emulsion. In addition, using colloidal clay to the mixture resulted in emulsions formation and its stability.

Keywords: Emulsion resolution; Water quality; bentonite; kaolinite; Persian Gulf water; surface tension.

1. Introduction

An emulsion is defined as two immiscible liquids wherein droplets of one phase (the dispersed or internal phase) are encapsulated within sheets of another phase (the continuous or external phase). There are two basic forms of emulsion. The oil-in-water (o/w) emulsion in which oil droplets are dispersed and encapsulated within the water and the water-in-oil (w/o) emulsion in which droplets of water are dispersed and encapsulated within the oil. The stability of water-in-oil emulsion is defined as the resistance by the dispersed water droplets against coalescence. Stable w/o emulsions may form during crude oil production and transportation, as co-produced water is mixed with the oil from reservoir to separation facilities [1]. The slow rate at which liquids may be naturally separated in many water-in-oil type dispersions has important consequences in many commercial operations. Stable water-in-crude oil emulsions are typically undesirable and can result in high pumping costs, reduced throughput and special handling equipment [2]. The understanding of the mechanisms and factors contributing to the stability of such emulsions is of both great economic and environmental importance [3-8]. For either type of stable emulsion to form, three basic conditions must be met [9-11]:

- The two liquids must be immiscible or mutually insoluble in each other;
- Sufficient agitation must be applied to disperse one liquid into the other; and
- An emulsifying agent or a combination of emulsifiers must be present.

Oil-in-water emulsions are stabilized by two main types of molecular emulsifying agents: small-molecule surfactants and water-soluble polymers. Emulsion structure, stability and rheology depends on the composition, thickness and visco-elasticity of the adsorbed stabilizing layer at the oil-water interface, as well as the strength and nature of the interactions between adsorbed layers on different droplets [12]. In water-in-oil emulsions, asphaltene, resins and paraffin waxes act as natural emulsifying agents stabilizing w/o mixture. Presumably, these agents provide the required film around the water droplets which resists rupture, thus preventing water-water coalescence [13,14]. There have been many studies on the parameters that affect stability and demulsification of crude oil emulsions. Sams and Zaouk showed that one of the important parameter is the process

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of production and recovering crude oil from beneath of the earth. They also showed that heating and cooling cycles may also promote a variety of undesirable effects, including oil dehydration accompanied by salt crystallization, wax or asphaltene precipitation accompanied by emulsion stabilization, bacteria formation accompanied by corrosion, and loss of light ends accompanied by increasing oil-specific gravity and viscosity [15]. Chen and Tao showed that temperature often has indirect effects on emulsification as a result of altering the interfacial tension, adsorption of emulsifier and viscosity. They investigate the effects of emulsifier dosage, ratio of oil to water, stirring intensity, emulsifying temperature and mixing time. The results showed that the optimum process conditions are: emulsifier dosage 0.5%; oil to water ratio 1:1; stirring intensity 2500 rpm; and mixing temperature 30°C [16]. Another parameter that affects stability of emulsion and quality of crude oil is type and amount of chemical demulsifiers that injected to crude oil [17]. Kang *et al.* showed that demulsifier molecules are adsorbed gradually on oil-water interfacial film and replace the emulsifiers. That replacement decrease both the strength and the life of oil film and film thickness until it collapse. The interfacial tension decreases with increasing of demulsifier concentration. When the demulsifier concentration reached a certain level, interfacial tension is changed drastically [18]. Strassner showed that the interfacial tension of some heavy crude oils depends on the pH of the contained produced water. Emulsions with pH<6 are highly stable, while those at pH>10 exhibited low stability or were highly unstable [19]. Yan *et al.* studied the stability of water-in-oil emulsions stabilized by fine solids with different hydrophobicities. The stability of the produced emulsions depended on the hydrophobicity of the particles. Only particles with intermediate hydrophobicity could produce very stable water-in-oil emulsions, and the hydrophilic particles leads to the stability of oil-in-water emulsion. Experimental results showed that hydrophilic colloidal silica could only stabilize oil-in-water emulsions for a short period of time [20]. Solids-stabilized emulsions are often encountered during the extraction of Bitumen from oil sands, crude oil de-watering, separation of fines from shale oil, and separation of oil from wastewater. The knowledge that fine solids can stabilize emulsions dates back to the beginning of the century when Pickering originally noted that colloid particles that were wetted more by water than by oil could act as an emulsifying agent for oil-in-water emulsions [21]. Tadros and Vincent have found that the fine particles adsorbed at the droplet surface act as a barrier preventing droplets form coalescing. They also pointed out that emulsion stability is dependent on the structure of the surfactant [22,23]. Different investigations showed that the surface tension of emulsion decreases with pH and oil contents. Also, the addition of surfactant resulted in the decrease of surface tension [24-26].

In the present work, the effects of water ions (quality), as well as the solid particles such as bentonite and kaolinite on the formation and stability of water-in-oil emulsions were studied. The formation of an emulsion is thermodynamically unfavorable because of the increase in surface area between the oil and water phases. In order to investigate these effects, the experiments were performed using Maroon crude oil of Iran as the oil phase. Distillated water and Persian Gulf water were selected as aqueous phase.

2. Experimental

The Maroon crude oil (before desalting process) was chosen. This crude oil was originated from oilfields in the Khuzestan province/Iran. The oil samples were degassed and dewatered before use. The general properties of Maroon oil were presented in Table 1.

Table 1. Physico-chemical properties of crude oil used

Crude oil	Maroon oil (without gas)	Standard
Density (60°F/60°F), °API	30.39	
Molecular weight	227.85	
Asphaltene, wt%	2.4	*IP-143*
Asphaltene, wt%	2.3	*ASTM: D 2007-80*
Light cut to C_{18}, wt%	36.13	
Viscosity (24.7°C), cP	16.32	

Experiments were carried out with two different water types, in order to investigate the effects of ions: Distillated water and Persian Gulf water. The general properties of Persian Gulf water are presented in Table 2.

Table 2. Persian Gulf water properties (pH=7.2)

Iones	Concentration (mg/l)
HCO_3^-	292.8
Ca^{2+}	499.5
Mg^{2+}	1452.5
Ba^{2+}	0.98
SO_4^{2-}	2100

The experiments were performed in two parts. In the first part, in order to evaluate the effect of water quality on the properties of the selected emulsions, the emulions were prepared as follows: the oil phase containing 10 ml of Maroon crude oil was introduced to the aqueous phase containing 10 ml of each types of water separately (Distillated water or Persian Gulf water). The emulsion samples were then injected into the cells and stirred totally for 2 min. The prepared emulsions were heated in the oven under desired temperature of 30°C or 70°C for a specific retention time. The volumes of the separated oil and water phases as well as the formed emulsion were measured at regular time interval. It should be noted that each sample was prepared twice and the mean values was reported. The second part of experiment was carried out to understand the role of aluminum silicate based particles on the emulsions properties. In this step, 0.5 gr of bentonite or kaolinite particles were added to the cells which prepared in part 1. The samples were placed in the oven and heated. Then, the samples were taken out of oven at different retention time. The mixture separated into three distinct layers, with the oil on the top, the separated water at the bottom, and a thin layer of emulsions in the middle. The volume percentage of each phase (emulsion, oil, water) was reported as a function of time for 1, 2, 4, 24, 48, 168, and 192 hours consequently.

The surface tension measurements were also performed by the Wilhelmy Plate technique. This method utilizes the interaction of a platinum plate with the surface being tested.

3. Results and discussion

3.1. Effect of water ions

To investigate the effect of temperature on the emulsion stability, the relative emulsion volume was determined at temperatures 30°C and 70°C. The results of relative emulsion volume versus time were shown in Fig. 1. Its shows the formed emulsion at 30°C become stable after one week resting, but the emulsion was disappeared at relatively high temperature of 70°C. Obviously, the emulsion was more stable at lower temperature, and the most stable emulsion was generated at 30°C, confirmed by Chen and Tao [16]. Temperature often has indirect effects on emulsification as a result of altering the interfacial tension, adsorption of emulsifier and viscosity. There is also some evidence that a sharp increase or decrease of temperature tends to coagulate the particles, thereby causing the deterioration of emulsions. The time is another important factor for emulsification. As a result of water and oil combination, the probability of formation of Distillated water-oil emulsion is existed at 30°C. The amount of formed emulsion increased as time increased from 4 to 168 hr. After 48 hr, the volume of formed emulsion was 1.0 ml, then with increasing time until 168 hr it asymptote to 2.0 ml, and after that remained unchanged.

The Persian Gulf water leads in un-stability of emulsions in comparison of distillated water as shown in Fig. 2. No emulsions were formed in the case of Persian Gulf water. This is due to the presence of ions in brine (sea) water. These ions play major roles in the deformation and break up of droplets, and this may be summarized as follows: these ions allow the existence of interfacial tension gradients which are crucial for the formation of stable emulsion. In the absence of surfactants (clean interface), the interface cannot withstand any tangential stress and the liquid motion will be continuous. The value of interfacial tension depends on the nature of the oil and ions/surfactant used; typically, ions such as Ca^{2+}, Mg^{2+}, and Ba^{2+} reduce interfacial tension to a great degree. More lower the interfacial tension, which in turn causes a reduction in droplet size and its coalescence. It is suggested that the film rupture, occurring during the hetero-coalescence of a water and a brine droplet, is closely associated with these water (and hydrated ion) transfer processes.

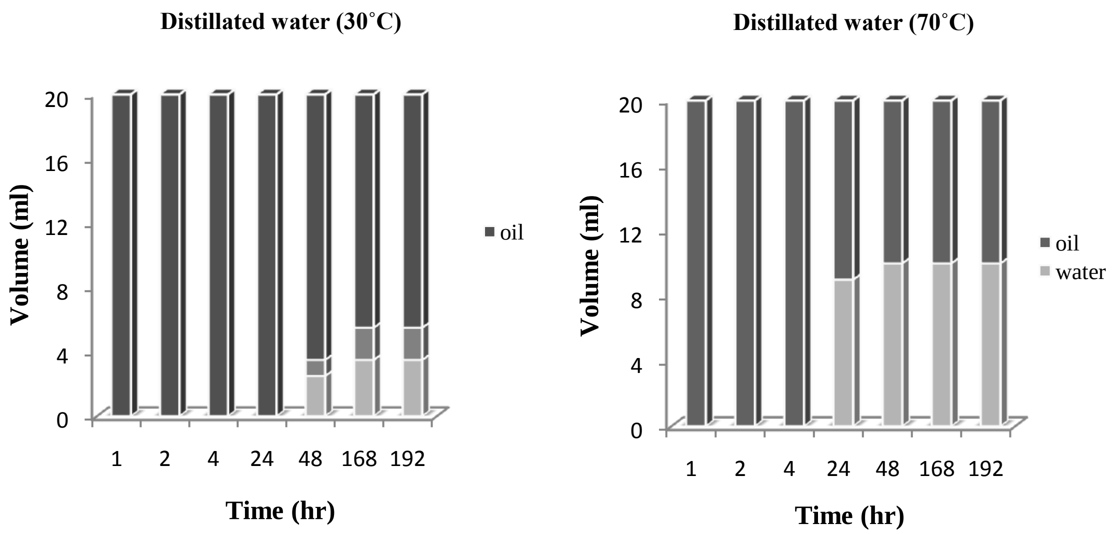

Figure 1. Effect of temperature on emulsion stability with distillated water

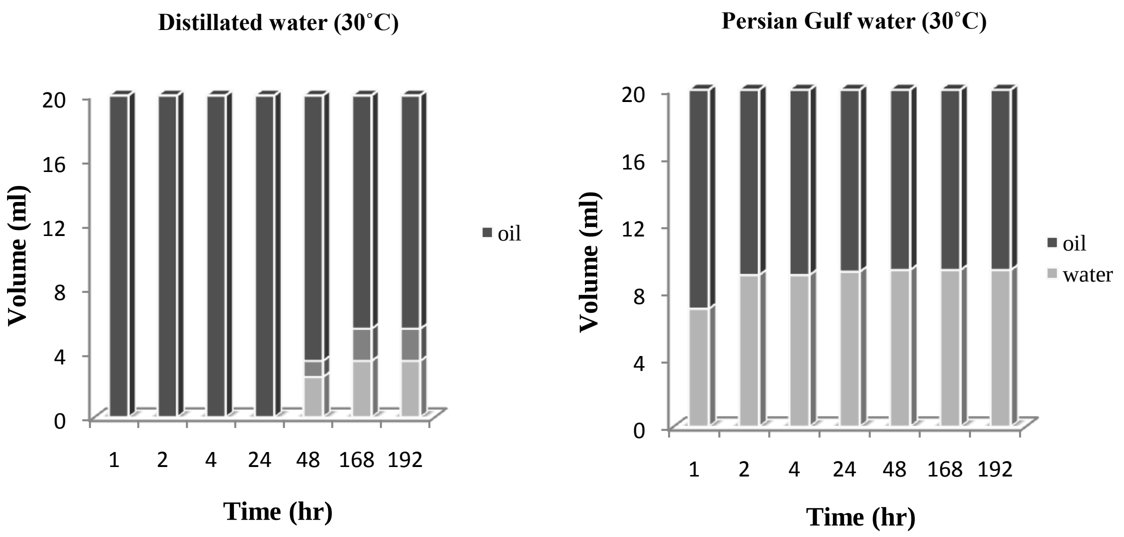

Figure 2. Effect of water quality (ionic strength) on emulsion stability

3.2. Effect of solid particles

Fig. 3 shows the mixture of Maroon oil and distillated water, where the bentonite particles were added to the mixture. After 4 hr retention time at 30°C, about 5 ml emulsion was formed and then it became stable (11 ml) after 168 hr. The emulsions were broken down at 70°C. For solids-stabilized emulsions, the solids should be initially in the continuous phase prior to emulsification. The inability to prepare water-in-oil emulsion indicates that the particles cannot transfer from aqueous phase across the oil-water interface to the oil phase even though they are hydrophobic. Particles adsorbed at the oil-water interface stabilize water-in-oil emulsions by providing a barrier preventing the droplets from coalescing. The stability of an emulsion depends, to some extent, on the partitioning and positioning of the particles at the oil-water interface, which are in turn related to the hydrophobicity of the particles. If particles are very hydrophilic, a large fraction of a particle's volume resides in the water phase. In this case, the particles cannot provide sufficient barrier to prevent water droplets from coalescing, and the emulsions became unstable. On the other hand, if the particles are very hydrophobic, a large number of the particles will stay in the oil phase, resulting in less protection for water droplet from coalescing [20].

Fig. 4 shows the effect of bentonite particles on the stability of Maroon oil-Persian Gulf water mixture. Bentonite has a positive role in emulsion stability, whereas the water ions have the negative role. This result demonstrates the important role of the electrostatic repulsive force in the thermal stability of o/w emulsions. This emulsion became unstable at 70˚C.

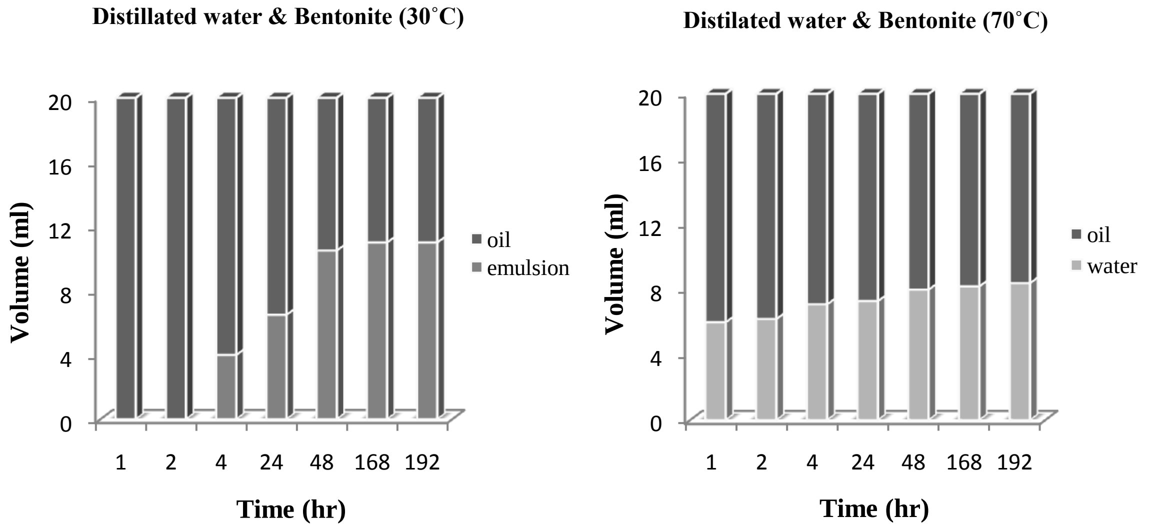

Figure 3. Effect of bentonite on emulsion stability with distillated water

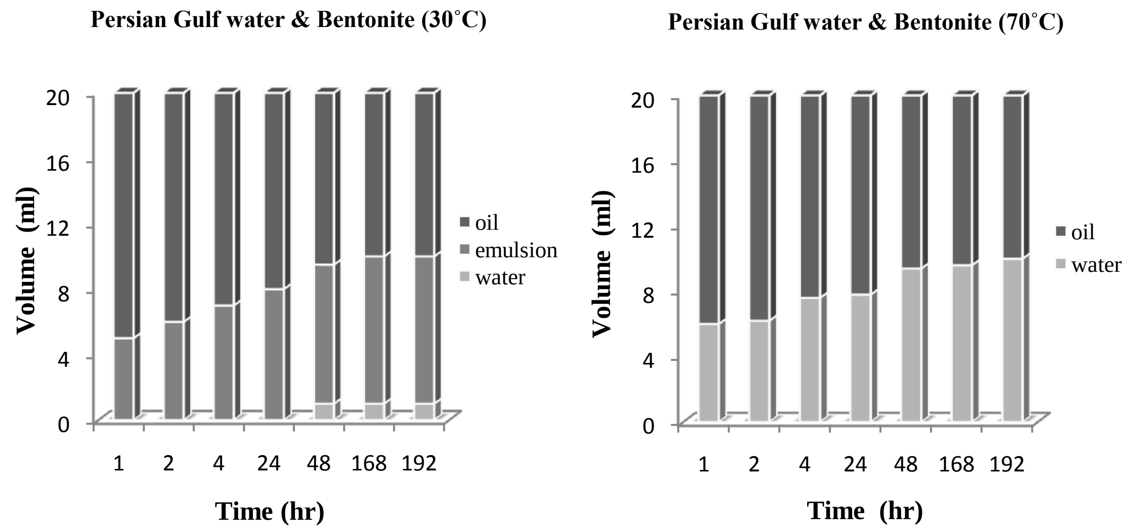

Figure 4. Effect of bentonite on emulsion stability with Persian Gulf water

Fig. 5 shows the effect of kaolinite particles on the stability of Maroon oil-Persian Gulf water mixture. The Kaolinite has nearly the same influence of bentonite, but any water layer was formed at 30˚C. The volume of formed water layer using this colloidal clay at 70˚C was less than that bentonite.

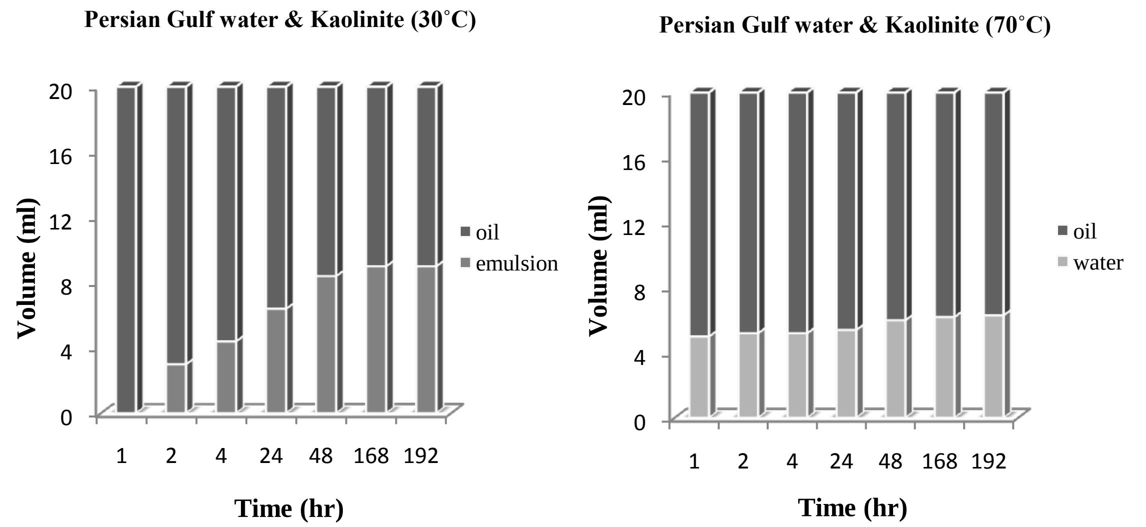

Figure 5. Effect of kaolinite on emulsion stability with Persian Gulf water

Table 3 summarized the experimental conditions and the volume of stable formed emulsion after 192 hr resting time. The maximum emulsion volume (11 ml) was formed in the case of Distillated water/Bentonite- in-oil emulsion and Persian Gulf water/kaolinite-in-oil emulsion.

Table 3. Volume of stable formed emulsion after 192 hr at different experimental conditions

Crude oil	Water	Solid particle	Temperature (°C)	Volume of emulsion (ml)
Maroon	Distillated water	-	30	2
Maroon	Distillated water	-	70	0
Maroon	Distillated water	Bentonite	30	11
Maroon	Distillated water	Bentonite	70	0
Maroon	Persian Gulf water	-	30	0
Maroon	Persian Gulf water	Bentonite	30	9
Maroon	Persian Gulf water	Bentonite	70	0
Maroon	Persian Gulf water	Kaolinite	30	11
Maroon	Persian Gulf water	Kaolinite	70	0

3.3. Effect of surface tension

An emulsion's stability can be measured in terms of Interfacial tension. Lower interfacial tension leads to the formation of more, smaller emulsified droplets, which are harder to coalesce. As oil contents of emulsion increase, it can be seen that surface tension of emulsion becomes lowered [24,27]. Reducing the surface tension of oil and water, droplets tend to join together to be less and water and oil droplets are spread most together thus the emulsion remains stable. Fig. 6 shows the surface tension of individual water and oil phases before and after emulsification.

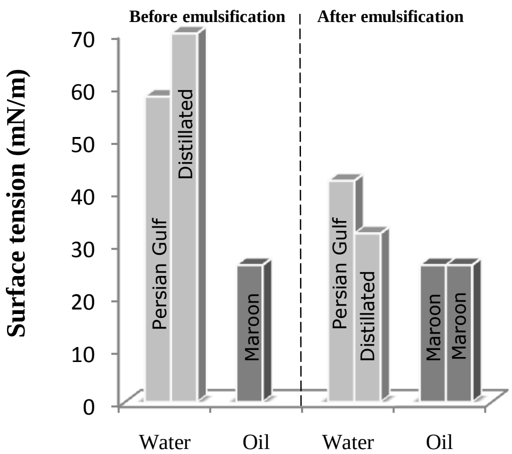

Figure 6. Surface tension of individual w/o phases before and after emulsification

4. Conclusions

The formation and stabilization of water-in oil (w/o) emulsions are investigated. This study demonstrated the effects of water quality (ionic strength) and the role of solid particles at different time and temperatures on w/o emulsions. The experiments presented here indicate that in mixed emulsions of water-in-oil and Gulf water-in-oil, heterocoalescence occurs reasonably rapidly. However, it also seems probable that prior to actual coalescence of a brine droplet and a water droplet, some transfer of water from the latter to the former (and possibly even of hydrated ions in the other direction) could well occur. It may well be that these diffusion processes, across the thinning oil film between the two aqueous phase droplets, form the basis of the film rupture mechanism. The stability and type of emulsions stabilized by solids particles depend on the hydrophobicity of the particles and the phase they reside in prior to emulsification. We have pointed out that the Bentonite and Kaolinite particles leaded to emulsions formation. An effective way to remove water and solids from w/o emulsions stabilized by solids was to make the solids more hydrophilic so that water and solids could be removed at the same time, resulting in clean oil. Although emulsions could also be demulsified by making the solids more hydrophobic, however, some of the resulting hydrophobic solids would remain in the oil, leading to difficulties in obtaining clean oil.

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