

## ENHANCEMENT OF SEPARATION EMULSIFIABLE OIL FROM OIL/WATER EMULSION FROM WASTE WATER BY THE SURFACTANT AND BARITE

Noura El Mehbad

Najran University, Chemistry Department, Najran, Saudi Arabia

Received April 16, 2018; Accepted June 27, 2018

---

### Abstract

The oil separation behavior of emulsifiable oil was studied using barium salt of heavy alkyl benzene sulphonate as the frother and calcium salt of heavy alkyl benzene sulphonate as de-emulsifier. In this research, the application of separation column technique was studied. A synthetic oil emulsion was prepared with different percentage of oil. The stability rate constant was determined under different conditions. The study showed that the critical concentration of the surfactant affects oil recovery depend on its critical micelle concentration CMC. The adsorption of the surfactant from the solution was investigated by measuring surface properties of the frother. The results were discussed in term of the adsorption isotherm and surface properties of the surfactant at the solution/oil/solid interfaces. The experimental data were analyzed as a first-order kinetic rate. The maximum oil removal obtained from the stable emulsion was 90% by weight. It can be enhanced by the addition 0.1% of barite.

Also, this paper deals with the influence of various thermodynamic parameters on the adsorption surfactant on the solid barite particles and will be discussed this synergism between the surfactant and the barite particles according to its adsorption isotherms at solid / oil interface and surface properties of the collector. It can be concluded that the column technique seems to be important separation methods and need to be modified using electro separation in the next research.

**Keywords:** Oil emulsion; frother; wastewater; barite.

---

## 1. Introduction

Microemulsion is formed when water is dispersed in a hydrocarbon-based continuous phase and is normally located towards the oil apex of an oil/surfactant. In this region, thermodynamically driven surfactant self-assembly generates aggregates known as reverse or inverted micelles, which minimize surface energy, are the most common form. Added amphoteric surfactants will become compartmentalized into the central cores of these reversed micelles. The oil-water emulsions are found in the petroleum industry, such as producing, and refining. The microemulsion is harmful to the environment. It is very important to develop different methods for destruction of oil emulsion for oil removal. Flotation technique which is used for recovering oil from clay and wastewater by Omar *et al.* [1]. The separation methods are developed, such as electroflotation and dissolved gas flotation [2-6]. The study of separation required preparation of the stable synthetic emulsion. Micelles in these systems can be described as "nanoreactors," providing a suitable environment for controlled nucleation and growth. Also, at the latter stages of growth, steric stabilization provided by the surfactant layer prevents the nanoparticles from aggregating. Some amphoteric surfactants such as N-octyl-N-benzyl-N-methyl glycine is used as oil separation. The physicochemical chemical characteristics were investigated. The adsorption behavior of these surfactants at oil/air interface was investigated by measuring the surface tension and interfacial tension as a function of concentration. Surface properties, in particular, the critical micelle concentration (CMC), the maximum surface excess ( $\Gamma_{CMC}$ ) and the minimum surface area ( $A_{min}$ ) were measured. It is found the surface, and thermodynamic properties of the prepared surfactants depend on its chemical structure.

Also, it is found that there is a good relationship between the surface properties of the surfactant and their efficiency in depressing oil recovery. The separation of waste oil from clay was studied using benzyl triethanol ammonium chloride as a phase transfer catalyst. The study showed that the surface tension affects oil recovery. The effects of various parameters including the concentration of catalyst, collector, and contact angle, and zeta potential for oil extraction were studied. The results depicted that, oil recovery increased with time of separation to a maximum and then levels off. The mechanism of oil separation was discussed according to micelle composition and the calculated oil recovery obtained was 87% [6].

This research aims to prepare stable oil emulsion at the optimum condition and studying the barium salt of heavy alkyl benzene sulphonate as anionic oil frother and its mixture with non ionic nonyl phenol ethoxylate at different mole fractions. Furthermore, at optimum conditions, addition different percentage of clay to best collector dose. Also, this paper suggests the relationship between the efficiency of adsorption at oil phase and solid phase. The used oil was pretreated with local clay by the Elmebad [7].

## 2. Experimental

Triton x -100 is the nonylphenol ethoxylate with a mean of 10 ethoxy units per nonyl phenol was used and supplied from Aldrich. The barium and calcium salts of heavy alkyl benzene sulphonate as anionic oil collector and de-emulsifier were prepared and confirmed their structures.

The surface tensions for various concentrations of the frother was measured using a Kruss type 8451 Duy Noy tensiometer at different temperatures with an accuracy of 0.2 mN/L [8].

Table 1 lists the physical properties of the oil uses in forming an emulsion. The oil content of each sample was determined gravimetrically to an accuracy of  $\pm 10$ mg /L [9]. Separation experiments were conducted using a column. The samples were conditioned with de-emulsifier for 10 minutes before separation. At optimum conditions, the recovered oil was collected, and its weight determined [9].

Emulsions were prepared from base oil and water, the emulsifier (Triton x 100) was used with a concentration of 50  $\mu$ mol/L according to its CMC. The physicochemical properties of the base oil are listed in table 1. The oil content of the sample was determined gravimetrically to an accuracy of  $\pm 10$  mg/L [9].

Table1. Physical properties of emulsified oil

Properties	Base oil	Test ASTM
Density ( g/mL) at 15.5°C	0.8951	D 1298
Refractive index $n_{D20}$	1.4954	D 1218
Kinematic viscosity cSt		
at 40°C	16.56	D 445
at 100°C	27.15	
Pour point, °C	14	D 97
Carbon residue content, wt%	1.5	D524
Ash content, wt%	0.0511	D482

In the separation process using the separation column. The emulsion poured in the column, different concentration of demulsifier was added and stirred at 1200 rpm with the pulp pH was adjusted only by adding, HCl. Then frother and barite added for 5- 20 min nitrogen was introduced.

## 3. Results and discussions

In the formation of emulsions, oil is broken up into particles that are dispersed into water. This emulsion is highly unstable according to the thermodynamic parameters. So addition Triton x-100 ethoxylate is to stabilize the emulsion for a definite time.

Figure 1, shows the change in oil concentration with time by adding this emulsifying agent. This compound adsorbs at the interface between oil/w interfaces. As the results, the interfacial

tension between the two phases decreases. Furthermore, agent forming a barrier film around oil droplets. As the results, the dispersed particles do not coalesce forming microemulsions. Flocculation or coagulation depends on interfacial tension and temperature. At low temperature, ethoxylate forming its micelle (CMC), then oil particles can be solubilized inside the micelles and forming o/w emulsions. As the temperature is increased, the solubilization of oil increases until 50 C°. Furthermore, as the temperature increases, the structure of the micelle change to a sandwich like by increasing temperature and the phase inverse and the micelle change from hydrophilic to oleophilic micelles (Figure 2).

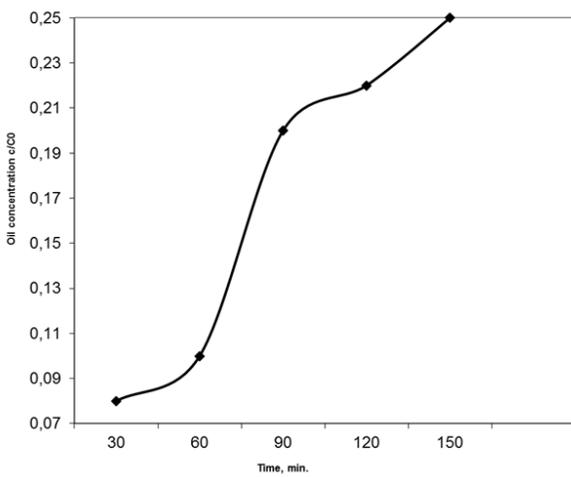


Figure 1. Effect different times on the oil concentration in oil/water emulsion, c/Co

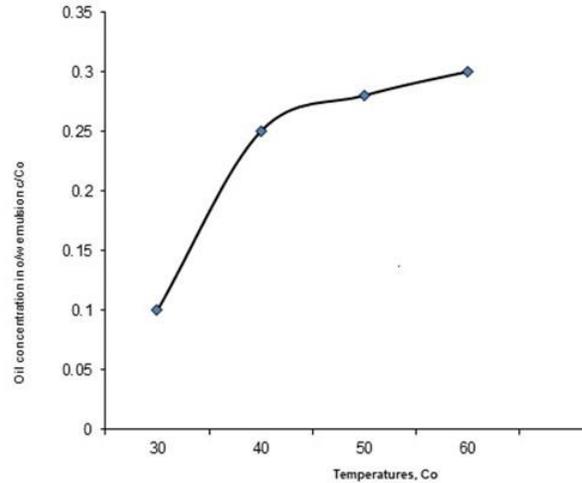


Figure 2. Effect different temperatures on oil content c/Co in o/w emulsion

At optimum conditions of formation emulsion o/w, the stable emulsion are conditioned with different concentration of demulsifier (calcium heavy alkylate sulphonate) for 10 min. and stirring rate 1200rpm. The results obtained are cleared in Figure 3.

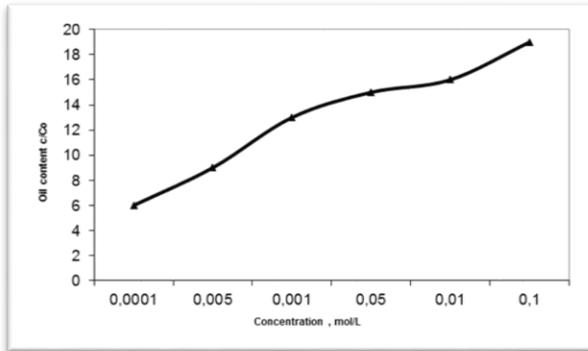


Figure 3. Effect of different concentration of the demulsifier calcium heavy alkylate sulphonate on oil separation

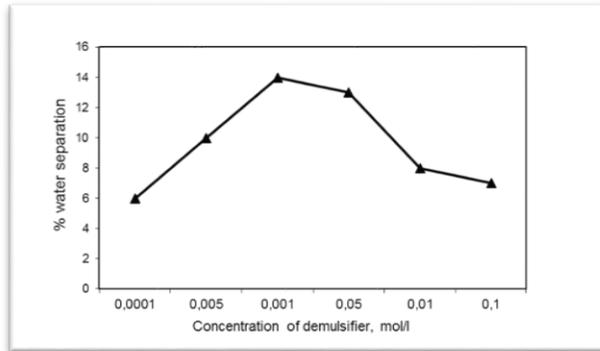


Figure 4. Effect different concentrations of the demulsifier in the presence of barite on oil content c/Co

The percentage of oil separation versus the concentration of demulsifier is depicted in the above figure. The oil separation was improved as the concentration of the demulsifier increased to 0.005 mol/L. These results can be discussed according to the role of the additive. The demulsifier is hydrophobic in nature, lead to the emulsion invert direction of its adsorption. As results, oil particles coagulate. The trapped water is surrounding by an interfacial film of demulsifier. As the results an increase in the interfacial tension between two phases, due to the rupture of a thin film formed between adjacent droplets. At the same time, the demulsifier counter acts as the emulsifier and promotes the formation of the aggregates oil and facilitate

the rupture of the droplet interface film, lead to separation of oil from water. A sample of barite with size 150 mesh and its surface area  $59.38 \text{ m}^2\text{g}^{-1}$ . The addition of 10 g of barite enhances the role of demulsifier in oil separation as shown in Figure 4.

The synergies between the demulsifier and the fine particles of barite are depicted in Figure 5. The author suggests the barite particles capable of forming oleophilic colloidal suspensions, as the results, the oil particles aggregate, and water separate from emulsifier micelle in the core. The interaction of barite at the emulsion interface and wettability of the barite. At the same time, the demulsifier adsorbs at the barite with oil phase indicated by formation the fragment number of particulates at the oil-water interface. As the results, demulsifier is effective in changing the wet ability of barite.

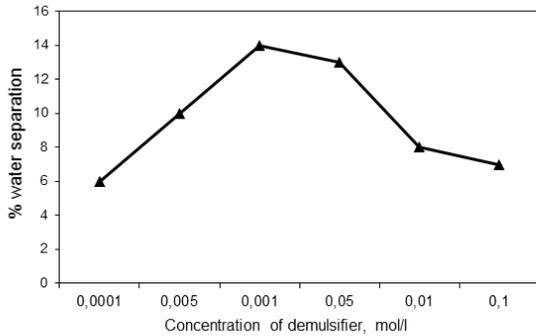


Figure 5. Relation between concentration of the demulsifier and % water separation

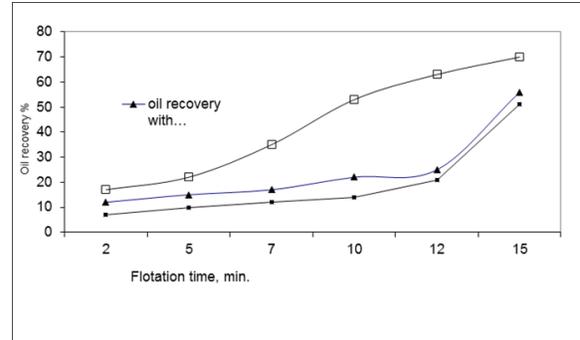


Figure 6. Effect of the separation time on the percentage of oil recovery at 0.01mole/l of collector, with and without the demulsifier and 1% of barite

At optimum conditions of demulsifying 1% of barite conditioned for 10 min. and stirring at 1200rpm. The effect of dose of barium heavy alkylate sulphonate as oil frother with a velocity of nitrogen 5l/s is shown in Figure 6. The percentage of oil recovery increase with increasing time of separation. We notice sharply increase in oil recovery after 2 minutes. The rate of oil recovery can be correlated to fit the first order kinetic rates the following:

$$dc/dt = -k$$

where the c is the oil concentration; t is separation time; k is removal rate constant.

$$\ln(c/c^0) = -kt$$

From the above equation, k value =  $2.5 \text{ min}^{-1}$  but by changing the dose of frother, the values of k increase as shown in Table 2 and Figure 7. The author calculates the degree of surface coverage of the additive on barite surface. It found that there is a good relationship between % of oil recovery and degree of surface coverage (Table 3).

Table 2. Effect of the separation time on rate constant

Dose of collector	k
0.0001	$2 \text{ m}^{-1}$
0.001	$2.2 \text{ m}^{-1}$
0.01	$2.5 \text{ m}^{-1}$
0.1	$3.1 \text{ m}^{-1}$

From the above equation, k value =  $2.5 \text{ min}^{-1}$  but by changing the dose of the frother, the values of k increase as shown in Table 2 and Figure 7.

The changes to the frother performance with an addition 1% of barite powder enhance separation and oil recovery as shown in figure 7. It found that, a significant increase in oil recovery and removal rate constants. The percentage of oil recovery changed from 45 to 73% for barite concentration 1% by weight and k changed from  $3.1 \text{ min}^{-1}$  to  $5.1 \text{ min}^{-1}$  (Table 3). These results can be discussed according to the adsorption isotherm of barium sulphonate on barite surface. The author suggests a method for measuring of the degree of surface coverage of the collector on barite surface according to Frumkin adsorption isotherm, the results are

listed in Table 3. Which the oil recovery increases with increasing contact angle and degree of surface coverage. The author thinks the degree of surface coverage computable with a contact angle of oil barite surface.

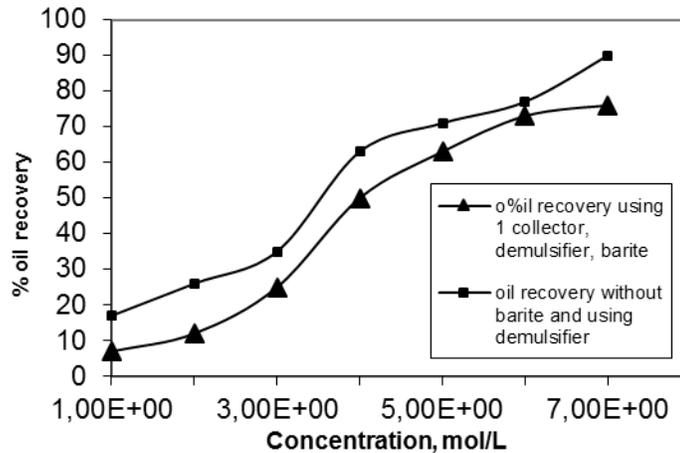


Figure 7. Effect of the frother concentration on % oil recovery in the presence demulsifier and with or without barite

Table 3. Effect degree of surface coverage of the additive at barite surface on % oil recovery

Dose of the frother	Degree of surface barite converge by the additives
0.0001	0.0042
0.001	0.00707
0.01	0.01
0.05	0.012

#### 4. Conclusion

Further work will study removal oil without using additive by design electro separation column of the frother barium heavy alkylate sulphonate necessary to enhance of oil recovery by separation techniques. There is a good enhancement between addition fine powders of barite in the presence of the frother, where the yield of oil recovery increase. These results depend on the degree of surface coverage of collector on barite surface, which affect on the contact angle of oil.

#### References

- [1] Omar AMA and Azzam EMS. Adsorption of some anionic surfactant on barite and at solution/air interfaces. *J. of Surfactants and Detergents*, 2004; 7(2): 141-145.
- [2] Omar AMA and Nagui AAK. Surface and Thermodynamic Parameters of Some Cationic Surfactants. *J. Chem. Eng. Data*, 1998; 43: 117.
- [3] Omar AMA, Mohamed MS and Ibrahim H. Recovery of Residual Emulsifiable Oil from Waste Water by Flotation. *Lubric. Sci*, 2001; 14(2):275-284.
- [4] Omar AMA, El Adly RA, Keera RA and Mohamed MS. Recovery of Residual Lubricating Oil from Waste Clay by Flotation. *Monatshefte für Chemie/Chemical Monthly*, 1998; 129: 387-392.
- [5] Omar AMA. Anionic/Nonionic Collector Efficiency as Related to the CMC of the Mixture. *Afinidad*, 1996; 53(464):262-266.
- [6] El Morsi AK, Omar AMA. Development of a Method for the Extraction of Oil from Clay by Friendly Phase Transfer Catalyst. *Petroleum Science and Technology*, 2010; 28(16):1674-1680.
- [7] El Mehbad N. Treatment and Refining of Used Lubricating Oil by Clay with Polymeric Surfactants. *Research Journal of Applied Sciences, Engineering and Technology*, 14(1): 7-9.

- [8] Gad EAM, Omar EAM and Zaki M. Surface and Thermodynamic Parameters Of Mixed N-Alkyl N- Trimethyl Ammonium-Chloride with Isooctyl Nonyl Phenol Ethoxylate. J. Surfactants and detergents, 1999; 2(1):39-43.
- [9] Oldham GF. Seminar on aspects of prevention of oik pollution in the Mediterranean action plan. UNEP, Athens 11-13 February, pp 2-15., 1985.

---

*To whom correspondence should be addressed: Dr. Noura El Mehad, Najran University, Chemistry Department, Najran, Saudi Arabia*