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Evaluation of a sulfanilic acid based surfactant in crude oil demulsification: an experimental study

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Abstract. In this study, 2-Amino-5-Dodecyl Benzene Sulfonic Acid (ADBSA) surfactant has been prepared and tested as crude oil emulsions demulsifier. Electrical conductivity method was used to obtain the critical micelle concentration of surfactant. A critical micelle concentration value of 0.225 wt.%. Bottle testing measurements were conducted to investigate the effect of several parameters including temperature, water content, salinity, demulsifier dosage and type of crude oil (composition) on the demulsification efficiency in presence of new synthetic demulsifier. A reduction of emulsion stability was observed with increasing water content or demulsifier dosage decrease. A water separation index of 98% was recorded at 60°C.

1 Introduction

Presence of water in crude oil as emulsions is a common subject in crude oil processing. The origins of formation of these emulsions are the shear and other restrictions created by the pumping of water-crude oil mixture through the valves, elbows and pipes. Water-in-Oil (W/O) emulsions are stabilized by asphaltenes and other natural occurring surfactants in crude oil [1–3]. Emulsion may be defined as a highly stable dispersion of droplets of a liquid with a certain size in a second immiscible liquid [4,5]. This emulsion causes many problems for petroleum industry. These problems include increased oil viscosity, associated corrosion problems, extra-expense of transportation, poisoning of downstream refinery catalysts, and required additional production equipment [6,7]. As a result, separation of this water from crude oil is very important in process operation [8–10].

Demulsification is the process of breaking emulsions with the aim of separating water from crude oil [11]. Emulsion-treating technologies are carried out when storage tanks cannot remove W/O emulsion [12]. There are several research studies in the open literature concerning the demulsification process and evaluation of the W/O emulsion [13–18].

There are two main demulsification methods: physical and chemical [19]. Some physical demulsification methods include supersonic demulsification [20], microwave radiation [21–24], centrifugation [25], and electro-sedimentation [26,27]. In chemical demulsification, demulsifiers are applied to extend the surface area at the water-crude oil interfaces and breaking the firm film around water droplets in order to separate water from oil [28,29].

The main goal of this article is study the impact of different parameters in presence of the new demulsifier. In present study 2-Amino-5-Dodecyl Benzene Sulfonic Acid (ADBSA) an amphoteric surfactant was prepared [30]. The demulsification properties of this surfactant were studied in detail. Synthetic brine in crude oil emulsions were used in bottle testing at different temperature, demulsifier concentration, water content, oil properties and water salinity [31,32].

2 Experimental

2.1 Materials

Anhydrous aluminum chloride (AlCl₃), acetonitrile, acetic anhydride, 1-bromododecane (dodecyl bromide), 2-Aminobenzene sulfonic acid, sodium hydroxide and hydrochloric acid were used as received without further purification. These chemicals were purchased from Merck Chemical Co. (Germany) and Aldrich Chemical Co. (Milwaukee, WI), USA.

2.2 Surfactant

2-Amino-5-Dodecyl Benzene Sulfonic Acid (ADBSA) an amphoteric surfactant was prepared with 85% yield. The following procedure was used in the synthesis of ADBSA
surfactant. 1.00 g of ortho-sulfanilic acid was placed in 50 mL 6.0 M hydrochloric acid and stirred using magnetic stirrer for 30 min some remained in the solution (container A). Then 8 mL of acetic anhydride was added to container A; at this time the remained ortho-sulfanilic acid was dissolved and a clear solution was obtained. In container B, 18.00 g of sodium acetate was dissolved in 35.0 mL of distilled water. Container B was placed in an ice water bath; then the solution from container A was added to container B and stirred for 4 h. At this time the container B was heated gently to evaporate water; when the volume of solution reduced to half, a greenish white precipitate formed; to complete precipitation it was placed in ice water bath for 24 h, it was filtered and washed then air dried (compound 2). In the next step, compound 2 was placed in a round bottom flask along with 0.10 g anhydrous aluminum chloride, 100.0 mL acetonitrile while it was stirring 2.0 mL dodecyl bromide was added slowly drop wise. After the addition was completed, the stirring was continued at reflux temperature for an additional 24 h. The flask was cooled and a white precipitate (compound 3) was formed; the acetonitrile was decanted; at this time 30.0 mL of 6.0 M hydrochloric acid was added to the flask and heated under reflux; compound 3 was dissolved and a clear solution was obtained. The flask was cooled to room temperature. 3.0 M sodium hydroxide solution was added to neutralize the acid, when neutralization was complete the solution turn cloudy. Finally, the flask was placed in an ice water bath a white precipitate was formed (compound 4), it was filtered and air dried. Compound 4 was recrystallized in ethanol. The synthetic pathway leading to the synthesis of target ADBSA surfactant is demonstrated in Figure 1.

2.3 Crude oil

The crude oils used in this study were dead oil samples from Iranian south oil reservoirs including Asmari (P1), Binak (P2) and Azadegan (P3).

2.4 Synthetic brine

A certain amount of NaCl was dissolved in sufficient distilled water to prepare brine. The details of the process will be explained in subsequent sections.

3 Methods

3.1 CMC measurement

The electrical conductivity technique was used to determine the Critical Micelle Concentration (CMC) of the surfactant. Jenway-4510 conductivity apparatus was used in these experiments. The conductivity of solutions was plotted versus surfactant concentrations; two distinct trend lines were observed. The CMC value corresponds to the point where a variation in the rate of conductivity occurs. Figure 2 exhibits the plot of solutions conductivity versus surfactant concentration at 25°C. The CMC value of ADBSA surfactant is 0.225 wt. %.

3.2 Preparation of water in crude oil emulsion

The demulsification tests were carried out using synthetic W/O emulsion. These emulsions were synthesized from mixing crude oil and brine. The aqueous phase is a NaCl solution. Appropriate volume of emulsion was prepared by shaking the fluids (oil phase and brine) in a JB-12KD (Zhengyuan Tongda Ltd.) homogenizer at 10000 rpm for 20 min. For example, 200 mL of an emulsion that contains 40% brine of 1 wt.% of NaCl was prepared as below:

- 0.8 g of NaCl was weighted and was poured in 80 mL of distilled water and was stirred by a magnetic stirrer until salt dissolved completely. This makes 1 wt.% brine;
- 120 mL of dead oil was added into the beaker containing brine that was made previously;
- brine must disperse in oil phase. For this purpose, a powerful shear stress is necessary. Homogenizer inserts this shear stress by stirring the emulsion with 10000 rpm and makes stable W/O emulsion that contains 40% v/v brine.

Fig. 1. Synthetic route of the target ADBSA surfactant.

Fig. 2. Conductivity of surfactant solution versus concentration to determine ADBSA CMC.

These emulsions are very stable within the experimental time frame and no water separation was observed for several days. At last, the emulsion demulsification was evaluated by bottle tests.

### 3.3 Bottle test

In this section, bottle testing was implemented in order to evaluate demulsification efficiency of ADBSA surfactant. The bottle test involves, shaking the content of the container to disperse the demulsifier in the emulsions and observing the phase separation (water separation) as a function of time. Figure 3 shows a typical bottle test that was carried out in this thesis. In each test, the labeled 25 mL graduated cylinder was filled with freshly prepared emulsion samples up to the 25 mL mark. About 0.5 mL of the demulsifier was added to the first test tube. Thereafter, 1, 1.5–3.5 mL was added sequentially into the remaining test tubes depend on which parameter was being studied. In most experiments, 2 mL of demulsifier was added to the emulsion. Then, the test tubes were shaken vigorously for 2 min by an electrical Orbital Shaker OS21 (Philip Harris Ltd.). At this time, the mixture was put in a water bath under desired temperatures (40 and 60 °C). The volume of the separated water was measured every 5 min for a period of 2 h.

The demulsification performance is evaluated by the percent of Water Separation Index (WSI%), which can be calculated from Equation (1), as below:

$$
WSI = \left[ \frac{\Sigma (SW)}{N} \right] \times 100, \tag{1}
$$

where N and SW are the number of measures of separated water and separated water (%) in a specific concentration/time, respectively. WSI is a simple and efficient index to demonstrate the efficiency of surfactants demulsification ability.

There are different criteria for evaluation of demulsification efficiency. In addition to WSI, as a simple and efficient index to demonstrate the efficiency of surfactants demulsification ability, other criteria such as separated water quality, settling time and presence of rag layer have been studied. Quality of separated water is related to the presence of oil droplets in separated phase which is not desirable due to environmental issues and wasting oil. Another parameter is settling time defined as the time span where the highest water separation takes place. Moreover, a gel-like emulsion that forms at the interface of the oil and water in a separation vessel is called the rag layer. Presence of rag layer and separated water quality are qualitative parameters, even though settling time and WSI are quantitative ones in demulsification process. Table 1 shows a summary of bottle test results of the ADBSA and CD demulsifiers. Demulsification was carried out in the following way: 2 mL of demulsifier was added to 25 mL crude oil emulsion containing 30% brine at the selected temperature (40 and 60 °C). The demulsification performance was improved at elevated temperature. Several factors may affect the demulsification efficiency are studied in subsequent sections. The effect water content, demulsifier dosage, brine salinity and temperature are investigated by means of Asmari oil.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Demulsifier</th>
<th>Settling time (min)</th>
<th>WSI (%)</th>
<th>Rag layer</th>
<th>Water quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>ADBSA</td>
<td>50</td>
<td>86</td>
<td>None</td>
<td>Excellent</td>
</tr>
<tr>
<td></td>
<td>CD</td>
<td>30</td>
<td>90</td>
<td>Yes</td>
<td>Good</td>
</tr>
<tr>
<td>60</td>
<td>ADBSA</td>
<td>30</td>
<td>95</td>
<td>None</td>
<td>Excellent</td>
</tr>
<tr>
<td></td>
<td>CD</td>
<td>25</td>
<td>97</td>
<td>Yes</td>
<td>Good</td>
</tr>
</tbody>
</table>

**Fig. 3.** Effect of temperature on demulsification efficiency of ADBSA.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Demulsifier</th>
<th>Settling time (min)</th>
<th>WSI (%)</th>
<th>Rag layer</th>
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<td>25</td>
<td>97</td>
<td>Yes</td>
<td>Good</td>
</tr>
</tbody>
</table>

**Table 1.** Results from bottle testing using demulsifier at 40 and 60 °C for 30% W/O emulsions.

4 Results and discussions

In this section, the effect of different parameters such as surfactant concentration, temperature, water content, emulsion stability, brine salinity and different crude oil properties are studied.
4.1 Effect of temperature

Figure 3 illustrates WSI versus time at various temperatures of 20, 40 and 60 °C. Water separation increases at elevated temperature. This could be due to an increase of dispersed brine droplets collision at the elevated temperature which causes more coalescence and separation. In other words, raising temperature decreases film stability and elasticity around water droplets lowering viscosity of oil, increasing oil mobility and growing settling rate of water droplets. Consequently, interfacial film breaking and coalescence of water droplets will be easier at elevated temperatures. Figure 3 demonstrated that when temperature increases the settling time of demulsification decreases and also a 95% separation of water was observed in 30 min.

4.2 Effect of water content

Figure 4 exhibited the effect of water content on demulsification efficiency at 60 °C. Generally, as water content of emulsion increases, WSI grows leading to an increase in demulsification efficiency. This increase of demulsification efficiency at higher water contents might be due to asphaltene content in the crude oil. As a result, the system tends to be unstable owing to the limited amount of asphaltenes that are adsorbed on the W/O interface. When asphaltene adsorption decreases through increasing water content, separation of water becomes easier. In addition, increasing water content of an emulsion may result to form large droplets that can coalesce and collide to each other. Thus, at any specific time in this study, WSI for emulsion containing 50% water content was larger than the others. The effect of water content on demulsification efficiency of emulsions at 60 °C is depicted in Figure 5, in which 2 mL of demulsifier were added to 25 mL of emulsions. The emulsion stability is usually considered as the requisite time for separating a definite volume of water content of an emulsion. In this study, stability is the time required for separating of 50% of water content of the emulsion with an accuracy of 10 s. As shown in Figure 5, minimum stability takes place in emulsion with 60% of water content. The minimum stability matches the emulsion inversion from W/O to O/W emulsion by increasing water content. This demulsifier is made to break w/o emulsions therefore they have a low performance in o/w emulsions treating. In addition to a minimum stability point, Figure 5 states that for water contents of 20 and 90%, very high emulsion stability was observed. In the other hand, when the volume of one phase significantly goes beyond the volume of another phase, the highest emulsion stability will occur which is not desirable.

4.3 Effect of demulsifier dosage

Effect of demulsifier dosage on demulsification efficiency of ADBSA in comparison with a Commercial Demulsifier (CD) is shown in Figure 6, in which different volumes of demulsifier were added to 30% of 25 mL w/o at the temperature of 60 °C. Figure 6 shows that adding demulsifier up to certain level increases demulsification efficiency then by formation of a second layer it lowers water separation efficiency. ADBSA surfactant dosage that causes the highest separation is in a reasonable range (±0.065–0.109 wt.%). At lower dosage, addition of demulsifier increases their adsorption at the interface of dispersed droplets with oil; thus, the Separation of Water (WSI) increases or emulsion stability significantly decreases. The decrease in stability can be explained in such a way that even a small amount of demulsifier molecules contributing at interface can diminish the rigidity of the interfacial film.

Fig. 4. Effect of emulsion water content on demulsification efficiency of ADBSA surfactant.

Fig. 5. Effect of water content on the stability of emulsion.
Moreover, for higher demulsifier dosage than a certain value the efficiency decreases because of formation of a new demulsifier layer. Since the interface is already saturated by the surfactant micelles consequently the demulsifier dosage keeps approximately constant at the interface. In other words, this phenomenon results in bonding between other water droplets and oil film. As a result of increasing demulsifier dosage, the inversion of the emulsion may occur to reduce WSI. Another important point obtained from Figure 6 is the gradual increase of water separation before a certain value, and then the sharp decrease of water separation after this optimum value, which occurs in the approximate range of 0.065–0.087 wt.%. As can be seen, the highest WSI for CD and ADBSA are 97% and 95%, respectively, which are approximately identical. It is noteworthy that the proposed demulsifier in this study is a single surfactant; however, the CD is a blend of several surfactant and compounds with a complex formula. It should be interesting to correlate the CMC value of the sulfanilic acid based surfactant demulsifier obtained in Section 3.1 (see Fig. 2) with the impact of demulsifier dosage in Section 4.5 (see Fig. 6). The comparison could lead to interesting interpretations. As shown in Figure 6, the region of acceptable separation can be achieved for demulsifier dosages much less than CMC value. In fact, the highest WSI occurs in concentration of 0.087 wt.% which is less than half of the CMC value (i.e., 0.225 wt.%).

### 4.4 Effect of brine salinity

Figure 7 demonstrates that the emulsions stability of ADBSA surfactant versus salinity at 60°C using 30% w/o emulsions. In accordance to this figure, by increasing brine salinity, stability of the emulsion decreases. In the other hand, adsorption of surfactant at interface of emulsion increases due to an electrostatic attraction between surfactant molecules and NaCl ions. In fact, the main effect of the addition of salt is to decrease the repulsion between surfactant molecules due to electrostatic forces which allows an increase of the surfactant density at the W/O droplets and therefore promote the emulsion destabilization.

This reduction leads to a specific salinity. This investigation reveals that a salinity of about 7% by weight enhances the demulsification efficiency. After that, increasing brine salinity does not have a substantial impact on demulsification efficiency or emulsion stability.

### 4.5 Effect of different crude oils (Composition)

To apply ASTM D6560-00 method, the asphaltene content of Asmari (P1), Binak (P2) and Azadegan (P3) oil samples were measured. In this section, the effect of different crude oil (crude oil composition) samples was investigated. Three different crude oils from Asmari (P1), Binak (P2) and Azadegan (P3) fields which have different composition and properties were studied. The properties of these crudes are given in Table 2. Based on this table, P2 and P3 are more asphaltene and more viscous samples than the P1. By

| Table 2. Properties of three crude oils labeled P1, P2 and P3. |
|---------------------------------|-----------------|----------------|-------------------|
| Crude oil | API gravity (°API) | Viscosity at 60°C (cP) | Asphaltenes (wt.%) |
| P1 | 28.4 | 20.5 | 5.6 |
| P2 | 19.0 | 185.4 | 11.0 |
| P3 | 10.9 | 511.3 | 9.5 |
knowing this fact, the demulsification experiments of these crude oil samples were conducted and compared with each other. Figure 8 illustrates the results of WSI versus time for ADBSA surfactant. Oil samples P1, P2 and P3, the amount of W/O emulsion, salinity, temperature and added volume of demulsifier were studied at 60°C. Both asphaltene content and viscosity of crude oil affect the emulsion stability. As Figure 8 shows oil samples of P2 and P3 that were more viscous and more asphaltic than P1, have made more stable emulsions. The final WSI was not very different but the settling time altered considerably. Settling time of P1, P2 and P3 were 30, 55 and 80 min, respectively. With increasing asphaltene content, the film rigidity increases, therefore emulsion becomes more stable. Moreover, movement, aggregation and coalescence of water droplets become more difficult by increasing oil viscosity.

5 Conclusion

In this study, bottle testing was conducted to investigate the efficiency of ADBSA surfactant as a demulsifier. Quantitative (settling time and WSI) and qualitative (presence of rag layer and quality of water) parameters were employed in our analysis. It is observed that ADBSA surfactant contains two powerful hydrophilic groups of ammonium and sulfonic ions, demonstrated excellent demulsification efficiency. Based on the obtained experimental results, the following conclusions are made:

– water separation increases at elevated temperature; in another word the stability of brine-crude oil emulsion decreases by increasing temperature;
– demulsification efficiency increases at higher water contents, this could be due to presence of limited amount of asphaltenes that are adsorbed on the W/O interface;
– demulsification efficiency increases by adding demulsifier up to certain level, and;
– the absorption rate of ADBSA surfactant is increased at interface of emulsion by growing salinity due to an increase in electrostatic attraction between surfactant molecules and NaCl ions;
– the most stable emulsions were achieved when the volume of one phase significantly exceeds the volume of another phase.

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References


