Preparation and evaluation of demulsifiers agents for Basra crude oil

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Abstract The present study relates to the preparation of demulsifiers from castor oil for dehydration (desalting) of Basra crude oil and water emulsions. It is an empirical application study. Two emulsifiers were compared, $R_p/6000$, which is commercially available and ammonium castor oil sulfonate that was prepared. The general physical properties and IR spectra were measured for the demulsifiers. The demulsification studies were performed at 50 °C, using a water–oil emulsion containing 15 vol% water and 3 wt% NaCl in the water. Parameters that were studied include demulsification time, demulsifier dose and the effect of pH. The best water separation was obtained at highest pH and demulsifier dose.

Keywords Demulsifiers · Basra crude oil

Introduction

Demulsifying agents are employed to break emulsions of polar solutes like water and nonpolar solutes like oil. They are used in functional fluids (for example, metal removal fluids, rust and oxidation fluids and transformer fluids) to inhibit the formation of emulsions and break emulsions that have developed (Golden 2003).

Among their industrial uses, demulsifiers are commonly used to dehydrate and desalt of crude oil (Berger and Hsu 2000). Salts and suspended matter are present in crude oil in varying concentrations, depending on the area where the oil originated. The water and crude oil emulsions are

formed naturally or artificially, by washing with water in a desalting unit (Ptister and Antoine 2000). The content of these emulsion ranges from 0 to 5% by mass of the emulsion (Ptister and Antoine 2000). The breaking of the emulsion results in the formation of an aqueous phase containing salts and suspended matter and of an organic phase (“crude oil phase”) containing the hydrocarbons (Durrieu and Havre 1992). The salts and water, unless removed, will cause problems in the distillation columns (Durrieu and Havre 1992; Hobson 1988). The salts present are the cause of corrosion observed in the production, transportation and refining of salt containing crude oils (Lorenz and Martin 1976; Kirk 1988). The water may also vaporize when exposed to high temperature, causing a rapid increase in pressure or even an explosion (Institute of Petroleum 1990; Gary and Handwerk 1975). It is consequently important to thoroughly remove water from crude oil before further refining, and demulsifiers play an important role in achieving this goal.

The present study investigates two demulsifying agents that are capable of aiding the separation of water and crude oil mixtures (Institute of Petroleum 1990). The one demulsifier, $R_p/6000$, is commercially available, and the other demulsifier, ammonium castor oil sulfonate (ASC), was prepared in our laboratory. This is an application report and it is empirical in nature.

Experimental work

Materials and instruments

All experiments were conducted with Basra crude oil (Table 1). The other materials and instruments employed are listed below.

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Suppliers	Materials and instruments
Iraq—Basrah oil company	Castor oil
Iraq—Basrah oil company	RP6000
B.D.H	Sulfuric acid
Fluka	Sodium hydroxide
Fluka	Ammonia
Fluka	Toluene
Germany	Mechanical stirrer
India	Separating funnel
Studios	Water bath
Germany	Evaporation rotary
BOUCK	IR spectrum
India	Micro sarong
India	Conductivity meter
India	pH meter

Table 1 Physical properties of the Basra crude oil employed in this study

Property	Basra crude oil
Specific gravity at 24 °C (g/mL)	0.8849
Salt content (wt%)	0.0006
Water and sediment content (vol%)	0.05
Asphaltene content (wt%)	2.22
Sulfur content (wt%)	2.1
Viscosity at 20 °C (cP)	50
Conductivity (mS)	0
API	28.4

Experimental procedure

Surfactant preparation

A mixture of 250 mL of castor oil and 50 mL of sulfuric acid were placed in a 500 mL three-neck round bottom flask, and the mixture was stirred for 3 h at room temperature. After the reaction, 50 mL of ammonia was added to the mixture and the mixture was heated to 80 °C, while stirring for 4 h. After the reaction completed, the mixture was transferred to a rotary evaporator to separate the water and any solvent that remained. This procedure was previously reported in the literature (Silverstein and Basslar 1981).

Emulsion preparation

The water in crude oil emulsion was prepared from crude oil by adding 30 vol% water to the oil at ambient temperature. The water contained 3% by mass sodium chloride (NaCl). The emulsion was formed by stirring the two-phase mixture with a mixer at a speed of 5,000 revolutions per

minute for 60 min. This gave a good stable emulsion without showing any signs of flocculation. The rate of water separation was monitored for a period of up to 24 h.

Evaluation of water separation efficiency of demulsifiers (Bottle test)

The demulsification tests were performed in 100 mL beakers all filled with the water and crude oil emulsion (w/o emulsion). In each beaker, the demulsifier was injected and mixed for one minute. The gravity separation of the water phase from the crude oil was allowed to take place while the temperature was kept constant at 50 °C using a temperature controlled water bath.

Effect of demulsifiers on water separation efficiency

In this set of experiments, the effect of ACS and Rp/6000 was investigated. The doses of these compounds were 10, 20, 30, 40 and 50 ppm.

Measurements

Salt content

The salt content in the crude oil was measured using a calibrated conductivity meter.

pH measurements

The acidity of the water that was separated from the w/o emulsion was measured using a pH meter that was calibrated with buffer solutions having a pH of 4, 7 and 9, respectively.

Residual water content

The residual water content in the w/o emulsion after breaking the emulsion was evaluated using the Dean–Stark method. The apparatus consists of a round bottom flask (500 mL) connected to a Liebig condenser through a receiving tube.

Density

The emulsion density was evaluated using picnometer.

Results and discussion

Physical properties of the demulsifier

The physical properties (density, pH, viscosity and flash point) of the ASC demulsifier were measured according to

Table 2 Physical properties of the demulsifiers R_p/6000 and ACS

Demulsifier	Color	pH	Flash point °C	Viscosity (cSt)	Specific gravity (g/mL)
R _p /6000	Brown	5.8	56	1.4905	0.8770
ACS	Brown/Black	6.7	60	1.4899	0.8766

the applicable ASTM standards and compared with the reference demulsifier, R_p/6000 (Table 2). It can be seen from Table 2 that the physical properties of ACS were similar to physical properties of R_p/6000. The flash point of the ACS demulsifier was high to improve safety during handling and transfer of the demulsifier.

Separation efficiency

The effect of R_p/6000 and ACS on water separation efficiency over time is shown in Figs. 1 and 2. Figure 1 shows an increase in water separation for R_p/6000 until it reaches 60 min, after that the separation levels off and the separation rate is low. The best separation recorded for R_p/6000 was 87% after 120 min. Figure 2 shows an increase in water separation for ACS over time. The separation rate of water was high only for the first 30 min, where after it decreased significantly. The best separation recorded for ACS was 85% after 120 min.

Both demulsifiers tested failed to improve separation beyond the threshold observed at 60 min. This threshold value correlated with the demulsifier concentration. The minimal additional increase in separation after 60 min that was observed for R_p/6000 and ACS is because the active chemical groups (OH, COOH, C=O, OSO₂, SO₂OH) on the hydrocarbons chains are fully engaged and are not available to improve separation.

Fig. 1 The influence of various concentrations of R_p/6000 on the separation of water. The water phase was 15 vol% and the temperature was 50 °C

Fig. 2 The influence of various concentrations of ACS on the separation of water. The water phase was 15 vol% and the temperature was 50 °C

Effect of pH on separation efficiency

The effect of pH value on separation efficiency is shown in Fig. 3. Over the pH range tested, the separation increased monotonically with an increase in pH, and the best separation was achieved at higher pH. The limiting values were the same as reported before.

Characterization of the prepared demulsifier

The infrared (IR) spectra of castor oil (Fig. 4) and the ACS demulsifier (Fig. 5) are shown for comparison. The unmodified castor oil does not exhibit the sulfur- and nitrogen-related absorption bands found in the ACS (Table 3).

Conclusions

The present study is an application report and is empirical in nature. The following conclusions could be drawn from

Fig. 3 Effect of pH on the water separation efficiency using R_p/6000 and ACS

Fig. 4 Infrared spectrum of castor oil **Fig. 5** Infrared spectrum of ammonium castor oil sulfonate (ACS)**Table 3** Assignment of prominent infrared absorption bands in castor oil (Fig. 4) and ammonium castor oil sulfonate (Fig. 5)

Compound	Infrared absorption (cm ⁻¹)				
	-S	N-H	SO ₃ -	C-H	CH ₂
Caster oil	-	-	-	680, 1450	2995, 2880
Ammonium caster oil sulfonate	1650	315, 350	1220, 1050	680, 1450	2995, 2880

the experimental work with the commercially available R_p/6000 demulsifier and the prepared ammonium castor oil sulfonate (ACS) demulsifier:

- 1) Water separation increases with increasing separation time for both demulsifiers tested.
- 2) There is a limiting water separation, which depends on the concentration of the demulsifier.
- 3) Water separation efficiency increases with increasing dose of demulsifiers.

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