



Evaluation of w/o emulsion stability in function of oil polarity: a study using asphaltenes C3I in kerosene

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Abstract

Emulsions are thermodynamically unstable colloidal dispersions of two immiscible liquids. The formation of w/o emulsions during production occurs when oil is mixed with formation water under strong turbulence in the presence of surface active agents as resins and asphaltenes. Emulsion formation during crude oil production is a very costly operational problem and many issues still remain poorly understood. Therefore, studies are carried out to verify the parameters that can affect the stability of these emulsions. In this work, the influence of oil polarity on the w/o emulsion stability was evaluated using model system. The oil phase was constituted of asphaltenes C3I dispersed in kerosene (concentration from 0.1 to 3.0 wt/v%) and the aqueous phase was 55,000 ppm NaCl:CaCl₂ 10:1. The following w/o emulsion compositions were used: 20/80, 40/60, 60/40 and 80/20. The demulsifier was used at concentrations of 0, 50 and 350 ppm. Higher asphaltenes concentrations are required to form emulsions containing higher water content. The emulsion stability increases as asphaltenes concentration is increased up to a threshold value, beyond which no change is observed. As expected, higher asphaltenes concentrations require higher concentration of demulsifier to achieve a satisfactory emulsion breaking.

Keywords

Oil polarity; w/o emulsion; emulsion stability

Introduction

An emulsion is a dispersion of one liquid in another, where they have a certain degree of immiscibility with each other. Emulsions are thermodynamically unstable systems that separate to reduce the interfacial area between the oil phase and the water phase, as a function of time [1-2]. Emulsion formation during crude oil production is a very costly operational problem. These emulsions do not form spontaneously, being necessary to supply energy for their formation as turbulence and shear. In addition, stable emulsions can be formed due to natural petroleum surfactants such as resins and asphaltenes [3-5]. Asphaltenes are the most polar molecules in the crude oil with high molar mass and are insoluble in aliphatic solvents such as pentane, hexane or heptane, and soluble in aromatic solvents such as toluene and benzene. The structure of asphaltene molecules consist of polycyclic aromatic clusters, substituted with varying alkyl side chains [3,6-7]. The accumulation of asphaltenes at the interface results in the formation of a rigid interfacial film, which creates a barrier to coalescence [5,8-9]. The state of asphaltenes in the crude oil has an effect on the stability of emulsions. There are strong evidences that emulsion stabilization is improved when asphaltenes are as precipitates [5,9]. The stability of these emulsions can be influenced by

temperature, pH, droplet size [5,8], and in some cases demulsifiers are used to cause emulsion destabilization through the coalescence of the droplets [10]. In this work, the influence of oil polarity on the w/o emulsion stability was evaluated using model system constituted of asphaltenes C3I dispersed in kerosene (concentration from 0.1 to 3.0 wt/v%) as oil phase, and brine 55,000 ppm NaCl:CaCl₂ 10:1 as aqueous phase, varying the w/o compositions (20/80, 40/60, 60/40 and 80/20).

Methodology

Experimental Procedure

Extraction of asphaltenes fractions

For this study, three fractions of asphaltenes were extracted from crude oil using propane, n-pentane, and n-heptane as flocculant, named, respectively, C3I, C5I and C7I [6].

Preparation of synthetic w/o emulsions

The oil phase was prepared at concentrations of 0.1, 1.0, 2.0 and 3.0 w/v% of C3I in kerosene, using magnetic stirring for 30 min, followed by ultrasound for 30 min for total solubilization of the samples. The aqueous phase was prepared by dissolving NaCl:CaCl₂ 10:1 at 55,000 ppm in deionized water under magnetic stirring for 30 min at room temperature.

The following procedure was performed: (1) oil and aqueous phases were put separately in the oven for 30 min at 80 °C; (2) brine was slowly added into the oil phase under stirring with glass stick at room temperature; (3) the mixture was stirred in Polytron at 15000 rpm with external heating of 60 °C for 6 min. 20/80, 40/60, 60/40 and 80/20 w/o proportions were used.

Bottle test

The fresh prepared w/o emulsion was poured into graduated conic glass flasks, which was put into the thermostatic bath at 60°C. For the additive samples, the demulsifier was added using micropipette and the glass flask was shaken manually for 1 min (the demulsifier was used at concentrations of 0, 50 and 350 ppm). After that, the glass flask was put into the thermostatic bath again and the test was started. At every 5 min the glass flask was removed from the bath and the volume of separated water was read in the first 30 min. From 30 to 60 min test, the volume was read at every 10 min. This generated a kinetic curve of percentage of separated water in function of time or simply the percentage of separated water at the end of the test, that is, after 60 min.

Results and Discussion

The solubility of the three asphaltenes fractions (C3I, C5I and C7I) was tested in kerosene. Only C3I fraction was soluble, which most likely is related to the low polarity of kerosene and higher polarity of C5I and C7I asphaltenes fractions compared with C3I. Therefore, the study was done using only asphaltenes C3I.

Concerning the emulsion formation using the model systems, it was observed that no emulsion was formed for the 80/20 w/o proportion using all asphaltenes concentrations tested (0.1, 1.0 and 3.0 wt/v%). The emulsification character of asphaltenes C3I is not strong enough to provoke the formation of emulsion containing so large content of water. When we reduced the amount of water in the emulsion to 60 v/v%, no emulsion was formed for the model system containing only 0.1 wt/v% of asphaltenes. However, by adding 1.0 or 3.0 wt/v% of asphaltenes, stable emulsions were obtained, that is, the increase in oil polarity did not affect the emulsion stability. By reducing the water content to 40 and 20 v/v%, it was possible to form emulsion even when adding only 0.1 wt/v% of asphaltenes, being the 20/80 w/o emulsion quite stable (only 4 % of separated water after 60 min of bottle test) (Table 1).

Table 1. Percentage of separated water after 60 minutes of stability test (bottle test at 60 °C) of emulsions prepared using kerosene + asphaltenes C3I, as oil phase, and brine, as aqueous phase, without and with adding demulsifier.

w/o composition (v:v)	Asphaltenes C3I concentration (%)	Demulsifier (ppm)	Separated water (%)
20/80	0.1	0	4.0 ± 0.0
		50	90.0
		350	93.0
	1.0	0	0.0
		50	60.0
		350	95.0
	2.0	50	50.0
		200	80.0
		350	97.5 ± 2.50
3.0	50	50.0	
	0.1	0	27.5 ± 2.50
		50	100.0
350		100.0	
40/60	1.0	0	0.0
		50	95.0
		350	95.0
3.0	1.0	0	0.0
		50	95.0
		350	95.0

The performance of demulsifier at different concentrations will be discussed separately for different w/o proportions (Table 1).

By analyzing the 40/60 w/o emulsion, it is observed that by increasing asphaltenes concentration from 0.1 to 1.0 wt/v%, the amount of water separated decreased from ~28 to 0,0 % and the performance of 50 ppm demulsifier slightly decreased from 100 to 95 % of separated water. The increase in asphaltenes concentration from 1.0 to 3.0 wt/v% did not change the performance to the demulsifier, confirming the observation done for 60/40 w/o emulsion in terms of no stability increase as

increasing asphaltenes concentration in the mentioned range.

Similar percentages of separated water were observed at the end of the bottle test (after 60 min) for the 60/40 (93%) and 40/60 (95%) w/o emulsion containing the same asphaltenes concentration (1.0 and 3.0 wt/v%) and the same demulsifier concentration (50 ppm). Nevertheless, for the 60/40 w/o emulsion the total separation occurred in the first 5 min of the test, while for 40/60 w/o emulsion the maximum amount of water separated was achieved after about 40 min of the test,

evidencing the influence of water content in the kinetic of the emulsion break.

20/80 w/o emulsion is the most stable emulsion among the w/o proportions tested, for this reason, the influence of asphaltenes and demulsifier concentrations could be observed in more details. The emulsion containing 0.1 wt/v% of asphaltenes was very stable (4 % of separated water), as mentioned before, and the addition of only 50 ppm of demulsifier was enough to destabilize the emulsion almost completely. Similar water separation percentages were obtained by the addition of 50 and 350 ppm of demulsifier, respectively, 90 and 93 % of separated water. When using 1.0 wt/v% of asphaltenes, the addition of 50 ppm of demulsifier was no longer enough to promote a good efficiency of the process: only 60 % of water was separated. To achieve 95 % of separated water, the demulsifier concentration must be increased to 350 ppm. The increase in additive performance as increasing its concentration was confirmed when using the emulsion containing 2.0 wt/v% of asphaltenes, nevertheless, such performances were quite similar to those observed for the emulsion containing only 1.0 wt/v% of asphaltenes. A test was carried out increasing the asphaltenes concentration to 3.0 wt/v% and adding 50 ppm of demulsifier, the percentage of separated water was similar to those observed for the emulsions containing 1.0 and 2.0 wt/v% of asphaltenes (~50%). This confirms that the emulsion stability increases as asphaltenes concentration is increased up to a threshold value, beyond which no change is observed

Conclusions

Higher asphaltenes concentrations are required to form emulsions containing higher water content. The emulsion stability increases by increasing the polarity of the model oil up to a threshold value, beyond which no change is observed. As expected, higher asphaltenes concentrations require higher concentration of demulsifier to achieve a satisfactory emulsion break. The performance of the demulsifier decreases as increasing asphaltenes concentration from 0.1 to 1.0 wt/v% and was quite similar for the emulsions prepared with oil phase containing 1.0 or 3.0 wt/v% of asphaltenes.

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Responsibility Notice

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