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INFLUENCE OF HPAM ON THE PEFORMANCE OF COMMERCIAL DEMULSIFIERS

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Abstract

Water/oil (w/o) emulsions are formed during oil production due to the shearing imposed during the flow and the presence of natural surfactants in oil. These emulsions are undesirable from an operational point of view, leading to a series of problems. Therefore, demulsifiers are used to contribute to the destabilization of these emulsions. The presence of partially hydrolyzed polyacrylamide (HPAM), used during the enhanced oil recovery (EOR) process, may interfere with the action of these demulsifying chemicals. Therefore, this work aims to evaluate the influence of HPAM, used in EOR, on the efficiency of two commercial demulsifiers. The emulsion stability test was carried out by bottle test. The stability results were compared with droplet size and interfacial tension analyses, aiming to verify possible correlations. It was observed that the emulsion was more unstable as increasing the demulsifiers concentration in the range analyzed. However, the performances of both demulsifiers were reduced in the presence of HPAM. The bottle test results, particle size and interfacial tension found good correlation, since the increase in the particle size and reduction in the interfacial tension promoted an increasing in the phase separation.

Keywords

water/oil emulsions; demulsifiers performance; physicochemical properties

Introduction

In oil production, around 80% is obtained in the form of water-in-oil (w/o) emulsions [1]. This fact arises from significant fluctuations in pressure, temperature and shearing, promoting a vigorous miscibility of the phases in the reservoir, resulting in the formation of a colloidal dispersion of two immiscible liquids, in the form of microdroplets present in a continuous phase [2, 3, 4]. This phenomenon results in increased production costs, as its formation causes an increase in viscosity, resulting in higher transportation and storage costs, corrosion of equipment, formation of salt deposits in apparatus and poisoning of refining catalysts [5, 6].

In the exploratory context, it is known that the presence of natural petroleum species such as asphaltenes and resins can act as emulsifiers, causing the stabilization of colloidal dispersion [7, 8]. Furthermore, recent studies speculate that the chemical components used in oil production, with emphasis on enhanced oil recovery additives (EOR), may also act to stabilize emulsions through an interfacial interaction mechanism, and may behave synergistically with the petroleum constituent species [9].

Although emulsions are kinetically stable, they represent thermodynamically unstable systems and capable of phase separation due to the action of destabilizing mechanisms [10]. However, the demulsification of this kind the emulsions cannot be achieved efficiently through gravitational techniques. Therefore, chemical demulsification techniques, with emphasis on the use of non-ionic polymers, has been widely used, considering the high efficiency of recovery of the oil phase with relatively low cost, short demulsification period and simple application for the treatment of crude oil [11, 12].

However, in addition to the kinetic aspects of efficiency in the volume of separated water, important considerations regarding the emulsified system have become increasingly investigated within the scope of research, based on different physicochemical properties that better describe the demulsification phenomena and justify the success in the application of chemical additives [13].

Therefore, studies carried out focused on exploring the droplet size distribution in conjunction with the interfacial tension between the phases emerge as a feasible way of interpreting the phenomena of increase or decrease in stability due to inequalities in working measurements between unstable emulsions and stable [8, 14, 15]. Therefore, based on the fundamental concepts of physical chemistry and the agreement of experimental results, it is possible to better understand the mechanisms of action of the chemicals involved in the emulsified system, covering gaps in the effect of EOR additives on the demulsifiers performance.

Therefore, the present work aims to evaluate the stability of w/o emulsions, without and with commercial demulsifiers used in oil production and partially hydrolyzed polyacrylamide (HPAM) used in EOR, correlating the results of phase separation by bottle test with those of droplet size, droplet size distribution and interfacial tension.

Methodology

To perform the experimental tests, asphalt oil was used with °API 13.2, measured by densimeter, water content of 2.8 wt/v%, determined by Karl Fischer, and asphaltene content of 12.9 wt%, obtained by a liquid-solid extraction method using Soxhlet extractor. The aqueous phase consisted of a synthetic brine at a concentration of ~90,000 ppm composed of a mixture of salts. The 40/60, 50/50 and 60/40 v/v w/o proportions were used. Two commercial demulsifiers, called A and B, were used at concentrations of 0, 50 and 650 ppm. Preliminary tests were carried out only with demulsifier A at a concentration of 350 ppm. The tests were performed without and with partially hydrolyzed polyacrylamide (HPAM) with a hydrolysis degree of 25-30%, at concentrations of 300 and 450 ppm. The stability of the emulsions was evaluated by bottle test. Droplet size and droplet size distribution were obtained by laser diffraction and interfacial tension was goten using a force tensiometer.

Experimental Procedure

Prepartion of syntetic brine

The brine was prepared at a total concentration of ~90,000 ppm by solubilizing the salts in deionized water under magnetic stirring at room temperature. The following salts were used at concentrations of: calcium chloride dihydrate (2,520 mg/L), magnesium chloride hexahydrate (523.8 mg/L), potassium chloride (424 mg/L), strontium chloride hexahydrate (236 mg/L). L), sodium bicarbonate (200 mg/L), barium chloride dihydrate (20.7 mg/L), and silicon dioxide (23.9 mg/L). After dissolution, glacial acetic acid was added at a concentration of 300 mg/L, followed by adjusting the pH to 7 using hydrochloric acid and sodium hydroxide. For tests containing HPAM, the polymer was inserted at a concentration of 300 or 450 mg/L into the saline solution at the end of preparation, maintaining under magnetic stirring and heating at 80 ºC for 90 minutes.

Preparation of synthetic w/o emulsions

The studies were conducted using the proportions 40/60, 50/50 and 60/40 (w/o), considering the water present in the crude oil. Thus, the emulsion preparation process was based on the following steps: (1) Heating the phases separately for 30 minutes in an oven at 80 ºC; (2) Addition of the brine to the crude oil, under manual stirring with a glass stick for 8 minutes; (3) Agitation in the Polytron with external heating at 60 °C and rotation at 15,000 RPM for 6 minutes.

Stability of emulsions by bottle test

After preparing the emulsion, it was transferred to a graduated conical tube and inserted into a thermostatic bath for 20 min, aiming to reach the test temperature of 100 ºC. Subsequently, in cases where demulsifier was added, it was added with the aid of an automatic micropipette, requiring manual shaking of the glassware for 1 min to disperse the additive throughout the emulsion. The bottle test then began, lasting a total of 1 hour at 100 ºC, with volume readings of separated water taken every 5 minutes in the first 30 min and every 10 min in the final 30 min. The analyzes were performed in duplicate.

Stability of emulsions by droplet size

For the average droplet size distribution tests, Mastersizer 3000 was used, which measures particle size in the range of 0.01 to 3,500 µm. The experimental procedure consisted of mixing the sample with mineral oil, under stirring at 80 ºC. A beaker containing 250 mL of pure mineral oil was placed in the equipment and then a quantity of the mixture (sample and mineral oil) was poured into the same beaker until minimum obscuration was reached (~10%) at a speed of 1500 rpm. The results are obtained as a graph of volume (%) versus size (µm) and a table containing D(10), D(50) and D(90), which means that 10%, 50% and 90% of the particles are below this size, respectively. The analyzes were carried out for the emulsions, without and with demulsifier, in the absence and presence of HPAM. The measurements were taken for emulsion just after being prepared, after 20 minutes resting in the thermostatic bath at test temperature, and at the end of the bottle test. The analyses were performed in duplicate.

Stability of emulsions by interfacial tension

For interfacial tension analyzes without demulsifier and without HPAM, the brine and oil were heated separately for 30 minutes at 80 °C. Then, the brine was added to the equipment's glass cuvette, followed by the oil. To carry out analyzes containing demulsifier, the oil sample was heated in an oven for 30 minutes at 80 °C, and then the demulsifier was added and manually homogenized for 1 minute, remaining at rest for at least 12 hours. Subsequently, the brine and the sample containing the demulsifier were heated separately for 30 minutes at 80 °C, before starting the analysis. For samples in the presence of HPAM, prior solubilization in brine at 80 °C for 90 minutes was necessary, the time required for complete solubilization of HPAM, followed by the same preparation method mentioned for samples without and with demulsifier. The Attension Sigma 700 force tensiometer was used, with a Wilhelmy plate accessory and a circulation bath at 60 ºC, with a total analysis time of 30 minutes. The analyzes were performed in duplicate.

Results and Discussion

Influence of demulsifiers and HPAM on emulsion stability by bottle test

To determine the best conditions for emulsion stability tests using demulsifiers and HPAM, preliminary tests were carried out in w/o proportions of 40/60, 50/50 and 60/40 v/v. All emulsions were very stable, with no percentage of water separated without demulsifier. With the addition of 350 ppm of demulsifier A, the percentage of separated water was 7.5, 45.0 and 70.0%, for the proportions 40/60, 50/50 and 60/40 (v/v), respectively. To study the performance of the demulsifier, we chose 50/50 emulsion, as the 40/60 emulsion is very stable, and the 60/40 emulsion is very unstable. Using the 50/50 emulsion, stability tests were carried out on emulsions with 50 and 650 ppm of demulsifiers A and B. A decrease in the stability of the emulsions was observed with an increase in the concentration of demulsifiers from 8.5 ± 0.5% to 55.0 ± 3.0 % (with demulsifier A) and from 24.0 ± 0.0% to 78.0 ± 2.0% (with demulsifier B), at concentrations of 50 and 650 ppm, respectively. When the emulsions were prepared with HPAM at a concentration of 450 ppm there was no emulsion formation and at 300 ppm a very stable emulsion was formed, with no phase separation observed at the end of the bottle test. When adding demulsifiers, a reduction in efficiency was observed in the presence of 300 ppm HPAM. Demulsifier A reduced the percentage of separated water from 8.5 ± 0.5% to 3.0 ± 1.0%, at a concentration of 50 ppm, and from 55.0 ± 3.0% to 39.0 ± 3.0% at a concentration of 650 ppm. For demulsifier B, the reduction was from 24.0 ± 0.0% to 14 ± 2.0%, at a concentration of 50 ppm, and from 78.0 ± 2.0% to 59.0 ± 1.0% at a concentration of 650 ppm. The presence of HPAM reduced the efficiency of the additives, but a better performance of demulsifier B was observed in relation to A.

Influence of demulsifiers and HPAM on emulsion stability by droplet size

Through the knowledge that supports physical-chemical studies of emulsion interfaces, it is known that the size of the droplets is inversely proportional to the stability of the system. The increase in droplet size can cause a collision between the dispersed phase due to the Brownian movement of the molecules, which consequently causes coalescence followed by phase separation [13,15]. In this study, it was observed that stable emulsions, without and with HPAM and without demulsifier, presented almost the same particle size distribution before and after resting in the thermostatic bath, and an increase in particle size after the bottle test (from ~160 to ~270 µm), taking into account the D(90) values, as they are the most representative values to evaluate stability of emulsions. For comparison purposes, analyzes with demulsifier were performed only at the end of the bottle test. An increase in particle size was observed with the addition of demulsifiers, showing larger particle sizes with 650 ppm of demulsifiers A and B and without HPAM, 1,495.00 ± 45.0 µm and 1,855.00 ± 45.0 µm, respectively. In the presence of HPAM, the sizes are reduced to 1.125 ± 5.0 µm and 1.435 ± 5.0 µm for demulsifiers A and B, respectively, confirming that the interface is more stable, which corroborates the bottle test results. As observed by bottle test, demulsifier B, which showed greater efficiency, also presented larger particle size at low and high concentrations of demulsifier, without and with HPAM proving its greater efficiency related to the demulsification mechanism due to the increase in droplet size from the change in chemical potential, as described by Lord Kelvin [16]

Influence of demulsifiers and HPAM on emulsion stability by interfacial analysis

Interfacial tension measurements reveal results that corroborate the bottle test data and droplet size distribution. In the mechanism of action of demulsifiers, a decrease in interfacial tension is observed. In this context, the additives migrate to the interface between water and oil, thus providing the displacement of the stabilizing substances, taking them back to the oil phase and, therefore, facilitating the breakdown of the emulsion through the least repulsive and/or sterically impeded type of interface [12]. Therefore, when demulsifiers A and B were added to the system, without and with HPAM, there was a reduction in interfacial tension. Samples without HPAM and without demulsifier showed interfacial tension values of 27.64 mN/m and with the addition of 650 ppm of demulsifier A and B they were 13.24 mN/m and 11.61 mN/m, respectively. Proving the greater efficiency of demulsifier B with 78.0% of water separated and larger droplet size 1,855.0. In the presence of HPAM the interfacial tension value was 22.04 mN/m and with the addition of 650 ppm of demulsifier A and B it was 11.35 mN/m and 9.46 mN/m, respectively. Indicating an interface more filled by HPAM, which makes the emulsion more stable, with a lower percentage of phase separation, smaller droplet size and less reduction in interfacial tension, when compared to the emulsion without HPAM. All bottle test results, droplet size and interfacial tension are presented in **Table 1**.

Conclusions

50/50 (w/o) emulsions were chosen to evaluate the performance of the demulsifier, since the 40/60 (w/o) proportion was very stable and the 60/40 proportion was very unstable, in the presence of 350 ppm of demulsifier. In 50/50 (w/o) proportion, more unstable emulsions were obtained with an increase in the demulsifier concentration, being the demulsifier B the that showed the greatest efficiency at both 50 ppm (24%) and 650 ppm (78%), without HPAM. This efficiency was reduced from 24% to 14% and from 78% to 59% in the presence of HPAM, with 50 and 650 ppm of demulsifier, respectively. More unstable emulsions, with a higher percentage of separated water, showed larger droplet size and lower interfacial tension values, without and with HPAM. However, in the presence of HPAM, the reduction in interfacial tension with demulsifier was smaller due to the interface being less available, presenting a lower tension value (22.04 mN/m) when compared to the sample without HPAM (27.64 mN/m).

Table 1. Results of Bottle test and droplet size of 50/50 w/o emulsion, and interfacial tension

Concentration Demulsifier A (ppm)	**HPAM (ppm)**	**Separated water volume (%)**	**Droplet size (μm)**			**Interfacial tension (mN/m)**
			D(10)	**D(50)**	**D(90)**	
0	0	0.0 ± 0.0	24.8 ± 2.8	109.5 ± 0.5	260.5 ± 7.5	27.64 ± 0.37
0	300	0.0 ± 0.0	25.0 ± 1.0	81.4 ± 0.7	279.0 ± 3.0	22.04 ± 0.25
50	0	8.5 ± 0.5	19.6 ± 12.9	115.5 ± 5.5	507.5 ± 31.5	18.32 ± 0.09
650	0	55.0 ± 3.0	20.8 ± 14.9	120.2 ± 21.8	1,495.0 ± 45.0	13.24 ± 0.43
50	300	3.0 ± 1.0	26.4 ± 0.6	90.7 ± 1.8	336.0 ± 8.0	19.96 ± 0.66
650	300	39.0 ± 3.0	36.4 ± 3.2	145.5 ± 20.5	1,125.0 ± 5.0	11.35 ± 0.62
Concentration Demulsifier B (ppm)	**HPAM (ppm)**	**Separated water volume (%)**	**Droplet size (μm)**			**Interfacial tension (mN/m)**
			D(10)	**D(50)**	**D(90)**	
0	0	0.0 ± 0.0	24.8 ± 2.8	109.5 ± 0.5	260.5 ± 7.5	27.64 ± 0.37
0	300	0.0 ± 0.0	25.0 ± 1.0	81.4 ± 0.7	279.0 ± 3.0	22.04 ± 0.25
50	0	24.0 ± 0.0	55.5 ± 7.7	210.5 ± 28.5	956.5 ± 53.5	14.04 ± 0.23
650	0	78.0 ± 2.0	5.8 ± 0.4	578.0 ± 117.5	1,855.0 ± 45.0	11.61 ± 0.13
50	300	14.0 ± 2.0	40.3 ± 8.4	139.0 ± 28.0	776.0 ± 13.0	13.58 ± 0.69
650	300	59.0 ± 1.0	51.6 ± 1.2	206.0 ± 3.0	1,435.0 ± 5.0	9.46 ± 0.31

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