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Evaluation of pH variation and calcium carbonate concentration on the performance of naphthenate inhibitor

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Abstract

Depositions of salts of naphthenic acid cause flow assurance problem. The formation of naphthenates can be influenced by factors such as pressure, temperature, pH of the co-produced water and the presence of nucleating agents. In a previous work we evaluated the efficiency of additives, formulated with commercial ethoxylated nonylphenol (EN) and monoacids (C4, C10 and C18), in inhibiting the formation of naphthenates. The most efficient formulation was that containing EN (U300) and butyric acid (BA) at 75:25 m:m. The current study aims to evaluate the influence of pH variation, as well as the concentration of carbonate ions (nucleating agent) on the performance of the same mixture at different proportions. The systems were evaluated by bi-phasic mixture test and oscillatory interfacial rheology using model system of ARN in toluene and brine. Without additive at pH 6.4, the bicarbonate concentration did not affect the deposit formation. On the other hand, at pH 8.0, the increase in bicarbonate concentration increased the amount of solid, which was formed more quickly. The best performances of the formulation U300:BA were obtained at 50:50 m/m and 75:25 m:m for pH 6.4 and 8.0, respectively. The increasing in bicarbonate concentration decreased the formulations efficiency in both pH.

Keywords

Tetraprotic Naphtenic acid; Naphtenates; Inhibitors.

Introduction

It is known that a large part of Brazilian oil has high acidity, due to the presence of carboxylic acids (found mainly in heavy, immature and biodegraded oils) called naphthenic acids (NAs) [1]. This class of compounds is a complex mixture of cyclic, acyclic and aromatic carboxylic acids [2].

NAs can form insoluble salts (through interaction with metal ions) during production. When oil is transported from the reservoir to the surface, there is a drop in pressure, a release of CO_2 and an increase in pH of the co-produced water, causing greater dissociation of naphthenic acids, which, at this stage, due to their amphiphilic nature, migrate to the interface water-oil and can interact with metal ions forming naphthenate deposits. Such insoluble deposits represent an important adversity for the oil industry, as they provoke flow assurance problems, generating financial damages [3,4].

Oil reserves, in addition to the deposition of naphthenates, may frequently present a deposition of low-solubility inorganic salts such as calcium carbonate, calcium sulfate, barium carbonate, barium sulfate, among others [5,6]. The presence of inorganic scale (such as calcium carbonate) can aggravate calcium naphthenate scale in oil fields, as heterogeneous nucleation causes a reduction in the energy required to form a starting point for the growth of calcium naphthenate deposition [7].

During the development of previous work, it was observed the existence of a synergistic effect between surfactants (based on ethoxylated nonylphenol) and monoprotic acids in preventing the formation of calcium naphthenates at additive concentrations of 100, 500, 1000 and 2000 mg/L. The systems were evaluated by biphasic mixture test and oscillatory interfacial rheology. The best results, among the formulations tested, were obtained by mixing a commercial molecule with a hydrophilic-lipophilic balance (HLB) of 17.1 (U300) with butyric acid (BA) at 75:25 m:m. However, it was not investigated all composition possibilities of the formulation at different conditions [8]. Therefore, this work aims to evaluate the influence of calcium carbonate concentration and pH on the formation of naphthenates deposits and the performance of the additive based on U300:BA at different proportion.

Methodology

Experimental procedure

To carry out the tests, a model system was used consisting of an aqueous phase containing salts generally found in oil fields and an organic phase containing naphthenic acids (ARN's), previously extracted from an industrial deposit, in toluene [6].

ARN characterization

ARN was characterized by nuclear magnetic resonance (H^1-NMR) using a Bruker Avance III spectrometer at 800 MHz and 25 °C. A mixture of ARN:benzoic acid (2:1 m/m) was solubilized in deuterated chloroform and poured into a 5 mm diameter NMR tube. The percentage of ARN in the industrial deposit was calculated by Equation 1.

$$P = \frac{m_{ba} . 2 . A_{2.11-2.30\,ppm} . MM_{ARN}}{m_{ARN} . 4 . A_{8.1\,ppm} . MM_{ba}} .100 \qquad (1)$$

Where m_{ba} is the mass of benzoic acid, m_{ARN} is the sample mass, MM_{ba} is the molar mass of benzoic acid, MM_{ARN} is the molar mass of ARN, considered to be 1230 g/mol, $A_{2.11-2.30\,ppm}$ is the peak area from 2.11 and 2.30 ppm, related to 4 hydrogens of tetraprotic acid, and $A_{8.1\,ppm}$ is the peak area from 7.5 to 8.1 ppm, related to the hydrogens of benzoic acid aromatic ring[8].

Biphasic mixture test

A preliminary study was carried out by biphasic mixture test, using a solution of ARN's in toluene at 3g/L and brines at two pH's (8.0 and 6.4) and two concentrations of sodium bicarbonate (0.7 g/L and 2.7 g/L for pH 6.4, and 0.2 g/L and 0.7 g/L for pH 8.0). The pH of the brines was adjusted using hydrochloric acid and sodium hydroxide. The composition of the brine was based on the mixture of salts present in the produced water considering a critical scenario for deposition of naphthenates and precipitation of calcium carbonate [9]. The test was carried out in a glass tube using 26 mL of brine and 2 mL of ARN solution. The tube was capped and shaken, manually and vigorously, for 1 min, to maximize the contact between the acid and the cations. Subsequently, the flask was kept under resting for 10 min to promote the possible agglomeration of solids, as well as phase separation. The aqueous phase containing the solid was filtered, and the recovered solid was identified and left to rest for 24 h in the hood to evaporate the solvent. After drying the material, the filter paper was photographed, to visualize the results, and weighed to quantify the mass of calcium naphthenate. The oily phase was transferred to a new glass tube where a new volume of brine was added, and the procedure was repeated. Three extractions of the same oil phase were conducted, aiming to convert as much naphthenic acid to naphthenate as possible. At the third extraction, it was not possible to recover a significant amount of solid.

Oscillatory interfacial rheology

Oscillatory rheology tests were carried out using a MARS 60 rheometer, Reotherm, coupled to a Du Noüy ring geometry sensor. All tests were performed in duplicate and at 25°C. In a glass cuvette, 20 mL of the aqueous phase were added. The sensor (Du Noüy ring) was positioned just below the air/water surface. Then, 20 mL of the oil phase was added on the aqueous phase and the sensor was repositioned at the water/oil interface.
The aqueous phase was the same as in the biphasic mixture test, however, the concentration of ARN in toluene was 25 mg/L. The formulations were commercial surfactant (U300):butyric acid (BA) at 50:50, 75:25 and 25:75 m:m, at a total concentration of 10 mg/L. The ARN concentration was 60% higher than that of the additive.

Results and Discussion

ARN characterization

It was calculated 91 % of tetraprotic acid, indicating that this kind of acid was the main component in the industrial deposit.

Biphasic mixture test

Figure 1 shows the results of biphasic mixture test. The upper images exhibit the phase separation after resting. The bottom images show the solids formed during the test, after drying. By analyzing brines with the same composition (0.7 g/L of sodium bicarbonate), at different pHs, it is observed that the results are very different from each other. The organic phase (upper) is clearer for brine at pH 8.0 than for that at pH 6.4, being observed a yellowish color in the latter. This is probably due to the presence of ARN (brown in color) which at pH 6.4 is less dissociated and more available in the oil phase.
It is also noticed a difference between the solids formed from brines with pH 8.0 and 6.4. In pH 8.0, the solid is dispersed in the brine (with a whitish appearance) and, after being extracted, it has a lighter color and is spread over the entire surface of the filter paper. For brine with pH 6.4, the solid is brown, and lumpier and smaller quantity than those for pH 8.0. This suggests that, at lower pH, there is the formation of less amount of calcium naphthenates, as already reported in the literature [10].

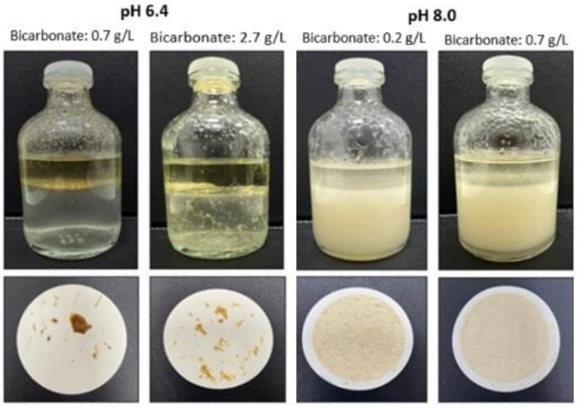

Figure 1. Photographs of the results of the biphasic mixture tests. Upper images: phase separation after resting. Bottom images: respective solids formed during the test. Source: prepared by the author.

Oscillatory interfacial rheology

Using oscillatory interfacial rheology, it was possible to evaluate the formation of the interfacial film over time, observing the values of G’ (elastic modulus) and G” (viscous modulus). In the beginning of the test, when no film exists at the interface, G” is higher than G’. If G’ increases and G” decreases until crossing each other, it means that a film of naphthenate was formed. Figure 2 shows G’ and G” as a function of time for the model systems with 0.7 g/L of sodium bicarbonate, at pH 6.4 and 8.0, without additive. At pH 8.0 (Fig 3a) the film is formed in a shorter time (12 min) than at pH 6.4 (30 min) (Fig 3b). This can be explained by pH 8.0 provoking greater dissociation of ARN’s to interact with metal ions present in brine [7].

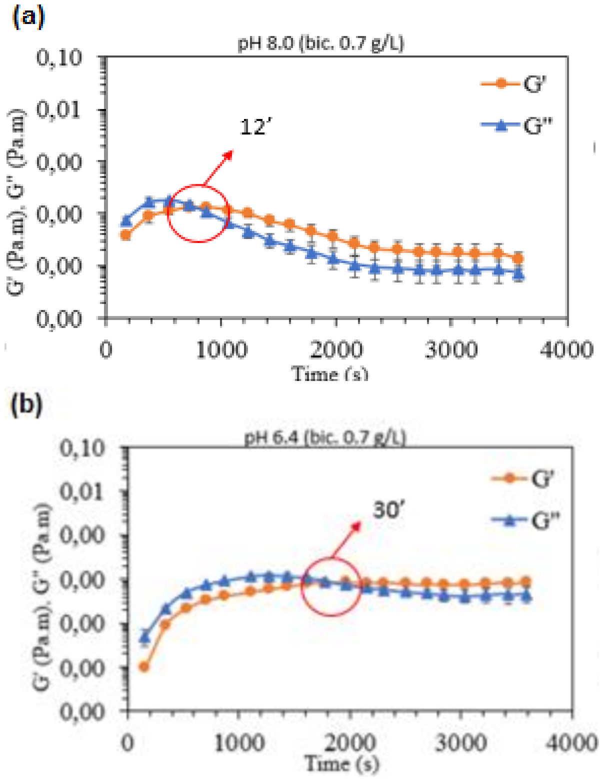

Figure 2. G’ and G” at the interface for the system constituted of brine (0.7 g/L of sodium bicarbonate) and ARN (25 mg/L) in toluene, as a function of time: (a) pH 8.0 and (b) pH 6.4.

Table 1 summarizes the crossing times of G’ and G’’ for the systems at pH 6.4 and 8.0, for different concentrations of sodium bicarbonate, without and with additives (at different proportions of surfactant:monoacid). For the model systems, without additive, using brine at pH 6.4, the time for the film formation (~30 min) was not changed as increasing the sodium bicarbonate concentration from 0.7 to 2.7 g/L, because the difference is within the error of the analysis. Most likely, this pH does not favor ARN dissociation. For model systems, without additive, using brine at pH 8.0, the time for film formation decreased ad increasing the concentration of sodium bicarbonate: at 0.2 g/L and 0.7 g/L of sodium bicarbonate, the crossing times were 20 min and 12 min, respectively. This confirms that calcium carbonate can act as a nucleation point for the formation of naphthenate. Moreover, the film formation is faster for pH 8.0 than pH 6.4: at the same sodium bicarbonate concentration (0.7 g/L), the G’ and G” crossing time were 12 min and 30 min, respectively. Even decreasing the concentration of sodium bicarbonate to 0.2 g/L, at pH 8.0, the crossing time is faster (20 min) than those observed for pH 6.4 and higher concentration of sodium bicarbonate (30 min at 0.7 g/L and 32 min at 2.7 g/L of sodium bicarbonate).

Table 1. Crossing time of G’ and G’’ at two pH’s and different sodium bicarbonate concentration, without and with 10 mg/L of additive (at different proportions of surfactant:monoacid).

Sample	**Crossing time of G' and G" (min)**
pH 8.0 (bicarbonate 0.7 g/L) + ARN	12’ ± 2
pH 6.4 (bicarbonate 0.7 g/L) + ARN	30’± 2
pH 8.0 (bicarbonate 0.2 g/L) + ARN	20’± 2
pH 6.4 (bicarbonate 2.7 g/L) + ARN	32’± 2
pH 8.0 (bicarbonate 0.7 g/L) + ARN + U300 (5 mg/L) + BA (5 mg/L)	51’± 2
pH 6.4 (bicarbonate 0.7 g/L) + ARN + U300 (5 mg/L) + BA (5 mg/L)	*
pH 8.0 (bicarbonate 0.2 g/L) + ARN + U300 (5 mg/L) + BA (5 mg/L)	*
pH 6.4 (bicarbonate 2.7 g/L) + ARN + U300 (5 mg/L) + BA (5 mg/L)	*
pH 8.0 (bicarbonate 0.7 g/L) + ARN + U300 (2.5 mg/L) + BA (7.5 mg/L)	17’± 2
pH 6.4 (bicarbonate 0.7 g/L) + ARN + U300 (2.5 mg/L) + BA (7.5 mg/L)	*
pH 8.0 (bicarbonate 0.2 g/L) + ARN + U300 (2.5 mg/L) + BA (7.5 mg/L)	31’± 2
pH 6.4 (bicarbonate 2.7 g/L) + ARN + U300 (2.5 mg/L) + BA (7.5 mg/L)	50’± 2
pH 8.0 (bicarbonate 0.7 g/L) + ARN + U300 (7.5 mg/L) + BA (2.5 mg/L)	*
pH 6.4 (bicarbonate 0.7 g/L) + ARN + U300 (7.5 mg/L) + BA (2.5 mg/L)	50’± 2
pH 8.0 (bicarbonate 0.2 g/L) + ARN + U300 (7.5 mg/L) + BA (2.5 mg/L)	*
pH 6.4 (bicarbonate 2.7 g/L) + ARN + U300 (7.5 mg/L) + BA (2.5 mg/L)	42'± 2

* No crossing was observed during the analysis time, that means, no film was formed

In all cases, the additive delayed or inhibited the film formation, when comparing with the same system without additive. For both pH (6.4 and 8.0), the increase in sodium bicarbonate concentration decreases the efficiency of the additive.

For pH 6.4, using the additive U300:BA 75:25 m/m, the film formation was delayed for both sodium bicarbonate concentrations. Using U300:BA 25:75 m/m, the film formation was inhibited for sodium carbonate concentration of 0.7 g/L, however for higher sodium carbonate concentration (2.7 g/L), the film formation was only delayed. The best performance was observed for U300:BA 50:50 m/m, since the film formation was inhibited for both sodium bicarbonate concentrations.

For pH 8.0, the best performance was observed for U300:BA 72:25 m/m, where the film formation was inhibited for both sodium bicarbonate concentrations. Using U300:BA 50:50 m/m, the film formation was inhibited only for lower concentration of sodium bicarbonate (0.2 g/L) and using U300:BA 25:75 m/m the film formation was only delayed for both concentrations of sodium naphthenate.

Conclusions

Biphasic mixture tests showed different aspect of naphthenates at different pH’s. Without additive at pH 6.4, the bicarbonate concentration did not affect the deposit formation. On the other hand, at pH 8.0, the increase in bicarbonate concentration increased the amount of solid precipitate, which was formed more quickly. This pH favors the formation of naphthenate, due to the greater dissociation of ARN, which interacts with metal ions at the interface to form naphthenates. Therefore, the decrease in pH shifts the reaction equilibrium, disfavoring the formation of naphthenates. The best performances of the formulation U300:BA were obtained at 50:50 m/m and 75:25 m:m for pH 6.4 and 8.0, respectively. The increasing in bicarbonate concentration decreased the formulations efficiency in both pH. These effects were expected since carbonate ions can act as nucleation point for the growth of naphthenate crystals and higher pH's favor the formation of naphthenates.

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