



## Evaluation of the influence of the hydrophilic-lipophilic balance of the additive on its performance in inhibiting the formation of calcium naphthenates

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### Abstract

Many crude oils present high levels of acidity due to the presence of naphthenic acids, which under certain conditions form insoluble salts in water and/or oil. In turn, these salts can accumulate at the water-oil interface, generating operational difficulties in the oil industries. Acids can be injected to minimize the problem; however, they contribute to the corrosion. Chemical additives are a good alternative to avoid formation of the deposits or, at least, provoke the formation of a weak film. In this work, four commercial molecules based on ethoxylated nonylphenol were used, varying the hydrophilic-lipophilic balance (HLB, 12.3-17.1), to evaluate their action on calcium naphthenate formation. Therefore, tetraprotic acid (ARN) was extracted from an industrial deposit and was characterized to be used in the tests. The additives were used at 100, 500, 1000 and 2000 ppm. The performance was evaluated by biphasic mixture test and oscillatory interfacial rheology (using Du Nouy ring). The performance increased as increasing additive HLB and concentration, within the range tested in this work. Although no precipitate was observed at all the conditions used, interfacial rheology shows the formation of a weaker deposit, which does not cause the operational problems as the hard one.

### Keywords

Flow assurance; naphthenic acids; calcium naphthenates

### Introduction

Technological advances and population growth have caused an increase in energy demand, generating a concern that oil reserves, under current production conditions, are not sufficient for this growth, with a rapid depletion of oil resources [1][2].

Unconventional crude oil reserves, which include heavy crude oils with high acidity, bitumen, and tar sands, represent more than 70% of the world's total reserves [3][2]. However, despite being abundant, these oils are very viscous and acidic, due to the presence of carboxylic acids, called naphthenic acids (NAs) [4]. The term "naphthenic acid", which corresponds to saturated cyclic compounds, is used to refer to all types of acids found in petroleum, including linear saturated and linear branched [5][6].

Pressure and temperature variations during oil production can induce the interaction of NAs with components present in the produced water. The existence of NAs in the medium has been associated with corrosion, stabilization of emulsions, deposition in processing units and blocking of formation pores [7]. The NAs, under certain conditions, have the potential to

form salts (through interaction with metallic ions) not soluble in water and/or oil, which accumulate at the interface, generating operational problems due to restriction or blockage of ducts and equipment, causing difficulties in flow assurance [8][9].

Although monoacids are more abundantly present in petroleum, a restricted group of high molar mass tetraprotic naphthenic acids, called "ARN", is dominant in the deposition of naphthenate salts, even though their mass concentrations are much lower than monoacids [10].

All types of naphthenates can cause production problems, but sodium and calcium naphthenates are the most commonly reported. The precipitate from calcium naphthenates appears as a hard deposit when exposed to air. This is because of the four terminal carboxylic groups, tetra acids can easily interact with calcium at the interface creating a lattice structure. On the other hand, sodium naphthenate is usually a soft emulsion or slurry [11].

The most widely used form of chemical control occurs with the injection of acid, usually acetic acid, aiming at lowering the pH to obtain a lower degree of ARN dissociation. This occurs because the interfacial tension

increases and reactions with metal ions are suppressed, also decreasing the stability of emulsions with naphthenic acids. However, this method requires high amounts of acid to achieve the desired effect, increasing corrosion and consequently decreasing the lifetime of the pipelines [5][13].

Another method concerns the addition of products that form complexes with the divalent cations, removing them from the aqueous phase, preventing them from reacting with the ARNs. However, it should be considered that the concentration of ions in the produced water can be very high, requiring large volumes of the additive [13].

Fouling by deposition of naphthenates is an adversity that has been reported for years to date. However, the understanding of its formation, deposition and mitigation is still not satisfactory.

## Methodology

### Experimental procedures

#### Naphthenic tetraprotic acids extraction and characterization

The procedure to extract the tetraprotic acids from the industrial deposit consisted of two steps: (i) to clean the deposit, which consists of removing excess of oil and impurities; and (ii) to extract the naphthenic acids, which consists of converting calcium naphthenate to naphthenic acid.

In the first step, deposit and toluene at 1g:6mL proportion were magnetic stirred four 3h. Then, the deposit was separated by vacuum filtration and dried at room temperature for 24 h. This procedure was repeated until the solvent was practically colorless. Using a Soxhlet extractor and toluene, the deposit was purified. After that, the deposit was dried at room temperature for 24 h. All this procedure was repeated sequentially using two other solvents: dichloromethane and methanol.

In the second step, the so purified deposit was mixed with a solution of chloroform and hydrochloric acid (150 mL of chloroform and 20 mL of 6M hydrochloric acid for each gram of the deposit) under magnetic stirring for 3 h, producing a biphasic mixture. Using a separation funnel, the organic phase (containing the ARNs) was recovered and the solvent was evaporated at room temperature [4].

$^1\text{H-NMR}$  was used to characterize the product.

#### Biphasic mixture test

In order to carry out the two-phase mixture tests, it was necessary to previously prepare the solutions for the organic and aqueous phases. The organic phase was composed of 1 g/L ARN in toluene. The aqueous phase consisted of a mixture of salts and especially with a concentration of 14 g/L, the pH being adjusted to a value between 8 and 9.

#### blank test

To perform the biphasic mixture blank test, 2 mL of saline solution and 2 mL of organic solution containing only naphthenic acids were added to a glass tube. Then, the container was capped and shaken, manually and vigorously, for 60 seconds, in order to maximize the contact between the acid and the cations. Subsequently,

the flask was kept at rest for 24 hours to promote the possible agglomeration of solids, as well as phase separation to observe the test result.

#### Test with commercial additive

The procedure performed was exactly the same as in the blank test, differing only in the addition of the additive to the 2 mL of toluene containing naphthenic acids. In this experiment commercial surfactants based on ethoxylated nonylphenol were used with HLB values of 12.3, 13.3, 14.1 and 17.1 [14], in different concentrations of 100 ppm, 500 ppm, 1000 ppm and 2000 ppm.

#### Oscillatory interfacial rheology

For the oscillatory rheological, a rheometer MARS III, Reotherm, coupled with a Du Noüy ring geometry sensor was used. All tests were performed at a 25°C.

To carry out the test, 20 mL of the aqueous phase were added to a glass cuvette. Then the sensor (Du Noüy ring) was positioned just below the air/water surface. Then, 20 mL of the oil phase were added upon the water phase, and the sensor was repositioned to the water/oil interface.

## Results and discussion

### Naphthenic tetraprotic acids extraction and characterization

The industrial deposit initially appeared as a hard solid with a very dark and lumpy color. After the cleaning and purification process, a beige color was observed, with a more powder-like and non-greasy appearance. This step exhibited a 33.32% yield.

From the clean deposit, naphthenic acids were recovered from the protonation of naphthenate ions. The material obtained was highly viscous and caramel colored. The yield of this step was 59% and the overall yield of the extraction of tetraprotic naphthenic acids, starting from the crude deposit, was 19.66%.

Nuclear magnetic resonance spectrum showed chemical shifts between 0.5 and 2.5 ppm, associated with carboxylic acids linked to aliphatic and cyclic hydrocarbon chains, which are the main structural characteristics of tetraprotic acids and other naphthenic acids. The peaks observed in the spectrum agree with literature for ARNs [15] [16].

### Additives evaluation

The biphasic mixture test is a qualitative analysis that is simple to perform that makes it possible to observe whether a given additive has the potential to inhibit the formation of calcium naphthenates. The formation of calcium naphthenates occurs at the oil/water interface, thus, the performance of the additives is evaluated in relation to the coalescence of droplets and the formation of an opaque film at the interface.

Figure 1 shows photographs of the results obtained in the tests performed. The best performance was observed for the additive with the highest HLB value (17.1) at the highest concentration (2000 ppm). As seen in Figure 1, the precipitate forms mainly in the aqueous phase, and the most water-soluble additive was the one that best fills the interface, inhibiting the contact between the acid

and the calcium cation. However, the interfacial oscillatory rheology results show a reduction in the elastic modulus for other HLB values and lower concentrations, indicating that the precipitates formed in the presence of the additive have a less elastic character and, therefore, less harmful to operations in the oil industry and gas.

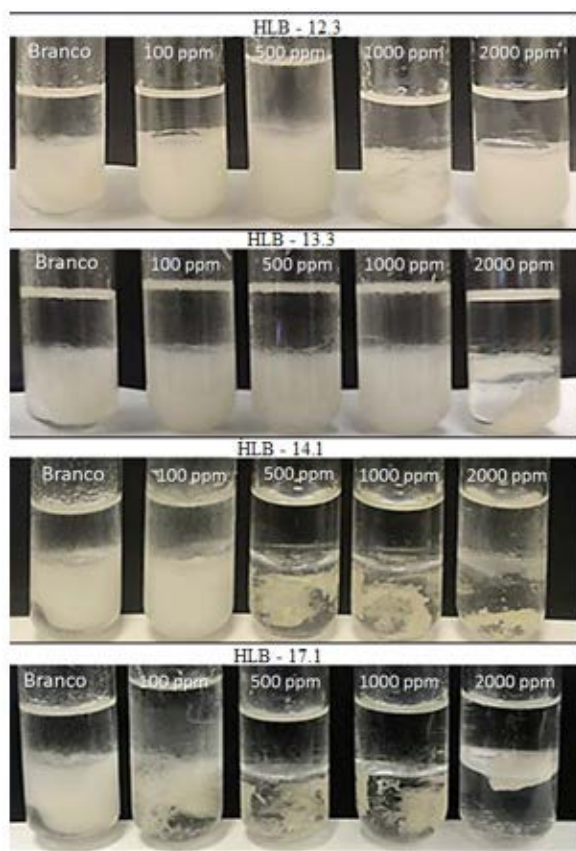


Figure 1: photographs of the results of the biphasic mixture tests with commercial surfactants. Source: prepared by the author.

## Conclusions

ARN type naphthenic acids were efficiently extracted from an industrial deposit with ~20% yield. Two-phase mixing tests qualitatively evidence the formation of precipitates, indicating that, in the range of 12.3 to 17.1 HLB, the additive with the highest HLB presented the best performance. Interfacial oscillatory rheology tests indicate the formation of film, quantify the strength of the precipitate, being able to perform a more assertive assessment regarding the performance of the additive, as well as the required concentration.

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## Responsibility Notice

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