EFFECT OF β-CHOLANIC ACID AND pH ON THE STABILITY OF WATER-IN-MODEL OIL EMULSIONS

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Asphaltenes fractionated from Hondo Crude Oil (a heavy crude from off-shore California) were dissolved in mixtures of toluene and heptane to create model oils. The emulsion stability of water-in-model oils was investigated over a range of pH. High pH (around 12) gave rise to water-in-oil emulsions with very high stability. However, the addition of 5-β-Cholanic Acid (β-CA), a carboxylic acid very similar to naphthenic acids found in petroleum fluids, to the model oil reduced dramatically the emulsion stability. This effect was more significant at higher pH (pH 12). Moreover, the amount of β-CA that destabilized the water-in-oil emulsion at pH 12 was around 500 ppm. These results suggested that the presence of β-Cholanic Acid or other naphthenic acids with similar structure could prevent the formation of stable W/O emulsions. With this in mind, water-in-petroleum emulsions were prepared in order to study the addition of β-CA to different whole crude oils and evaluate the stability of the emulsion formed at high pH. The results from the later study were very satisfactory and demonstrate that carboxylic acids with a similar molecular structure to β-CA (that is, a carboxylic acid for which its hydrophobic moiety is largely aliphatic) could break asphaltenic-film-stabilized emulsions.

Introduction

The existence of emulsions in both the production and refining of crude oil is one of the most persistent problems facing the petroleum industry. At the production end, emulsions are generated when water is coproduced with petroleum or pumped into the well to aid in petroleum recovery and this mixture passes through the wellhead, pipe bends, and choke valves. At the refinery, water is added to generate a large oil-water interfacial area to aid in the extraction of salts from the crude oil. The emulsions produced from the processes mentioned above do not easily resolved into neat crude and water phase and a certain volume of the emulsion remains [1-3].

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The mechanism of water-in-oil emulsion stabilization is not fully understood. The primary means, however, by which water-in-petroleum emulsions are stabilized is by mechanically strong elastic films formed by self-assembling asphaltenes [4-6]. Asphaltenes are the portion of petroleum insoluble in an n-alkane solvent (usually n-pentane or n-heptane). Asphaltenes are polydisperse with respect to molecular weight and chemical functionality. The common structural theme among asphaltenes is a planar, polyaromatic, fused ring core imbedded with polar functionality, surrounded by aliphatic side chains and naphthenic rings [7-10]. Asphaltenes contain many heteroatom functional groups. Some of the functional groups are hydrophilic while the hydrocarbon structure of asphaltenes is hydrophobic. Hence, the asphaltenes can be surface active and may adsorb on the water-oil interface and stabilize emulsions. Since the asphaltenes in crude oil are known to contain acidic and basic groups, the pH of the water in an emulsion can be expected to affect both the quantities and types of materials constituting the interfacial film. The aqueous-phase pH was indeed found to significantly affect the physical properties of the adsorbed films (e.g. rigidity and mobility), which led to laboratory tests of pH adjustment in emulsion breaking [11-12].

In the recent years the production of crude oils with high amounts of naphthenic acids has increased [13]. Certain problems are related to this type of crudes and a better understanding of the chemistry of the naphthenic acids is therefore of interest. The naphthenic acids can affect the emulsion stability directly or through interactions with other crude oil components. The naphthenic acids and their soaps are surface/interfacially active. Hence, they will accumulate at water-oil interfaces and stabilize colloidal structures [13-16]. Naphthenic acids are defined as carboxylic monoacids with the generic formula RCOOH, where R is any cycloaliphatic structure. However, in general, the term “naphthenic acid” is used to describe all carboxylic acids present in crude oils, also including aromatic and acyclic acids. This class of material is, like most petroleum fractions, a complicated mixture of compounds. Characterization studies of these acids have been carried out by means of many different methods and analytical techniques [14]. Based upon these studies naphthenic acids can be described mainly as C_{10}–C_{50} compounds with 0–6 fused rings, most of which are saturated, where the carboxylic acid group is attached to a ring through a short side chain [13]. The fact that naphthenic acids with similar molecular weight and total acid number (TAN) might have remarkably different molecular structures [13] and ability to stabilize emulsions increases the complexity of mixtures of these materials.

Ese and Kilpatrick [13] have studied a variety of acids and their corresponding soaps in order to investigate how these compounds interact in aqueous solutions at different pH, and how the association structures relate to emulsion formation and stability. The formation of aggregates

and hence, the stabilizing properties of this class of material were strongly sensitive to the relative proportion of uncharged acid and charged soap anion.

It is observed that the nature of the hydrophobic moiety of the acidic species and the pH of the aqueous has a very strong influence on the stability of the water-in-oil emulsions formed [13]. Specifically, with naphthenic acids for which the hydrophobic moiety is largely aliphatic, such as naphthenic rings and alkyl or alkenyl tail groups, the emulsions are strongly destabilized at high pH (that is, when the acidic species is charged at the oil-water interface). On the other hand, when the hydrophobic moiety is aromatic or fused aromatic, the emulsion stability is strongly enhanced. With this in mind, an alternative approach to destabilizing water-in-oil emulsions is with acidic species which strongly solvate the asphaltenic aggregates and which, when charged, strongly adsorb to the oil-water interface and prevent the creation of an ordered asphaltenic film.

In the present work, the effect of a model naphthenic acid (5-β-Cholanic Acid) on the emulsion stability as an alternative approach in order to prevent the asphaltenic-film stabilization was studied. The 5-β-Cholanic Acid have been used as a model compound because the structure of this chemical is believed to resemble the naphthenic acids found in crude oils.

Materials and Methods

Chemicals

All chemicals utilized in the experiments were high purity compounds delivered from different suppliers. They were used as supplied without further purification. The naphthenic acid used was 5-β-Cholanic Acid (99%, Sigma). It was used as a model compound. The chemical structure of the β-CA is presented in Figure 1. Toluene and *n*-heptane (HPLC grade) obtained from Fisher Scientific were used in order to prepare model emulsions. NaOH (98%, Fisher) was used to adjust the pH in the aqueous phase. NaCl (99.5%, Fluka) was added to the water phase in order to modify the ionic strength of the solution.

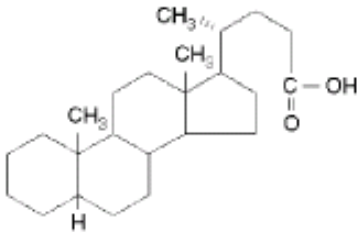

Figure 1. Chemical Structure of β-CA

Asphaltene and Petroleum Source

Asphaltene precipitated from Hondo Crude Oil (a heavy crude oil from off-shore California) were used to prepare water-in-model oil emulsion dissolving them in mixtures of heptane and toluene (HepTol). Different amounts of β-CA were added to the mixture in order to study the effect of this carboxylic acid on the stability of the emulsions.

Whole crude oils doped with β-CA were used to prepare water-in-crude oil emulsion in order to evaluate the results obtained with the above-cited model emulsions. The crude oils used in the present study were: a) Hondo Crude Oil (a heavy crude oil from off-shore California); and b) Brazil Crude Oil (a heavy and acidic crude oil from Brazil). These crude oils are asphaltene rich and vary in viscosity, resin content and asphaltene H/C ratio. Basic crude oil and asphaltene properties are summarized in Table 1.

Table1. Summary of Crude Properties.

Crude	Asphaltene Content, wt%	Resins-asphaltene ratio	TAN (mg KOH/g)
Hondo	14.8	1.39	0.39
Brazil	3.08	2.3	3.83

Asphaltene precipitation and fractionation

The crude oils were stored near 0°C in sealed containers under an argon blanket to minimize possible oxidation. The crude oil was warmed to room temperature and shaken vigorously to ensure homogeneity before sampling. Aliquots of 10–15 grams of Hondo Crude Oil were diluted with *n*-heptane 40:1 by volume and gently shaken for 24 hours. Since the crude oils were viscous and only partially soluble in heptane, the flasks were initially hand shaken to completely disperse all material. After the continuous shaking, the precipitated asphaltenes were removed by vacuum filtration through 15-cm-diameter 1.5 μm Whatman 934-AH glass microfiber filter paper. The filter cake was rinsed with 10-ml aliquots of *n*-heptane to remove any maltenes. All solvents used were HLPC grade (from Fisher Scientific). Additional aliquots of heptane were added to the filter cake until the washings eluted through the filter paper were clear in color. The filtrate was isolated and methylene chloride was used to redissolve the asphaltenes under partial vacuum. The methylene chloride–asphaltene solution was rotary evaporated under partial vacuum at 40°C. After evaporating a substantial volume of solvent, the remaining solution was transferred to glass jars and placed under an argon stream for further drying. Once nearly dry, the samples were moved into a nitrogen-flushed vacuum oven at 50°C for 24–36 hours.

Emulsification and Stability Measurements

Water-in-oil emulsions were prepared by homogenizing water and model oil solutions containing asphaltenes and 5-β-cholanic acid (or even just asphaltenes) or whole Crude Oils.

Preparation of the oils.

For the model oil experiments, Hondo asphaltenes were weighted into 20-ml jars and dissolved in toluene, the mixture was shaken overnight to ensure the complete dissolution/dispersion of asphaltenes. The heptane was added to adjust the state of asphaltene solvency and shaked again overnight. The final asphaltene concentration was 1% (w/w) in 4 mL of HepTol. The range of heptol was varied from 10 to 100% (v/v) of toluene.

The emulsions containing the model carboxylic acid were prepared by adding the appropriate amount of this compound to the overnight-shaked mixture of asphaltene/toluene above mentioned, and shaking the new mixture (β-CA/asphaltene/toluene) again for 12-24 hours before adding the heptane. The concentration of β-CA used to study the effect of this naphthenic acid on asphaltene-stabilized emulsions was from 0.005 to 2% (w/w). The asphaltene concentration was 1% (w/w) and the Heptol ratio was 50:50 (v/v).

For the experiments with crude oils, the whole crudes were heated at 60°C for 2 hours and shaken by hand from time to time to ensure homogeneity of the crude oil samples. After this homogenization process an appropriate amount of petroleum was weighted into 20-ml jars. Then, a 40:60 (v/v) mixture of HepTol (heptane: toluene) was added to decrease the viscosity of the crude. The crude:heptol ratio was 1:1 or 3:7. It permits a better handling of the final sample. After shaking for 3 hours, to ensure a good homogenization between the crude and heptol, the β-CA was added to the mixture and shaking overnight.

Preparation of the aqueous-phase and Emulsification.

The aqueous phase (deionized water) with 1% (w/w) NaCl was used for preparing the emulsions. After NaCl dissolution, the pH of the aqueous-phase was adjusted to 6, 7 or 12 with NaOH. A 6-ml volume of the water phase was added to the prepared model oil or whole crude oil solution (4 mL). The emulsification was carried out using a 750-W Virtis Cyclone IQ Homogenizer with a 6 mm rotor-stator mixing head. The oil and water phases were mixed at 15000 rpm for 5 minutes.

Following a 24-hours period of aging, a known mass of the emulsion was transferred into 2-ml microcentrifuge tubes. The emulsions were centrifuged for 1 hour at 14500 rpm in an Eppendorf MiniSpin Plus centrifuge. Each sample was centrifuged by triplicate. Usually, three

layers were observed following centrifugation corresponding to creamed oil, emulsion and coalesced water. Creamed oil was discarded and the resolved water was recovered by means of a glass pipette, and transferred to a pre-weighted vial. Emulsion stability were calculated from the volume of water resolved as the following expression:

$$\%\ water\ resolved = \frac{Mass\ water\ resolved}{Initial\ mass\ water\left(6\,ml\right)} * 100 \qquad (1)$$

Results

The effect of varying the aromaticity of the oil medium on the stability of the emulsion formed with 1% (w/w) Hondo asphaltenes in HepTol at pH 7 and 12 is shown Figure 2. The aromaticity of the oil medium, the heptane/toluene mixture, was modified increasing the proportion of toluene in the mixture. In the cited figure, higher amounts of water resolved indicate weaker emulsions because of increased droplet coalescence. In the other hand, lower values indicate reduced droplet coalescence and more stable emulsions.

The results shown in Figure 2 indicate that the aromaticity of the oil (% toluene in the heptol mixture) is an important factor in determining the stability of asphaltene-stabilized emulsions. Moreover, there is a range in the aromaticity of the medium for which a maximum stability is observed. Regarding to the aqueous-phase pH, it significantly effects the emulsion stability.

The effect of the aromaticity on the emulsion stability can be explained in light of the solubility state of the asphaltenes [12, 17]. The extent to which that asphaltenes are solvated is the controlling factor in determining the surface-active nature of the colloidal aggregates. That is, emulsion stabilized by individual asphaltene molecules, which are dissolved in the oil phase in the form of a molecular solution, are of little significance for crude oil, when compared with stabilization by colloidally dispersed asphaltenes. In highly aromatic solvents (toluene-rich) the aggregation of asphaltenes is presumably minimized by disrupting the π-π and hydrogen bonding associated with polar aromatic asphaltenes moieties. By reducing the toluene volume fraction, asphaltenes aggregated to a greater extend and were more prone to adsorb in the oil-water interface. The results obtained shown that the emulsions formed at pH 7 exhibit their highest stability between 40-50% toluene in Heptol. According to the literature [12, 17-18], the asphaltenes which are at or near the point of precipitation are more surface-active than those which are sufficiently solvated or molecularly dispersed. In the middle range of crude aromaticity (30-

50% toluene), the asphaltenes are most likely near or at the point of its solubility limit in the form of a fine dispersion, which is capable of adsorbing and stabilizing the water/oil interface by forming a barrier mechanically resistant to the coalesce of the water droplet. At pH 12, the emulsions were stable even in high aromatic solvent. It suggests that Hondo asphaltene can be solvated by forming aggregates bigger than the aggregates formed at pH 7 and/or a different type of association between asphaltene can occur. Moreover, it is likely that more surface-active compounds are available and/or they adsorb more strongly at the oil-water interface.

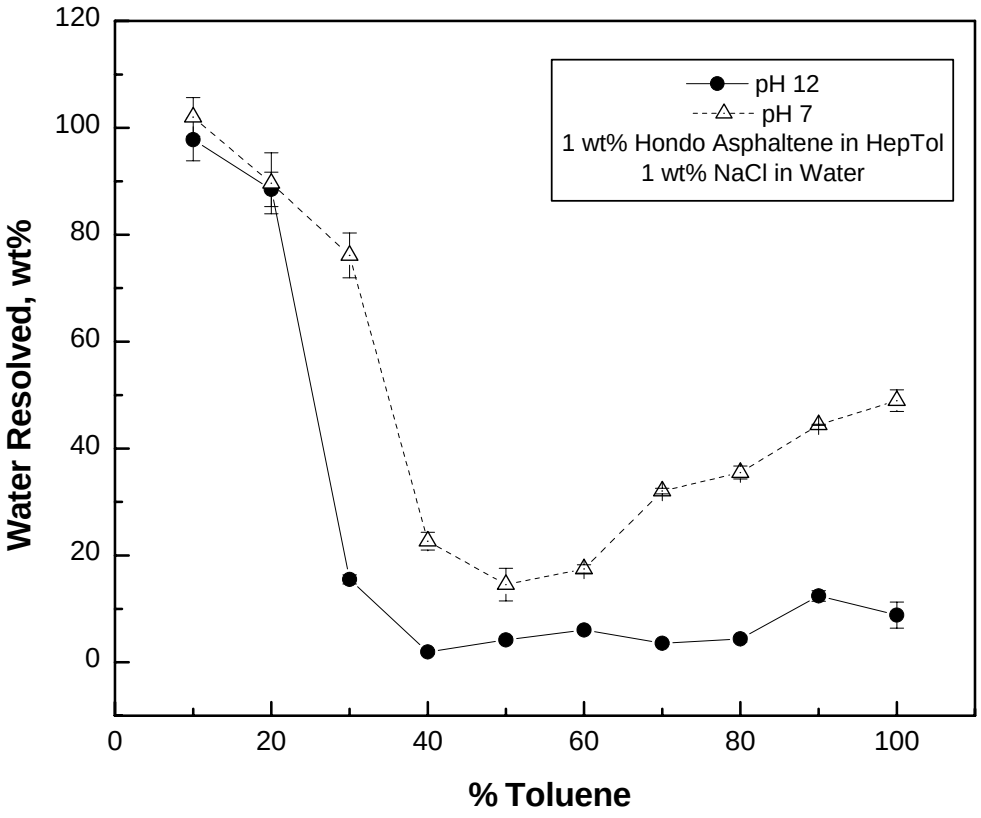

Figure 2. Effect of aromaticity and pH on the stability of the emulsion formed with 1 wt% Hondo Asphaltene

Finally, at pH 7 as well as at pH 12, in highly aliphatic solvents (i.e. at oil aromaticities lower than 20% toluene), the asphaltenes are precipitated out of solution. These larger aggregates were not simply able of effectively stabilizing the oil-water interface due to their size and inability to form cohesive film.

These previous results demonstrated that Hondo asphaltene itself can form very stable water-in-oil emulsions, being the maximum stability at 50% (v/v) of toluene. Thus, they were used to study the effect of a model carboxylic acid (β-CA) on the stability of asphaltene-stabilized emulsions.

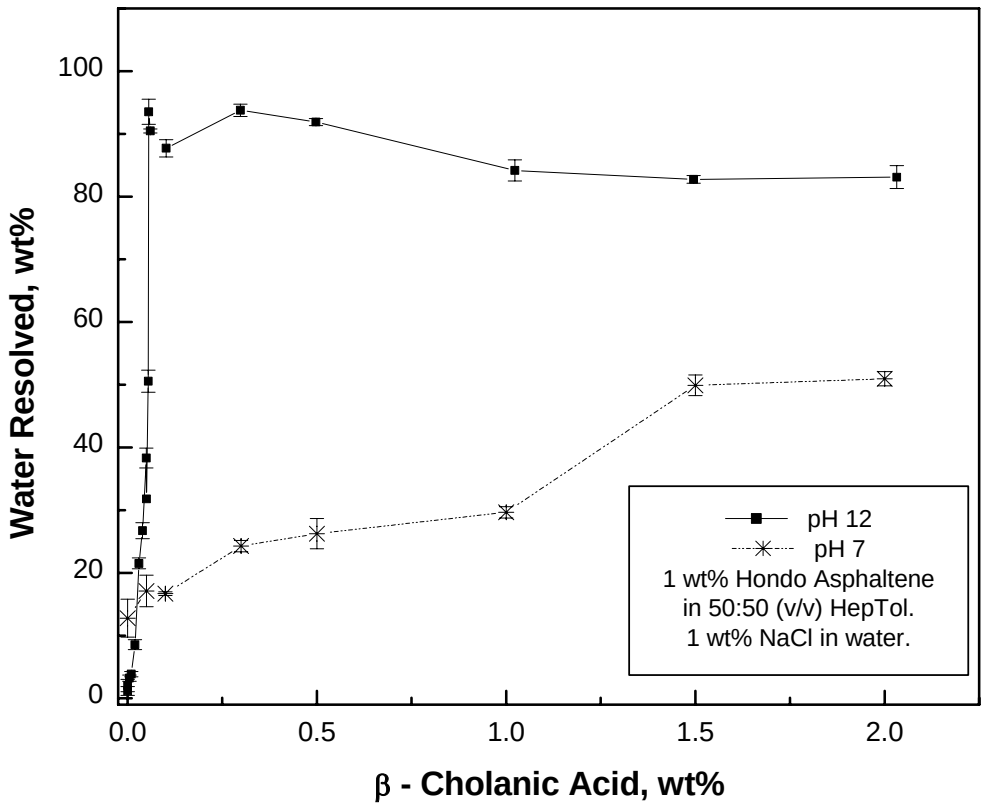

Figure 3. Effect of adding β-CA on the stability of asphaltene-stabilized model emulsions (1 wt% Hondo Asphaltene in 50:50 (v/v) heptol mixtures).

The Figure 3 presents the effect of the amount of β-Cholanic Acid added to the model oil on the stability of the emulsion at pH 7 and 12. As can be observed, at both pH's, the addition of β-CA reduced the stability of the emulsion, being this effect more noticeable at pH 12. Figure 3 shows that at pH 7 a moderate increase of the water resolved as the increase of the carboxylic acid. However, it was necessary around 1.5 wt% of β-CA in order to obtain around 50% of resolved water after centrifugation. On the other hand, at pH 12 the effect of adding the β-CA is highly significant in order to prevent the asphaltene-stabilization of the emulsion. That is, around 500 ppm of β-CA was enough to recover around 90-95% of the water after centrifugation.

The noticeable effect of the β-CA on the stability of asphaltenic-stabilized emulsions at pH 12 can be attributed to two possible effects. At high pH the acid/soap ratio is low. According to previous studies [13], no emulsion stability in acid/soap/oil mixtures is observed until protonated acid molecules dominate the chemistry in the systems, and then W/O emulsions are formed. As a second and more important effect, the β-CA could displace and/or compete with the asphaltenes aggregates for the W/O interfaces. Hence, it suggests that the presence of the 5-β-Cholanic Acid or

other naphthenic acids with similar structure (i.e. a structure with a high-aliphatic hydrophobic moiety) can prevent the formation of water-in-oil emulsions. Moreover, different optimal combinations between the size and type of the aliphatic hydrophobic moiety and the pH of the aqueous-phase could be implemented in order to use lower amounts of a carboxylic acid or a lower pH to destabilize emulsions.

The next step in this study was prepared water-in-crude emulsions to test the effect of adding β-CA on the stability of these emulsions. In Figures 4 and 5 the stability of the emulsions prepared with different whole crude oils (Hondo and Brazil, respectively) as a function of the β-CA concentration is presented. In all cases, the pH of the aqueous phase was 12 and the whole crude oils were diluted in heptol (it was described in the *Materials and Methods* Section).

The Figure 4 presents the effect of the addition of β-CA to Hondo whole crude oil on the water resolved after centrifugation for a crude/heptol-ratio of 1:1 and 3:7 (v/v). It means that the total asphaltene concentration of the mixture was around 7.5 and 4.5% (w/w), respectively. For the mixture with 30% (v/v) of Hondo Crude oil in heptol an important reduction of the stability (80% of water resolved) was reached with around 0.5 wt% of β-CA. In the case of the mixture with 50% (v/v) of Hondo Crude about 1 wt% of the carboxylic acid was necessary to destabilize the emulsion. It is important to mention that in a 10:90 (v/v) crude/heptol-ratio mixture (data not shown in the Figure) around 0.3 wt% of β-CA was enough to recover about 88% of the water after centrifugation. For this rich-asphaltenic crude oil, the amount of β-CA added to the mixture in order to get an important reduction of the stability was higher than for the model oils. It can be associated with the marked difference of the asphaltene concentration in the mixture and the presence of others indigenous-stabilizers present in the crude that could contribute to the observed stability. An increase of β-CA as the increase of the asphaltene content was necessary to break down the asphaltenic-stabilized emulsions. These results satisfactory show that naphthenic acid with a structure like to β-CA can be useful to prevent the stabilization by asphaltenic-films in water-in-oil emulsions. In the case of a crude oil with a high asphaltene content an alternative option to increase the concentration of the carboxylic acid can be the addition of a compound with a higher aliphatic hydrophobic moiety than β-CA.

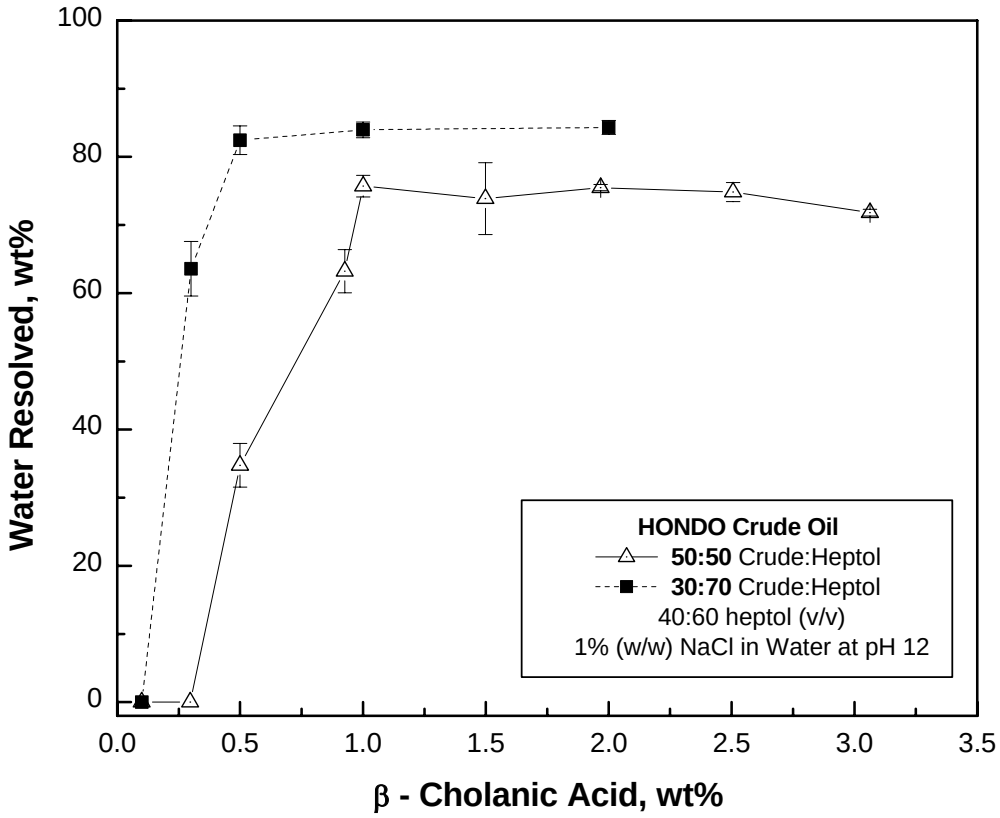

Figure 4. Effect of adding β-CA on the stability of emulsions formed with Hondo Crude Oil.

The water recovered from emulsions formed with Brazil crude doped with β-CA is illustrated in Figure 5. The asphaltene content of the crude is about 5 times lower that Hondo crude. However, for Brazil petroleum, around 2% (w/w) of β-CA was necessary to recover about 80% of the initial water. It can be explained from the fact that the Total Acid Number (TAN) of Brazil crude is around 3.73 mg KOH/g crude. It suggest that a very complex mixture of carboxylic acids can be present naturally in Brazil crude, which can interact with the petroleum components. Moreover, the average hydrophobic moiety of this complex mixture of naphthenic acid could be aromatic and enhance the stability of the emulsion. Thus, higher amounts of β-CA were required in order to destabilize the emulsions formed with the acidic Brazil crude oil. It can be support by the fact that the addition of 9-Antracene carboxylic acid (a model carboxylic acid which its hydrophobic moiety is purely aromatic) to the same model-oil used with β-CA (i.e., 1 wt% Hondo asphaltene in 50:50 (v/v) heptol) slightly enhanced the stability of the water-in-model oil emulsions (data not presented in this work).

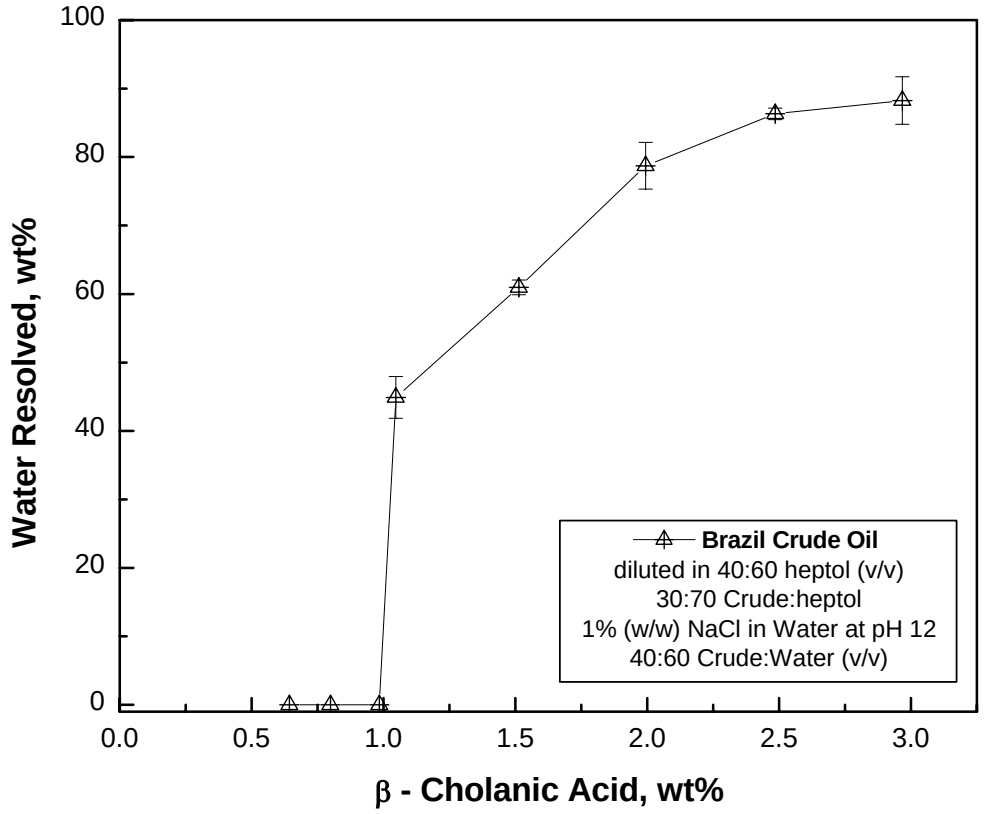

Figure 5. Effect of adding β-CA on the stability of the emulsions formed with Brazil Crude Oil.

Conclusions

In the present work, the effect of the addition of a model carboxylic acid on the stability of water-in-model oil and water-in-petroleum emulsions was studied. The results from this study tend to support the concept that the presence of naphthenic acids for which their hydrophobic moiety is highly aliphatic can reduced the stability of water-in-oil emulsions stabilized by asphaltenic-films, being this effect significant at high pH (around 12).

The evaluation of the effect of the addition of β-CA on water-in-petroleum emulsions demonstrated that this carboxylic acid was capable of destabilizing the emulsions formed with different whole crude oils. However, the amount of β-CA necessary to recover around 80% of water after centrifugation was higher than in the case of model oil emulsions, owing to the higher asphaltene content of the crude oil or the presence of a high concentration of indigenous-naphthenic acids.

The use of different optimal combination between the size and the type of the aliphatic hydrophobic moiety and the pH of the aqueous-phase instead of increasing the concentration of the

carboxylic acid could be used as an alternative option in order to destabilize high asphaltenic-stabilized emulsions.

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