Breaking of Water-in-Crude Oil Emulsions. 4. Estimation of the Demulsifier Surfactant Performance To Destabilize the Asphaltenes Effect

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ABSTRACT: Surfactant molecules are tested as water-in-crude emulsion breakers to attain the quickest separation rate in the so-called "proportional regime". A concept of demulsifier performance is proposed on the basis of the required demulsifier concentration to offset the effect of a given amount of asphaltenes. The experimental evidence allows one to rank the tested products and relate their performance to their hydrophilicity and molecular weight. Some evidence indicates that the presence of acids in the crude makes it easier to break emulsions and suggests that so-called "extended surfactants" can significantly shorten the demulsifying process.

■ INTRODUCTION

The breaking of the water-in-crude emulsions is still a technical challenge in the petroleum industry.[1] As discussed in the previous papers of this series,[2−5] the crude oil dehydration optimization may be seen as finding a synergistic effect between the natural (lipophilic) surfactants (referred to as asphaltenes in what follows) and the added demulsifier (usually a hydrophilic surfactant mixture). It has been known for more than two decades[6] that the proper dehydrant additive is such that the overall amphiphilic mixture at the interface, i.e., the asphaltenes and added demulsifier, exhibits an equal affinity for the oil and water phases according to the general phenomenology.[7,8] This physico-chemical circumstance corresponds to the so-called optimum formulation, which exhibits a very deep minimum in emulsion stability.[6−12] Fan et al.[13] established a relationship between the HLB and the concentration of demulsifier and its dehydrant effect. Peña et al.[14] found a relationship between systematic changes in the demulsifier and the stability of water-in-crude emulsions.

The affinity of the interfacial mixture depends on the hydrophilicity of the asphaltenes and demulsifier species and their proportions at the interface (indicated as X). For the sake of simplicity, the reasoning is carried out using the hydrophilic−lipophilic balance (HLB) concept of the amphiphiles. The characterisitic hydrophilic−lipophilic balance of the interfacial surfactant mixture at optimum formulation (HLB_{opt}) must be determined experimentally; however, it is generally close to 10, as a first approximation, according to a previous discussion.[2] If "A" (for asphaltenes) and "D" (for demulsifier) are the subscripts that describe the two amphiphilic species, then the optimum formulation is attained when the following relationship is satisfied at the interface:

$$X_A HLB_A + X_D HLB_D = HLB_{opt} \qquad (1)$$

According to the general phenomenology, the quickest phase separation is attained when X_D satisfies eq 1. In practice, the persistance of the emulsion is measured as a function of the concentration of the demulsifier (C_D), which is added to the system, and C_D^* is the optimum demulsifier value, which, in this case, corresponds to the minimum emulsion stability. The value of X_A and X_D in the interfacial mixture are not known; however, at low asphaltenes concentration, it was shown that they depend directly on the overall concentration of asphaltenes (C_A) and demulsifier (C_D) originally introduced in the bulk phases. The previous papers[2,3] have reported the demulsifier optimization as a function of the asphaltenes content, by means of the dilution of the crude oil with a solvent such as cyclohexane. They have shown that, when the concentration of asphaltenes (C_A) is higher than a so-called "threshold" T (typically 1000 ppm), then the value of C_D^* is essentially constant, regardless of the asphaltenes concentration. This result is consistent with the presence of a thick layer of asphaltenes gathered at the interface, with only the first layer interacting with the demulsifier. The remaining asphaltenes are acting out of the interface, according to some form of segregation or aggregation.[5]

What was reported as a new insight in the previous articles[2,3] was the fact that, below that threshold, the concentrations C_A and C_D^* are proportional; i.e., if there is twice as much asphaltenes in the oil phase, twice as much demulsifier is needed in the water phase. This range was called the proportional regime,[3] since it corresponds to the fact that, at optimum formulation, $X_D^*/X_A = X_D^*/(1 - X_D^*) = k_{interf}$. Because most of the amphiphilic species taken into consideration in C_D and C_A are finally adsorbed on the large interfacial area of the emulsion, it has been assumed[3] that

$C_D^*/C_A = k = k_{interf}$. Hence, the experimental map data plot of log C_A vs log C_D^* allows one to estimate k and calculate X_D^*, which is the proportion of D at optimum, calculated from

$$(1 - X_D^*)HLB_A + X_D^* HLB_D = HLB_{opt} \qquad (2)$$

HLB_{opt} may be accurately estimated with the same oil and water phases at the same temperature with a mixture of known surfactants, and it is generally close to 10; on the other hand, HLB_D may be also estimated by characterizing the demulsifier, as discussed elsewhere.[7,8] As a consequence, and as shown previously,[3] HLB_A may be estimated from eq 2 as a way of characterizing the natural surfactant (asphaltenes) lipophilicity.

As seen in eq 2, the contribution of the demulsifier is the term $X_D^* HLB_D$; hence, the attainment of an optimum formulation with demulsifier D depends on two factors, i.e., its hydrophilicity (HLB_D) and its concentration (C_D^*). It was shown, on a poly-ethoxylated surfactant series,[3] that, at higher HLB (more hydrophilic demulsifier), the C_D^* required is lower and, hence, X_D^* is lower.

In the present work, the main criterion to estimate the performance of the demulsifier will be the dosage needed to attain the quickest breaking at a given asphaltenes concentration, particularly at and above the threshold point T, since the corresponding C_D^* value is the concentration required at high asphaltenes content (i.e., in the real case).

■ REAGENTS AND EMULSION PREPARATION

The systems are composed of 5 mL of an aqueous phase containing the demulsifier at the proper concentration C_D and 5 mL of an oil phase, which is a crude oil diluted with a solvent (cyclohexane, unless otherwise specified), so that the asphaltenes concentration is C_A. Tested demulsifiers or pseudo-demulsifiers were the following substances, used alone: a very hydrophilic ethoxylated (20EO) sorbitan monololeate, sold as Tween 80 (symbolized as SM-15) with HLB = 15, provided by Sigma; triblock copolymer (CP) polyethylene oxide–polypropylene oxide–polyethylene oxide of the Pluronics series from BASF, sold as PE 4300, PE 6800, and PE 9400, and respectively labeled as CP-1750-14, CP-8000-21, and CP-4600-19, where the first number indicates its molecular weight and the second its HLB number.

Two so-called "extended surfactants"[15,16] that contain an intermediate polarity spacer between their head and tail groups were dodecyl-polypropylene oxide(14)-polyethylene oxide(20) $C_{12}PO_{14}EO_{20}$, synthesized in our laboratory, and dodecyl-poly-propylene oxide(12)–polyethylene oxide(2)-sulfate sodium salt $C_{12}PO_{12}EO_2SO_4Na$, supplied by Huntsman. Pure-grade cyclohexane was obtained from Fisher Scientific.

The oil phases were prepared as a crude oil diluted with cyclohexane to attain a certain asphaltenes concentration C_A for each of the tested crudes oils, which included the following: Boscan heavy crude oil (10° API, 14% asphaltenes, acidity = 0.8 mg KOH/g) from southwest of Maracaibo, Venezuela; Hamaca extra heavy crude oil (8–9° API, 11% asphaltenes, acidity = 2 mg KOH/g) and Cerro Negro extra heavy crude oil (8–9° API, 13% asphaltenes, acidity = 6 mg KOH/g), both from the Orinoco oil belt in western Venezuela; and San Jacinto heavy crude (10° API, 12.6% asphaltenes, acidity = 3–4 mg KOH/g), from the Amazonian Flank of the Andes in North Peru. The experimental procedure to prepare the samples is the one described in detail in previous papers.[2,3] It is worth remembering
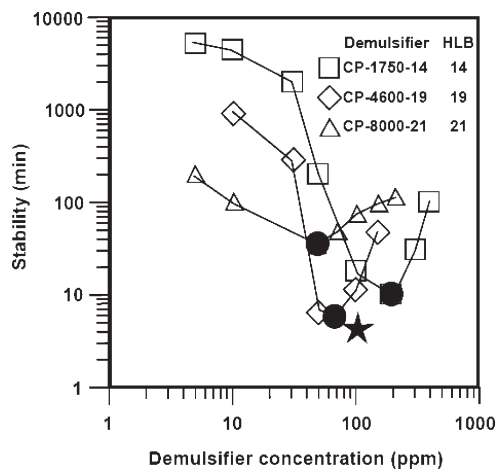

Figure 1. Emulsion stability versus demulsifier concentration C_D for different triblock copolymers. The asphaltenes concentration of 500 ppm is attained by diluting Hamaca crude oil with cyclohexane.

here that the demulsifier, which is a hydrophilic substance, is placed in the aqueous phase, which is a situation that mimics the equilibrated system condition, and thus allows better control of the process (to avoid any diffusion delay). This is not the case in actual practice, in which the demulsifier is added to the crude as a solution in an organic solvent, and then must migrate by convection and diffusion to the interface to combine with the natural surfactants. By placing the demulsifier in the aqueous phase, the lag time introduced by the migration to interface through the oil phase is eliminated and the time for coalescence is essentially that which is related to the formulation effect on the interdrop film (i.e., the one that depends on the demulsifier action to destabilize the emulsion). This also eliminates the influence of the oil viscosity in the transfer process of the demulsifier to the interface.

The 10-mL systems are pre-equilibrated at ambient temperature for 24 h. They then are poured into a 50-mL beaker and emulsified for 30 s at 11 000 rpm with a IKA Werk Ultraturrax turbine blender; finally, they are poured in a test tube, which is closed and kept at constant temperature (22 ± 2 °C). The water separation is monitored as the time elapses. The stability criterion is taken as the time (in minutes) required for 2.5 mL of the water phase (i.e., 50 vol %) to separate.

■ DATA PROCESSING AND DEFINITION OF THE PERFORMANCE CONCEPTS

For a given crude oil dilution with an asphaltenes concentration C_A, the emulsion stability is plotted versus the demulsifier concentration C_D. The value corresponding to the minimum stability is noted as C_D^* and refers to the optimum concentration or dose. Figure 1 indicates such plots for three different copolymers whose HLB is indicated as the last two digits. As in the previous article,[2] the black circle indicates the experimental or interpolated minimum stability for each plot, and determines the optimum C_D^* value of each demulsifier to produce the minimum stability. The star indicates the approximately best interpolated case for the series.

The variation of the optimum demulsifier dose C_D^* then is represented versus the asphaltenes concentration in a log–log graph, as in Figure 2. The plot has been found in the previous study[3] to exhibit two straight-line segments. At low concentrations, a line slope of unity indicates that C_D^* and C_A are proportional;
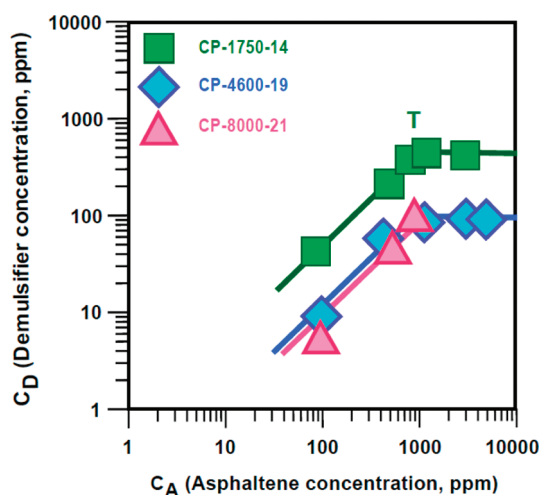
Figure 2. Plot of C_D^* vs C_A with three triblock copolymers in Hamaca crude oil diluted in cyclohexane.

this region is called the "proportional regime",[3] in which the asphaltenes/demulsifier mixture at the interface, indicated as X_D^* in eq 2, is constant. At high asphaltenes content, C_D^* is constant, regardless of the asphaltenes concentration C_A, in what has been called the "saturation regime".[3] In this case, only a part of the asphaltenes are mixed with the demulsifier at the interface, and an excess is located elsewhere, probably in a multilayer close to the interface.[5] The break point T between the two regimes is the so-called "threshold", and it is typically located at $C_{AT} \approx 1000$ ppm, and at a C_D^* value that is dependent on the demulsifier.

When the variations in C_D^*/C_A for different demulsifiers are plotted on the same map, as in Figure 2, two comparison criteria may be used. At a given concentration C_A in the proportional regime (unity slope zone), a lower C_D^* value indicates that less demulsifier is required to attain the optimum dose, hence exhibiting a higher-performance substance, as far as its effect in the interfacial mixture with asphaltenes is concerned, according to eq 2. The time required to separate 50% of the water for a given C_A concentration at the black circular points in Figure 1, brings additional information concerning the dehydration kinetics.

On the other hand, if the comparison is carried out above the threshold T in Figure 2, the result indicates the appropriate C_D^* concentration to use in practice, and it is useful, although it does not allow one to use eq 2 to determine the interfacial composition and the asphaltenes characteristic parameter.[3] The systems reported up to now tend to exhibit a threshold close to $C_{AT} = 1000$ ppm, which seems to be essentially constant for a family of demulsifiers and a given crude. If this is a general trend, it means that the second criterion (comparison of the C_D^* values for two demulsifiers above C_{AT}) lead to the same ranking as that in the proportional regime. Since the generality of this point is not known, the performance index concept is selected according to the first criterion, i.e., as the vertical location of the unity-slope segment of the proportional regime.

Figure 2 map allows one to evaluate the performance of different demulsifiers for the same crude oil. On the other hand, comparing the C_D^*/C_A plots for a given demulsifier with two crude oils allows one to estimate the relative performance of this demulsifier when mixed with different asphaltenes types.

Table 1. Basic Characteristics and Optimum Formulation for Different Demulsifiers with Hamaca Crude Oil Diluted in Cyclohexane at C_A = 500 ppm

demulsifier	HLB	MW	C_D^* (ppm)	t_{500}^* (min)
CP-1750-14	14[a]	1750	220	10
CP-4600-19	19[a]	4600	55	6
CP-8000-21	21[a]	8000	42	40
extended nonionic	6[b]−11[c]	1836	150	5
extended ionic	39[b]−20[c]	1140	50	4
SM-15	15[a]	1310	100	62

[a] Given by the manufacturer. [b] Determined using the Davies formula.[17] [c] Determined from the optimum formulation in mixture.[18]

■ RESULTS AND DISCUSSION

Test with Various Triblock Demulsifiers. Table 1 and Figure 2 show the results obtained with three triblock demulsifiers of different HLB values and molecular weights. In Table 1, the stability value, which is indicated as t_{500}^*, is the minimum time required for the separation of 50% of the aqueous phase at $C_A = 500$ ppm, and it corresponds to a C_D^* dose for each demulsifier at this asphaltenes concentration. The vertical shift in the proportional regime line of Figure 2 indicates that the more hydrophilic the surfactant is, the more performing it is, i.e., the lesser is its required amount C_D^*. This result is given in ppm, which is noteworthy, because the molecular weights (MW) are quite different. The trend corroborates that which was found with ethoxylated nonylphenol series[3] and is a consequence of eq 1; i.e., when HLB is higher, X_D is lower. In the present case, it may be said that CP-4600-19 is 4 times better than CP-1750-14, since the required amount to attain the best formulation is 4 times lower. Nevertheless, this improving tendency, along with the hydrophilicity, seems to fade away when the surfactant becomes too hydrophilic, and tend to partition in water, as discussed previously.[2] For the most hydrophilic triblock CP-8000-21, the C_D^* reduction is just 25%, when compared to CP-4600-19. However, the stability value is quite altered by the surfactant type, and some explanation may be presented. As the hydrophilicity increases (from CP-1750-14 to CP-4600-19), the breaking time becomes shorter, i.e., the performance is improved not only because the C_D^* is much less (from 220 ppm to 55 ppm), but also because the time required to break 50% of the emulsion is shorter, despite a higher MW of the demulsifier. As the hydrophilicity increases even more (from CP-4600-19 to CP-8000-21), the gain in C_D^* is not very significant; however, on the other hand, the (minimum) breaking time increases considerably, probably because of the presence of a lower driving force to adsorb and a slower migration process, because of an increased MW. This confirms that increasing the hydrophilicity of the demulsifier is surely a good move, but that two drawbacks should be avoided, i.e., a too-high hydrophilicity and a too-large MW. In addition, a hydrophilicity that is too high is, of course, an intrinsic disadvantage in the actual practice, because it reduces the solubility of the demulsifier in the oil phase, thus resulting in some difficulty for its introduction in the crude.

Another difference shown in Figure 2 is that the threshold is not attained for CP-8000-21 at $C_A = 800$ ppm. Above this last reported C_A value (at 1000 ppm and higher), the stability of the emulsion is quite high, i.e., over three days; hence, the experiment is not performed up to the occurrence of the minimum stability and the threshold is not determined.
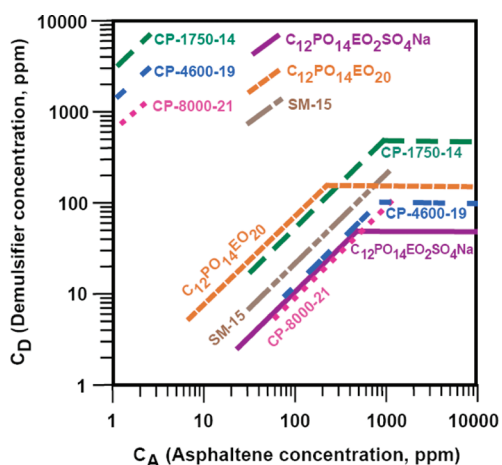
Figure 3. Plot of C_D^* vs C_A for different demulsifiers with Hamaca crude oil that has been diluted with cyclohexane.

As a partial conclusion, it may be said that the best practical performance from the C_D^* dose and the kinetics result is attained by CP-4600-19, which is a rather hydrophilic (but not too hydrophilic) surfactant, and a rather high (but not too high) MW surfactant. In other words, the 30% gain in C_D^* from CP-4600-19 to CP-8000-21 is not compensated by the factor-of-6 increase in the shorter separation time scale.

Test with Various Surfactant Families. In Figure 3, the same types of plots are shown for different types of surfactants, i.e., the previous triblocks, an ethoxylated polysorbate (SM-15), and two extended surfactant species with anionic and nonionic head groups. The experimental points are not shown in Figure 3, to allow a better comparison; however, as may be seen in Figure 2, the fit is generally satisfactory.

First of all, the general phenomenology with a proportional regime and a saturation zone is exhibited by all types of surfactants with a threshold, which is well-defined for some surfactants at $C_{AT} \approx 1000$ ppm. For other surfactants, there is not enough separation after 3 days and only the proportional regime is shown in the map.

Second, the vertical location of the unity-slope straight line segment (proportional regime) allows one to establish a performance comparison on a C_D^* weight concentration basis of all of the cases of tested surfactants:

- The performance ranking based on the required dose to attain the optimum is essentially in the same order as the hydrophilicity, although with some slight shifts.
- The extended nonionic surfactant $C_{12}PO_{14}EO_{20}$ exhibits a similar performance as the triblock copolymer CP-1750-14, although the threshold point T is higher for the triblock species. For these two surfactants, the ethylene oxide contents are, respectively, 47% and 30%; the propylene oxide weight content are, respectively, 46% and 63%; and the molecular weights are, respectively, 1862 and 1750. Note that the HLB value of the extended surfactant is 6, according to the Davies formula estimation,[17] which is not a logical value, because it is readily water-soluble. The HLB = 11 value calculated from an experiment on the optimum formulation of a mixture[18] for three-phase behavior is much more consistent and is closer to the CP-1750-14 value, at which they behave similarly.
- The extended nonionic surfactant $C_{12}PO_{14}EO_{20}$ and the ethoxylated sorbitan monooleate SM-15 have a similar
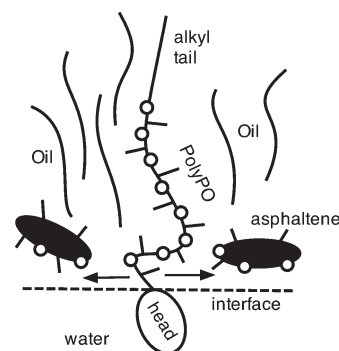
ethoxylated chain (20 EO); however, because of the polypropylene oxide spacer (14PO), the extended nonionic surfactant is less hydrophilic, and, as expected, it is less performing (by a factor of $\sim$3), in accordance with the previous trend and eq 2.

- The extended anionic surfactant $C_{12}PO_{14}EO_2SO_4Na$ is much more hydrophilic than the extended nonionic surfactant, typically because of the sulfate group that accounts for $\sim$40 HLB units in the Davies formula,[17] which is somehow arbitrary but extremely high. The actually estimated HLB from phase behavior[18] is $\sim$20, which also is quite high, and, consequently, it is also one of the most performing species, according to the map. This tends to support the tendency that a better performer is a quite hydrophilic surfactant with a MW that is not too high.
- As far as the MW is concerned, it seems that a relatively low MW (1000–2000, which is of the same order of magnitude as that of asphaltenes, exhibits a shorter t_{500}^* in Table 1, i.e., a quick destabilization process.

Recently published results[19,20] indicate that the extended surfactant location at the interface is such that the first 2–4 propylene oxide groups in the spacer remain close to the interface. This means that the polypropylene oxide chain is not straight, but is somehow folded close to the interface as indicated in Figure 4. In other words, the polypropylene oxide spacer tends to produce some looseness and a lack of packing where the asphaltenes molecules are likely to be positioned (i.e., close to the interface on the oil phase side). Consequently, such extended surfactant structures are likely to inhibit the formation of asphaltenes gel and favor a short breaking time scale, as evidenced in Table 1 data.

Dehydration of Different Crude Oils. Figure 5 indicates the C_D^*–C_A plots for two different demulsifier surfactants and four different diluted heavy crude oils: Boscan, Cerro Negro, and Hamaca (from Venezuela), and San Jacinto (from Peru).

The maps indicate that the demulsifier concentration required to attain the optimum formulation (C_D^*) is dependent on the crude oil used in the emulsion stability evaluation. The vertical location of the proportional line indicates the performance of the demulsifier for the crude oil, as discussed previously. However, if the comparison is conducted at a constant demulsifier concentration, along a horizontal line in the region where the proportional regime takes place, for instance, at $C_D^* = 40$ ppm in Figure 5a and 5 ppm in Figure 5b, it may be said that a certain amount of demulsifier counterbalances much more asphaltenes from one type of crude oil than that from another. The most
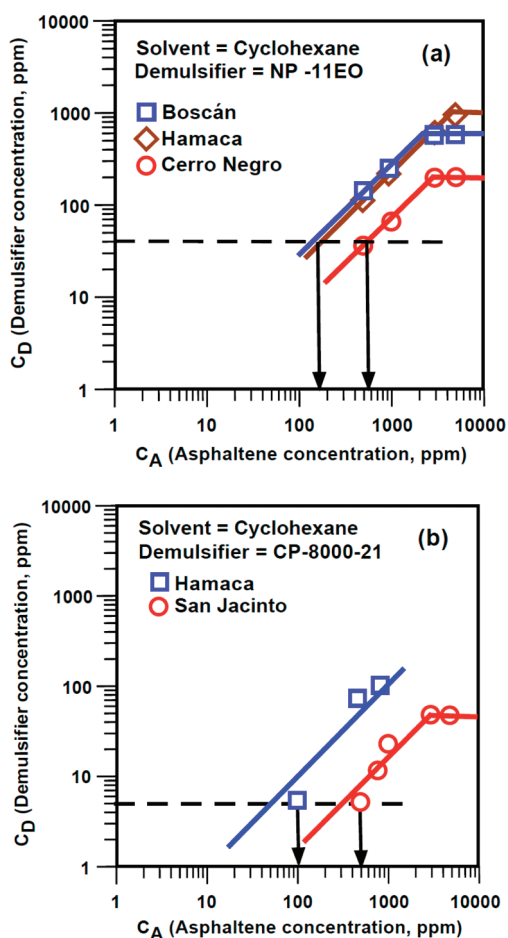

Figure 4. Scheme of the possible effect of the extended surfactant with a polypropylene oxide interaction with the asphaltenes close to the interface.

Figure 5. Plot of C_D^* vs C_A, using different crude oils and different demulsifiers: (a) Nonylphenol-11EO and (b) CP-8000-21.

CONCLUSIONS

The comparison of the different formulation cases in the proportional regime allows one to rank the performance of demulsifiers on a given crude oil. The few available results indicate that the performance tends to increase with higher demulsifier hydrophilicity, but that trend may be curtailed by a significant partitioning in the water phase, or a molecular weight that is too high, which could result in a slower diffusion. On the other hand, there is some evidence that the disorder resulting from the presence of small amphiphiles such as acids or those from the twisted polypropylene oxide intermediate in extended surfactants make the water-in-acidic-crude emulsions easier to break.

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ACKNOWLEDGMENT

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probable explanation for this behavior is based on the different molecular structure of the asphaltenes present in each particular crude oil, or on their different maltenic fractions (e.g., the proportions of its saturates, aromatics, and resins). The comparison allows one to rank the crude oils in such way that, for a given demulsifier, it is possible to say than some crude oils are more difficult to dehydrate than others.

For instance, for dehydration, the Cerro Negro crude requires much less NP-11EO (HLB = 13.7) that the Hamaca and Boscan crudes, and, in some way, it may be said to be easier to treat. It is the same for the San Jacinto crude, when compared to the Hamaca crude with the CP-8000-21 species, which is a better demulsifier than the ethoxylated phenol, because it is larger and more hydrophilic. No general statement could be securely advanced with such a small number of cases, but it could be noted that the emulsions with Cerro Negro and San Jacinto crudes, which are the most acid ones, seem to be easier to break. It may be conjectured that this is associated with the presence of natural surfactants such as smaller-sized acidic resins that could be better combined with demulsifiers, or are less likely to form asphaltene aggregates. This is consistent with some reports[21,22] suggesting that small-MW carboxylic acids are promoting the rupture of the interfacial film between water drops. Conversely, the case of Furrial crude that was exhibited in a previous paper[3] indicates that the asphaltenes aggregation and precipitation behavior is likely to result in some gel formation that delay the breaking process.

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