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ARTICLE *in* ENERGY & FUELS · OCTOBER 2007

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## Breaking of Water-in-Crude-Oil Emulsions. 2. Influence of Asphaltene Concentration and Diluent Nature on Demulsifier Action<sup>†</sup>

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Received July 9, 2007. Revised Manuscript Received August 27, 2007

The stability of water-in-oil emulsions formed during oil slicks or petroleum production operations is ensured by natural surfactant molecules (principally asphaltenes) that are present in the crude oil. These persistent emulsions may be broken by adding a suitable demulsifier at the proper concentration to attain a so-called optimum formulation at which the stability of the emulsion is minimum. In this report, the concentration of asphaltenes is varied by diluting the crude oil with a solvent such as cyclohexane, toluene, or mixtures of them. The experimental evidence shows that there exists some critical asphaltene concentration at which the interfacial zone seems to be saturated. Beyond this threshold, which is typically around 1000 ppm of asphaltenes, the demulsifier concentration necessary to attain the emulsion's quickest breaking is constant. Below it, e.g. when the crude is highly diluted with a solvent, the optimum demulsifier concentration is found to be proportional to the asphaltene concentration. The map of emulsion stability versus asphaltene and demulsifier concentrations exhibits a typical pattern for different demulsifiers and diluents, which contributes to improving the interpretation of the demulsifying action.

### Introduction

Emulsified water is generally present in crude oil as a result of the mixing occurring during production operations. Because it adds up to the cost of petroleum transportation and refining, water must be separated, and since the emulsion ageing tends to increase its stability, the breaking must be carried out as soon as possible in the production facility close to the well. These water/oil (W/O) type emulsions are mostly stabilized by naturally occurring surfactants, e.g., asphaltenes and resins, which adsorb at interfaces and tend to inhibit or delay the interdrop film drainage, hence preventing drop-drop coalescence and water separation.<sup>1</sup> Several approaches have been reported to study the associated phenomena, and some trends and correlations have been found between properties.<sup>2–9</sup> However, the general phenomenology is not completely understood,

certainly because there are (too) many concomitant effects in extremely complex systems from the chemical point of view, so that direct and clear-cut analysis is essentially impossible.

Natural surfactants are referred to as asphaltenes in the present paper because these species have been shown to play the major role in stabilizing the emulsion. However, and contrary to some other studies, the asphaltenes are not extracted by precipitation and dissolved back in a easier-to-handle model system. Instead, the crude oil is diluted with a solvent so that the complete range of natural surfactants originally present in the crude is kept with the same relative proportions of all species. As will be shown in the present paper, this approach allows the establishment of a relationship between the effect of asphaltene and demulsifier species, as well as the influence of the oil phase polarity.

In the first paper in this series,<sup>10</sup> the physicochemical principle of the breaking of a water-in-crude-oil emulsion by a hydrophilic demulsifier was discussed in terms of formulation. The principle of the dehydration process<sup>11</sup> is to make use of the fact that when the hydrophilic–lipophilic balance of the surfactant is varied, a minimum stability of the emulsified system is attained when the surfactant adsorbed at the interface exhibits the same affinity

<sup>†</sup> Presented at the 8th International Conference on Petroleum Phase Behavior and Fouling.

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for the oil and water phase. This phenomenon has been verified for a variety of surfactant–oil–water systems,<sup>12–16</sup> and the corresponding formulation has been called “optimum” formulation. Natural surfactants are lipophilic, whereas W/O demulsifiers are hydrophilic;<sup>10</sup> hence, their mixture in different proportions may exhibit a continuously changing affinity from lipophilic to hydrophilic. When demulsifier and asphaltene species form at an interface a mixture which has exactly the same affinity for the aqueous phase and the crude oil,<sup>11</sup> the emulsion quickly breaks down.

Part 1 of this series<sup>10</sup> reported that the contribution of the demulsifier depends on both its intrinsic hydrophilicity and its concentration. The more hydrophilic it is, the lesser the required amount to attain the optimal formulation for the emulsion quickest breaking. However, a compromise must be found in order to obtain the best conditions in practice, i.e., the demulsifier must not be too hydrophilic nor its concentration too low.

The precedent results have been obtained for an oil phase containing a constant asphaltene concentration (1000 ppm) attained by diluting the crude oil with cyclohexane. In the present paper, the asphaltene concentration is varied (by changing the dilution ratio) to determine its influence on the demulsifier formulation required to attain the emulsion quickest breaking situation. Then, the effect of the nature of the solvent used for diluting the crude oil is reported.

### Experimental Procedure

The systems studied were composed of a water phase (containing the demulsifier) and an oil phase (containing crude oil, hence asphaltenes).

**Water Phase.** Distilled water and aqueous solutions of demulsifier at different concentrations were used as water phases. All system samples contained 5 mL of aqueous phase. Demulsifiers used were, on the one hand, polyethoxylated nonylphenols with the ethoxylation degree labeled as their average ethylene oxide number (EON) and, on the other hand, an ethoxylated (20 ethylene oxide groups per molecule) sorbitan mono-oleate, sold as Tween 80. Polyethoxylated nonylphenols were provided by SEPPIC (France), and Tween 80 was provided by Aldrich. Their relative hydrophilicity is expressed through their HLB value, which is taken as  $1/5$  of the weight percent of ethylene oxide in the molecule. These surfactants are known to be able to produce a demulsifying effect similar to commercial demulsifier products as shown in the first paper in this series,<sup>10</sup> although not as efficiently. However, they are much better defined than industrial demulsifiers, and consequently, it is easier to use them for accurate formulation scans. Surfactants with nondirectly available EON values were obtained by blending two polyethoxylated nonyl-phenols having the nearest EONs to the desired value.

**Oil Phases.** Oil phases are not solutions of precipitated asphaltenes in a solvent. They are constituted by diluting a crude oil in cyclohexane (or other solvent as indicated). Vic-Bilh crude oil comes from a field located in southwest France. Its density is 0.946 g/cc, and it contains 10 wt % asphaltenes; hence, the asphaltene concentration in the undiluted crude is 100 000 ppm. Hamaca (and Furrial) are extra heavy (and intermediate) crudes from eastern Venezuela with quite different characteristics, i.e., 8° API and 11 wt % asphaltenes (and, respectively, 21° API and 7 wt %

asphaltenes). The indicated asphaltene content has been determined by precipitation with a large excess (20 times) of pentane for Vic-Bilh and of heptane for the other crudes. In what follows, the asphaltene concentration in the oil phase is deduced from the concentration of the crude oil in cyclohexane or other solvent, by applying the dilution ratio. All system samples contain 5 mL of oil phase.

**Emulsion Formation and Stability Measurement.** Demulsifiers were dissolved in water, and crude oils were diluted in cyclohexane or other solvent, to attain the desired asphaltene concentrations. Samples of 10 mL total volume were prepared with a water–oil volume ratio equal to unity. These samples were slightly agitated, then left at rest for 24 h at ambient temperature in order to reach equilibrium. This pre-equilibration process warrants the absence of transient mass transfer and related nonequilibrium phenomena which are likely to complicate matters, as recently discussed elsewhere.<sup>17,18</sup>

Emulsification was then carried out in a plastic conical beaker with an Ultra Turrax turbine blender at 1800 rpm over 30 s; then, the emulsion was poured in a graduated test tube and left to rest at ambient temperature ( $21 \pm 2$  °C). The emulsion stability was appraised by monitoring the volume of water separated as a function of time, according to the bottle test described in detail in the first paper in this series.<sup>10</sup> The time (in minutes) necessary for 50% of the total volume of water to separate was taken as a measurement of the emulsion stability. As discussed in previous papers,<sup>14–16,19,20</sup> the general variation of stability with formulation is not altered by the selected separation amount (here 50%) used to define stability, nor by the water/oil ratio (here WOR = 1).

### Experimental Results on the Influence of Asphaltene Concentration

Emulsion stability data were collected over wide ranges of asphaltene and demulsifier concentrations.

**1. Influence of Asphaltene Concentration for a Given Ethoxylated Nonylphenol Demulsifier.** The first results correspond to the use of a nonylphenol with EON = 5.5 as a demulsifier. The demulsifier concentration ( $C_D$ ) scans were carried out at a fixed asphaltene concentration in cyclohexane ( $C_A$ ) ranging from 100 to 10 000 ppm.

The left plot of Figure 1 shows that, for any of the  $C_A$  asphaltene concentration cases, the emulsion stability undergoes a minimum at a concentration of demulsifier which is noted as  $C_B^*$  in what follows to indicate that it is the optimum one, as far as the quickest breaking is concerned along the  $C_D$  variation. This result corroborates the pattern reported in the previous paper for an asphaltene concentration of 1000 ppm. It is worth noting that the value of optimum demulsifier concentration  $C_B^*$  remains essentially constant at about 200 ppm for asphaltene concentration ranging from 10 000 ppm down to approximately 1000 ppm. When asphaltene concentration is lower than 1000 ppm,  $C_B^*$  is no longer constant but rather decreases as  $C_A$  decreases.

The right plot of Figure 1 shows the isostability contours in a  $C_D$ – $C_A$  map with log–log scales. The locus of the stability minima (as  $C_B^*$  when  $C_A$  is held constant) is indicated as a bold black line. A secondary line of stability minima (found this time by varying  $C_A$  at constant  $C_D$  above 200 ppm) is indicated as a corrugated line.

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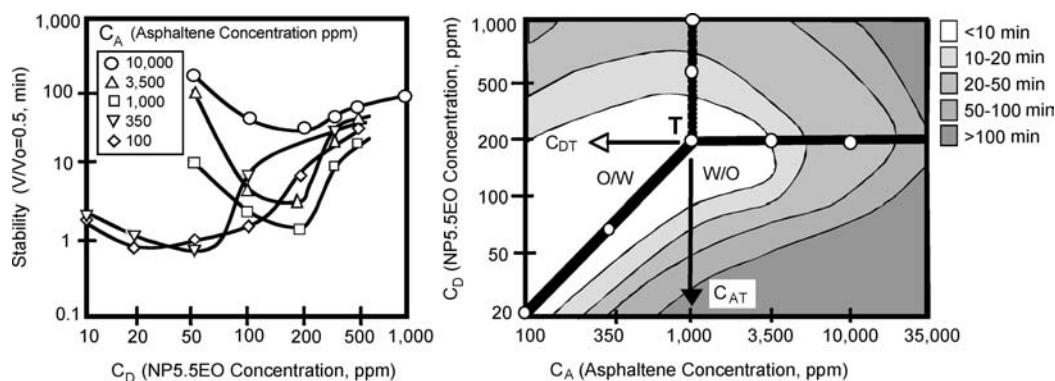
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**Figure 1.** Effect of asphaltene and demulsifier concentrations on the stability of water-in-crude-oil emulsions containing a nonylphenol (EON = 5.5) as a demulsifier. (left) Emulsion stability versus demulsifier concentration for different asphaltene concentrations. (right) Isostability contours and locus of minimum stability in a log  $C_A$ –log  $C_D$  map. Vic-Bilh crude oil is diluted in cyclohexane.

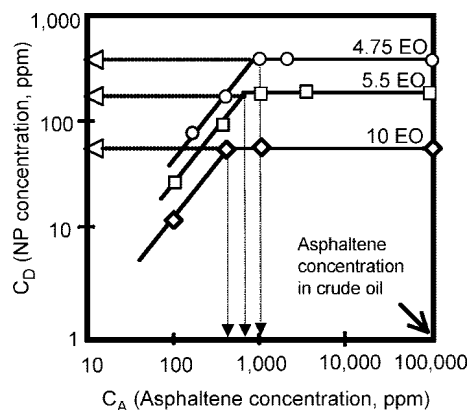
The locus of minima is composed of three straight line segments. First, for  $C_A$  lower than 1000 ppm, the locus is a slanted segment, with an approximately unit slope and the emulsion breaking rate is very fast, e.g., about 1 min according to the left plot of Figure 1. It is worth remarking that this line corresponds to the stability minimum found by changing  $C_D$  at constant  $C_A$  as well as by changing  $C_A$  at constant  $C_D$ .

Second, for  $C_A$  higher than 1000 ppm, so-called  $C_{AT}$  with subscript T for reasons to be explained later, the locus is a horizontal segment at  $C_D^* = C_{DT} = 200$  ppm. Moreover, in this branch, the emulsion stability minimum is much higher than in the slanted branch and it is increasing as asphaltene concentration increases.

The third segment, which is a vertical line located at  $C_A = C_{AT} = 1000$  ppm for  $C_D > 200$  ppm, corresponds to a slight stability minimum found along a variation of  $C_A$  at constant  $C_D$ . With the present system, the minimum is not very significant; hence, the corresponding branch is indicated as a corrugated line.

Point T ( $C_{DT}$ – $C_{AT}$ ) at the intersection of the three branches appears to be some kind of threshold, which is why a T subscript is used. Below it, i.e. at lower concentrations, there is an unambiguous minimum of stability with a very low value, from which a stability increase is found by changing either  $C_D$  or  $C_A$ . Above this threshold, there is a stability minimum only in one direction. At constant  $C_A$  larger than  $C_{AT}$ , i.e. along a vertical variation, the optimum  $C_D^*$  is found to be independent of  $C_A$ ; however, the minimum stability value increases with increasing  $C_A$  as if the optimum demulsifier dose would offset the effect of only a certain amount of asphaltenes, i.e.  $C_{AT}$ , which is the one likely to be located at interface. The rest of the asphaltenes might be somewhere else, either as micellar or particular aggregates, or may be in some kind of gel phase adjacent to the interfacial layer. A similar situation occurs when the demulsifier dose is also in excess, i.e., when it is larger than  $C_{DT}$ . A minimum stability is found for a certain asphaltene concentration  $C_{AT}$  that offsets the demulsifier amount present at the interface, with the rest of it contributing to an increase in stability along the (vertical) branch. The minimum effect is however not as obvious as in the other (horizontal) branch.

**2. Influence of Asphaltene Concentration for Different Demulsifiers from the Same Family but with Different Hydrophilicities.** The experiment is repeated for nonylphenols with different ethoxylation degrees as in the first paper in this series,<sup>10</sup> but this time for different asphaltene concentrations, which are adjusted as done previously by changing the crude dilution. The research of the locus of the stability minimum is performed at a constant  $C_A$  by varying  $C_D$ , as in the left plot of Figure 1. Whatever the EON of the demulsifier, the locus



**Figure 2.** Locus of minimum stability in a log  $C_A$ –log  $C_D$  map for three differently ethoxylated nonylphenols as demulsifiers. Vic-Bilh crude oil is diluted in cyclohexane.

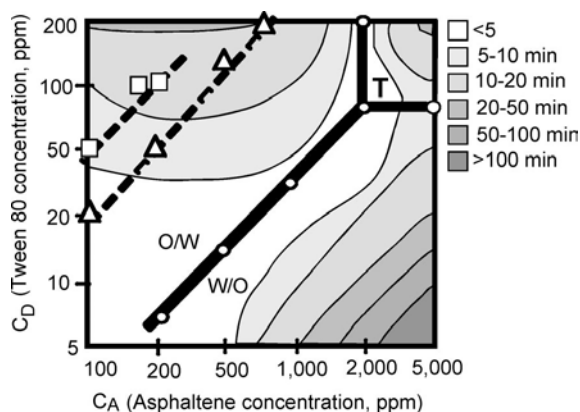
exhibits the same pattern in the log  $C_A$ /log  $C_D$  diagram, as shown in Figure 2. There is a straight line branch with an approximately unit slope at low concentrations and a horizontal segment at high  $C_A$ , i.e., above the threshold.

The coordinates ( $C_{AT}$ ,  $C_{DT}$ ) of the threshold are found to depend on the EON. As the demulsifier is more hydrophilic (higher EON), both  $C_{DT}$  and  $C_{AT}$  decrease. The decrease in  $C_{DT}$ , which is quite significant, is expected from the trend presented in the first paper in this series,<sup>10</sup> according to which the more hydrophilic the demulsifier, the lesser the amount required to produce a hydrophilic countereffect to the adsorbed lipophilic asphaltenes. The decrease in  $C_{AT}$  is much less perceptible and is in fact within experimental error, i.e.,  $C_{AT}$  could actually be constant.

Figure 2 shows that when the crude oil is used without dilution ( $C_A = 100\,000$  ppm), the quickest breaking is attained for the value of the demulsifier concentration corresponding to  $C_{DT}$ , which is the same as when  $C_A$  is in the 1000 ppm range. This backs up the suggestion that the horizontal segment of the minimum stability locus corresponds to some “overconcentration” in the asphaltene species and that only a fraction of them ( $C_{AT}$ ) participates in the optimum formulation of the interfacial mixture.

**3. Influence of Asphaltene Concentration for Tween 80 as a Demulsifier.** Figure 3 shows the isostability contour map in a  $C_A$ – $C_D$  log–log plot for emulsions containing Tween 80 as a demulsifier. The aspect of the map and the minimum stability locus for Vic-Bilh crude (circle data point) is exactly the same as that for other surfactants used as demulsifiers. The slanted part of the locus has an approximately unit slope, and this time the data is significant enough to warrant the tracing of the





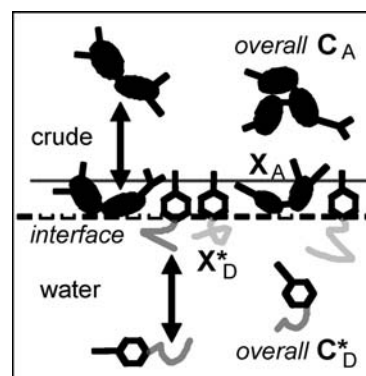
**Figure 3.** Isostability contours and locus of minimum stability (circle data points) in a log  $C_A$ –log  $C_D$  map for Vic-Bilh crude oil. Triangular (respectively square) data points indicate the minimum stability for Hamaca (respectively Furrial) crude oils in the low asphaltene concentration zone. In all cases, Tween 80 is used as a demulsifier, and crude oils are diluted in cyclohexane.

(vertical) branch of the minimum stability locus at  $C_{AT}$  for  $C_D > C_{DT}$ . The threshold point  $T$  is located at  $C_{AT} = 2000$  ppm and  $C_{DT} = 80$  ppm. It is worth noting that the  $C_{DT}$  value for Tween 80 (HLB = 15) is about the same as the one found with the ethoxylated nonylphenol with 10 EO (HLB = 13.5), which could be considered as roughly the same (high) hydrophilicity, since the HLB scale is quite inaccurate when comparing different surfactant families. The  $C_{AT}$  value is higher than for the ethoxylated nonylphenol surfactants, which means that Tween 80 is able to mix with asphaltenes up to a higher concentration before some maximum interfacial filling is attained, which could be an indication of a better compatibility. Another way to look at this change is that the ratio of Tween 80 demulsifier to asphaltene at the threshold is lower, which could be viewed as a better efficiency of Tween 80 with respect to the ethoxylated nonylphenols.

Figure 3 also contains the minimum stability locus data for two other crude oils which are known to be difficult to dehydrate. Hamaca (triangular data points) is a heavy crude, whereas Furrial (square data points) is a light crude whose asphaltenes are known to be extremely unstable and to precipitate readily. In both cases, efficient dehydration with Tween 80 is only attained at high dilution, i.e. at a low content of asphaltenes, e.g.  $C_A$  below 200 ppm for Furrial and below 1000 ppm for Hamaca. Above these values, Tween 80 is not effective enough as a demulsifier to cause water separation in a reasonable time span. This poor behavior could be also deduced from the fact that, at a given asphaltene concentration, much more Tween 80 is required for Hamaca and even more for Furrial, to attain the minimum stability locus (dashed lines). Hence, only the slanted part of the plot is experimentally accessible for these two crudes when using Tween 80 as a demulsifier. Nevertheless, the trend at low concentration, i.e., the approximately unit slope variation, is preserved.

**4. Modeling of the Asphaltene–Demulsifier Interfacial Mixture in the Proportional Regime.** At a concentration below the threshold, the approximately unit slope variation of the locus of the stability minimum (in a log–log scale) indicates that the overall concentrations of asphaltene  $C_A$  and demulsifier  $C_D$  are proportional to each other along the slanted branch; in other words,  $C_D^*/C_A$  is constant and its value  $k_{\text{overall}}$  may be calculated from the experimental data.

$$C_D^*/C_A = k_{\text{overall}} \quad (1)$$



**Figure 4.** Adsorption model in the proportional regime.

This part on the locus will be called the “proportional regime” in what follows. The interfacial model illustrated in Figure 4 uses the notation of the previous paper,<sup>10</sup> in which both asphaltenes (A) and demulsifier (D) are each assumed to be a single component for the sake of simplicity. Both A and D molecules which are adsorbed at interface (occupancy fractions  $X_A$  and  $X_D$ , respectively) are in equilibrium with the molecules present in the bulk phases.

Along the proportional regime branch, the demulsifier concentration is noted as  $C_D^*$  and its molar fraction in the interfacial mixture is noted as  $X_D^*$ . The asterisk indicates that in this case the interfacial formulation corresponds to the mixture with the same affinity for the oil and water phases. Because it is well-known that the minimum stability is associated to the optimum formulation, it may be taken for granted that the interfacial formulation remains invariable all along the branch up to the threshold point; hence,  $X_D^*/X_A$  is constant along this branch, even though its value cannot be calculated unless the hydrophilicities of both species are known (see eq 3 in the first paper in this series<sup>10</sup>).

$$X_D^*/X_A = k_{\text{interf}} \quad (2)$$

Consequently, both ratios of interfacial concentrations and overall concentrations are constant, as indicated by eq 1 and 2. In the present case, the overall concentrations are low, the surface area provided by the emulsion is high, and the adsorption takes place from either bulk phases onto the interface just after emulsification. Hence, most surface active species are likely to be adsorbed at the interface, with little remaining in the depleted bulk phases. In such an approximation, the overall and interfacial ratios are essentially the same (noted as  $k$ ):

$$X_D^*/X_A = C_D^*/C_A = k \quad (3)$$

It is worth noting that more sophisticated statistical mechanics considerations, discussed elsewhere,<sup>19</sup> lead to the same result with less restrictions and assumptions, but the discussion is limited here to the simplest approach since there is no need for more intricacies.

Equation 4 (reproduced from the first paper in this series<sup>10</sup>) is an expression of the invariability of the optimum formulation attained by the proper mixture of A and D at the interface for a given oil/water pair:

$$HLB_m = X_A HLB_A + X_D^* HLB_D \quad (4)$$

where the HLB is a measurement of the hydrophilicity of a surfactant.  $HLB_m$  is the hydrophilicity of the surfactant or surfactant mixture that produces optimum formulation, and it may be determined by experiment<sup>20</sup> using a proper procedure with the same oil and water phases. Likewise,  $HLB_D$  may be

also determined by experiment. Dividing eq 4 by  $X_A + X_B^* = 1$  and combining with eqs 1–3, the following relationship is attained:

$$HLB_m = \frac{HLB_A + kHLB_D}{1 + k} \quad (5)$$

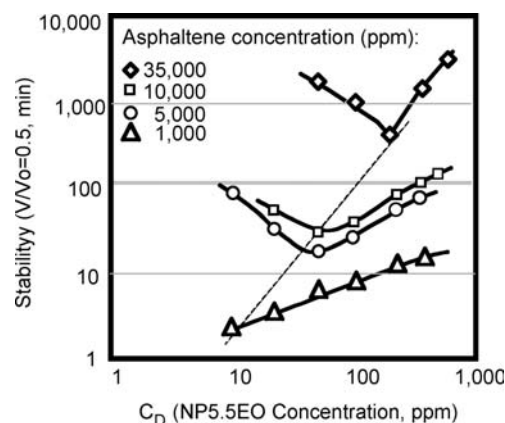
Since  $k$  may be calculated from the  $C_D^*/C_A$  map data, then  $HLB_A$  may be calculated from eq 5 once  $HLB_D$  and  $HLB_m$  are available. The proportional regime thus allows the estimation of the asphaltene hydrophilicity, valuable information as a crude characteristic parameter which would lead to help predicting the formulation of optimum demulsifiers. For Vic-Bilh crude oil, an approximate calculation from a mass balance reported elsewhere<sup>19</sup> lead to  $HLB_A = 6.9$ , which is indicative of a reasonable lipophilicity for the asphaltenes.

As far as the two other (vertical and horizontal) branches of the locus are concerned, they correspond to a situation in which the concentration of one of the two components in the (respective) bulk is too high to be in equilibrium as a molecular solution with the interface. Hence, some precipitation, segregation, or aggregation occurs elsewhere, and only a part of the amount of the component present in the system participates in the interfacial mixture monolayer. This is particularly fortunate in the case of the horizontal branch, since a few tens or hundreds of parts per million of the proper demulsifier are enough to attain an optimum formulation, i.e. to produce a hydrophilic countereffect to the ten or hundred thousands of parts per million of lipophilic asphaltenes contained in the crude. However, it is worth noting that the stability contours of Figures 1 and 3 indicate that the actual time required to separate 50% of the water at optimum formulation tends to increase quickly as asphaltene concentration increases beyond  $C_{AT}$ . This is quite important in practice, because it means that though the optimum demulsifier dosage remains the same, its efficiency is quite altered when the asphaltene concentration goes beyond the threshold  $C_{AT}$ . Above the threshold, the instability associated to optimum formulation is hindered by any assembly resulting from the asphaltene overconcentration. Nevertheless, the comparison of ethoxylated nonylphenols and Tween 80 data indicates that threshold  $C_{AT}$  also depends on the demulsifier nature; thus,  $C_{AT}$  may be used as some effectiveness yardstick to estimate the demulsifier performance.  $C_{DT}$  is also another performance index since it indicates how much demulsifier should be introduced in the system to attain an optimum formulation, but this time it deals with the demulsifier efficiency. Figure 3 data also indicates that the demulsifier performance is also dependent on the crude oil, thus probably on the asphaltene maltene characteristics.

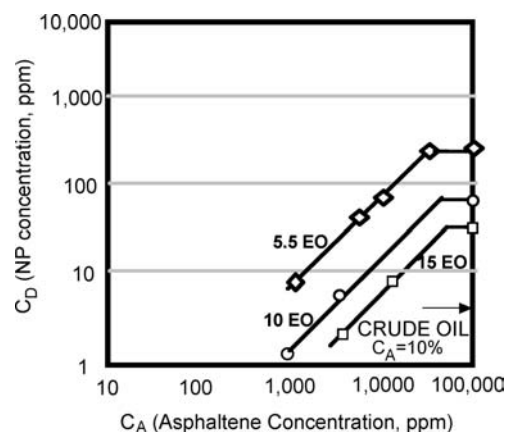
### Experimental Results on the Influence of the Nature of the Oil

In the previously shown results, the crude oil is diluted with cyclohexane in different proportions in order to vary the asphaltene concentration. According to the basic phenomenology, both the optimum formulation A/D mixture and the equilibrium between the bulk phases and the interface depend on the oil and water phase nature and should be altered by changing them.

In what follows, the diluent is changed (toluene or cyclohexane/toluene instead of cyclohexane) and the stability experiments are repeated at different dilution values, i.e. different asphaltene concentrations. As previously, the formulation is changed along the scan by varying the (ethoxylated nonylphenol) demulsifier dosing.



**Figure 5.** Emulsion stability when using different asphaltene and surfactant concentrations. Vic-Bilh crude oil is diluted in toluene.



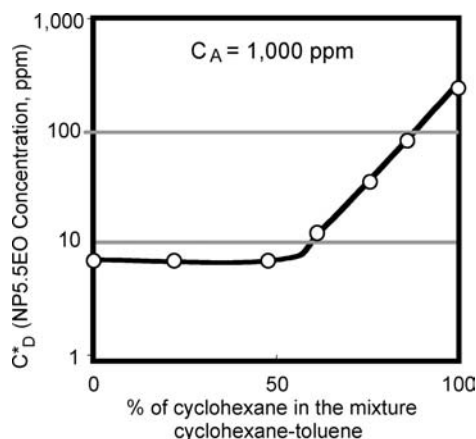
**Figure 6.** Ethoxylated nonylphenol demulsifier concentration for optimal formulation depending on asphaltene concentration and EON. Vic-Bilh crude oil is diluted in toluene.

**1. Dilution with Toluene.** Figure 5 shows the same kind of data as the left plot of Figure 1, but this time the Vic-Bilh crude oil is diluted in toluene, an aromatic substance which is likely to produce a higher solvability of asphaltenes in the bulk and thus a lesser adsorption at the interface. As previously, the stability exhibits a minimum at some optimum  $C_D^*$  value, but several changes are observed when a comparison is carried out with the previous case: (a) at a given asphaltene concentration, e.g. 1000 ppm, the optimum  $C_D^*$  is much lower, e.g., 10 ppm instead of 200 ppm in Figure 1, and the stability minimum is also lower; (b)  $C_D^*$  varies with asphaltene concentration even at very high  $C_A$  values, and hence, the  $C_{AT}$  threshold, if any, is quite high, probably beyond 35 000 ppm.

Figure 6 shows the minimum stability locus for different emulsifiers when using toluene as a solvent. For all demulsifiers, the straight-line variation with approximately unit slope, i.e. the proportional regime, is found. On the other hand, the same downward shift revealed in Figure 2 is exhibited when the demulsifier hydrophilicity increases.

Although the plateau  $C_D^*$  value seems to be approximately the same in both solvents, the threshold is found at a much higher asphaltenes concentration  $C_{AT}$ . This indicates that a higher asphaltene concentration is required in the toluene bulk phase to produce the same interfacial contribution. This is consistent with the higher solvability of asphaltenes in toluene.

The previous observations corroborate that, with toluene diluent in large proportion in the oil phase, the asphaltenes are less prone to migrate to the interface, their surface-active properties are diminished, as well as their stabilization capacity, and consequently, the demulsifier is more effective.



**Figure 7.**  $C_D^*$  as a function of cyclohexane percentage in a toluene–cyclohexane mixture to dilute Vic-Bilb crude.

It means in practice that more asphaltenes are present in the bulk oil at the threshold conditions. However, since the  $C_{BT}^*$  value seems to be the same for nonylphenol +5.5 EO demulsifier for systems containing cyclohexane and toluene (around 200 ppm), this means that the amount of demulsifier required for compensating a “saturated” adsorption of asphaltene seems to depend only on the demulsifier, not on the asphaltene concentration when this one is larger than the  $C_{AT}$  threshold. This could be a very simple explanation for a puzzling experimental fact, which is that a very small amount of demulsifier, e.g., a few hundreds of parts per million, is able to dehydrate a crude oil containing a huge amount of asphaltenes.

**2. Dilution with Toluene–Cyclohexane Mixtures.** In this section, the same 5.5 EO nonylphenol demulsifier is used and the asphaltene dilution is carried out with mixtures of cyclohexane and toluene, in order to vary the asphaltene solvability in a somehow continuous way. However, the results clearly indicate that the variation does not actually continuously follow the proportion of toluene in the mixture. As shown in Figure 7, the optimal demulsifier concentration  $C_D^*$  for  $C_A = 1000$  ppm remains essentially the same as the one corresponding to the system diluted with pure toluene, when up to 50% cyclohexane is used in the mixture. This result tends to indicate that when the diluent contains 50% toluene and 50% cyclohexane, the oil phase close to the interface is essentially pure toluene. This behavior has been reported before and has been called interfacial segregation;<sup>21</sup> it has been related with the so-called lipophilic linker effect.<sup>22–24</sup> It was found to be typical in systems containing oil components with different polarities, the most polar oil (here toluene) tending to be preferably segregated close to the interface with water.

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The same segregation could take place in any crude oil, with the more aromatic or polar oil species segregating close to interface. This will tend to increase the solvability of asphaltenes and thus to reduce their adsorption at interface. This might explain why most commercial dehydration formulas have been routinely prepared with aromatic solvents in huge proportions. Maybe this explains why so little demulsifier is needed, given that the solvent that carries it is also affecting the stability of the emulsion.

## Conclusions

A new kind of map showing the optimum demulsifier concentration as a function of asphaltene concentration is found to exhibit a typical phenomenology for different surfactants used as demulsifiers (polyethoxylated nonylphenols and Tween 80). The variation in asphaltene concentration is obtained by diluting a crude oil containing 10 wt % asphaltenes with solvents like cyclohexane or toluene, or their mixtures.

The locus of optimum demulsifier concentration exhibits three branches in the log–log scale map: a slanted branch of approximately unit slope, a vertical branch, and a horizontal branch. At low concentrations of asphaltenes, the unit slope branch corresponds to a so-called proportional regime in which the proportions of asphaltene and demulsifier molecules to attain the optimum formulation is constant. This regime allows the understanding of the interaction of asphaltene and demulsifier molecules and the estimation of the required dosage of emulsifier for each specie. It paves the way toward the determination of the hydrophilicity of asphaltenes. The two other branches correspond to some overconcentrated states in which one of the surfactant species (asphaltenes and demulsifier) is in excess with respect to the required amount to adsorb at interface. The meeting point of the three branches is a threshold whose location allows the estimation of the efficiency of the demulsifier. Above the threshold, the optimum demulsifier concentration remains the same whatever the asphaltene concentration. However, its breaking efficiency decreases as the asphaltene concentration increases.

The actual concentration of demulsifier for the quickest emulsion breaking at or above the threshold is found to depend on the demulsifier and on the diluent polarity. In the proportional regime, the presence of a small amount of aromatic hydrocarbon in the oil phase is found to ease the breaking process much beyond its expected contribution, presumably because of some interfacial segregation process.

**Acknowledgment.** The authors thank the French Ministry of Research for the financial support Nr 04 G 366 within the framework of RITMER. They also acknowledge the financial backing provided by FONACIT-Venezuela (Grant S1-2001-001156, PCP program on “Petroleum Emulsions”) and the University of the Andes Research Council (Grants I-834-05-08-AA and I-815-05-08-A).

EF7003877