

Demulsification of Crude Oil Emulsions: Correlation to Microemulsion Phase Behavior

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The search for the appropriate demulsifier for a water-in-crude oil emulsion is generally carried out through the well-known “bottle test” technique. A comprehensive approach is proposed here, which is based on earlier work on the rate of separation of surfactant–water–hydrocarbon mixtures, where it was found that “optimal” type III systems, in Winsor’s nomenclature, exhibits the fastest separation rate. It is shown that the rules developed for microemulsion optimization apply to the selection of the demulsifier. They allow one to take into account the variation of salinity, temperature, crude-oil type, and so forth and provide an explanation for the demulsifier concentration effect. Interfacial tension measurements have been carried out. They show that the kinetics of demulsifier adsorption at the water–crude oil interface (or alternatively the Gibbs elasticity modulus) is correlated to the phase separation rate, as already described in the literature: the higher the kinetics, the faster the separation rate.

Introduction

When crude oil is produced from an oil field well, it is generally accompanied with variable proportions of water. This water is emulsified by surface-active substances naturally present in the crude, which makes the separation of water prior to crude commercialization difficult. A number of research groups have investigated the various mechanisms of water-in-oil emulsion stabilization, a good review of which has been issued recently.¹ Various techniques are used to break these emulsions, among which the most widely used consists of adding small amounts of so-called “demulsifiers”. These surface-active molecules adsorb at the oil–water interface and accelerate the phase separation.

Nowadays, the mechanism for this destabilization is however not yet fully understood. A number of demulsifiers are proposed by suppliers and the choice of the most efficient one is a long and difficult task. Moreover, during the well life, the production conditions (temperature, salinity) can change and it is very often necessary to proceed to the selection of another additive.

The different demulsifiers are generally tested through a “bottle-test” method, which consists of adding a given demulsifier in small bottles containing freshly sampled emulsion from the field production and following the percentage of decanted water as a function of time. Screening of additives is then performed rather empirically.

In this paper, we present first, on the basis of bottle testing, a physicochemical approach of demulsification that gives some insight into the operative mechanisms. This approach is based on earlier observations carried out while the phase behavior of surfactant–water–hydrocarbon mixtures for microemulsion formulation was being investigated.^{2,3} It was then found that the rate of phase separation is maximum when a particular three-phase behavior, namely, a microemulsion phase in equilibrium with both excess water and oil phases, is observed when the system has reached its final equilibrium.

A correlation is then established with interfacial tension measurements, which sheds further light on the above-mentioned mechanisms.

Materials and Experimental Procedures

Commercial demulsifiers are generally complex mixtures, the precise chemical structures of which are not easy to figure out. A series of four products, so-called resins R1, R2, R3, and R4, has been supplied by CECA S.A. They are nonionic type and contain various amounts of ethylene oxide and propylene oxide. According to their hydrophile–lipophile balance, they can be ranked as $R1 > R2 > R3 > R4$, R1 being the more hydrophilic species. Molecular weights are in the range 4000–5000.

Ethoxylated nonylphenols, supplied by CECA S.A., have also been used as representatives of more conventional surfactants. Their ethylene oxide number (EON) ranges from 4 to 24. Similarly, TRS 10 is a petroleum sulfonate (molecular weight 430) supplied by Witco.

Two different crude oils were used: Afia (naphthenic African crude) and Vic-Bilh (asphaltenic French crude).

Water-in-crude oil emulsions were prepared in the laboratory by mixing of brine and crude oil in 10/90 or 20/80 volume ratios and stirring for 2 mn at 2000 or 4000 rpm with an Ultra-Turrax turbine; 500-mL emulsions were thereby prepared and distributed in 10 graduated bottle tests. Less than 5 min after the preparation of the emulsion, a known amount of demulsifier was then added to each bottle test, which was shaken and placed in a temperature-controlled bath. The percentage of separated water was then recorded over time. A given emulsifier was characterized by the fraction of water separated after 30, 60, or 90 mn of settling. The additive free sample (reference) was showing no separation after this time.

Interfacial tension measurements were carried out with a drop tensiometer (Tracker, from IT CONCEPT-France). A drop of crude oil (in which the demulsifier had already been added) was created with a thermostated syringe in thermostated brine, and the interfacial tension was obtained from the analysis of the drop

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contour. This can be done over time, allowing one to determine the kinetics of the interfacial tension evolution.

Background of the Physicochemical Approach

Earlier work^{2,3} on the stability of emulsions, in relation to the phase behavior of microemulsion systems, has shown that the rate of phase separation of emulsions is maximum when three-phase behavior is observed after equilibrium is reached. Such a phase behavior, called type III in Winsor's nomenclature,⁴ corresponds to the equilibrium of a surfactant-rich (microemulsion) phase with, simultaneously, an excess aqueous phase and an excess organic phase.

According to Winsor, type III systems are obtained when the ratio of interactions of the surfactant with water to its interactions with oil is close or equal to 1. This ratio can be written, to incorporate the other interaction energies involved in the system equilibrium,³ as

$$R = \frac{A_{CO} - A_{OO} - A_{LL}}{A_{CW} - A_{WW} - A_{HH}}$$

where C, O, and W stand for surfactant, oil, and water, respectively, and L and H designate the lipophilic and hydrophilic moieties of the surfactant. The interaction terms A_{CO} and A_{CW} tend to promote miscibility of the components of the system, while A_{OO} , A_{WW} , A_{LL} , and A_{HH} tend to promote separation in several phases.

To obtain $R = 1$, or close to 1, it is thus clear that different methods are possible, by changing any one of the factors involved in the R ratio: salinity of water, temperature, nature of surfactant, nature of the oils, and so forth can be used to modify the balance of interactions.

The situation where $R = 1$, where the average interface curvature is believed to be 0 (plane interface, as an average^{3,4}), has been shown to present several interesting features: the interfacial tension between the phases is very low and the solubilizing power of the surfactant is maximum. This is thus the most favorable situation to formulate single-phase microemulsions because the required surfactant concentration is then minimum.³ The R ratio concept constitutes therefore a very powerful tool for microemulsion formulation. It will be shown below that it can also be very useful for demulsification optimization.

Figure 1² shows the time required for one-half of the excess phase to separate from the emulsion as a function of EON.

Increasing EON amounts to increase the interaction of the surfactant with water, namely, the A_{CW} term in the R ratio. There are two stable maxima that correspond to the most stable water-in-oil (low EON) and oil-in-water (high EON) emulsions. Between these two maxima, a deep minimum is observed, corresponding to type III behavior at equilibrium.

A similar pattern, with a different system, is shown in Figure 2, where the surfactant is a petroleum sulfonate. Its interactions with water are progressively decreased with increases in the water salinity.

Figures 1 and 2 both reflect a profound relationship that correlates emulsion stability to surfactant phase behavior, which has also been recognized by other researchers.⁵⁻¹⁰

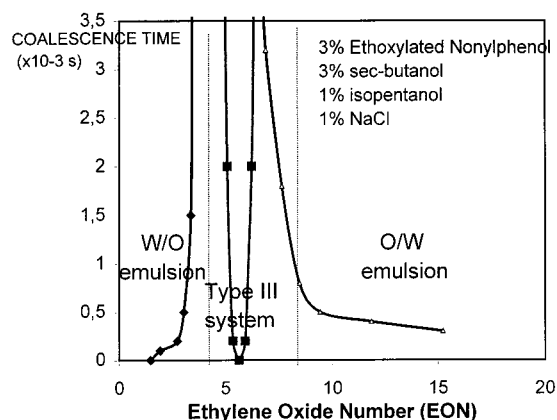


Figure 1. Emulsion stability in terms of time for one-half the clear phase to appear versus EON of a series of ethoxylated nonylphenols of known EON. The concentrations refer to the aqueous phase. Aqueous phase/nonane = 4 (by volume).

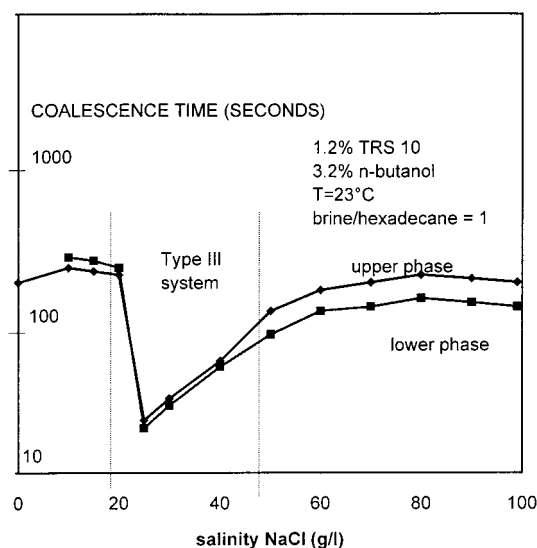


Figure 2. Time required for one-half the clear phase to appear as a function of brine salinity.

For the sake of simplicity, we will consider that the stable, deep minimum corresponds to $R = 1$, which thus appears as a key point for demulsification.

Hazlett and Schechter¹¹ showed that it is the result of greatly increased coalescence efficiency.

The typical pattern displayed in Figures 1 and 2, which relates to the important matter of emulsion coalescence, was recently theoretically investigated by Kabalnov and Wennerstrom.¹² These authors argue that coalescence is controlled by hole nucleation in the film separating two droplets of the dispersed phase, which involves a strong curvature at the edge of the hole. They consider that the interfacial tension at the edge is different from that of a planar film: the result is the dependence of the interfacial tension of emulsion films on the monolayer spontaneous curvature, H_0 , the absolute value of which can be changed by the addition of surfactant. The bending energy penalty involved, related to H_0 , is thus strongly affected by the addition of surfactant. A very steep change in film stability with H_0 is predicted in the so-called "balanced state", where $H_0 = 0$. This balanced state corresponds to the situation where $R = 1$ in our approach. Similarly, $H_0 > 0$ (O/W droplets) and $H_0 < 0$ (W/O droplets) correspond to $R < 1$ and $R > 1$, respectively. The interest in using the R

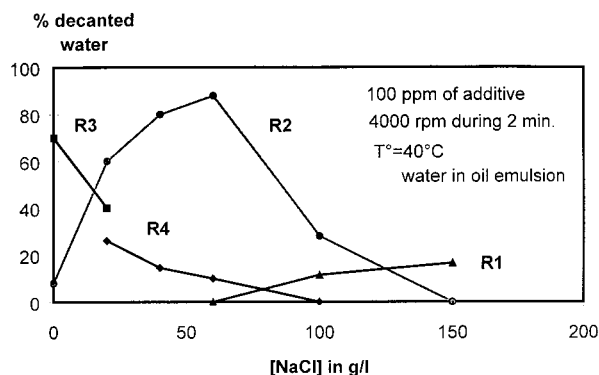


Figure 3. Effect of emulsion brine salinity on demulsifier efficiency (crude oil: AFIA, % of decanted water measured after 30 min).

ratio is that it makes clear the various ways of promoting phase transitions.

Alternatively, Ivanov et al.¹⁴ discuss the relative importance of droplet deformation, surfactant transfer, and interfacial rheology for the stability of emulsions. The rheological and dynamic properties of the surfactant adsorption monolayers (Gibbs elasticity, surface diffusivity, surface viscosity, and surfactant adsorption kinetics) are found to be major factors for the stability of emulsions under dynamic conditions. The solubility of the surfactant in one of the two phases is claimed as being able to determine the type of emulsion to be formed. It must be pointed out however that, in their work, no mention is made of the typical pattern displayed in Figures 1 and 2.

With regard to demulsification, the latter type of an approach has been thoroughly used for interpreting the results.^{15–18}

Experimental Results and Discussion

Bottle Tests. In Figure 3 is shown a typical result obtained with the Afia crude using the resin series. A clear maximum is observed with R2 when the water salinity is varied. With the other additives it can be conjectured that if they should exhibit a maximum, they would be located at higher salinity for R1 and at lower values for R3 and R4; that is, these “optimal” salinities would be ranked in the same order as the hydrophilicity of the resins: the more hydrophilic the additive, the higher the salinity for the maximum separation rate. This is in accordance with the *R*-ratio concept because it is known that increasing the salinity decreases the interactions of a nonionic surfactant with water.

Further illustration of this concept is provided by Figure 4 where the interactions of the surfactant with water have been decreased by increasing temperature. A maximum in the separation rate is observed with each additive, at the temperature ranked as expected from the respective hydrophilicity of the resins.

It is important to insist that the existence of an optimum when the temperature is changed is a strong element in favor of the relevance of the concept used in this study. A temperature increase is known to increase the phase separation rate by a viscosity decrease and an increase of the fluctuations in the system. In the case presented in Figure 4, this effect, although important at higher temperatures, is not strong enough to dominate the effect of the interaction ratio in disfavor of a high coalescence rate: the decantation rate decreases.

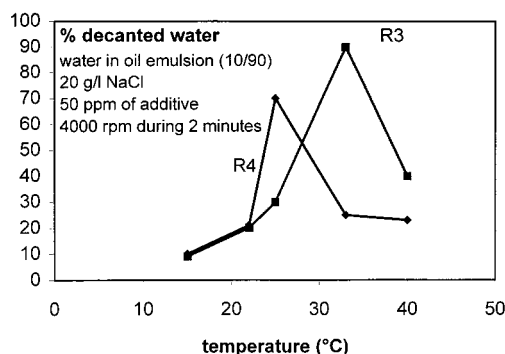


Figure 4. Temperature effect on demulsifier efficiencies (crude oil: AFIA, % of decanted water measured after 30 min).

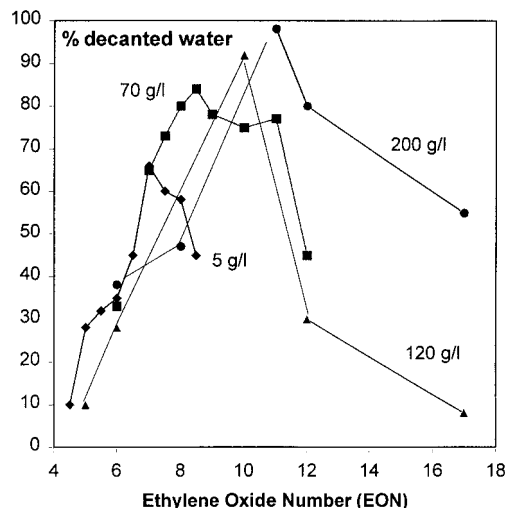


Figure 5. Effect of additive hydrophilicity (ethoxylated nonylphenol) on demulsifier efficiency. Crude oil: VIC BILH, % of decanted water measured after 60 min, 2000 ppm of additive, $T = 60^\circ\text{C}$, x g/L refers to brine salinity. Brine-in-oil emulsion, 20/80.

At much higher temperatures, this effect could however become predominant.

It is also interesting to point out that the maxima may look sharper in Figure 4 than in Figure 3. This can be attributed to the higher sensitivity of a nonionic surfactant to temperature than to salinity. The equivalence between these two parameters has been discussed elsewhere.¹⁹

From an applicative point of view, temperature and salinity are imposed by the production well, and the problem is then to find the best demulsifier. The approach is illustrated in Figure 5, where ethoxylated nonylphenols are used and their interaction with water adjusted through the ethylene oxide number. The experiments have been carried out at different salinities.

It is seen that if the field salinity were 5 g/L NaCl, for example, the optimal demulsifier would have EON ~ 7 , while for a salinity of 200 g/L, it would have EON ~ 12 . Again, this is in agreement with that expected from the *R* ratio.

Interestingly, such a maximum in demulsification efficiency when the EON varies has been reported on in the past by Mukherjee and Kushnick.¹⁵ These authors, who were comparing this property to interfacial tension at equilibrium, concluded, “In general, there is no correlation between the ability of a demulsifier to lower the oil–water interfacial tension and its effectiveness”.

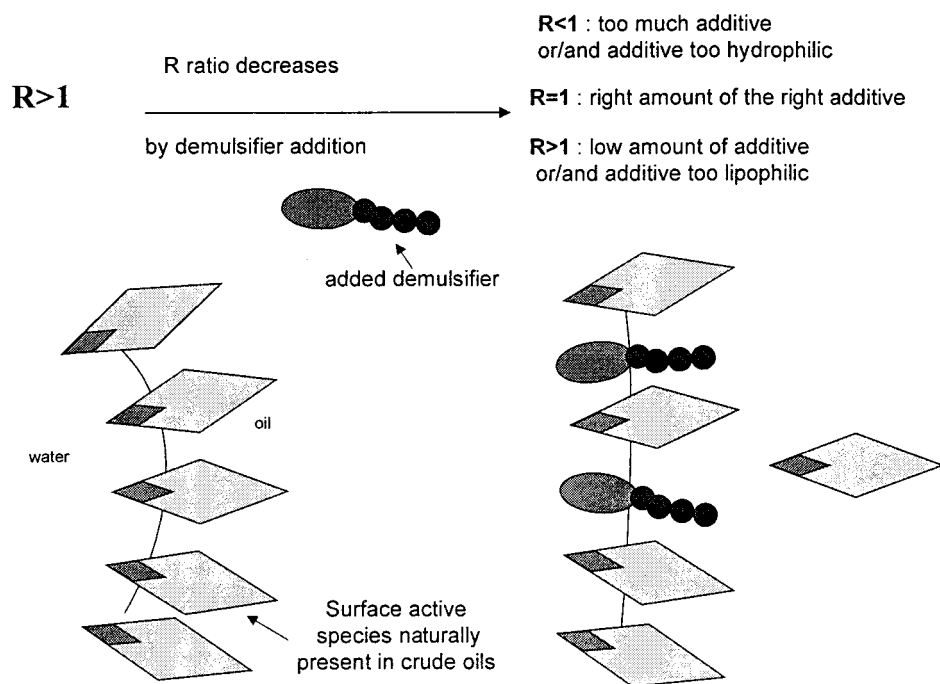


Figure 6. Schematic representation of the demulsifier concentration effect.

The above results show that there exists optimal conditions for a demulsifier to display high efficiency. These optimal conditions correspond to equilibrated interactions of the adsorbed surface-active species with oil and water and, from conclusions drawn from the phase behavior of surfactant–water–oil mixtures,^{3,4} to an average plane, although fluctuating, water–oil interface. Indeed, these adsorbed surface-active species include both the naturally present species in the crude and added demulsifiers molecules as schematically represented in Figure 6. In this picture, the demulsifier may adsorb at the interface with or without replacement of the crude oil surface-active species.

In the above-reported experiments, the emulsifier was added in a given amount and the interactions were varied by scanning salinity, or temperature or ethylene oxide number. It is clear that it is also possible to vary the average interactions of the crude surface-active species and added emulsifier mixture by changes in the demulsifier concentration.

In Figure 5, for example, if we consider the 120 g/L salinity curve, a nonylphenol ethoxylated at 8 or 9 mol and used at 2000 ppm is not hydrophilic enough to achieve complete phase separation within 1 h. It can be conjectured however that increasing the overall concentration of this surfactant should increase its concentration at the interface, thus enhancing the interactions with water. Complete phase separation should then be achieved.

This is shown on a slightly different system (different crude oil) in Figure 7. Three different ethoxylated nonylphenols are used.

An optimal concentration is observed for each additive, and as expected, it occurs at lower concentrations when the hydrophilicity (EON) increases: less additive is required to reach the interaction equilibrium when it is very hydrophilic. Of course, once the concentration is increased, the equilibrium is lost also at a high rate. This explains why the maxima becomes sharper when the demulsifier hydrophilicity increases. Reciprocally, it can be conjectured that if the hydrophilicity is not

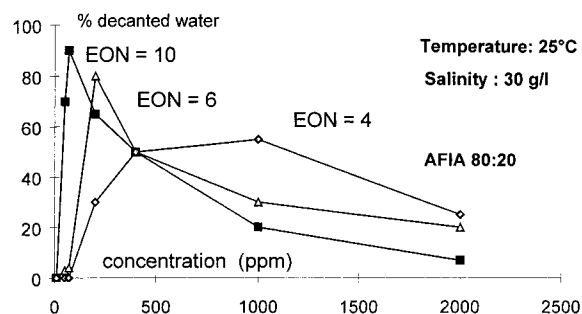


Figure 7. Concentration effect of three ethoxylated nonylphenols. Crude oil: AFIA, % of decanted water measured after 90 min.

high enough, no maximum may be observed, and rather a plateau can be reached. Such a behavior has actually been observed. In Figure 7, the differences in separation efficiencies at optimum have to be explained as well. It is conjectured that increased surfactant concentration at the interface enhances lateral interactions, which in turn promotes interfacial film rigidity. This is indeed detrimental to phase separation, as described in the literature.¹ It thus appears that an additive that is optimal at high concentration has also the drawback of being less effective. From an applicative point of view, however, an additive modifying very effectively the R ratio is not necessarily the most practical because its efficiency window (with respect to concentration) is rather narrow, and it may not thus be able to afford the variations of production conditions that are generally encountered.

Interfacial Tension Measurements

Regarding the investigation of the mechanisms of additive adsorption at the interface, as depicted in Figure 6, interfacial tension measurements, and more specifically dynamic measurements, appear to be particularly relevant. They have been used by several authors.^{15–18,20–22}

Figure 8 shows the results of interfacial tension measurements carried out with the drop tensiometer

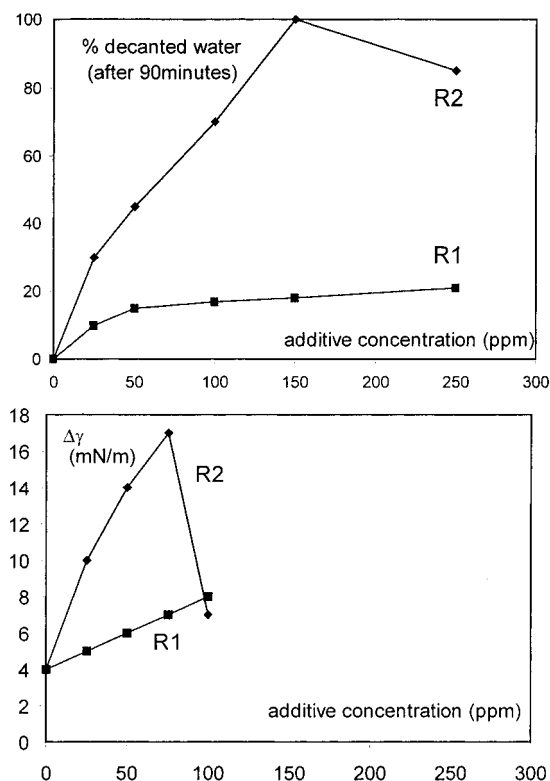


Figure 8. Comparison of the bottle-test results with interfacial tension decrease after 2 min ($\Delta\gamma$). Crude oil: AFIA, salinity 30 g/L NaCl, $T = 30^\circ\text{C}$.

on the Afia crude with resins R2 and R1; they are compared to bottle tests results. It must be pointed out that a drop of oil (containing the additive) is created with a syringe in an aqueous phase, to facilitate the observation and recording of the shape change over time. The water–oil ratio is thus far from the one in an emulsion. To assess the kinetics of additive adsorption, the decrease in interfacial tension, $\Delta\gamma$, after 2 min is recorded. It is plotted in Figure 8 as a function of the additive concentration. (Alternatively, the kinetics can be characterized by a relaxation time, defined as the time required to decrease the interfacial tension by a given fraction of its initial value.¹⁸) A correlation is observed with the phase separation kinetics: resin R2, which is the most effective for emulsion breaking in the range of concentration investigated (and exhibits a maximum), displays also a maximum in adsorption kinetics. In comparison resin R2 does not present any maximum in the same range of concentration and has low $\Delta\gamma$ values. This correlates with a poor separation efficiency in bottle tests.

Indeed, there is a difference in the “optimal” additive concentrations obtained from the two methods. It is likely that it has to be attributed to the large difference in the condition where the two types of experiments have been carried out (the amount of oil–water interface created in the two experiments is very different and the same concentration of additive given in ppm does not correspond to the same concentration per interfacial area unit).

The drop tensiometer can also be used for measuring the Gibbs elasticity modulus of the interface: once the drop has reached its equilibrium shape (equilibrium interfacial tension), a piece of software allows it to vary its volume (mean volume, $10\ \mu\text{L}$; variation, $\pm 2\ \mu\text{L}$), and thus the water–oil interfacial area, in a sinusoidal

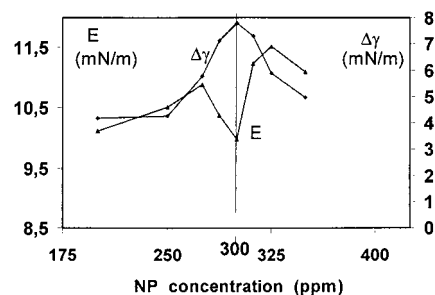


Figure 9. Concentration (NP 12.5) effect on elastic modulus E and lowering of interfacial tension kinetics $\Delta\gamma$ (crude oil: VIC BILH).

manner (period, 9 s). The Gibbs elasticity modulus is then derived,

$$E = \frac{d\gamma}{d \ln A} \quad (1)$$

where γ is the interfacial tension and A the droplet area. (More precisely, in this particular type of experiment, a complex interfacial dilational modulus is measured and E is its modulus). A typical result is reported in Figure 9, together with the decrease in interfacial tension $\Delta\gamma$ after 20 s, as a function of the additive concentration. The elasticity modulus presents a minimum, which coincides with the maximum in surfactant adsorption kinetics. Such a correlation is not surprising because eq 1 can be rewritten, as pointed out by Breen,¹⁸

$$E = \frac{d\gamma}{d \ln A} = \left(\frac{d\gamma}{dt} \right) \left(\frac{dt}{d \ln A} \right) \quad (2)$$

where t is the time. For the situation where $dt/(d \ln A)$ is imposed, the elasticity will vary with the rate at which γ changes with time.

To reconcile both types of information presented in this paper, namely, the relevance of the R ratio for demulsification and of the kinetics of the additive adsorption at the water–oil interface, it can be proposed that the additive that yields balanced interactions of the interface (which includes the crude surface-active species) with water and oil is the fastest to reach its equilibrium state at this interface. A concomitant change in spontaneous curvature is then likely to occur. This would be in agreement with Breen's results,¹⁸ showing that the relaxation time for adsorption is not diffusion-controlled. This is tentatively depicted in Figure 10.

Conclusions

The relevance of earlier observations on the phase behavior of surfactant oil–water mixtures for demulsification has been demonstrated. Consequently, the rules established for microemulsion optimization apply to the optimized selection of demulsifiers. Namely, the interactions of all the surface-active species located at the water–oil interface, which include those coming from the crude and the added demulsifiers molecules, have to be equilibrated with oil and water, and simultaneously, the interface must display a fluctuating character. A correlation has been found between the demulsification efficiency and the kinetics of demulsifier adsorption at the interface (or, alternatively, the Gibbs elasticity modulus).

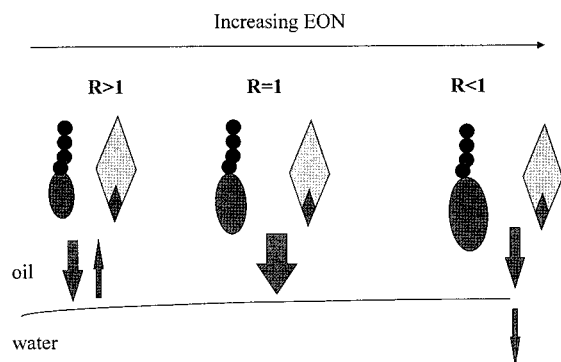


Figure 10. Schematic representation of the effect of additive hydrophilicity (ethylene oxide number) on adsorption kinetics at the oil-water interface. The kinetics is maximum at optimum ($R = 1$).

The results presented in this paper are typical of a number of systems investigated in the laboratory. It is not claimed however that they are universal. In particular, in the case of extremely rigid interfacial films stabilized by solid particles, different behaviors may be obtained.

A practical consequence of the above results is that they provide a rationale to achieve the selection of the demulsifier for a given oil field and to adjust it to a possible shift of production conditions. Useful indications can be provided by interfacial tension measurements carried out on small samples.

From a more fundamental standpoint, the correlation between phase behavior of microemulsion systems and demulsification is information to be taken into account when the mechanisms of coalescence are being discussed. The results presented in this paper suggest that coalescence is favored by the fastest adsorption of demulsifier molecules, which is achieved when the average interactions of the surface-active species are equilibrated with oil and water.

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