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Breaking of Water-in-Crude Oil Emulsions. Part 9. New Interfacial rheology characteristics measured using a spinning drop rheometer at optimum formulation

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Abstract

Water-crude oil interfaces are often exhibiting a viscoelastic film with a high mechanical resistance, consisting of natural surfactants in crude oil, mainly asphaltenes, which stabilize water-in-oil emulsions. Shear and dilational interfacial rheological properties of these systems have been studied for more than 40 years. However, a clear understanding of the role of interfacial rheological behavior in water-in-oil emulsions destabilization at optimal formulation (when the hydrophilic lipophilic deviation $HLD = 0$) has been established only a few months ago thanks to the use of an oscillatory spinning drop rheometer. In the first articles using this equipment, the dilational interfacial rheological properties of water-oil interfaces has been measured for very simple systems, with pure cyclohexane and pure surfactant, showing a very consistent new behavior. In the present article different oils are used and the system complexity is increased up to be close to actual petroleum cases by including asphaltenes. As in systems without asphaltenes, a deep minimum in dilational modulus and phase angle is found at optimum formulation, thus showing that the reported interfacial rheology phenomenon is very general. Then, a practical approach for crude oil dehydration is designed, and the formulation scan is carried out by adding an increasing concentration of a surfactant acting as a demulsifier, as in the bottle test method usually used. For the first time with oil containing asphaltenes, the occurrence of a deep minimum of interfacial dilational rheological properties is shown to happen at the point of minimum interfacial tension and maximum instability of emulsions, i.e. at optimum formulation. This is a significant advance in the evaluation of the selected demulsifier performance for crude oil dehydration.

Key words:

Formulation, HLD, interfacial tension, emulsion instability, interfacial rheology, asphaltenes, demulsifier.

Abstract

When demulsifier surfactants are added, W/O emulsions containing asphaltenes in the oil phase, are shown to exhibit several properties at the so-called optimum formulation, where the interfacial tension is minimum. A deep minimum in emulsion stability is correlated with minima of various interfacial properties, i.e. interfacial dilational modulus, interfacial viscosity and phase angle. These results are similar to our previous observations with simpler oils. The formulation variation was obtained by two kinds of scans which were shown to be equivalent. In the first type of scan, the temperature, the salinity or the EON (ethylene oxide number of a nonionic surfactant) was continuously changed. In the other type of scan, a demulsifier (surfactant soluble in both oil and water) was used in variable concentrations. A deep minimum in interfacial tension is reported for demulsifier concentration scans for the first time. The usual optimum formulation rules can predict the conditions at which the demulsifier's efficiency is optimized

1. Introduction

The persistence of water-in-oil emulsions that are generated in petroleum production processes is in general related to the properties of the interfacial layer formed on the drop surface. This ~~film~~ layer is made up of natural surfactants such as asphaltenes, most of the time existing as aggregated structures^{1,2} which can form strong inter- and intra-molecular bonds that hinder the breakdown of emulsions³⁻⁷. There is evidence that after the initial adsorption of these species, a molecular densification and re-arrangement takes place, forming a rigid layer (which in some cases has been called “skin”) that can favor a high stability of water-in-oil emulsions^{6,8-10}.

Several authors have studied the interfacial rheological behavior of oil/water systems confirming these phenomena^{1,11-17}. It has been determined that when the asphaltenes molecules are adsorbed at the interface, the stability of the emulsions thus formed appears to correlate with the elastic dilational modulus^{6,18-21}. However, these conclusions refer to systems which are not at the so-called “optimal formulation”, which is the selected one to break emulsions in dehydration or crude oil dewatering processes according to our previous work²²⁻²⁴. The main reason is that the equipment generally used for evaluating interfacial rheology (i.e. the oscillating pendant drop apparatus) is not compatible with the optimum formulation conditions used in dehydration, when the interfacial tension is lower than 1 mN/m. At such a low tension the pendant drop elongates, detaches and falls. Consequently, up to now it has not been known how the above interfacial rheology conclusions apply in actual dehydration conditions with a very low tension occurrence.

Emulsion breakage has been casually related to the physicochemical formulation of surfactant-oil-water (SOW) systems a long time ago²⁵⁻²⁶. Then, a number of research studies have clearly demonstrated in a direct or indirect way, the role of surfactants in the destabilization in emulsions²⁷⁻³⁴. In a pioneering work on the petroleum dehydration principle, the process of destabilizing emulsions was explained through a model in which natural petroleum surfactants, i.e. asphaltenes, originally tend to produce stable water-in-oil emulsions²². This model indicates that, in order to destabilize these emulsions, it is necessary to add a surfactant called demulsifier agent, until the so-called optimum formulation situation is reached. This general method was supported later by some more fundamental studies³⁵.

It is worth noting that the optimum formulation concept has been presented first as a linear empirical correlation^{28,30} between the variables describing a SOW system. When such simple equation was satisfied, a very low minimum in interfacial tension was found to be attained, as required for improving the enhanced oil recovery (EOR) efficiency. It was discovered some time later^{27,29,31,32} that a deep minimum in emulsion stability was occurring exactly at the same condition. The optimum formulation correlation was associated with some physicochemical concepts related to the interactions of the surfactant with the oil (Aco) and with water (Acw) molecules according to Winsor’s early proposal of the ratio $R = Aco/Acw$, with $R = 1$ at optimum. It was later presented as the Hydrophilic-Lipophilic Deviation³⁶ (HLD) equation which was found to be equivalent to a Aco-Acw difference and to be quite accurate in practice for very simple systems.

The HLD is presented now as the following physicochemical formulation equations for anionic and nonionic surfactants:

$$HLD_{AI} = SCP_{AI} + \ln S - k EACN - a_T (T-25) \quad (1)$$

$$HLD_{NI} = SCP_{NI} + b S - k EACN + c_T (T-25) \quad (2)$$

where SCP is the Surfactant Characteristic Parameter. In original presentations^{28,30} SCP was

called σ for an anionic surfactant system and $\beta = \alpha - \text{EON}$ for a nonionic one, where EON was the average ethylene oxide number and α the contribution of the tail³⁶. In the previous equations, S is the salinity in wt%, EACN is the equivalent alkane carbon number of the oil phase, when it is not a n-alkane (ACN), T the temperature in °C, and b, k, a_T and c_T are positive constants that vary according to the type of components^{36,37}. The optimum formulation condition is expressed as $\text{HLD} = 0$ and results in the occurrence of a minimum interfacial tension (and eventually a WIII three-phase behavior), as well as a deep minimum in emulsion stability^{23,24,27,32}.

The two equations are essentially the same in principle, only with slight variations due to the facts that the salinity and temperature effects are different for the two types of surfactants. In the present case dedicated to a petroleum reservoir, the brine salinity, the oil nature and the temperature are fixed, and the correlation becomes very simple, with the HLD only depending of the surfactant characteristic parameter SCP, i.e.

$$\text{HLD} = \text{SCP} + \text{Q} \quad (3)$$

Where Q is a constant depending on the brine salinity, oil EACN and temperature, but independent of the surfactant.

In the case the formulation is changed by mixing two surfactants (at constant oil, brine and temperature and thus at constant Q) the HLD of the mixed surfactant systems has been supposed to linearly vary with the contribution of each component, i.e. according to

$$\text{HLD}_M = X_1 \text{HLD}_1 + X_2 \text{HLD}_2 \quad (4)$$

Where X_1 and $X_2 = 1 - X_1$ are the volume or mass fraction in the surfactant mixture. According to equation (3) this is equivalent to the same linear rule with the surfactant characteristic parameters

$$\text{SCP}_M = X_1 \text{SCP}_1 + X_2 \text{SCP}_2 \text{ or } \text{SCP}_M = X_1 \text{SCP}_1 + (1 - X_1) \text{SCP}_2 \quad (5)$$

Where SCP_M is the surfactant mixture characteristic parameter. This equation has been found to be exact in many cases³⁸, particularly when the two surfactants species are similar in structure, for instance in alkyl benzene sulfonates with different tails²⁸, or alcohols with different ethoxylation³⁰. It might not be the case if the surfactant are quite different or if they strongly interact³⁸.

In the present case, the asphaltene-demulsifier mixture is assumed for simplicity to correspond to a linear relation^{38,39} to calculate its SPC, according to equation (5)³⁷.

$$\text{SCP}_M = X_D \text{SCP}_D + X_A \text{SCP}_A = X_D \text{SCP}_D + (1 - X_D) \text{SCP}_A \quad (6)$$

where X_A and X_D are the volume or mass fractions of asphaltenes acting as surfactants (A) and added demulsifier (D), whereas SCP_A and SCP_D are the surfactant characteristic parameters for asphaltenes and demulsifier respectively, and SCP_M for their mixture.

There are two ways²³ to determine the optimum formulation according to equation (6) when the asphaltenes type (and its parameter SCP_A), the salinity, the oil EACN, and T are given to characterize the system and calculate Q. Equation (3) corresponds to an optimum formulation, i.e. to $\text{HLD} = 0$ for a $\text{SCP}^*_{\text{SYS}}$ value expressed as follows.

$$SCP^*_M = X_D SCP_D + (1-X_D) SCP_A \quad (7)$$

The first method is to use a selected demulsifier D (with a given SCP_D value) and to change its X_D fraction by changing its added concentration (C_D) in a bottle test experiment. At some C^*_D concentration, equation (7) is satisfied and an optimum formulation is attained, exhibiting all the usual properties, i.e. a minimum interfacial tension, eventually a three-phase behavior, and for our specific interest here, a minimum emulsion stability.

The alternative way is having a given dose of demulsifier (i.e. a fixed concentration C_D and thus a fixed X_D) and thus changing the nature of the demulsifier (and its SCP_D), e.g., making it more or less hydrophilic, as in an EON scan for ethoxylated surfactants^{23,24}, until equation (7) is satisfied.

The first method is generally used to determine the best demulsifier dosis to be added to break the emulsion, whereas the second one might also be used to select a more efficient demulsifier with a lower C_D^* .

Equation (7) can be re-written to predict the optimum demulsifier concentration C_D^* as:

$$C_D^* = k_D X_D = k_D (SCP_M - SCP_A)/(SCP_D - SCP_A) \quad (8)$$

Where k_D is a coefficient relating the demulsifier concentration to its fraction in the mixture^{24,37}. It is seen that with equation (8) that the exact demulsifier concentration C_D^* to attain the minimum stability of crude oil-in-water emulsions, can be calculated when k_D , SCP_{SYS} , SCP_A and SCP_D are available.

The second issue in the efficiency of a demulsifier has to do with the reduction of emulsion persistence at its minimum when $HLD=0$, particularly by increasing the drainage rate of thin films that form between approaching emulsion drops and the reduction of rheological parameters, particularly the dilational modulus. This has been studied recently⁴¹⁻⁴³ for very simple SOW systems, and is presented here for the first time with crude oil components.

A third important requirement for a demulsifier to be effective, whatever the formulation, is that there must be a very efficient mass transfer of the hydrophilic demulsifier from one of the phases to the interface, a situation which depends on its molecular weight and structure. For instance, it has been known that a demulsifier molecule of smaller size^{34,44-46}, branched⁴⁷, and partitioning well between the aqueous and oily phase, will be more rapidly transported to the interface and will perform better^{34,23,24}. The interfacial activity of the demulsifier at optimum formulation results in a low tension and considerably reduces interfacial tension gradients^{23,24,34,44,48,49} so that the dilational modulus becomes very low and the Gibbs-Marangoni effect vanishes. The fact that at optimum formulation fast surfactant exchanges occur⁵⁰ as well as a very low interfacial rheological modulus^{41,42} thus favors the third requirement.

It has also been shown that the best demulsifiers are those with a faster progression of dynamic interfacial tension^{21,34,51}. The presence of additives such as alcohols (sec-butanol in particular)^{42,51} or short chain acids⁵², also increases the rate of mass transfer at interface, and thus contributes to decrease the interfacial viscosity and to increase the coalescence of the droplets^{45,53}. All these phenomena may be optimized to improve the quality/performance of the formulation on the emulsion instability as shown in previous articles in the present journal^{37,54,55}.

Since the late 1970's a possible relationship between interfacial rheological properties and the stability of water-in-oil emulsions versus demulsifier action has been examined^{21,35,44,45-48,53,55-59}. The conclusions of these studies are consistent and indicate that interfacial tension outside the optimum formulation zone is not related to the stability of water-in-oil emulsions in the presence of demulsifiers. They have also proved that demulsifiers tend to decrease the interfacial elasticity and viscosity^{44,47,53,57}, and that a good performance tends to occur when there are similarly soluble in oil and water^{22,24,46,57}. In this situation, the dilational modulus and interfacial viscosity are in general low³⁴.

Outside the optimal formulation zone, i.e. for $HLD < 0$ or $HLD > 0$, it was found that systems where the dilational elastic modulus is less than 5 mN/m exhibit a low stability^{34,44,47}. However, systems with larger elastic modulus or large interfacial shear viscosities were also found sometimes to produce unstable emulsions^{35,48,59} and systems with small interfacial shear viscosities can form stable emulsions^{34,57}.

Nevertheless, the consistency is not wholly warranted, and no phenomenology has been clearly established yet. Some studies argued that the interfacial shear viscosity plays a more important role than the dilational elasticity⁵³, while another reports that this elasticity is more significant²¹. On the other hand, the minimum stability is said to correspond⁶⁰ or not³⁵ with the minimum interfacial viscosity or elasticity close to the optimum formulation.

The influence of the interfacial shear modulus is yet far from clear. However, this modulus is generally zero at short interfacial ages (less than one day for good asphaltene solvents and a few hours for asphaltenes in heptol⁶). Its influence could therefore be important only for aged emulsions. When relating emulsion stability to interfacial rheology, it must be kept in mind that various processes with different timescales are involved: sedimentation or creaming of drops, slower if the drops are smaller, Ostwald ripening, slower if the drop concentration is smaller, and coalescence that involves two distinct processes: drops approach, which is rather rapid, and drop coalescence, that can be very long if the surface layer is densely packed. This means that there are many different timescales in the problem, and that measuring the rheological parameters in a small frequency range cannot lead in general to meaningful correlations.

A simple case is found with unstable emulsions close to optimal formulation, which lifetime is of the order of a few minutes: sedimentation or creaming and Ostwald ripening have no time to proceed, and the stability is controlled by the approach of emulsion drops. Because surfactant can quickly exchange between the drops and the continuous phase, the Marangoni forces opposing thinning of films between drops are much reduced. They are controlled by an effective dilational modulus close to that measured by compressing the oil-water interface at a frequency comparable to the inverse thinning time, i.e. of the order of 0.1 s^{-1} , thinning times being of the order of 10 s.

Only very few studies investigated interfacial rheology close to the optimum formulation. The early studies have been performed with interfacial shear rheology methods⁵³, not with dilational rheology, which is said to be the most important issue for demulsification^{21,61}. In these previous investigations, the minimum stability of emulsions was measured, but the interfacial dilational rheology evaluation was never performed near $HLD = 0$ until recently.

The FIRP Laboratory and CITEC-ULA workshop jointly developed an oscillatory spinning drop interfacial rheometer⁶², that allows the measurement of the dilational interfacial rheology at low and ultralow interfacial tension, i.e. at less than 1 mN/m. This technique opened a new field of research to study the relationship between the dilational elasticity and the film formation at the water/oil interface, with the instability of emulsions at the optimal formulation with applications in crude oil dewatering and enhanced oil recovery.

In our previous research, the interfacial dilational rheological properties were determined for very simple systems, i.e. cyclohexane, water and a pure surfactant using the oscillatory spinning drop interfacial rheometer at low frequencies ($\sim 0.1 \text{ s}^{-1}$)⁴¹⁻⁴³. The new fundamental result was that at optimal formulation (HLD = 0) with ultralow interfacial tension, the interfacial elastic modulus is minimum and close to zero, while at a certain “distance” (HLD > 0), particularly far away from the optimal formulation (HLD \gg 0) it is much larger. This explains why the thinning of the films formed between approaching drops is fast, and leads to instabilities and to film rupture⁴².

So far, no studies of interfacial dilatational rheological properties at the optimum formulation were performed with oils representative of real crudes. The purpose of the present article is to fill this gap and to investigate if minima of interfacial properties are also observed at optimum formulation in complex SOW systems. If the HLD effect on the interfacial rheology is very general, it could straightforwardly be used in demulsifier applications to break crude oil emulsions

In the following results, the same oscillatory spinning drop interfacial rheometry technique is used to evaluate the interfacial behavior of systems with more complex structures of oil, such as long alkane, natural triglycerides mixture and a very light paraffinic crude, as well as cyclohexane dilutions of heavy crude oil containing asphaltenes. In the first type of experiments presented here, the physicochemical formulation is scanned by changing the temperature for an extended ethoxylated surfactant, to complement the other scans previously reported. The second type of experiments are bottle tests scans used for crude oil dewatering in previous articles of this series; it is the concentration of demulsifier C_D which is varied at a fixed asphaltene concentration C_A , in order to change the SCP formulation parameter. The influence of the resulting formulation scan on the interfacial dilational rheology is then shown and the probable mechanism explained.

2. Experimental conditions

2.1 Products used

Liquid phases

N-heptane and N-hexadecane are from Sigma, and soybean oil is from an ordinary food store. The very light paraffinic crude oil (40 ° API) from Abu Dhabi has a low density (0.79 g/cm^3 at 60°C) essentially without clearly detectable asphaltenes (less than 1 wt% using heptane precipitation). Hamaca crude oil (8 °API) is from the Orinoco oil belt (Venezuela). It contains 17 wt % asphaltenes and is diluted in different proportions with cyclohexane, technical grade from Sigma Aldrich (USA), as the oil phase. The aqueous phase in nonionic systems always contains 1 wt% NaCl to easily measure the emulsion conductivity and determine the emulsion type. For the extended anionic surfactant systems the aqueous phase is a NaCl brine solution of variable salinity. Sodium chloride is analytical grade from J.T. Baker (Mexico). Milli-Q water was used.

Surfactants

Ethoxylated nonylphenols, i.e. small size nonionic surfactants were obtained from Witco Chemicals. Two products were used. Their average number of ethylene oxide groups per molecule were EON=6 (MW = 440 Da, HLB = 10.9, surfactant characteristic parameter, SCP = 0.5) and EON=8 (MW = 572 Da, HLB = 12.3, SCP = -1.5). They are designated as NPEO6 and NPEO8 respectively as in a previous article⁴¹. Continuous variation of EON is obtained by mixing NPEO6 and NPEO8 in different molar proportions. Data with ordinary anionic surfactant like sodium dodecyl sulfate has been shown in a previous article⁴². The large anionic surfactant molecule used here is an extended molecule $\text{C}_{12}(\text{PO})_{14}(\text{EO})_2\text{SO}_4\text{Na}$ obtained from our industrial partner Lipesa (Venezuela) with an average molecular weight of 1188 Da and a surfactant characteristic parameter SCP = -0.92.

The molecule of purely nonionic extended surfactant $\text{C}_{18}(\text{PO})_{18}(\text{EO})_{10}$ with the head consisting of a long polyethoxylated group, is selected as another type of species. This surfactant is doubly sensitive to an increase in temperature which decreases the hydrophilicity of the polyEO head group³⁰ and increases the lipophilicity of the polyPO tail part⁶³. It was recently shown⁶⁴ that its SCP parameter value is considerably increasing with a rise in temperature, about 2-3 times more than for an ordinary polyethoxylated nonionic surfactant with the same EON. It was used to carry out a temperature scan to strongly vary the formulation for different oil types.

2.2 Methods.

Typical Formulation scans

The formulation scans were made according to the standard procedure: the surfactant is dissolved in 5 ml of the aqueous phase which is then equilibrated with 5 ml of the oil phase in graduated test tubes. The samples were gently shaken and left in a thermostated bath at 30°C (unless another experimental temperature is indicated) for 24 h, which is the time that warrants a thermodynamic equilibrium before evaluation. The surfactant concentrations used were very small, often close to the critical micellar concentration in water, so no third phase microemulsions were seen close to the optimal formulation. Only two phases, oil and water were observed as in the pure oil systems studied previously⁴¹. Equilibrium was considered to be reached when the interfacial tension remained constant, typically after one hour. The different

studied samples correspond to a HLD scan. In the ~~small aqueous volume of the~~ nonionic surfactant system, the EON was varied between 6 and 7. In the anionic extended surfactant systems, the salinity of the aqueous phase was changed from 2.5 to 4.5 wt% NaCl. In the nonionic extended surfactant system, the temperature is the formulation variable. In all samples, the surfactant concentration was taken as 1 mg/L (indicated as 1,000 ppm), unless otherwise mentioned. It is worth noting that asphaltenes and surfactant concentrations are indicated as ppm in volume or weight (essentially equivalent to mg/L or mg/Kg) to use the same unit than in previous papers of this series and facilitate the comparison. Such surfactant concentration is small, often close to the critical micellar concentration in water and thus no microemulsion formation was observed. In particular, no middle phase is found near HLD=0 in the equilibrated test tubes even in asphaltene free oil, as it was the case in similar systems presented in previous research⁴¹. The EON and S formulation scans with diluted crude were made at both low and high asphaltene concentrations, i.e., $C_A = 300$ and 10,000 ppm, which are extreme cases in practice. The optimal formulation corresponds to the point where the interfacial tension is minimum as in original EOR studies^{28,65}.

Surfactant (demulsifier) concentration scan

The nonionic surfactant NPE of EON=6 and the anionic extended $C_{12}(PO)_{14}(EO)_2SO_4Na$ surfactant are the same than in a previous article⁴ and are tested here as demulsifiers. They were diluted at variable concentration in the brine. For the anionic surfactant, the aqueous phase contains 4 wt% NaCl. The oil phase was Hamaca crude diluted in cyclohexane, containing two extreme asphaltene concentrations C_A at 100 and 10,000 ppm. In the formulation scan the demulsifier surfactant concentration C_D is varied from 0 to 500 ppm, a range which allows to pass from HLD > 0 to HLD < 0 at both low and high C_A , i.e from below to above the threshold point T.

Interfacial tension

The interfacial tension between the equilibrated water and oil phases was measured using a spinning drop tensiometer. A small oil drop is placed in the capillary containing the aqueous phase and then rotated at an angular frequency ω_{rot} . The drop then elongates due to the centrifugal force and takes an equilibrium shape when this force is equilibrated by the interfacial tension. The interfacial tension (IFT) was calculated according to Vonnegut⁶⁶ who considered the oil drop in rotation with the shape of a cylinder with a diameter d , a length l , and hemispherical edges. For a length/droplet diameter > 4, the interfacial tension is given by:

$$\gamma = \Delta\rho \omega_{rot}^2 d^3/32 \quad (9)$$

where γ is the interfacial tension (in N/m), d is the diameter of the droplet at middle equator (in m), $\Delta\rho$ is the density difference between the two fluids (in kg/L), and ω_{rot} is the rotational velocity (in rev/s).

Interfacial rheology

A oscillating spinning drop tensiometer modified as interfacial rheometer (RI-1000 model made by Lab. FIRP-CITEC, Universidad de Los Andes, Venezuela) is used to perform interfacial rheology measurements. It is equipped with a device allowing to sinusoidally modulate the rotational velocity at a frequency F . Consequently, the droplet is periodically extended and contracted, and the instrument allows the determination of the interfacial dilational elastic modulus, surface viscosity and phase angle, as discussed previously^{41,62}. When the drop area varies sinusoidally, the interfacial tension also changes sinusoidally. The amplitude of the

variation of ω_{rot} used was 1,000 rpm (revolution per minute) and the average value of ω_{rot} was depending on the interfacial tension (and the drop elongation). For ultralow interfacial tension systems ω_{rot} was varied from 3,000 to 4,000 rpm.

The dilational viscoelastic modulus, is calculated according to equation (10),

$$E = (\Delta\gamma/\Delta A) A_0 \quad (10)$$

where $\Delta\gamma$ is the interfacial tension variation and ΔA is the area variation, A_0 being the average area of the drop. The phase angle ϕ corresponds to the phase shift between the sinusoidal curves of interfacial tension and the interfacial area. The storage and loss moduli, respectively E' and E'' , and the interfacial viscosity η are given by equations (11),:

$$E' = E \cos\phi, E'' = E \sin\phi \text{ and } \eta = E \sin\phi/F \quad (11)$$

In the absence of relaxation processes affecting the dilational modulus, phase angle ϕ equals 0 and the interfacial layer is purely elastic, whereas if the viscous dissipative losses dominate, the phase angle is close to 90°. Interfaces with a phase angle between 0 and 90° have viscoelastic behaviors. The instrument is equipped with a software that automatically calculates interfacial dilational rheological properties E , ϕ , and η ⁶².

In the experiments performed, the frequency F was fixed to 0.1 s⁻¹ and the amplitude of the oscillations to 10%, for which the interfacial response was found to be linear.

Two remarks should be made here. Because the surfactants are not irreversibly adsorbed at the interface (at least not fully), exchanges between interface and bulk are possible. The measured modulus is therefore not the intrinsic modulus that could only be measured at very high frequencies, much larger than the inverse exchange times.

A second remark concerns the type of modulus measured: the surface is periodically extended and compressed along the axis of the drop; this deformation is equivalent to that used to measure the Young modulus. In two dimensions this modulus is the sum of the pure dilatation and of the pure shear moduli. In the systems studied, the interfacial layers are fluid, so the elastic shear modulus is zero and the measured elastic modulus is the pure dilational modulus. The viscosity measured is in turn the sum of the shear and of the pure compression surface viscosities. In the following, we will continue to use the notations E and η for simplicity.

When oil contains asphaltenes, it has been reported that a finite shear modulus develops after some time, a few hours in oils diluted with heptol, and days in oils diluted with toluene. The dilution oil used here is an asphaltene solvent intermediate between toluene and heptol, so the shear modulus is likely to remain negligible in the experiments performed. The emulsions studied were not aged either, so the surface layers were analog to those studied in the spinning drop technique

Stability of emulsions

Emulsions are obtained by first shaking a blend of equal volumes of oil and water. The oil-water system is subsequently pre-equilibrated for a period of 24 h and then re-emulsified with an Ultraturrax turbine blender at 30,000 rpm for 30 s. The emulsion persistence, so-called stability in the following, is taken as the time necessary for the separation of 60% of the aqueous phase as in previous publications^{23,24,41-43,67,68} This particular selection is arbitrary but it has been found to be appropriate to characterize emulsion stability.^{32,42}

3. Results and discussion

3.1. Complementary data on interfacial rheology with different systems

In the previous articles on interfacial rheology dealing with very simple systems⁴¹⁻⁴³ the oil phase was pure cyclohexane (EACN = 3.5) or a kerosene mixture (EACN = 9-10), and the surfactant were sodium dodecyl sulfate, a mixture of alkylphenol ethoxylates or an anionic extended surfactant.

To complement these data, other oil phases are taken here: short and long liquid alkanes (heptane and hexadecane), a vegetable triglyceride mixture (soybean oil) and a very light paraffinic crude oil with almost no asphaltene, but likely to contain other polar substances like resins or naphthenic acids.

The selected surfactant for these experiments is $C_{18}(PO)_{18}(EO)_{10}$ which is known to produce a low tension with polar oils⁶⁴. It has an extended structure and a nonionic polar head, at the difference of the extended surfactants with anionic polar heads studied previously.

This surfactant contains two alkoxyated parts which are both very influenced by the temperature. This is why the temperature is taken as the scanned formulation variable, instead of the brine salinity and EON scans previously used.

Figure 1 shows the interfacial tension variation for these different systems when a temperature scan is carried out. As for all formulation scans, a minimum interfacial tension is found at a temperature T^* corresponding to the optimum formulation at which $HDL = 0$ according to equation (2). This indicates that T^* depends of oil nature, i.e. its EACN, since all other variables are kept constant. This temperature is essentially the same than the phase inversion temperature (PIT) value introduced by the Shinoda's group⁶⁹⁻⁷¹ in the 1960's for other applications; the temperature has been systematically used as a scan variable even with complex systems^{72,73}.

As in the data previously reported for very simple systems containing cyclohexane and kerosen^{41,43}, the rheological properties shown in Figure 1. It is seen that the interfacial dilational modulus E , the interfacial viscosity η and the phase angle ϕ are all minimum at the optimum formulation T^* where the minimum interfacial tension γ is also found.

This figure 1 is thus some kind of first generalization of the relation discussed previously only with systems containing cyclohexane oil and kerosen⁴¹⁻⁴³. This exact matching of the interfacial rheology minimum occurrence at $HLD = 0$, is thus probably quite general as the minimum emulsion stability happening at the same specific formulation^{27,29,30-32,34,67}.

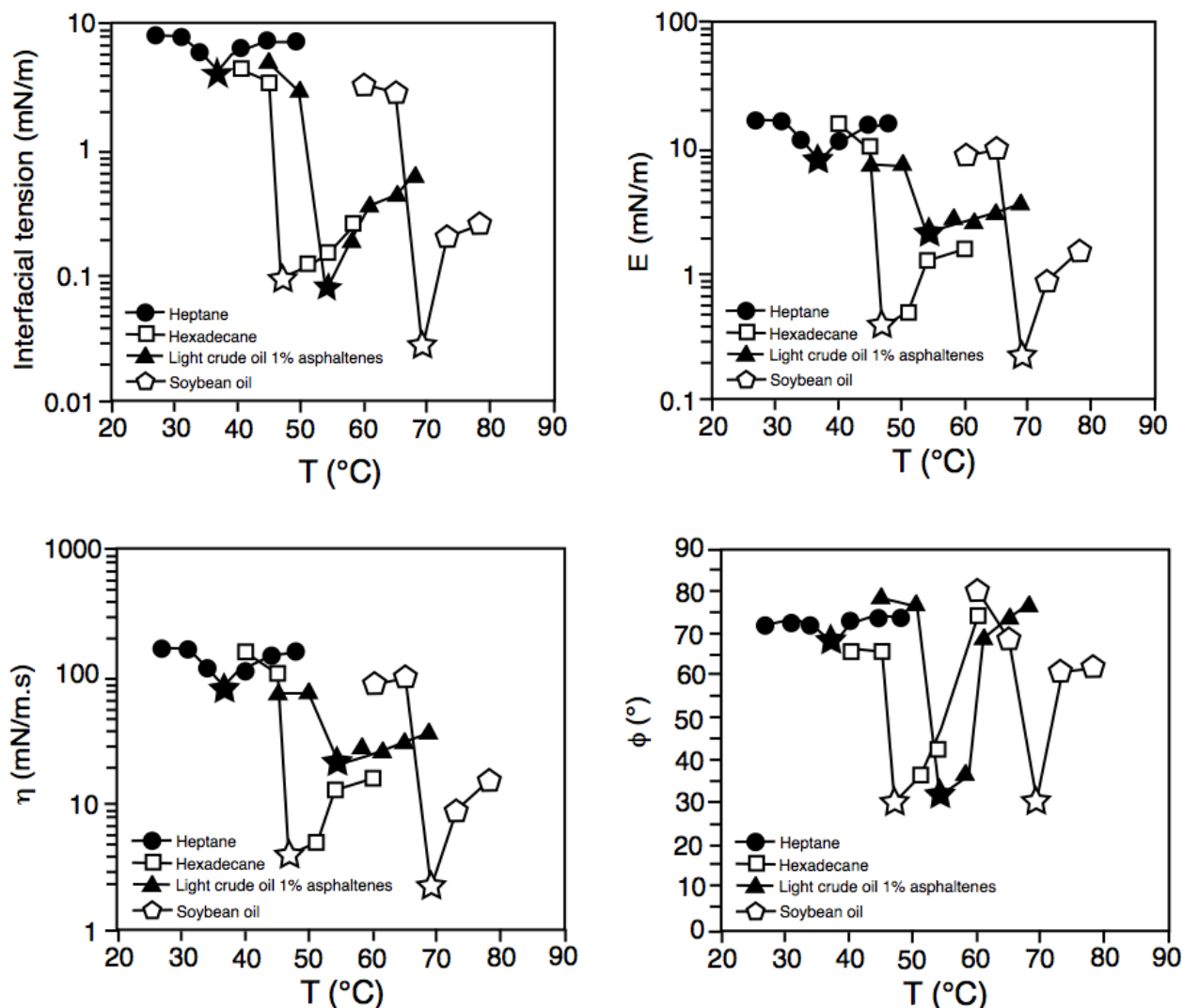


Fig 1. Interfacial tension (γ) and interfacial rheological properties (E , η , ϕ) along a temperature scan for systems containing 0.1 wt% of nonionic extended surfactant $C_{18}(PO)_{18}(EO)_{10}$ for all oils but soybean (where it is 0.05wt%), 1 % wt NaCl brine, and various oil phases. Light crude oil from Abu Dhabi is a paraffinic crude of 40°API with less than 1 wt% asphaltenes.

It is worth noting in figure 1 that the change of the minimum temperature T^* with the oil ACN is fast, e.g. $T^*=38^\circ\text{C}$ for heptane, and 47°C for hexadecane. The variation in the HLD_{NI} equation (2) may be thus calculated as $dEACN/dT = 0.75^\circ\text{C}^{-1}$, i.e. it is much higher than the value (0.45°C^{-1}) found for alkylphenol ethoxylates with the same EON³⁰. This is obviously due to the additional effect of increasing temperature on the dehydration of the polypropyleneoxyde intermediate zone, as shown previously⁶³. If this $dEACN/dT$ tendency is extrapolated to the other oils, the EACN of the light crude oil is relatively high (about 22) but quite acceptable since it is paraffinic. However, the EACN of the triglyceride soybean oil is found to be above 30, i.e. higher than usually reported elsewhere for this kind of substance^{72,74-77}. Such a deviation might be due to many reasons, not only the probable impurities in an ordinary commercial product, but also to the fact that the surfactant concentration is very low and the actual EON of the interfacially active mixture is thus likely to be higher because of the partitioning of the oligomers as discussed elsewhere^{74,78}. According to the HLD_{NI} equation, a higher interfacial EON would result in a higher EACN if the average EON is used. More studies, with a high surfactant concentration as recently proposed⁷⁹ are thus required to accurately estimate the EACN.

The minimum tension values at optimum formulation with heptane and hexadecane in figure 1 confirm the occurrence of an unusual trend found with extended surfactant having a long polypropylene oxide chain intermediate. The data shows that the performance of this surfactant, i.e. its attainment of a lower tension minimum, is improved when the n-alkane gets longer, as casually reported some time ago^{80,81} contrarily to the usual tendency. The minimum of the rheological properties follows the same trend in Figure 1. As shown a long time ago as a specific attractive characteristic of extended surfactant^{74,82,83} a low tension can be attained with oils containing polar species like triglycerides or heavy crude oils. This was found to happen also when the extended surfactant is only one component of a mixture with up to three surfactant species⁸⁴.

The light crude oil of Figure 1 contains very little (if not) asphaltenes, although it forms stable emulsions and a dehydration process might be necessary at the well head. In the following section, we will describe the behavior of oils containing large amounts of asphaltenes, which form extremely stable emulsions, quite difficult to break

3.2 Formulation scans for surfactant/crude oil in cyclohexane/brine systems.

Interfacial tension

The Hamaka crude oil used in this study is very viscous, so dilutions have been performed. This required to use an oil phase being a good solvent of asphaltenes in order to avoid precipitation, but not too good, not to alter the asphaltene behavior^{1,2}. Indeed, when asphaltenes are well solubilized in aromatic solvents, such as toluene or xylene, they are less adsorbed at the interface.

Cyclohexane is an asphaltene solvent with intermediate properties that has been used in previous studies^{23,24}. It was also selected here because it exhibits a good solubilization of the surfactants used, e.g. $C_{12}(PO)_{14}(EO)_2SO_4Na$ extended anionic and ethoxylated alkylphenol nonionic NPEON. Cyclohexane has been the oil phase in the reference simple systems experiments^{41,43} which will be used for the sake of comparisons (their composition being the same, excepted from the presence of asphaltenes).

The data is reported for two extreme cases 300 ppm and 10,000 ppm of asphaltenes. As reported in the previous article of this series², a high concentration of asphaltenes alters the EACN. Figure 2 displays the interfacial tension of the surfactant/crude oil diluted in cyclohexane/brine systems as a function of a formulation variable, which is the aqueous phase salinity when the surfactant is an extended anionic, and the EON of a NPE6/NPE8 mixture of nonionics. Using the Winsor terminology, the phase behavior is indicated as WI (or respectively WII) for two phase systems in which the surfactant-rich phase is the lower aqueous (or respectively the upper oily) phase:

The HLD was calculated through equation (1) for the anionic extended surfactant and equation (2) for the nonionic one, where the values of σ (here SCP_{AI}), S , k , EACN, a_T and T for the anionic and α -EON (here SCP_{NI}), b , S , k , EACN, c_T and T for the nonionic are the known ones in the literature³⁶

A strong minimum of interfacial tension is observed for the anionic system, when formulation is changed by varying salinity. The minimum is still significant, although shallower, for the nonionic system in an EON scan, especially at high asphaltene concentration.

It is worth noting that close to the minimum, the interfacial tensions are significantly higher than those found with the same systems without asphaltenes⁴¹. It may be also remarked that the tensions are higher for $C_A = 10,000$ ppm than for $C_A = 300$ ppm, and that this increase of

minimum interfacial tension is particularly important in the nonionic system.

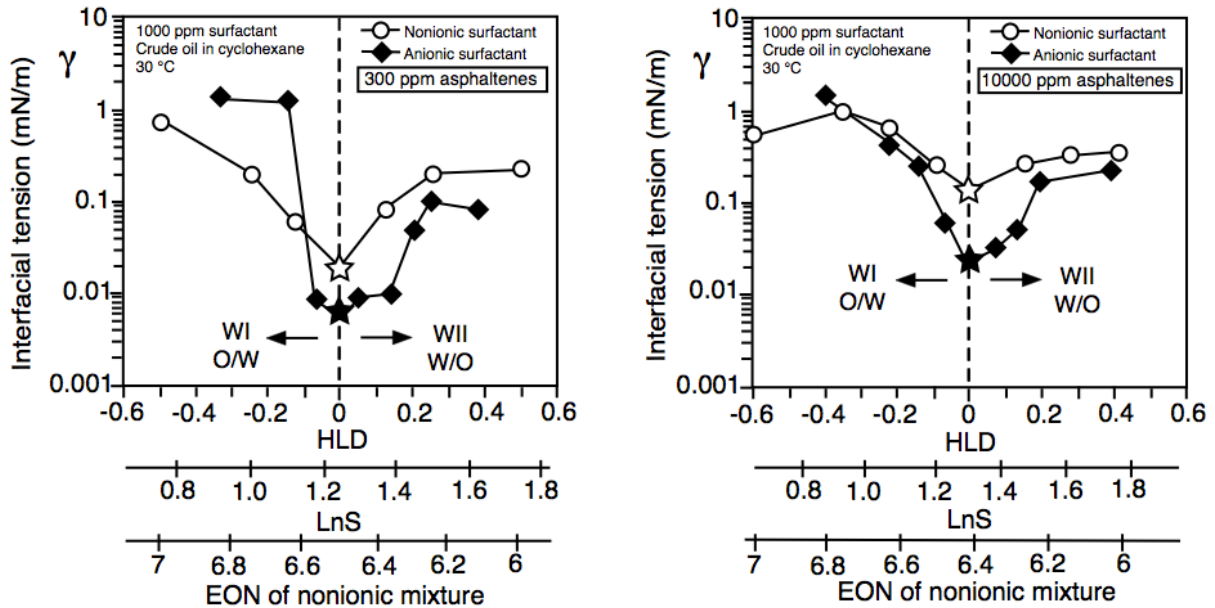


Figure 2. Interfacial tension (γ) as a function of salinity for the extended anionic system and EON for the nonionic one in brine/crude oil diluted in cyclohexane (at asphaltene concentrations $C_A = 300$ ppm and 10,000 ppm) systems. Surfactant concentration 1,000 ppm, $T = 30$ °C. 1 wt% NaCl in the aqueous phase of nonionic system.

Emulsion Stability

Figure 3 shows the variation of emulsion stability for the same systems than in Figure 2. A minimum in emulsion stability is observed at $HLD = 0$ in all cases. This feature is general as reported in the past 40 years and recently reviewed^{85,86},

Fig 3 indicates the occurrence of similar low stability values at optimum formulation for extended anionic systems with very different asphaltene concentrations ($C_A = 300$ and 10,000 ppm). On the contrary, there is a huge difference in the minimum stability value with the nonionic systems; it seems that the ethoxylated surfactant is losing its efficiency to break emulsion at optimum when the asphaltene concentration is high ($C_A = 10,000$ ppm). It is not known whether this is general.

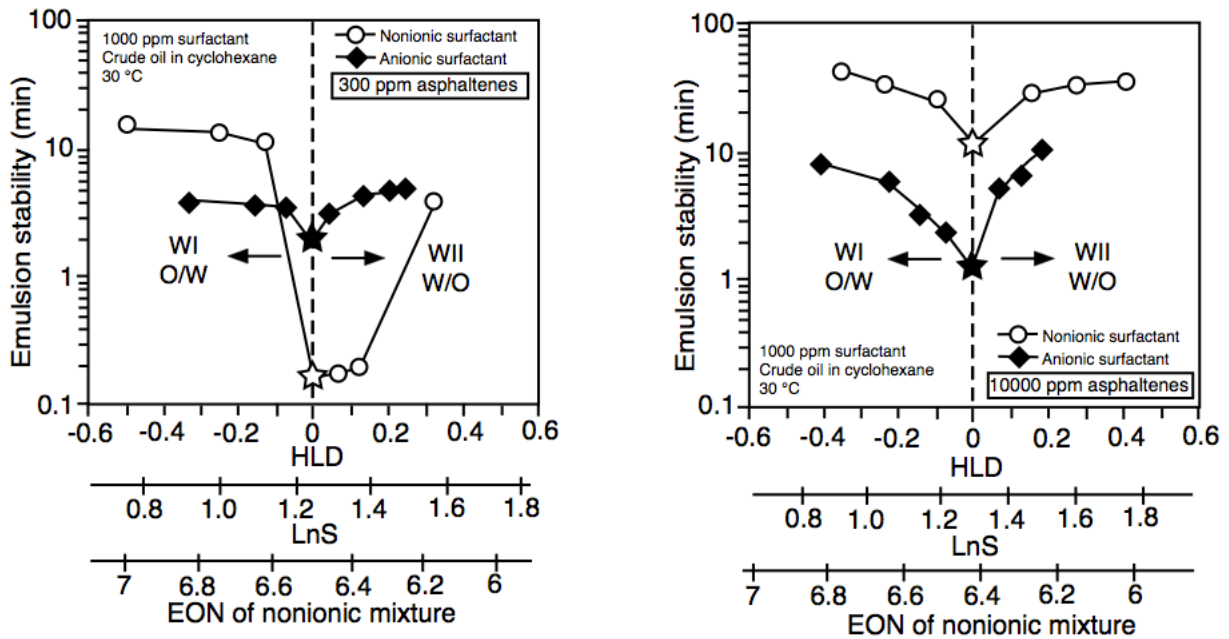


Figure 3. Emulsion stability as a function of salinity for anionic extended surfactants and EON for nonionic surfactant in brine/crude oil diluted in cyclohexane (at asphaltene concentrations $C_A = 300$ ppm and 10000 ppm) systems. Surfactant concentration 1,000 ppm, $T = 30$ °C. 1 wt% NaCl in the aqueous phase of nonionic system.

Interfacial Rheological Properties

Figure 4 shows the dilational modulus and interfacial viscosity variation when salinity and EON are scanned in the systems studied.

A minimum in dilational elastic modulus and interfacial viscosity is found at optimum formulation $HLD=0$, deeper for the ionic extended surfactant system as was also observed for the interfacial tension, especially at large C_A . The occurrence of a deep minimum in the dilational modulus at optimum formulation and its relationship with emulsion instability was presented for the first time very recently for SOW simple systems⁴¹⁻⁴³. It is also seen that the dilational modulus close to optimum formulation is higher at large C_A .

It is worth noting that the minimum of the rheological parameters is also deeper when there is no asphaltene at all⁴¹⁻⁴³. The influence of asphaltene concentration is likely related to their interfacial activity.

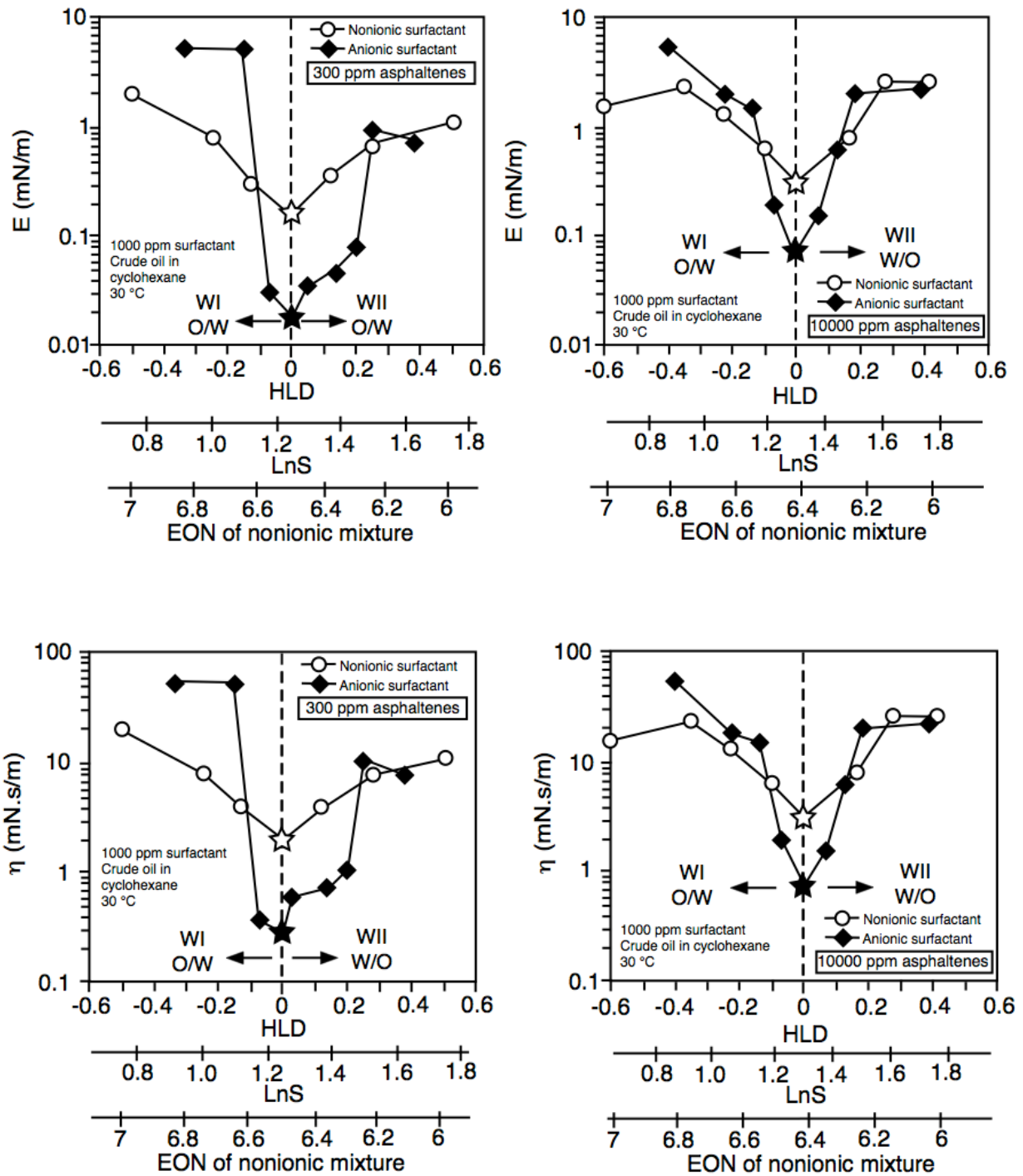


Figure 4. Dilational modulus (E) and interfacial viscosity (η) as a function of EON for nonionic and salinity for extended anionic surfactant in brine/crude oil diluted in cyclohexane (with asphaltenes concentrations $C_A = 300$ ppm and 10,000 ppm) systems. Surfactant concentration 1,000 ppm, $T = 30$ °C. Sinusoidal frequency $F = 0.1$ Hz. Salinity is 1 wt% NaCl in the aqueous phase of nonionic system.

For all the systems, the dilational modulus goes through a significant minimum at $HLD=0$. This indicates that the surfactant film layer covering the interface at $HLD = 0$ has a very low rigidity

at the frequency of measurement, 0.1 s^{-1}) and rapid exchanges between interface and bulk oil are present, thus confirming previous results^{41,42,50}.

Figure 5 shows the phase angle ϕ variation in both formulations scans. The phase angle decreases similarly for both systems, reaching a minimum at the optimum formulation of the EON and salinity scans, as was found for very simple systems^{41,43}. Nevertheless, the angle falls below 45° at high asphaltene concentration, indicating that the layers become more elastic than viscous close to HLD=0. As for the other interfacial properties there is a trend, i.e. as asphaltenes concentration increases from 0 to 300 ppm, and then to 10,000 ppm, the phase angle tends to decrease⁴¹. These results suggest that asphaltenes are not fully expelled from the interface close to HLD=0 and that they confer some elastic behavior to the monolayer.

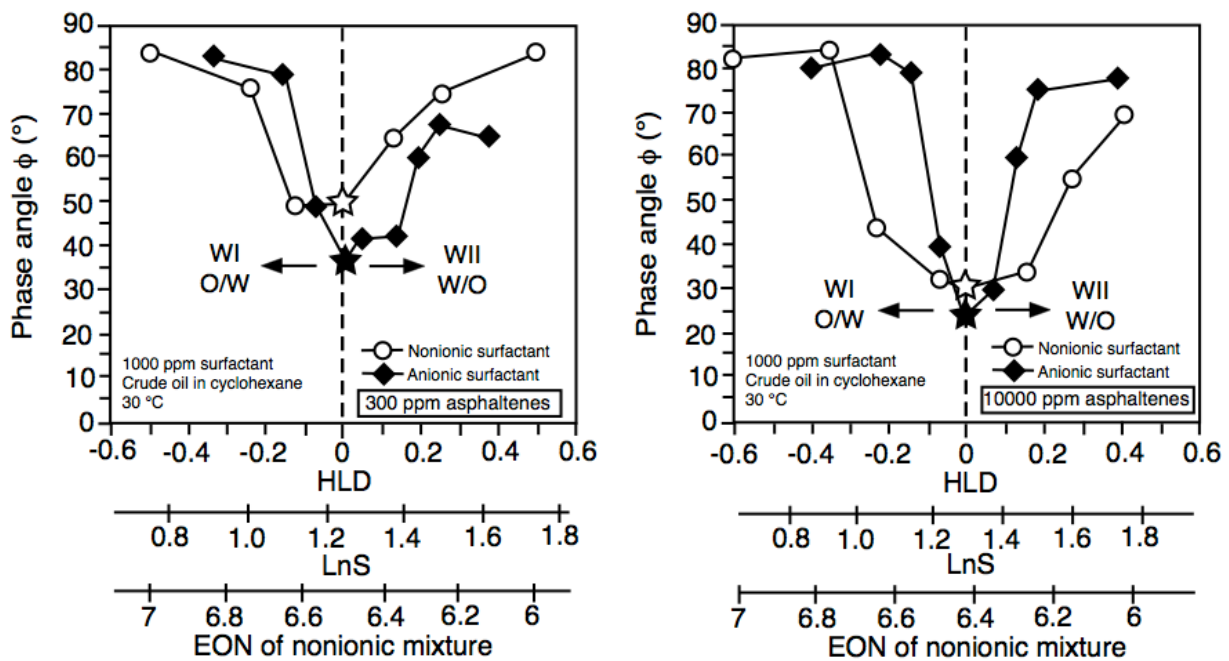


Figure 5. Phase angle as a function of EON for nonionic and salinity for extended anionic surfactant /crude oil diluted in cyclohexane (at $C_A = 300$ and $10,000$ ppm)/brine systems. Surfactant concentration $1,000$ ppm, $T = 30^\circ \text{C}$. Sinusoidal frequency $F = 0.1$ Hz. Salinity is 1 wt% NaCl in the aqueous phase of nonionic system

3.3 Surfactant (demulsifier) concentration scan for nonionic and anionic extended surfactant/crude oil in cyclohexane/brine systems

These kinds of nonionic and extended anionic surfactants are used as demulsifiers to break crude oil emulsions. They are in general efficient at a low concentration (generally < 100 ppm), when they are close to the optimal formulation. In this section, we will present the corresponding interfacial properties during demulsifier concentration scans (up to 500 ppm).

Interfacial tension

Figure 6 shows the demulsifier surfactant concentration (C_D) scan for the nonionic and the anionic ease systems with crude oil diluted in cyclohexane systems. In the first case, The selected EON=6 was selected and in the second case S=4% NaCl for the nonionic and extended anionic surfactants used as demulsifiers at a low concentration (generally < 100 ppm), corresponding to

systems near optimum on the WI side (HLD < 0 in absence of asphaltenes).

Two C_A concentration levels are shown (100 ppm and 10,000 ppm) corresponding to C_A lower and higher than the threshold point T, according to the procedure presented in our previous publications in emulsion breaking^{24,37,52,54,55}. This point T separates the regimes where the optimum demulsifier concentration C_D^* varies linearly with asphaltene concentration C_A and the regime in which C_D^* no longer depends on C_A as explained in detail elsewhere^{24,37}. Point T has been found to be at about $C_A = 1,000$ ppm³⁷.

It can be seen in Figure 6 that the interfacial tension presents a deep minimum at a certain optimum demulsifier concentration C_D^* (indicated with a star data point) where HLD = 0 formulation is attained.

It is worth noting that this is the first time that a deep minimum in interfacial tension is reported for a demulsifier concentration scan. It is thus shown here that such an interfacial tension minimum can be found, if the right physicochemical situation is selected (mainly by selecting an adequate demulsifier for the crude oil) to reach a HLD=0, as was proposed 30 years ago²². Figure 6 data clearly show that the optimum formulation indicated with a star in the plots depends on both the demulsifier nature (SCP_D) and the asphaltenes concentration C_A in the oil which influences their contribution (X_A) according to equation (6) applied at optimum formulation.

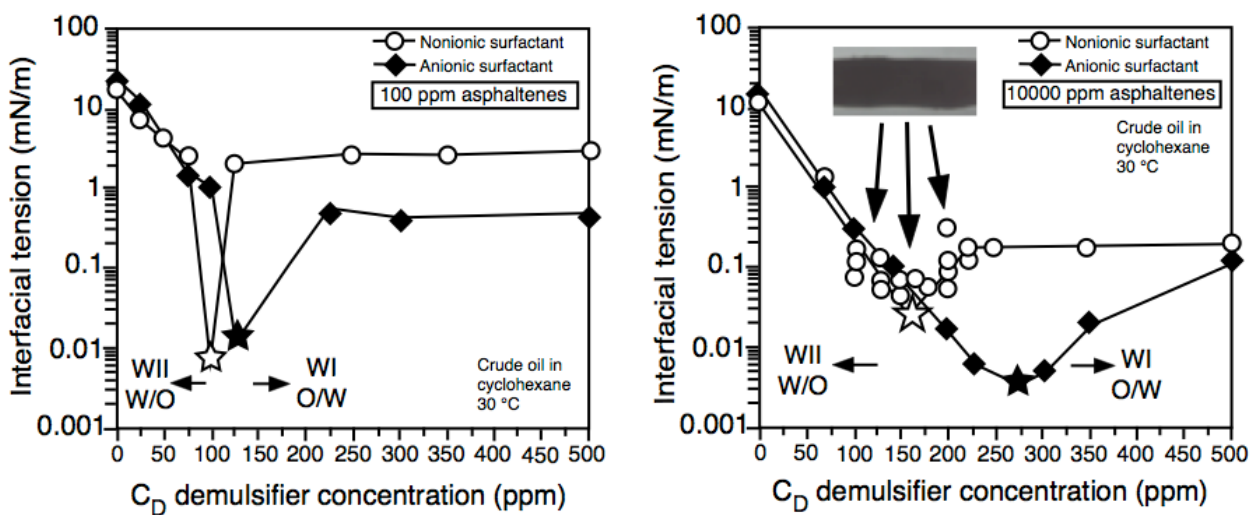


Figure 6. Interfacial tension when a surfactant concentration (C_D) sweep is carried out in the nonionic NPE6 and extended anionic surfactant/crude oil diluted in cyclohexane (at $C_A=100$ ppm and 10,000 ppm of asphaltenes) /brine system. Salinity is 1 wt% NaCl for nonionic and 4 wt% for anionic). $T = 30$ °C.

It should be noted that some inconsistencies were found with the measurements close to optimum formulation (indicated by arrows) with the nonionic surfactant at high asphaltenes concentration. Repeated experiments tend to sometimes show the presence of some nonwetting third phase on the spinning drop (which could be a microemulsion or liquid crystal gel), resulting in irregularities on the drop diameter as seen in the elongated drop picture.

These measurements were discarded and the tensions to determine the optimum star point in figure 6 are measured in the absence of third phase. It has been shown that the microemulsion

phase coexisting with excess oil in water at optimum formulation does not wet the oil-water interface, and form lenses at this interface⁸⁷⁻⁹¹. The interfacial tensions are not supposed to be affected by the presence of these lenses anyway, they are isolated and move freely at the surface.

Figure 6 additionally indicates that the nonionic surfactant is more efficient than the anionic one in the interfacial mixture with asphaltenes since less nonionic demulsifier C_D^* is required to attain the optimum formulation in both C_A cases. On top of this, the efficiency of the nonionic to attain $HLD = 0$ is found to be quite better, since its C_D^* increase (from 100 to 160 ppm) to compensate the asphaltenes increase (from 300 to 10,000 ppm), is much less than the corresponding increase required for the anionic species (from 125 to 275 ppm).

It is also worth mentioning that this might be due to another phenomenon; the presence of a high proportion of asphaltenes is likely to alter the formulation through an EACN reduction that would require an increase of C_D^* at higher C_A ².

Emulsion stability

Figure 7 displays the emulsion stability for the C_D scan in both the anionic and non ionic systems. As in earlier studies^{22 24,37}, the increase in concentration (C_D) of a hydrophilic demulsifier (NPEO6), produces a change in formulation to reach $HLD = 0$ at a concentration C_D^* ^{23,37}, where a deep minimum in interfacial tension and emulsion stability is found.

It is worth noting in Figure 7 that outside optimum formulation at $C_D < C_D^*$, including the case without any demulsifier, emulsion stability is much higher for the $C_A = 10,000$ ppm system. In other words, it can be said that the asphaltenes considerably stabilize the W/O emulsions, e.g. it is hundred times more persistent without demulsifier. Notwithstanding this evidence, it is worth remarking that at optimum formulation the emulsion stability minimum is more or less the same, at a quite low value, for the two C_A levels. This is an extremely significant result showing the importance of having a proper formulation for crude oil dehydration or dewatering, since no matter the amount of asphaltenes in the system, even if it is really high, at optimum formulation the emulsion stability is quite low.

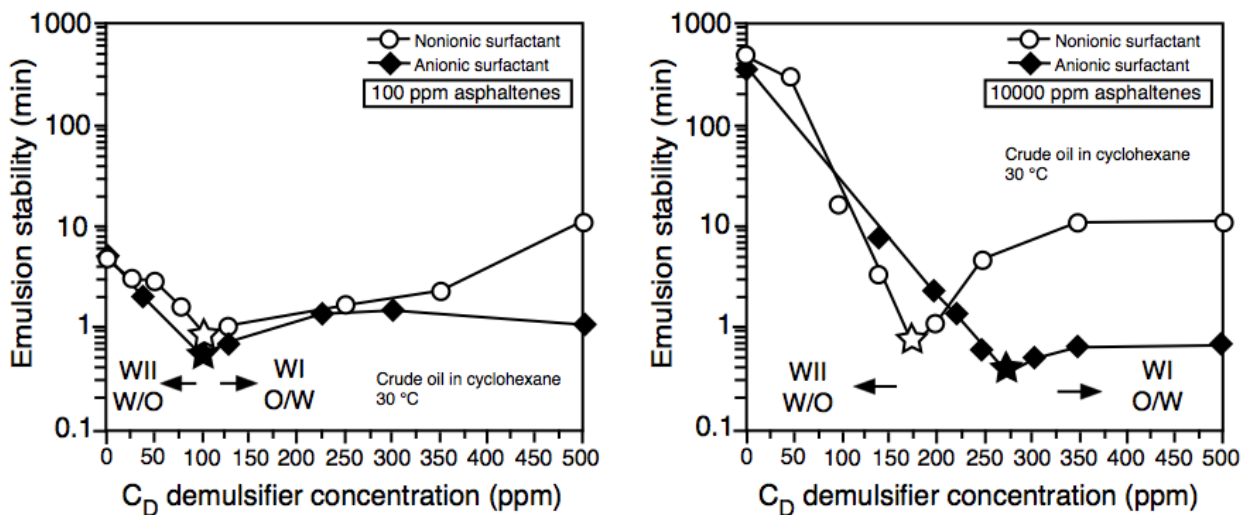


Figure 7. Emulsion stability when a surfactant concentration (C_D) sweep is carried out in the nonionic NPE6 and extended anionic surfactant/crude oil diluted in cyclohexane (at $C_A=100$ ppm and 10,000 ppm of asphaltenes) /brine systems. Salinity is 1 wt% NaCl for nonionic and 4 wt% for anionic). $T = 30$ °C.

Interfacial Rheological Properties

Figure 8 presents the variations of the interfacial dilational modulus E and interfacial viscosity η along the demulsifier surfactant concentration scan in the anionic and nonionic systems. A deep minimum in the dilational modulus E (as well as in interfacial viscosity η) is found to coincide with the interfacial tension minimum at optimum formulation presented in Figure 5.

As discussed previously, many authors have mentioned that the emulsion stability is related to E and η , particularly with a lower stability when the interfacial rheological parameters are small. It is seen in figure 8 that for both asphaltenes concentrations and for both demulsifiers, E and η are similar in WII systems (at $C_D < C_{D}^*$, e.g. $C_D = 50$ ppm), while in WI systems (at $C_D > C_{D}^*$ for both cases, e.g. $C_D = 400$ ppm), E and η are only slightly lower for the anionic surfactant demulsifier. This might be related to a greater performance of the extended surfactants for crude oil dewatering⁵⁵. For $C_A = 10,000$ ppm it is seen that the interfacial rheological properties (E and η) are much lower for the extended surfactant system at optimum formulation, although the occurrence of a minimum stability requires more demulsifier.

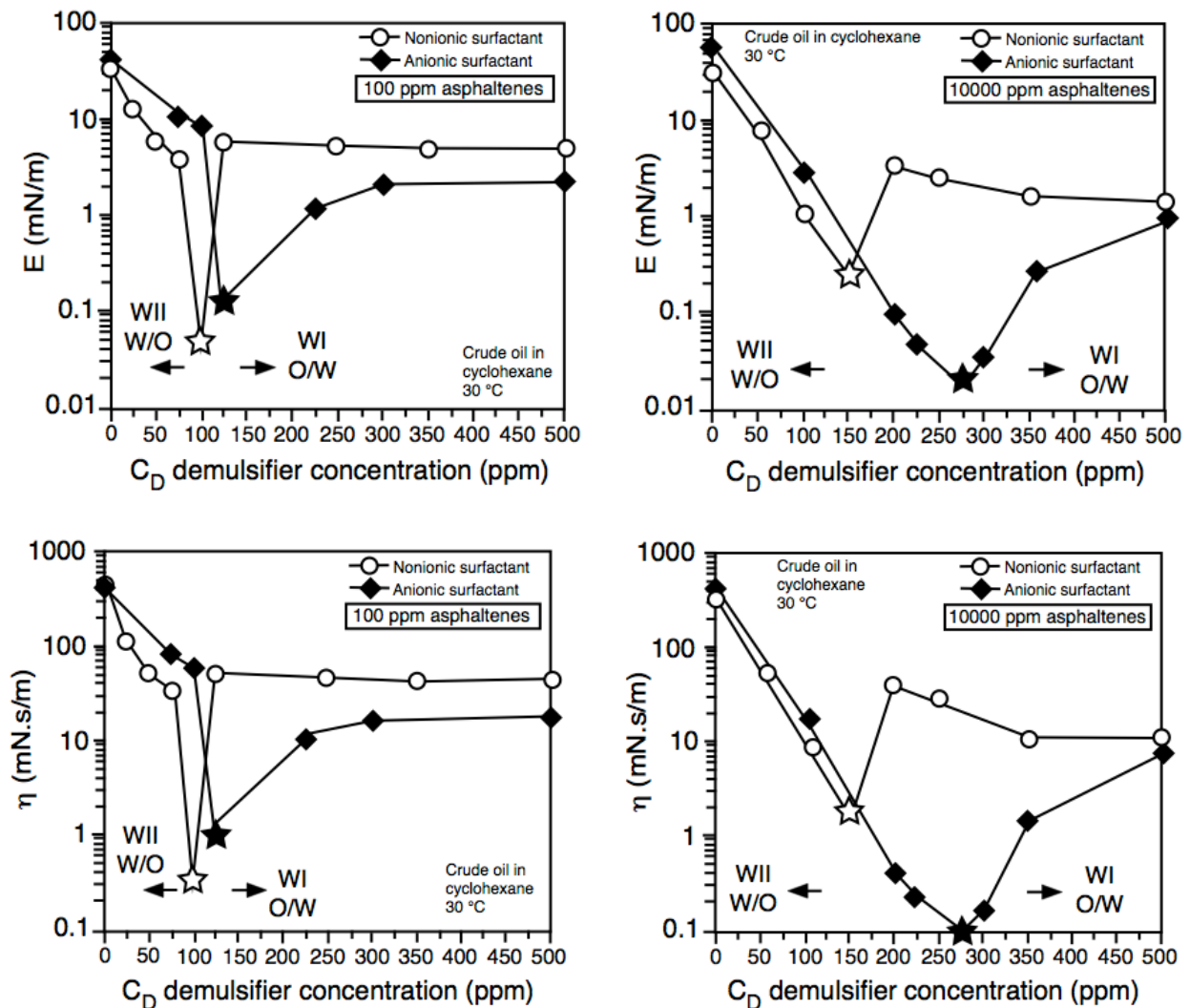


Figure 8. Dilational modulus when a surfactant concentration (C_D) sweep is carried out in the nonionic NPE6 and extended anionic surfactant/crude oil diluted in cyclohexane (at $C_A=100$ ppm and 10,000 ppm of asphaltenes) /brine system. Salinity is 1 wt% NaCl for nonionic and 4 wt% for anionic). $T = 30$ °C.

In Figure 9 the phase angle for the anionic and the nonionic surfactant systems is presented. Phase angles go through a minimum at optimum formulation for both C_A levels.

The wide range low ϕ minimum at about 20° may be related to the performance of the extended anionic surfactant when a high content of asphaltenes is present in the system^{55,85,86}.

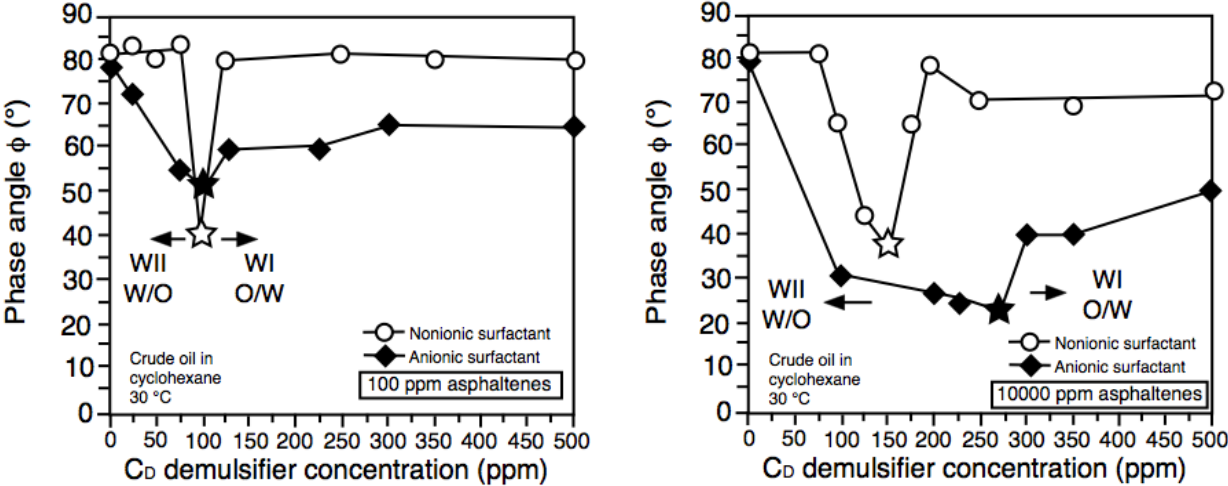


Figure 9. Phase angle when a surfactant concentration (C_D) sweep is carried out in the nonionic NPE6 and extended anionic surfactant/crude oil diluted in cyclohexane (at $C_A=100$ ppm and 10,000 ppm of asphaltenes) /brine system. Salinity is 1 wt% NaCl for nonionic and 4 wt% for anionic). $T = 30^\circ\text{C}$.

4. Discussion

The results presented in this paper confirm the observations made previously with simpler systems⁴¹⁻⁴³, but this time in a case which is realistic in the petroleum industry. In the present study, asphaltenes and surfactants adsorb at the oil-water interface, and at optimum formulation for which $HLD=0$, the exchanges between the bulk and the interface are accelerated, as evidenced by the minimum in rheological properties E and η .

As in simpler systems^{37,41-43,55}, when the demulsifier surfactant concentration C_{D^*} corresponds to the optimum formulation, the interfacial tension is minimum and the emulsions are always quite unstable, (e.g. lifetimes, less than a few minutes). Creaming/sedimentation or Ostwald ripening being longer, the only destabilization process at play is the emulsion drop coalescence.

In order to have two drops coalescing, they have first to approach and the (thin) liquid film between them has to drain before drop fusion can proceed. The fusion step in moderately stable emulsions is shorter than the film drainage⁹².

Film drainage is closely related to interfacial rheology: indeed, when a film thins, the surfactant at the film surfaces is entrained, surface concentration changes and create interfacial tension gradients. This results in huge forces opposing the film thinning (Marangoni forces), the magnitude of which is determined by the interfacial elastic dilational modulus E . Interfacial viscosity can also limit the surfactant motion and can slow down the thinning process.

When the surfactant is soluble in the droplet phase, it can however exchange rapidly by demulsifier diffusion between interface and drops, and replenishes film surfaces during film thinning, so that the Marangoni forces almost vanish. But when the surfactant is soluble in the emulsion external phase and when the film between two drops is thin enough, there is not enough surfactant to replenish the surfaces and the surfactant has to come back from the film boundaries; this motion takes time and film thinning proceeds as if the surfactant were insoluble. This is the basis of the Bancroft rule according to which in the emulsion that forms, the external phase is the phase in which the surfactant is soluble^{93,94}.

Experiments with water films in air have indeed shown that thinning is then controlled by the intrinsic film elastic modulus⁹⁵ and is slower than that of air films in water⁹⁶. When the surfactant is partitioned equally between oil and water, one sees that exchanges between the interface and oil or water are both very fast, and everything happens as if there were no or very little surfactant at the interface and the emulsion will become very unstable, as actually observed^{38,39,97}.

The close relationship between emulsion stability and elastic modulus can also be rationalized. In the experiments performed at optimum, there is some amount of surfactant in both oil and water to replenish the surface when the drop is stretched. Because we have chosen to use a small amount of surfactant, the replenishment is controlled by diffusion and is relatively slow (convection would be more rapid, but the velocity is essentially parallel to the drop surface).

The elastic modulus is therefore small, but non-zero, even at its minimum for $HLD=0$. Going back to the film thinning problem, because exchanges are possible between the interface and both oil and water, the effective modulus measured at a frequency equal to the thinning time to estimate the thinning velocity has to be compared. Recently, Denkov and coworkers⁹² have measured thinning times for emulsion systems that present stabilities comparable to those reported here, of the order of 1-10 s for drops of radius 10-1,000 μm . This time scale corresponds well to the frequency of 0.1 Hz used in the present measurements. Hence, it may be said that emulsion stability is correlated with the dilational rheology performed at the proper time scale.

The measurements also indicate that asphaltenes behave as a lipophilic surfactant when the

formulation scans are performed by changing the demulsifier concentration. Addition of hydrophilic (demulsifier) surfactants change the phase behavior from Winsor II to Winsor I system types, confirming a behavior previously proposed^{22,35}. It should be stressed however, that Winsor III systems could be present at the demulsifier optimum concentration C_D^* used in dewatering or dehydration. However, microemulsions are not seen, probably because their amount is insufficient to be visible.

The present measurements of dilational rheology for crude oil systems with very low interfacial tensions are the first of their kind. The oscillating spinning drop technique opens the way for the measurements of useful properties to master applications in crude oil dehydration and dewatering. It is seen in particular that E is much greater for the nonionic system for both asphaltene concentrations, and lower than 1 mN/m only at $HLD=0$, whilst for the extended anionic surfactant system, E is lower than 1 mN/m in a wide demulsifier concentration range. The high performance of the extended anionic surfactants in heavy crude oil dewatering has been explained elsewhere^{55,85,86}, and it may be said that this behavior is favorable for crude oil dewatering applications, with a robust action obtained in a relatively wide range of demulsifier concentration, e.g. $C_D=250-500$ ppm.

Optimum demulsifying action is correlated with small dilational elastic modulus (typically less than 0.1 mN/m) and small phase angle (typically around $30-40^\circ$ or lower). The discussion presented explains why the modulus should be small, but the exact reason why the phase angle is small is unclear. In view of the rapid exchanges between bulk fluids and interface, the dispersion should be large (in a model incorporating diffusion, $\phi=45^\circ$ at surfactant concentrations below the cmc). Because the shear viscosity contributes to the dispersion in the measurements, ϕ should be even lower. It is however possible that the shear modulus reaches values of about 0.1 mN/m near the optimum. More research is needed to quantitatively account for emulsion lifetimes in relation to interfacial rheology.

5. Conclusions

For over 35 years, researchers have been looking for an experimental proof of the relationship between interfacial dilational rheological properties and the destabilization of water-in-crude oil emulsions with demulsifiers. However, up to very recently, no such evidence could be found mainly because of the lack of an apparatus that could measure dilational interfacial rheology in systems of very low interfacial tension, where the emulsion stability has been found to be minimum 40 years ago.

This is thus the first time that an experimental evidence is provided of a clear relationship between a deep minimum in interfacial tension, dilational interfacial rheological properties and emulsion stability in crude oil systems,, which opens the way to applications for crude oil dehydration or dewatering.

These experimental facts are presented for two types of scans. The first is a formulation scan in which a typical variable is changed at constant surfactant concentration; the second is the demulsifier dosification one, which is used to study water-in-crude oil emulsion breaking, this time with a variable concentration of surfactant mixture composed of asphaltenes and demulsifier. It was shown that the two types of scans are equivalent, but at a much lower concentration with the demulsifier effect.

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Notes

The authors declare no competing financial interest.

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Selected figure for Abstract graphic:

