Dynamic interfacial tension measurement of heavy crude oil–alkaline systems
The role of the counterion in the aqueous phase

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Abstract

The dynamic behaviour of the interfacial tension at the oil–water interface $\gamma_{(t)}$ for oleic acid and a 90% v/v Cerro Negro–xylene solution had been studied under alkaline conditions. For the system oleic acid in paraffin, aqueous sodium carbonate with or without added sodium chloride, the usual $\gamma_{(t)}$ behaviour was observed, i.e. γ drops to low or ultralow values at short times, remains low during a short period, and then rises to high (> 1 N m^{-1}) values. However, when alkyl amines (ethyl, diethyl and triethyl amine) were used as alkalis in the aqueous phase, $\gamma_{(t)}$ first dropped to a relatively high value ($1.5 < \gamma < 3$ N m^{-1}) and then remained almost constant afterwards. The presence of sodium chloride in the aqueous phase was required to observed the aforementioned usual $\gamma_{(t)}$ behaviour. From these results it is clear that the presence of sodium ions is esential for both reducing (to very low values) and increasing $\gamma_{(t)}$. It is suggested that ultralow transient (values and the formation of spontaneous emulsion are due to a phase inversion (from w/o to o/w) going through a microemulsion intermediate. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Due to its ability to form water emulsions, the natural surfactants of crude oils have been the subject of many studies [1–5]. Depending on conditions, both water-in crude oils (w/o) as well crude oil in water (o/w) emulsions could be formed.

Secondary production by steam injection leads to w/o emulsions that must be dehydrated before using the oil for any purpose (marketing, refining). These emulsions are stabilized by a very strong and the thick film formed by asphaltenes, resins [6, 7] and other compounds such as long chain carboxylic acids. Dehydration is usually perform by treating the w/o emulsion with surfactants that displace the asphaltenes from the interface. A mechanism for this displacement, based on interfacial tension arguments, has been suggested by Eley et al. [8].

Low gravity viscous hydrocarbons are found in large supply in Canada, Russia, USA, China and Venezuela, and are normally liquids with high viscosities ranging from 10.000 to more than 500.000 cp at ambient temperature [9]. Once produced, desalted and dehydrated these oils are useful as combustible fuel. However, these oils are too viscous for practical use, and therefore they are mixed with water and surfactant to form o/w emulsion with improved (lower) viscosity and a high ratio of oil to water. Since commercial surfactants are expensive, we have investigated the use of the natural surfactants present in Cerro Negro bitumen for preparing these o/w emulsions [9]. It is well known that under alkaline conditions o/w emulsions are formed due to adsorption of natural surfactants which contain carboxylic acids groups. These acids ionize at the interface, thereby reducing the interfacial tension by orders of magnitude. A common observation has been that the time behaviour of the interfacial tension $\gamma_{(t)}$ for several crude oil–water systems, determined using the spining drop method, is such that $\gamma_{(t)}$ first reaches a very low and steady value for some time and then rises to higher values. For simplicity this $\gamma_{(t)}$ behaviour will be referred to as $\gamma_{(t)}$ ''minimum'' hereafter. This peculiar behaviour have been analyzed by several research groups and interpreted in different ways. Rubin and Radke suggested that the $\gamma_{(t)}$ minimum was mainly due to differences in mass transfer of surfactant from oil to water [10]. According to them, if surfactant adsorption exceeds desorption a minimum should appear. Based on the formation of caboxylates at the

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interface and in a mass transfer model proposed by England and Berg [11], Trujillo [12] reported a model to account for the decrease of γ with pH and the increase of γ with concentration of $CaCl_2$. He found that the interfacial tension remained lower for a longer time for the more acidic crude oils. This finding was consistent with others reported [13, 14]. A $\gamma_{(t)}$ minimmum was also found by Isaacs and Smolek for an extraheavy crude (8.9° API) using D_2O, NaOH and $T = 50°C$ [15]. In some cases (pH = 13), γ remained low (0.06 N m^{-1}) for a long time (~100 min) and afterwards rose to relatively high equilibrium values [15] (~10 N m^{-1}). Sharma et al. reported a maximum as well as a minimum for $\gamma_{(t)}$ when working with a Long Beach crude (22° API) for certain alkali (NaOH or Na_2SiO_4) and salt (NaCl) concentrations [16]. This behaviour was accounted for in terms of mass transfer phenomena [16]. The interfacial tension increase in a Long Beach crude had been attributed to the formation of insoluble high molecular weight sodium carboxylates [17]. Spontaneuous emulsification before the $\gamma_{(t)}$ increase was reported by Wasan and atributed to negative interfacial tensions due to high surface pressure [18]. These authors [18] also discussed the role of the sodium ion in both decreasing and increasing $\gamma_{(t)}$. Bansal et al. [19] reported a correspondence between the γ minimum and the maximum electrophoretic mobility for a crude oil/aqueous alkaline interface. They found that the maximum electrophoretic movement, associated with a high concentration of carboxylates, occurs within the spontaneous emulsification region (0.1–1% NaOH) [19]. These results were confirmed in a latter publication [20]. Rudin and Wasan [21] suggested that the very low γ value found for the crude oil/alkaline system was due to a synergistic effect between the acid and the carboxylate, and that the increase in γ with the sodium hydroxyde concentration was due to mass transfer from the interface to micelles in the aqueous phase. It is now well known that ultralow or zero γ values are associated to micellar solutions which could be formed for specific combinations of water, oil, surfactant and salt concentrations [22]. Usually these micellar solutions are stable, provided the composition remains constant. For instance, relatively small changes in salt or surfactant concentration could lead to the formation of a new phase, i.e. γ changes from zero to a finite value.

From the above review it is clear that factors such as mass transfer, acidic pKa, pH, ion pair formation, synergistic and salt effects, micelle formation, and spontaneous emulsification are all probably involved in the $\gamma_{(t)}$ behaviour observed at the crude oil–alkaline water interface. Also the complex mixture of acids that should be present at the crude oil–water interface is another factor to consider. Another important aspect to be considered is the relationship between $\gamma_{(t)}$ and the phase change from (w/o) to (o/w) that takes place when the aqueous phase is alkalinized. As discussed below this phase change is related to the ultralow or zero $\gamma_{(t)}$ values.

In this paper the role of sodium ion in reducing as well as increasing $\gamma_{(t)}$ was studied using oleic acid as a model. Two different aqueous alkaline systems were used; in the first one sodium carbonate was employed, whereas in the second alkylamines were the alkalis. Also a $\gamma_{(t)}$ study for the system Cerro Negro/aqueous sodium carbonate is presented here.

2. Experimental

2.1. Materials

Cerro Negro crude oil is an extraheavy crude (8° API) from the Orinoco Valley in Venezuela. Analytical degree oleic acid was employed. For interfacial tension measurements, a 90% v/v solution of crude oil in xylene was used and a commercial liquid paraffin was used for dissolving oleic acid. Stearic, lauric, palmitic and tricosanoic acids were also tried, but the results were poor and they are not presented here.

2.2. Spinning drop measurements

Equipment similar to that described in [23] was used. The sample was rotated at 6600 rpm and, as usual, the interfacial tension was obtained from Eq. (1) below:

$$\gamma = \frac{\omega^2 D^3 \Delta\rho}{32} \tag{1}$$

Where ω, D and $\Delta\rho$ are the angular velocity, drop diameter and difference in density respectively. $\Delta\rho$ was determined using a PAAR Digital Densimeter provided with a DMA-512 cell and a DMA-60 console.

Several concentrations of oleic acid in paraffin were tried in the range from 0.1 to 0.4% w/v (3.5 and 14.2 mM). In the range 0.2–0.4%, we found difficulties due to emulsion formation in the spinning drop capillary. For instance at 0.4% and sodium carbonate concentrations above 200 mg l^{-1}, spontaneous emulsions were formed. Below this concentration the interfacial tension was too high to be measured by this method. The best compromise was to work with acid oleic concentrations of 0.1%. In order to inquire whether these emulsions were promoted by rotation, a drop of solution (oleic acid or crude oil) was placed within the capillary and observed throught the microscope without spinning. Under these conditions, the drop elogated spontaneously and broke apart into tiny drops. Measurement of $\gamma_{(t)}$ for the xylene solution of the crude oil was straightforward, except for the conditions where spontaneous emulsions were formed. This was the case for 1 g l^{-1} < [NaCl] < 3 g l^{-1} and [Na_2CO_3] = 4 g l^{-1}. Evolution of $\gamma_{(t)}$ with time was followed for at least 3 h and ''equilibrium'' values of γ were measured after 4 hours.

Several experiments were performed at different pHs using buffer mixtures of Na_2CO_3 and NaOH. They show that a minimum in $\gamma_{(t)}$ will develop, provided the
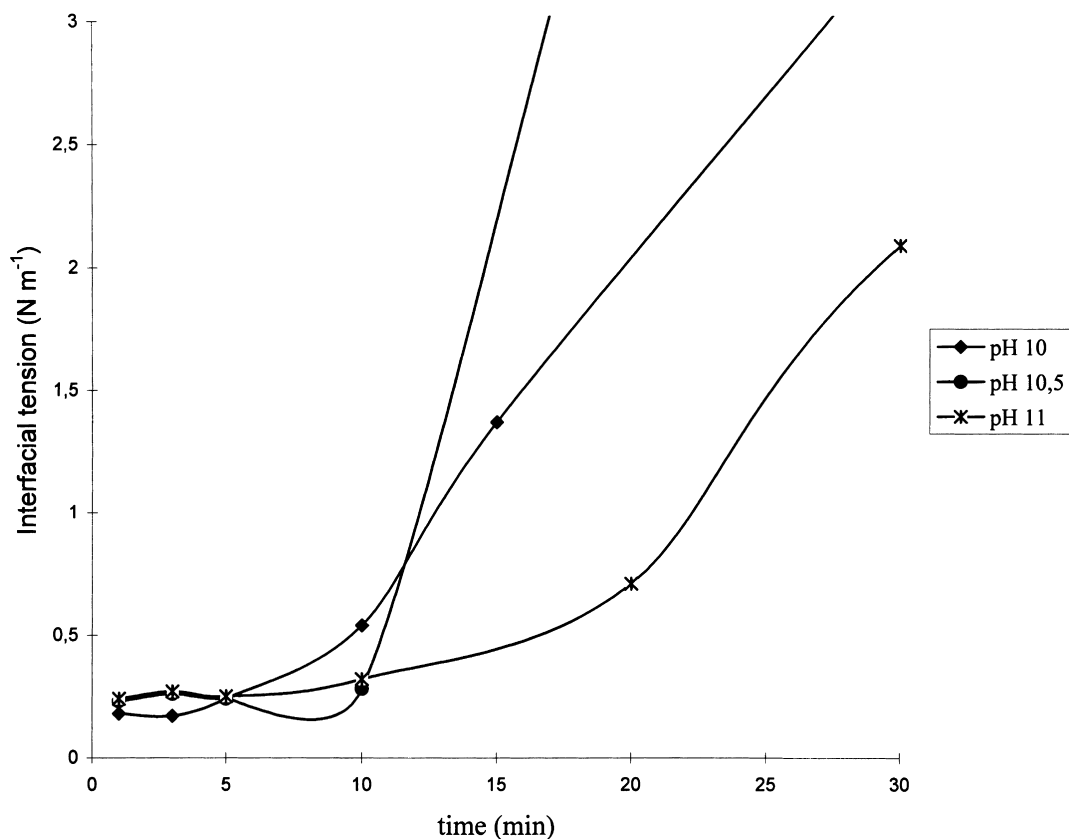
Fig. 1. Dynamic of interfacial tension for the system: 0.1% oleic acid in paraffin at different pHs.

aqueous pH is above 10. Good behaviour in this sense was observed when working near pH 11 as shown in Fig. 1.

After many trials, we found it convenient to use the following conditions for the measurement of interfacial tension in the case of amines: amine and oleic acid concentration, 0.2%. Under these conditions the aqueous pH was near 11.4. Due to the very high vicosity of the extraheavy Cerro Negro crude oil it was necessary to dilute the oil.

Thus the γ measurements were performed with a 90% w/w crude oil–xylene solution.

3. Results

3.1. Crude oil

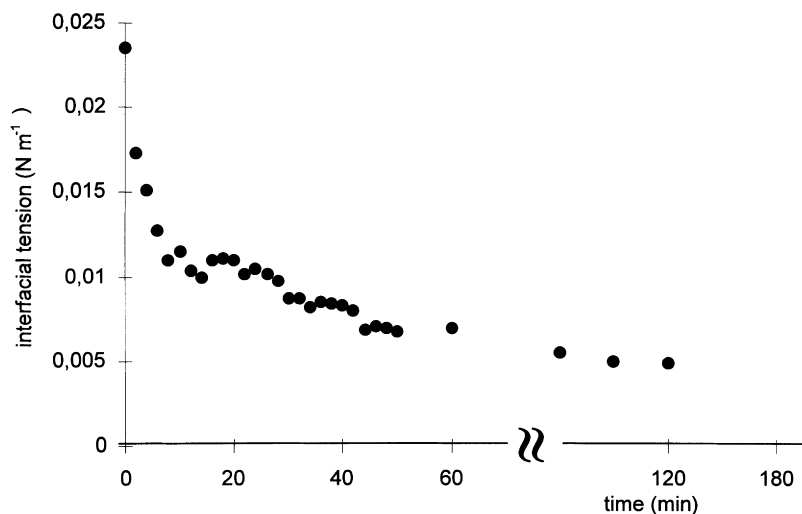Figs. 2–5 show the time evolution of the interfacial

Fig. 2. Time evolution of the interfacial tension for the system: crude oil–xylene (90% w/w)/sodium carbonate (3 g l^{-1}). $T = 25°C$.
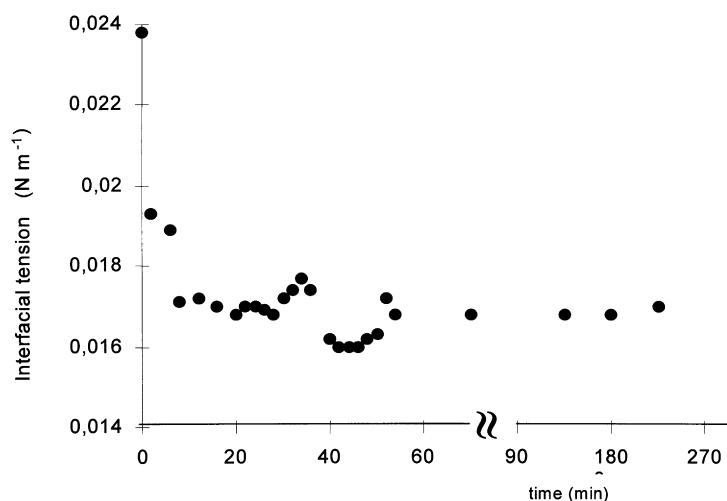
Fig. 3. Time evolution of the interfacial tension for the system: crude oil–xylene (90% w/w)/sodium carbonate (5 g l^{-1}). $T = 25°C$.

tension $\gamma_{(t)}$ of the crude oil–xylene mixtures at several sodium carbonate concentrations. As mentioned in the previous section, spontaneous emulsions were formed at alkali concentrations below 3 g l^{-1}. For simplicity we could analyze $\gamma_{(t)}$ in terms of the general behaviour of the derivate $d\gamma/dt$ or $\gamma_{(t)}'$. There is a first region where γ drops very fast; that is, $\gamma_{(t)}'$ has a very high negative value within the first minutes. Also, there is a second region where on average $\gamma_{(t)}'$ is either negative with a small value or zero, and finally a third region where $\gamma_{(t)}'$ is positive. In all cases, the γ value reached after the first region was very low; in particular, the behaviour of $\gamma_{(t)}$ under the conditions used to obtain the data of Fig. 2 is interesting since to our knowledge, a similar time dependence has not been reported. As shown in these Figures (Figs 2–5) the γ values in the second region have a trend of increasing with the Na$_2$CO$_3$ concentration.

Fig. 6 shows the dependence of γ with the concentration

of added sodium chloride at a fixed sodium carbonate concentration (4 g l^{-1}). It is noteworthy that even at high salt concentrations the interfacial tension remains very low.

3.2. Oleic acid and sodium carbonate

The results of $\gamma_{(t)}$ for the system oleic acid 0.1% (w/v) in paraffin, aqueous sodium carbonate (0.5 g l^{-1}) for several sodium chloride concentrations are shown in Fig. 7. The first region, corresponding to the fast drop in γ (see above), was too fast to be measured in this case. As with the crude oil, regions two ($\gamma_{(t)}' \sim 0$) and three ($\gamma_{(t)}' > 0$) are present here, although in general, after the first region the trend is for γ to increase much faster than for the crude oil system. Adding sodium chloride reduces the interfacial tension and there is a tendency for γ to remain low for a longer time as the salt concentration is increased.
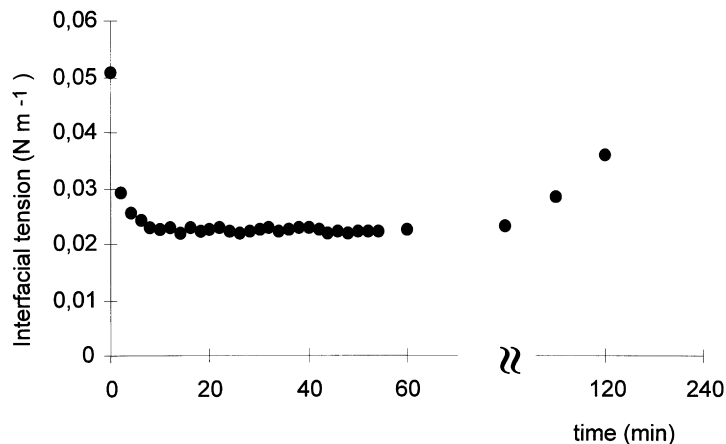

Fig. 4. Time evolution of the interfacial tension for the system: crude oil–xylene (90% w/w)/sodium carbonate (8 g l^{-1}). $T = 25°C$.
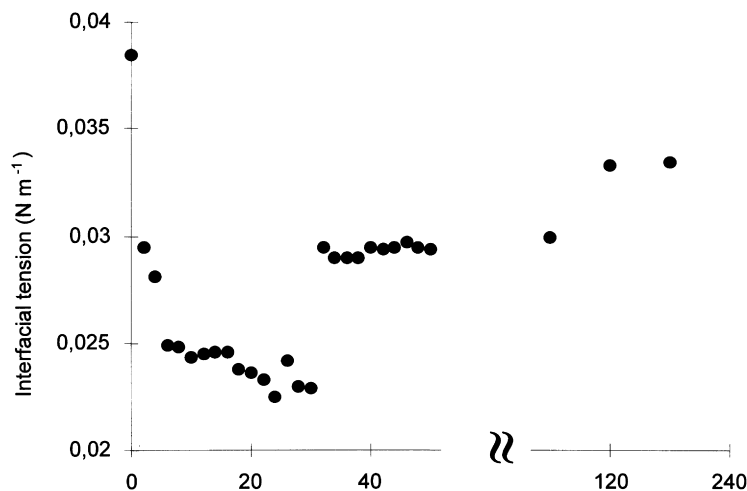
Fig. 5. Time evolution of the interfacial tension for the system: crude oil–xylene (90% w/w)/sodium carbonate (9 g l^{-1}). $T = 25°C$.

3.3. Oleic acid and amines

In Fig. 8, the $\gamma_{(t)}$ values for the three amines studied are shown. Three features in this figure deserve comments: First, no sodium ions are present; second the $\gamma_{(t)}$ reached after the first region is significatively higher than those obtained with sodium carbonate; and third, there is not a third region where $\gamma_{(t)}'$ is positive. In other words, after the first region $\gamma_{(t)}' \approx 0$. However, as shown in Figs. 9–11, low interfacial tension values and positive $\gamma_{(t)}'$ appear in the presence of added sodium chloride.

4. Discussion

Comparison of results with the different bases (Na$_2$CO$_3$ versus amines) shows a significant difference in the corresponding $\gamma_{(t)}$ curves (see Figs 7–11). Also, when the $\gamma_{(t)}$ behaviours for any particular amine with and without salt are compared, it is evident that the existence of transient low interfacial tension values are associated to the presence of sodium ion. In general, the $\gamma_{(t)}$ behaviour in the presence of Na$^+$ is such that the very fast drop in γ is followed by a slow

increase, pointing to a two quite different kinetic mechanism. The first one in the usual carboxylic acid ionization at the interface where the Na$^+$ stabilizes the carboxylates more efficiently than any ammonium ions N$^+$HR$_1$R$_2$R$_3$. Possibly, differences in ion size are the main source of the differences in $\gamma_{(t)}$. The other mechanism, responsible for the slow increase in $\gamma_{(t)}$, has been the subject of the controversy commented on in Section 1. A similar mechanism has been proposed for the Na$^+$ case [17]. As mentioned above this is strongly associated to the presence of Na$^+$, and at least for the oleic acid case, the behaviour of $\gamma_{(t)}$ is consistent with the formation of sodium carboxylate ion pairs at the interface. Thus, the dynamics of the process could be described as follows:

$$RCOOH + M^+X^- \xrightarrow{k_1'} RCOO^- + M^+ + XH \qquad (2)$$

$$RCOO^- + M^+ \xrightarrow{k_2'} RCOO^-M^+ \qquad (3)$$
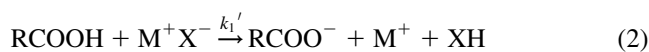
Step one represents the usual acid neutralization. When M$^+$ is sodium, a larger acid neutralization could be
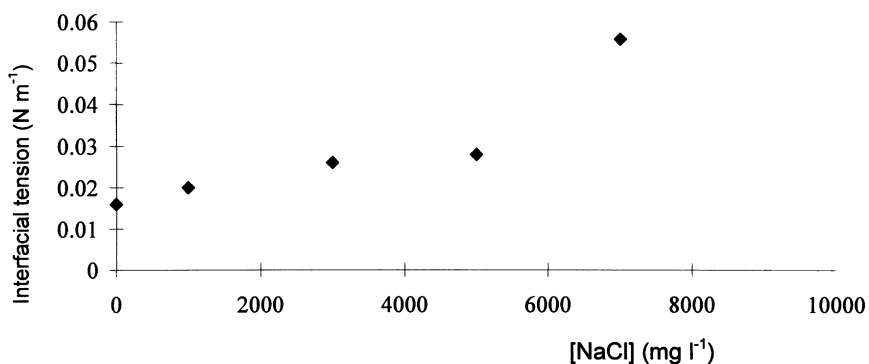

Fig. 6. Dependence of interfacial tension with the concentration of added sodium chloride for the system: crude oil–xylene (90% w/w)/sodium carbonate (4 g l^{-1}).
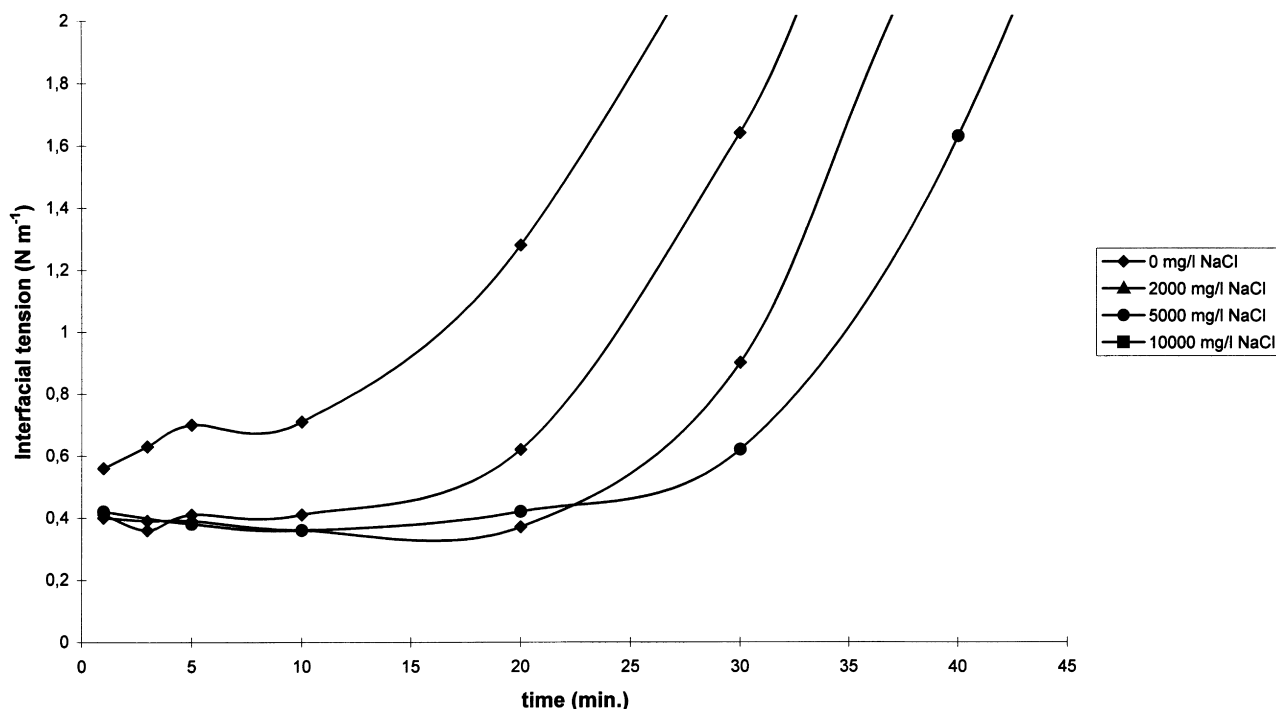
Fig. 7. Effect of NaCl added on the dynamic of interfacial tension for the system: 0.1% oleic acid in paraffin–alkaline solution ($Na_2CO_3 = 0.5 \, g \, l^{-1}$).

expected, equivalent to an acid stronger than the one present when M^+ is an ammonium ion. In other words, changing from amines to sodium carbonate in the aqueous phase would be equivalent to decreasing the pKa of the oleic acid at the interface. The same argument could be used for amines in the aqueous phase with and without added

sodium chloride. Therefore, a larger interfacial tension decrease is expected in the presence of sodium.

The second step corresponds to ion pair formation and would be the mechanism for the $\gamma_{(t)}$ increase. Ion pair formation in this case is equivalent to the well known counter ion binding in micelles [24]. Combining the steps Eqs.
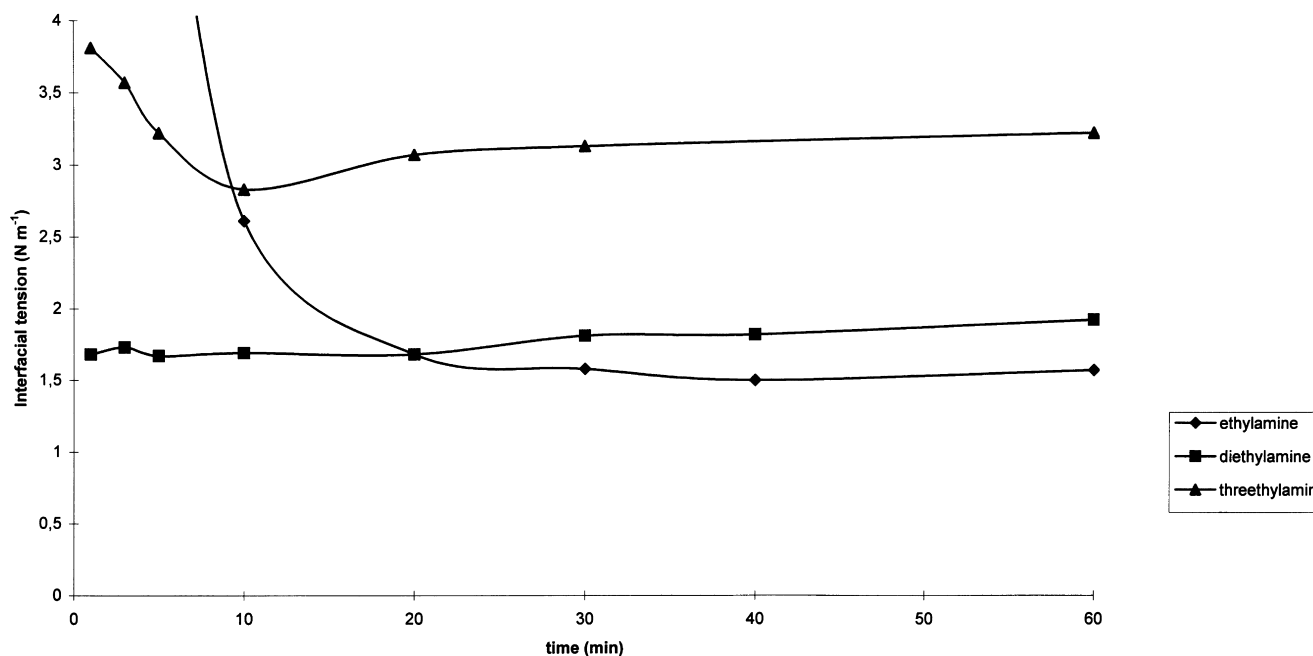

Fig. 8. Dynamic of interfacial tension for the system: 0.2% oleic acid in paraffin–alkaline solution (amine = $0.2 \, g \, l^{-1}$).
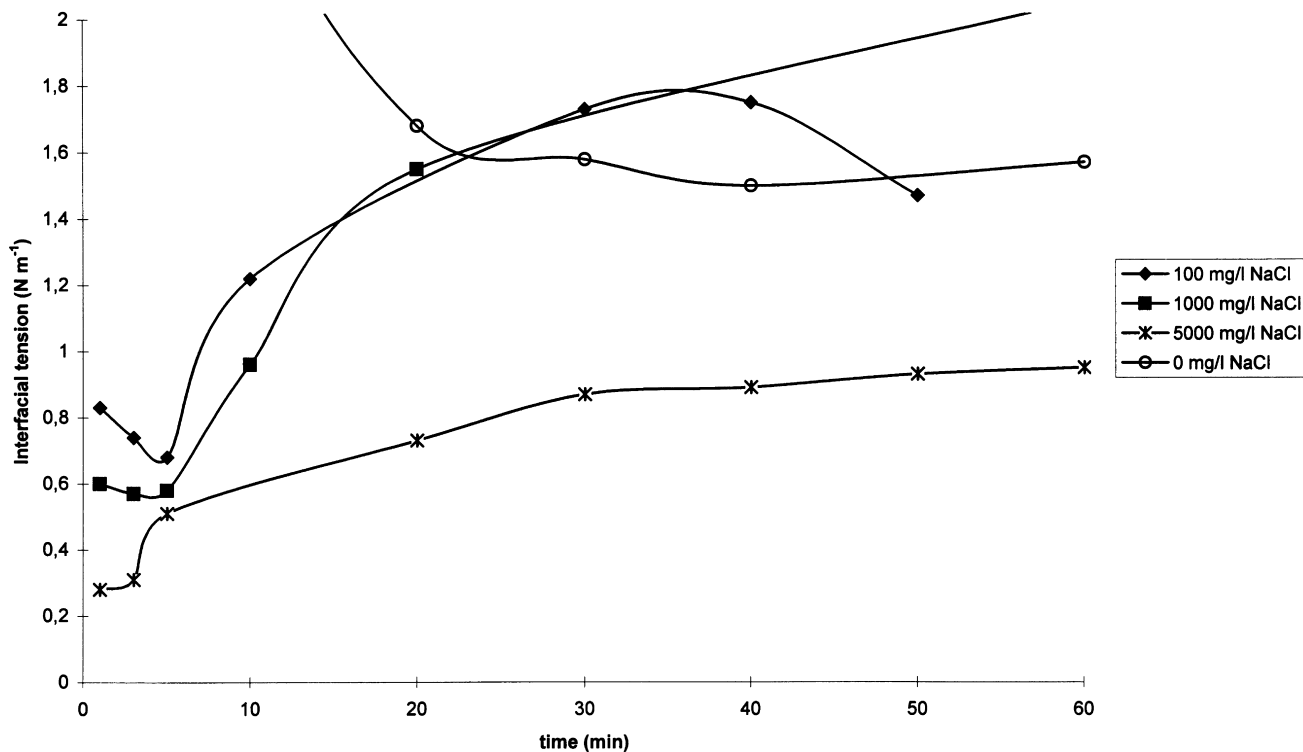
Fig. 9. Effect of NaCl added on the dynamic of interfacial tension for the system: 0.2% oleic acid in paraffin–alkaline solution (ethylamine $= 2$ g l^{-1}).

Fig. 10. Effect of NaCl added on the dynamic of interfacial tension for the system 0.1% oleic acid in paraffin–alkaline solution (diethylamine $= 2$ g^{-1}).
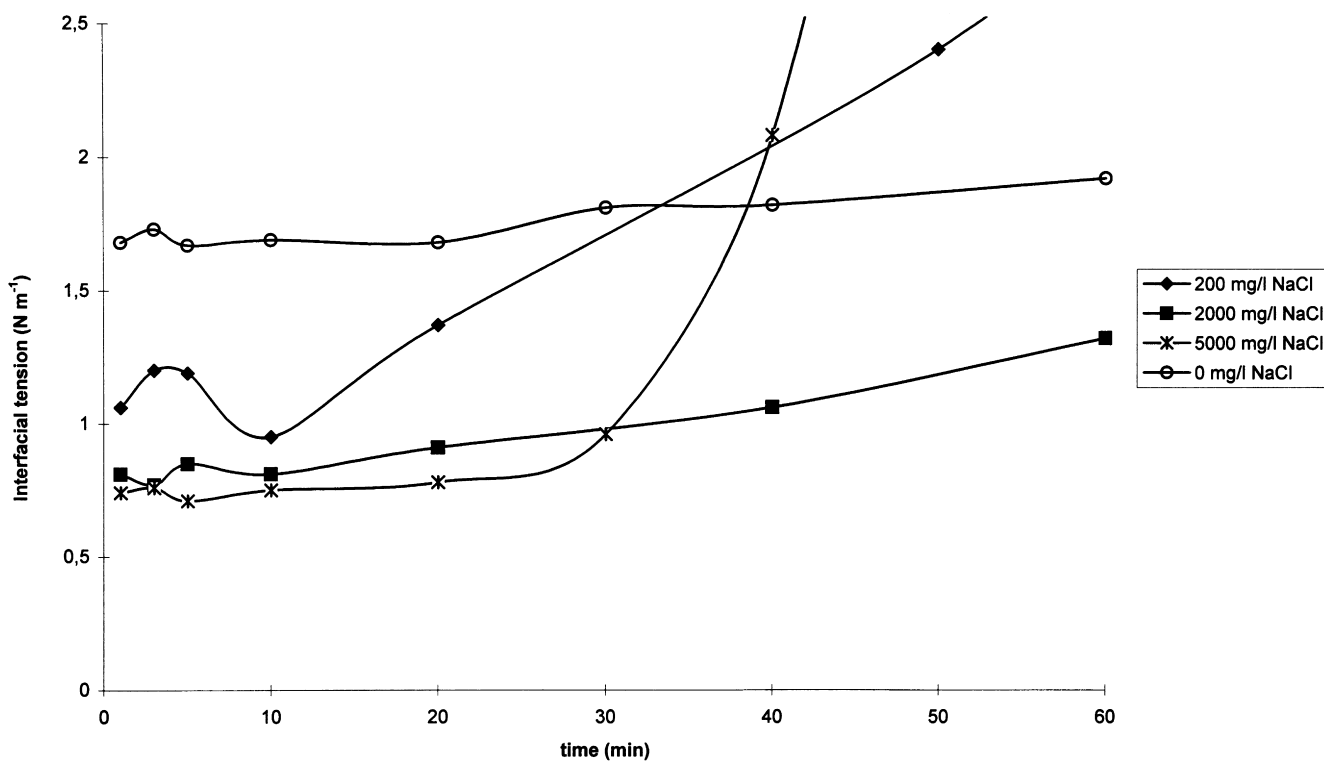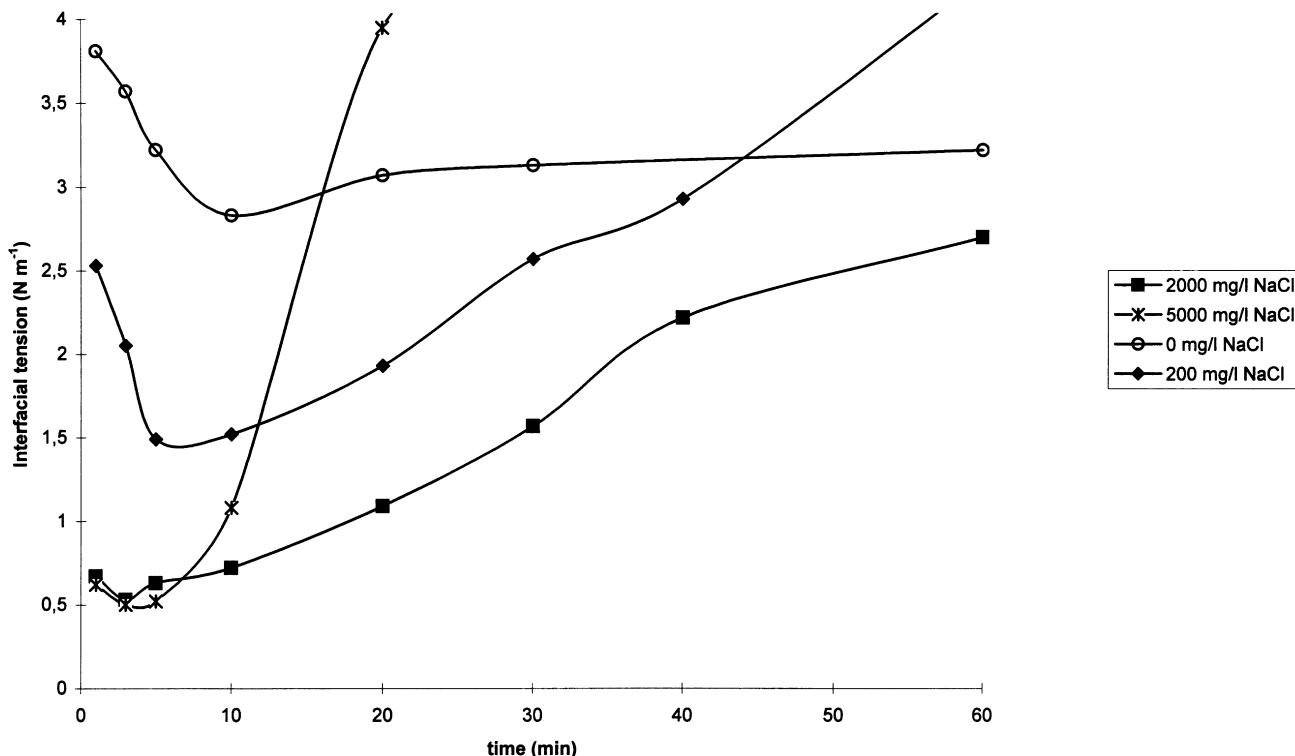
Fig. 11. Effect of NaCl added on the dynamic of interfacial tension for the system: 0.1% oleic acid in paraffin–alkaline solution (thriethylamine = 2 g^{-1}).

(2) and (3) above for M = Na$^+$ and assuming simple kinetics, Eq. (4) is obtained:

$$-\frac{d\gamma}{dt} = k_1(\text{RCOOH})(\text{Na}^+)(\text{X}^-) - k_2(\text{RCOO}^-)(\text{Na}^+) \quad (4)$$
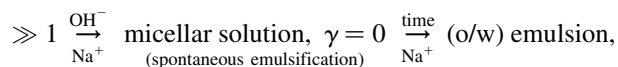
Of course, Eq. (4) is only an approximation; for instance it does not account for diffusion or material transport through the interface, asumes first-order in each reagent, etc. However, for the purposes of this paper it is sufficient for summarizing the above results: sodium ion will both decrease and increase $\gamma_{(t)}$ values. Since $k_1 \gg k_2$ a minimum, or low γ values, is observed at very short time and the γ value at this minimum depends on the sodium concentration. Near complete ionization [RCOOH] is very small and $\gamma_{(t)}'$ approaches zero. According to the results in Fig. 7 this ''steady state'' condition is best described by the results at high sodium chloride concentration. Although undoubtly other effects should be considered in the case of crude oils, we believe that the obtaining of very low interfacial tension in crude oils, when using sodium bases, is due to the presence of sodium ions. Possibly factors such as adequate size, charge density and hydration result in a better negative charge stabilization at the interface. For instance, it has been reported [25] that the very low interfacial tension (0.005–0.04 m N m^{-1}) at the aqueous alkali Lloydminster crude oil (a heavy oil, density = 0.9705 g cm^{-3}) interface changes with time in different ways depending on the nature of the hydroxide counter ion. Thus, the following interfacial activity was found: KOH > Ca(OH)$_2$ > NaOH > LiOH.

Since the above charge stabilization requires the ion to approach the carboxylates to close distances, ion pairs or even sodium carboxylates are likely to form, thereby increasing $\gamma_{(t)}$ values [16].

Permanent ultralow or zero γ values are, of course very well known in the microemulsion field, and type I, oil in water and type II, water in oil microemulsions in equilibrium with micellar solution or microemulsion of ionic surfactant in the presence of salt are commonplace [22]. Usually the phase behaviour of these systems could be changed continuously (for instance from o/w to w/o) by increasing the sodium chloride concentration, i.e. by decreasing surfactant hydrophilicity. For instance it has been shown that type I oil in water emulsion for the system oleic acid, decane, NaOH and brine change to type III and then to type II after increasing the sodium chloride concentration [26], while keeping the sodium hydroxide concentration constant. Type III is a microemulsion containing substantial amounts of oil, water and surfactant. Of course, transitions such as I → III or II → III go through zero interfacial tension [22]. In general, the $\gamma_{(t)}$ behaviour for the oleic acid and for crude oil in contact with aqueous sodium alkaline system could be conveniently interpreted from a similar change of phase perspective. Initially (at low or zero carboxylate concentration) a water in oil emulsion system prevails; as the carboxylate concentration increases in the presence of sodium ions, hydrophilicity increases, promoting emulsion or phase inversion to oil in water. Under the proper system composition the above phase inversion will go through a

microemulsion system ($\gamma_{(t)} = 0$) acting as a sort of ''transition state''. However, this microemulsion or micellar system is not stable due to the above sodium carboxylate formation, and thereby it evolves to an ordinary oil in water emulsion. Thus, under conditions where ultralow or ''spontaneous'' emulsions appear, the behaviour could be summarized as follows:

(o/w) emulsion, γ

$$\gg 1 \xrightarrow[\text{Na}^+]{\text{OH}^-} \text{micellar solution, } \gamma = 0 \xrightarrow[\text{Na}^+]{\text{time}} \text{(o/w) emulsion,}$$
$$\text{(spontaneous emulsification)}$$

$\gamma > 0$

As shown in Figs 2–5, the interfacial tension for the crude oil system remains very low even for relative high salt concentrations, suggesting that carboxylate formation, or better, sodium carboxylate ion pair formation is low. It is expected that the $\gamma_{(t)}$ increase would depend on the natural surfactant composition of each crude. For instance, if the molecular weight distribution of these surfactants is very wide, the formation of precipitates or any other organized structures such as liquid crystals is unlikely. Such a wide molecular distribution has been found for Cerro Negro and other extraheavy crude oils from Venezuela [5, 27].

Acknowledgements

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