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ORIGINAL CONTRIBUTION

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Interactions between synthetic and indigenous naphthenic acids and divalent cations across oil–water interfaces: effects of addition of oil-soluble non-ionic surfactants

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Abstract Interactions between naphthenic acids and divalent metal cations across model oil–alkaline water interfaces were investigated by correlating changes in dynamic interfacial tension (IFT), to plausible reaction mechanisms. The measurements were carried out by using a CAM 200 optical instrument, which is based on the pendant drop technique. The naphthenic acids used were synthesised model compounds as well as commercial acid mixtures from crude distillation and extracted acid fractions from a North Sea crude oil. The divalent cations involved Ca^{2+}, Mg^{2+}, Sr^{2+}, and Ba^{2+}, which are all common in co-produced formation water and naphthenate deposits. The results show that the dynamic IFT strongly depends on naphthenic acid structure, type of divalent cation, and the concentration of the compounds as well as the pH of the aqueous phase. Introducing divalent cations to systems involving saturated naphthenic acids caused mostly a permanent lowering of the IFT. The decline in IFT is due to electrostatic attraction forces across the interface between the cations in the aqueous phase and the carboxylic-groups at the o/w interface, which cause a higher interfacial density of naphthenic acid monomers. The permanent lowering in IFT is likely due to formation of positively charged monoacid complexes, which possess high interfacial activity. On the other hand, in the case of the aromatic model compounds, the cations affected the IFT differently. This is mainly discussed in light of degree of cation hydration and steric conditions. Various oil-soluble non-ionic surfactant mixtures were also introduced to systems involving a model naphthenic acid and Ca^{2+} in order to investigate how the interfacial competition affected the local interactions. Based on the behaviour of dynamic IFT, probable inhibition mechanisms are discussed.

Keywords Naphthenic acid · Metal naphthenate · Non-ionic surfactant · Pendant drop · Dynamic interfacial tension · Interfacial reaction

Introduction

The naturally occurring naphthenic acids in crude oil are complex mixtures consisting of saturated and aromatic rings connected by aliphatic chains [1, 2]. The acids show polydispersity in stoichiometry and molecular weight [2–5] and due to the complex distribution of different structures, the physico–chemical behaviour of naphthenic acids is quite different from normal fatty acids.

From an operational point of view in crude production, the naphthenic acids are causing several problems. Since they are amphiphilic molecules, they may accumulate at water–oil interfaces and stabilize emulsions [6–9], which in turn cause enhanced separation problems. When the pH of the co-produced water increases due to release of CO_2 during fluid transportation from the reservoir to the topside, the acid monomers dissociate at the water–oil interface, making them even more interfacially active. In combination with the co-produced formation brine, the dissociated carboxylic groups may also react with cations in the brine to form metal soaps/naphthenates. At certain conditions, these metal soaps can stabilize foams and emulsions [10, 11]. In addition, naphthenates may precipitate during the processing [12–14], mainly in topside facilities like heat exchangers and separators, which may lead to the worst scenarios in cleaning processes and regular production shutdowns.

Reaction mechanisms

Basically, there are two main approaches, how the naphthenic acids may react with cations to form metal naphthenates. The first and more traditionally one is a reaction between water-soluble acids and cations in the water bulk. The fraction of the acids with the lowest molecular weight is soluble in the aqueous phase, even at pH values near the pKa. However, normally this accounts only for a limited part of the total amount of naphthenic acids: the major part, consisting of larger molecules, is preferably oil-soluble at normal operational conditions and will rather be accumulated at the oil–water interface. According to this, and by taking into account the tremendously large interfaces created when the formation water is emulsified with the crude oil during the transport from the reservoir to the topside, it is obvious that the contact and the interactions between the compounds across the interface may lead to the second approach, i.e. interfacial reactions.

When naphthenic acids and divalent cations react at oil–water interfaces, it is reasonable to suppose that the process involve two reaction stages where the acid monomers sequentially bind to one cation, according to Eq. 1

$$M^{2\oplus} + RCOO^{\ominus} \rightleftarrows [RCOO - M]^{\oplus} + RCOO^{\ominus} \rightarrow (RCOO)_2{-}M \quad (1)$$

The rate of formation of naphthenate will thus depend on the stability of the positive monovalent complex. For fast reactions, the occurrence of the intermediate might be neglected as the two monomers will bind almost simultaneously. This is likely the normal case for bulk reactions due to high chain-flexibility and free diffusion. However, when the monomers are distributed at an interface, their location is much more fixed, and effects like steric hindrance might thus have a reducing impact on the reaction rate or even counteract 2:1 structures to form. Consequently, this would increase the lifetime of the intermediate complex.

Formation of positively charged metal–mono-acid complexes has also been discussed in earlier studies, e.g., by Albers and Overbeek [15] in their investigations in correlating emulsion stability to electrokinetic potential. Later McLaughlin et al. [16] found that divalent cations adsorbed on phosphatidylserin gave rise to positively charged surfaces. A 1:1 binding of cation and acid would probably lower the IFT as the surfactants penetrate deeper into the interfacial layer. On the other hand, if Eq. 1 is fully switched to the right, more hydrophobic structures are formed, which most likely will tend to migrate away from the interface and towards the oil bulk [17]. This is especially the case if multiacidic naphthenates are formed. These electrochemically neutral structures might then accumulate and start to agglomerate in the oil phase, normally in combination with inorganic materials like clay and scale, and further adhese to surfaces of the process units. Naphthenate deposits are becoming a common problem in a number of fields where highly acidic crude oils are processed, like in West Africa [12, 18] and in the North Sea [18, 19]. An improved basic understanding of how the naphthenic acids react to form naphthenates is thus of essential importance for future elimination of related problems.

Naphthenate inhibition

In order to reduce the extent of naphthenate formation, chemical mixtures of various compositions are nowadays commonly injected into the well stream. Naphthenate deposition is a problem only if the aqueous pH exceeds the pKa of the naphthenic acids. Anything which keeps the pH low, like injecting short-chain organic acids, may thus avoid naphthenate to form [20]. In addition, acid demulsifiers, consisting of acetic acid in an aromatic solvent mixture, and non-acid demulsifiers, consisting of ethoxylates and alcohol, have shown to reduce deposition significantly [21]. The main mechanism behind naphthenate inhibition by using non-ionic surfactants is likely a competitive process, which takes place at the interface. Etoxylates are highly interfacially active and have normally a much higher affinity towards water–oil interfaces than naphthenic acids. Consequently, they may occupy the interface and thus hinder the naphthenic acids to reach it and to further react with the cations. In addition, it is reasonable to assume a diluting mechanism to take place. As pointed out earlier, the lifetime of positively charged 1:1 complexes of naphthenic acid and divalent cations is among other factors that depend on the interfacial conditions. Due to lateral steric hindrance, 2:1 complexes of branched structures will be less favoured than more aliphatic ones. A similar effect is also achieved by introducing surfactants with large polar headgroups. First, these will cause an increased average intermolecular distance between the naphthenic acid monomers. Second, due to inhibitors located in between the acid monomers, the naphthenic acids also have to restructure in the interfacial layer in order to complete the reaction. Obviously, this will slow down the rate of reaction step 2 in Eq. 1.

During the last decades, interfacial behaviour of organic acids in combination with metal cations in oil–water systems has been an object of several studies [22–27]. A lot of work has also been carried out on systems involving crude oil and caustic water [17, 28–31]. However, a trend in most of the previous work has been to characterize systems after the reaction between the compounds has taken place. As a consequence, and particular for fast reactions, the detection of the initial stages of diffusion and electrostatic interaction across the interface might be lost. In this study, on the other hand, the dynamic IFT is continuously measured during in situ addition of metal cations to the aqueous phase. In this way, we can follow the entire process during one single experiment.

The study is a direct continuation of a recent work in which interfacial interactions between a model naphthenic acid (*p*-*n*-dodecyl benzoic acid) and various divalent cations were investigated by the same experimental technique [32]. Now, several more naphthenic acids, model- as well as indigenous compounds, are involved. Changes in IFT are discussed and correlated to plausible reaction mechanisms. In addition, mixtures of oil-soluble non-ionic surfactants have been introduced in order to investigate their influence on the interfacial interaction between a synthetic naphthenic acid and calcium ions.

Experimental

Chemicals

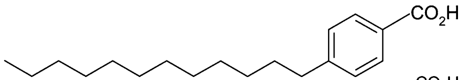
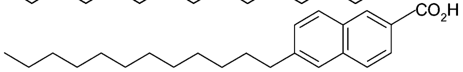
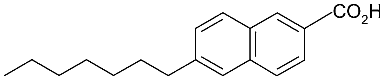
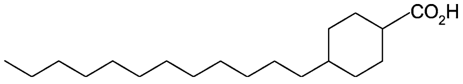
The chemicals were all of high purity delivered from various suppliers. The oil phase employed was a 1–9 volume mixture of toluene and n-hexadecane (99%, Acros Organics). The water phase consisted of ultra-pure water buffered to pH 8.0 or pH 9.0 by using a mixture of sodium tetraborate and hydrochloric acid (>99.5%, Acros Organics). The divalent cations were Ca^{2+}, Mg^{2+}, Sr^{2+}, and Ba^{2+}, all in form of chloride salt with hydration water (>99%, Chiron).

Totally, eight different naphthenic acids/acid fractions were involved, of those four were model compounds (>99%, Chiron), one commercial acid mixture (Fluka), and three were extracted acid fractions from different distillation cuts of a North Sea crude. The extraction procedure has been described in the literature [33].

Table 1 summarizes all the naphthenic acids used in the experiments, comprising both model compounds and indigenous acid mixtures. Concentrations are given in Table 2.

For the experiments, where surfactant mixtures were introduced to the system, pure n-decane (99%, Acros Organics) was used as solvent. Buffer of pH 9.0 was used as water phase. The surfactant mixtures (products 1–5) consisted of different oil-soluble non-ionic compounds.

Table 1 An overview of the naphthenic acids utilized in the experiments

Name	M (g/mol)	Naphthenic acid structure	Source
p-(*n*-dodecyl) benzoic acid	290.4		Chiron AS
6-dodecylnaphthalene- 2-carboxylic acid	340.6		Chiron AS
6-heptylnaphthalene- 2-carboxylic acid	270.4		Chiron AS
4-*n*-dodecyl-cyclohexane carboxylic acid	296.5		Chiron AS
Fluka naphthenic acid	250*	Mixture	Fluka
Naphthenic acids from North Sea crude; cut 1	200*	Mixture	Statoil ASA
Naphthenic acids from North Sea crude; cut 2	290*	Mixture	Statoil ASA
Naphthenic acids from North Sea crude; cut 3	310*	Mixture	Statoil ASA

*Average values calculated from total acid number (TAN) by assuming only monoprotic acids

Table 2 Naphthenic acid (NA) concentrations and divalent cation—naphthenic acid concentration ratios selected for the experiments, correlated to figure numbers

Figure	NA	Conc. NA (mM)	Conc. M^{2+}/Conc. NA
1	*p*-(*n*-dodecyl) benzoic acid	0.1	3/1
2	4-*n*-dodecyl-cyclohexane carboxylic acid	1.0	3/1
3	6-dodecylnaphthalene- 2-carboxylic acid	0.1	3/1
4	a) 6-heptylnaphthalene- 2-carboxylic acid	0.1	3/1
	b) 6-heptylnaphthalene- 2-carboxylic acid	1.0	10/1
5	Fluka naphthenic acid	100	3/1
6	a) Naphthenic acids from North Sea crude, cut 1	10	1/1
	b) Naphthenic acids from North Sea crude, cut 2	20	1/1
	c) Naphthenic acids from North Sea crude, cut 3	20	1/1

Equipment

All measurements were carried out by using a CAM 200 equipment from KSV Instruments, which is based on the pendant drop technique. Reviews of the theory behind the technique have frequently been presented [34–38]. The instrument consists of a CCD video camera with telecentric optics, a frame grabber, and a LED based background light source. The resolution is 512×512 pixels and the frame interval is between 40 ms and 1,000 s. The LEDs are housed in a reflective sphere, which integrates their light and directs it towards the sample. The light is also strobed and monochromatic, and all these features help to assure sharp images and high accuracy.

Method

To ensure a high degree of dissociation of the naphthenic acids, it is crucial to operate at an elevated pH when compared to pKa. In this work, buffer solutions of pH 9.0 were employed for all systems. At the selected concentration levels, pH 9 is also the upper limit to avoid precipitation of magnesium hydroxide. For the naphthenic acids/acid, mixtures showing high water solubility at pH 9.0, measurements were also carried out at pH 8.0.

All experiments were conducted by forming an oil droplet containing dissolved naphthenic acid upward in the aqueous solution. The concentration of acid was adjusted so that the initial IFT was in the range of 25–30 mN/m. The system was then equilibrated before dissolved metal salts were added to the water phase. The IFT was continuously captured during the entire process with a constant frame interval of one second. The measurements continued for 30 min.

In order to measure interfacial activity, dynamic IFT measurements were also carried out for oil-droplets containing 100 ppm of the oil-soluble non-ionic surfactants. The surfactants showing highest interfacial activity were further combined with one of the model naphthenic acid (*p*-(*n*-dodecyl) benzoic acid). The concentrations of acid and non-ionic surfactants were 0.25 mM and 50 ppm, respectively. Dissolved $CaCl_2$ was added to a concentration of 0.75 mM after 500 s.

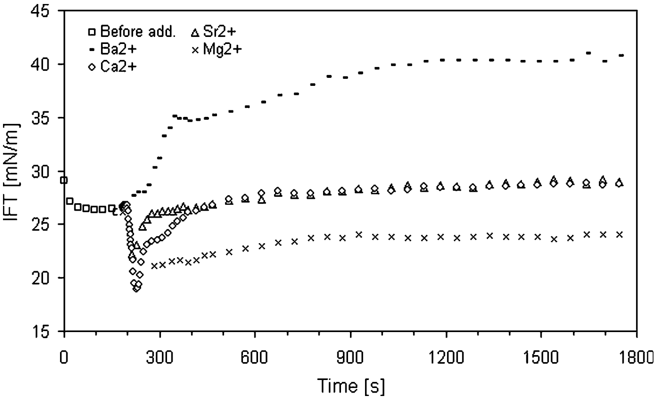


Fig. 1 Effects of addition of divalent cations on dynamic IFT for o/w systems with p-(n-dodecyl) benzoic acid

Results and discussion

All results are plotted as IFT versus time. The first period of time is ascribed to the initial diffusion stage, where the naphthenic acid monomers diffuse towards the o/w interface and, after reaching it, undergo dissociation when brought in contact with the alkaline aqueous phase. For most of the experiments, the initial equilibrium was reached within 3 min. Before divalent cations were added, the systems with the same pH and naphthenic acid structure were identical and showed very similar dynamic IFT. Thus, for reasons of clarity, this period is given by one single curve only, although it represents four individual experiments.

Model compounds

Naphthenic acids comprising one ring

Result from measurements on the *p*-(*n*-dodecyl) benzoic acid, also presented in a previous work [32], is given in Fig. 1 for the sake of comparison. As the plots show, the acid monomers equilibrate quite fast at the interface and the divalent cations were thus added after 3 min. This caused either a sudden decrease or an increase in the IFT, depending on type of added cation. In the case of Ba^{2+}, a steep increase in the IFT is observed before the curve gradually flattens out and reaches an almost constant tension value. Introducing the other cations, however, results in a sudden drop in the IFT. For Ca^{2+} and Sr^{2+}, the drop is followed by a steep increase where the curves elevate to a level slightly above the starting IFT. The curve of Mg^{2+}, on the other hand, differs from the others by showing a permanent decrease in the IFT. In this case, the curve monotonously rises only a few units above the lowest value as a function of time. The effect of adding different cations is also concentration dependent, and lower concentrations of counterions cause more similar trends in the cases of Ca^{2+}, Sr^{2+}, and Mg^{2+} (see Fig. 1.2 in the electronic supplement).

The fact that various cations affect the stability of interfacial films in different ways is well established. During the past, a lot of work has been done in order to investigate these effects. One hypothesis is that the interfacial activity of a cation and thus its reactivity with interfacial negative charges is affected by the amount of water of hydration that surrounds the ion [39–41]. Since the degree of hydration decreases with increasing ionic size, Ba^{2+} will bind less water than the other cations in this study, and should hence show a higher affinity towards the interface. The interfacial distance between acid monomers and approaching cations (especially for Ba^{2+}) might thus be sufficiently short for most of the acid monomers to convert to stoichiometric 2:1 structures. The suggestion that the reaction involving Ba^{2+} is fast is further supported by the observation that the IFT increases immediately after addition of divalent cations, i.e. no preliminary drop is observed under the current experimental conditions with a camera-speed of one picture a second. According to Eq. 1, this indicates that the lifetime of any monovalent complex is much shorter for Ba^{2+} than for the other cations under study.

Formation of naphthenate structures increases the hydrophobicity and decreases the interfacial activity, especially in the case of multivalent cations. The observed increase in IFT is thus a consequence of migration of the formed complexes from the interface and into the oil bulk phase. It is however noteworthy that, after 30 min of time when the curves have flattened out, the IFT is still 10–15 units below the value of the pure o/w interface. This indicates that some interfacially active material still has to be present at the interface. This was also demonstrated in a previous study where mechanical properties of interfacial Langmuir films were investigated [42]. However, since the interface is being compressed in a Langmuir film, the result is a much higher density of interfacial species than in the case of a pendant drop study. Hence, it is not fair to directly compare the results from these two techniques.

For Mg^{2+}, the situation is somewhat different than for Ba^{2+}. This cation binds six molecules of hydration water, giving it a higher affinity towards water than Ba^{2+}. Hence, a steric energy barrier against adsorption is created, which in turn may hinder the interfacially bound Mg^{2+} to react further with the second acid monomer. The observed decline in IFT most likely reflects an interfacial coverage of positively charged mono-acid complexes, where the concomitant small monotonous increase in IFT is a result of a gradual diffusion of some magnesium-diacid formed structures into bulk solution.

As indicated by the plots in Fig. 1, addition of Ca^{2+} or Sr^{2+} gave curves with slopes somewhere in between the cases discussed above. This is in accordance with the correlation between ionic size and amount of hydration water. The monovalent complexes of Sr^{2+} and Ca^{2+} will be converted into 2:1 structures at a higher rate than in the case of Mg^{2+} and, accordingly, the curves of IFT versus time will ascend steeper.

Figure 2 shows the results from the measurements carried out on 4-*n*-dodecylcyclohexane carboxylic acid. The hydrogenated ring gives a more hydrophobic and less interfacially active substance than the corresponding unsaturated structure. This is clearly demonstrated by comparing the levels of the IFT at the beginning of the experiments; the IFT has a higher value than for *p*-(*n*-dodecyl) benzoic acid, even though the concentration of acid is ten times higher. The larger decline in the IFT observed after introducing cations is thus a result of more acid monomers entering the interface. Contrary to the systems with the aromatic C12 naphthenic acid, all the plots of the saturated acid show a permanent lowering of IFT after addition of cations. The decline is even more drastic at increased concentration. Also this effect can be attributed to the hydrophobic structure of the naphthenic acid. A saturated ring will not penetrate so deeply into the interfacial layer as an aromatic one and this will cause longer interfacial distances between

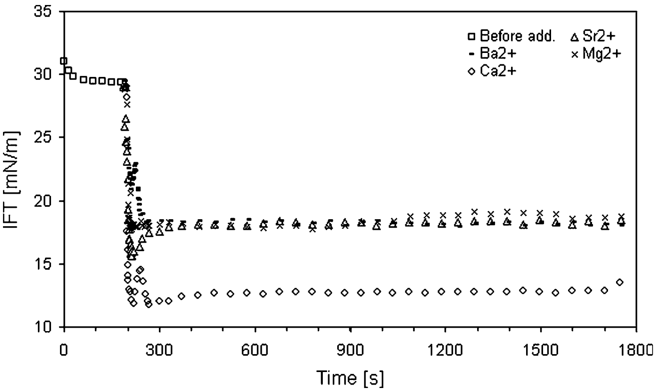


Fig. 2 Effects of addition of divalent cations on dynamic IFT for o/w systems with 4-*n*-dodecylcyclohexane carboxylic acid

the acid monomers and the divalent cations as an average. Consequently, the interfacial conditions will not promote a completion of the reaction into a final 2:1 ratio between acid and cation. Since the effect is caused by the nature of the acid, an introduction of all cations will influence the IFT in a similar way.

Complementary to the discussion above, the steric hindrance between acid monomers would also affect the rate of reaction. Due to different conformations, the intermolecular distance between molecules containing aromatic rings will be shorter than between corresponding saturated ones. This difference in packing is enhanced by the π-bonds between the aromatic entities which keep the monomers at a closer distance. As a consequence, a formation of 2:1 stoichiometric complexes will be more favourable in the case of aromatic rings.

It is worthwhile noticing that in the case of the condensed structure introduction of Ca^{2+} brings about the lowest IFT. This has also been observed at lower concentrations of cations (see figure 2.2 in electronic supplement). The reason for this is, however, not clear and no further explanations are given in order to explain this effect.

Naphthenic acids comprising two rings

The results from the measurements performed on 6-dodecylnaphthalene-2-carboxlic acid are given in Fig. 3. As in the case of the aromatic single-ring structure, addition of Mg^{2+} causes a permanent reduction in the IFT, which is more pronounced for 3:1 ratio than for 1:1 ratio of cation and acid (as compared with figure 3.2 in the electronic supplement). The reaction between acid and Ba^{2+}, Ca^{2+}, and Sr^{2+} gives a rise in the IFT and the final levels in all three cases are in the range of 40–50 mN/m. The structure comprising two aromatic rings seems thus to form 2:1 stoichiometries (with the exception of Mg^{2+}) at a higher rate than the corresponding single-ring structure. This may be attributed to the π-bonds; since two aromatic rings now are involved, the acid monomers will pack even denser at the interface than in the case of a single ring.

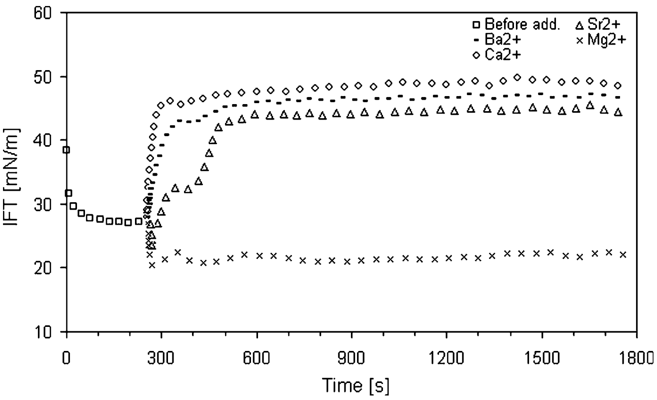


Fig. 3 Effects of addition of divalent cations on dynamic IFT for o/w systems with 6-dodecylnaphthalene-2-carboxylic acid

Figure 4 displays the results from the measurements carried out on 6-heptyl-naphthalene-2-carboxylic acid. Shortly, after initiating the experiments at pH 9 (Fig. 4a) and without any addition of divalent cations, the IFT gradually increases towards the tension value of the pure interface between oil and water. This indicates a migration of the ionized acid from the interface into the aqueous phase, i.e. high water-solubility. This interfacial adsorption and desorption of monomers results in a highly dynamic interface which in turn makes it difficult to identify any effect of added counterions.

At pH 8, given by the plots in Fig. 4b, the situation is very different as a more stable interface is formed. When the divalent cations are added at this pH, a steep decline in IFT is observed. This is in contrast to the curves of Ba^{2+} combined with the C12 aromatic single-ring structure, where the initial drop was lacking. In spite of this, the dynamic IFT proceeds in a quite similar way as for the aromatic single-ring acid.

The different behaviour of the curves for Ba^{2+} might be attributed to the aqueous pH; a lowering of the pH causes a lower degree of dissociation of naphthenic acid monomers and the interface will be covered by more undissociated molecules. This increases the lateral distances between the charged carboxylic groups at the interface, which in turn lower the reactivity with divalent cations. The lower degree of dissociation is also the reason why much higher concentrations of acid and counterions are required to reach the desired initial IFT.

Indigenous compounds

Fluka naphthenic acid

The Fluka naphthenic acid, obtained from crude oil distillation, consists of a number of different acid structures. Analysis by FT-IR and NMR (^{1}H and ^{13}C) has shown that the mixture mainly consists of saturated naphthenic acids with cyclic- as well as acyclic hydrocarbon moieties.

The results from the pendant drop study are given by Fig. 5. As for the aromatic two-ring structure with C7 aliphatic chain, the water-solubility is high at pH 9 (see figure 5.2 in electronic supplement). By decreasing the pH to 8, a fairly stable IFT is obtained, disregarding the slight monotonous decrease of about 3 units during the first 500 s of time. Due to lower degree of dissociation, however, higher concentrations of acid and cations had to be added than in the case of pH 9. The acid monomers equilibrate quite fast at the interface, as

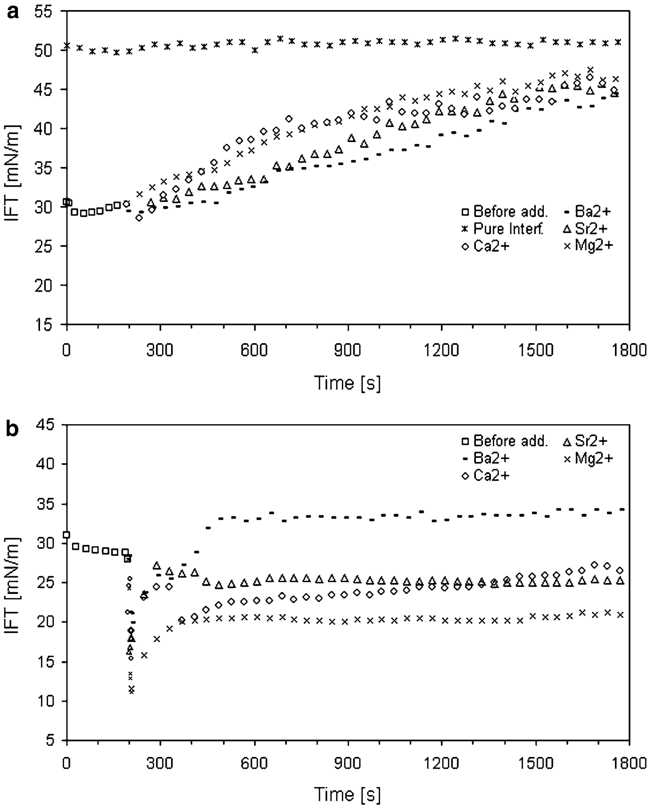


Fig. 4 Effects of addition of divalent cations on dynamic IFT for o/w systems with 6-heptylnaphthalene-2-carboxylic acid at **a** pH 9.0, and **b** pH 8.0

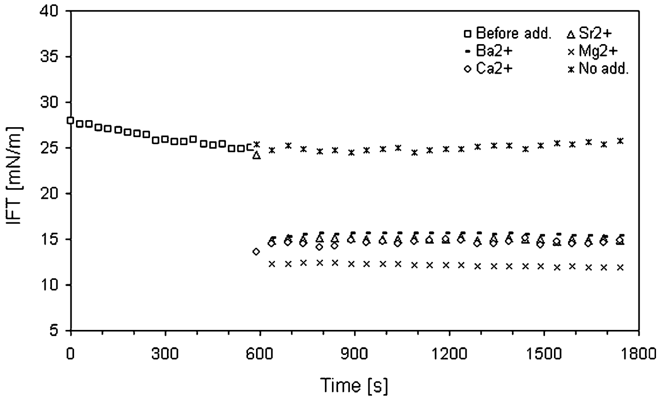


Fig. 5 Effects of addition of divalent cations on dynamic IFT for o/w systems with Fluka naphthenic acid at pH 8.0

shown by the almost linear curve from the origin of the experiment. This indicates a presence of fast diffusing monomers with high interfacial activity, causing an almost immediate drop in IFT from 51 mN/m, representing a pure o/w interface, to 28 mN/m. The following small decrease in IFT is probably due to a slow process where the polydisperse monomers are reorientated at the interface.

The divalent cations were added after 500 s. This caused a sudden and permanent decline in the IFT for all systems. After addition of counterions, the compounds also equilibrate quite fast at the interface since no points were captured during the drop. The permanent lowering of the IFT is similar to what observed for the saturated model acid, although addition of Mg^{2+} now brings about the lowest tension value. Hence, the behaviour is likely a result of the same mechanism as discussed before, i.e. formation of mono-acid complexes, which remain at the interface. The lower pH will also favour the formation of such complexes as more undissociated molecules are occupying the interface.

Naphthenic acids from a North Sea crude

The naphthenic acids from a North Sea crude oil were selected from three different distillation cuts at temperatures 230–250, 330–350, and 350–370°C. NMR-studies have shown that all acid fractions mainly consist of saturated structures with primary and secondary carboxylic groups, where the molecular weight increases with boiling point of the fraction.

The results from the measurements performed on the distillation cut at 230–250°C are given in Fig. 6a. After addition of cations, the IFT shows a step-wise progress until it equilibrates 10–15 units below the starting value. The step-wise curve is most likely a result of a combination of two processes. First, since the mixture is polydisperse, small molecules will be the first ones to reach the interface due to higher diffusion rates than larger ones. Gradually, however, the smallest molecules will be replaced by larger molecules. Due to their higher water solubility, the low-molecular weight species will cross the o/w interface and dissolve into the aqueous phase. A stepwise adsorption of monomers, to the interface might thus occur depending on the level of interfacial activity. Second, for polydisperse mixtures, more dynamic processes are taking place at the interface than for monodisperse surfactants and, normally, longer times are required for the system to reach equilibrium. This was also the case for the commercially available Fluka naphthenic acid before addition of cations. The sequential steps in IFT might thus refer to temporary states of equilibrium before the real equilibrium is reached as the curves flatten out. At this final state, the interface is covered by a film comprising more interfacially active molecules in combination with divalent cations.

Figure 6b gives the result from the measurements carried out on the 330–350°C fraction. With the addition of divalent cations to systems containing this acid mixture, a decline—followed by a small increase in IFT occurs, before all curves reach a steady state. The small increase might be due to film restructuring or that a minority of the monomers react to form 2:1 complexes.

The curves of the fraction at 350–370°C, given in Fig. 6c, have very similar shapes at equilibrium as of those at 330–350°C. This indicates the presence of similar structures, which is also in accordance with the overlapping intervals in temperature.

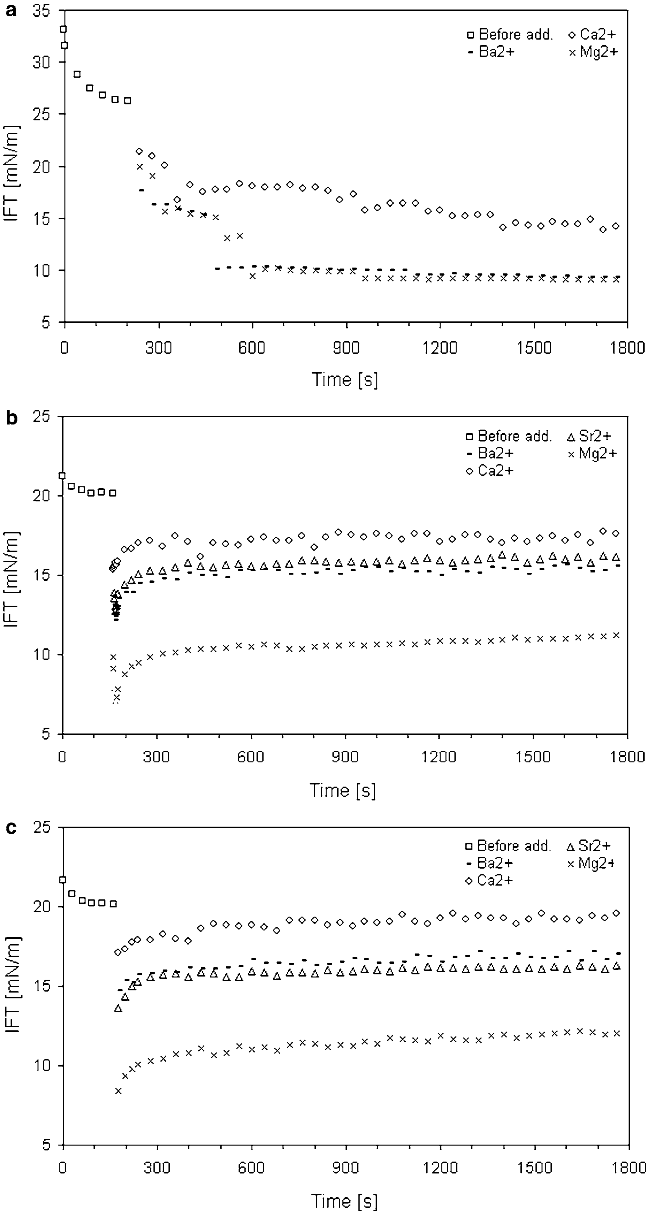


Fig. 6 Effects of addition of divalent cations on dynamic IFT for o/w systems with North Sea naphthenic acid of **a** distillation cut 1, **b** distillation cut 2, and **c** distillation cut 3

Introduction of oil-soluble non-ionic surfactants

Oil-soluble non-ionic surfactants have been introduced together with the ionized naphthenic acids in order to create a competitive situation at the o/w interface and to undertake a dilution of the reactive species when multivalent ions are present in the aqueous phase.

Interfacial activity of additives

Figure 7 shows the results from the measurements of dynamic IFT of the added non-ionic surfactants. In the case of product 1, 2, and 3, the IFT decreases continuously towards a stable value, while product 4 and 5 cause a monotonous increase in the IFT, most pronounced for product 5. This increase reflects a considerable solubility in water. In the case of product 5, an almost pure oil-water interface is obtained within a period of about 20 min.

Surfactants in combination with naphthenic acid and Ca^{2+}

In the upper part of Fig. 8, dynamic IFT is plotted for a system consisting of an oil droplet of *n*-decane and 0.25 mM *p*-(*n*-dodecyl) benzoic acid in aqueous borate buffer at pH 9.0. As the oil phase now is changed compared to the former studies, the reaction kinetic is a bit different as observed by comparing the result with that in Fig. 1. However, the trends are very much alike as addition of Ca^{2+} causes a sudden decrease followed by a steep increase in the IFT. The main difference is the part of the curve during the increase, which ascends steeper in the case of *n*-decane.

The lower part of Fig. 8 shows a typical result from an inhibition experiment based on the surfactants in Fig. 7. As an example, we have chosen product 2. The equilibrium IFT is now lowered several units and consequently, the decline in IFT caused by the reaction with Ca^{2+} becomes less prominent, since the interface now is mainly covered by non-ionic surfactant molecules instead of reactive acid monomers. Another conspicuous observation is that, after addition of Ca^{2+}, the curve ascends slower than in the case when no non-ionic surfactant is present. This is a consequence of the interfacial dilution and steric effects, causing a lower rate of completing the reaction to stoichiometric 2:1 compounds.

Conclusions

The pendant drop technique has proved to be a suitable tool to investigate interfacial reactions between naphthenic acids and divalent cations across oil–water

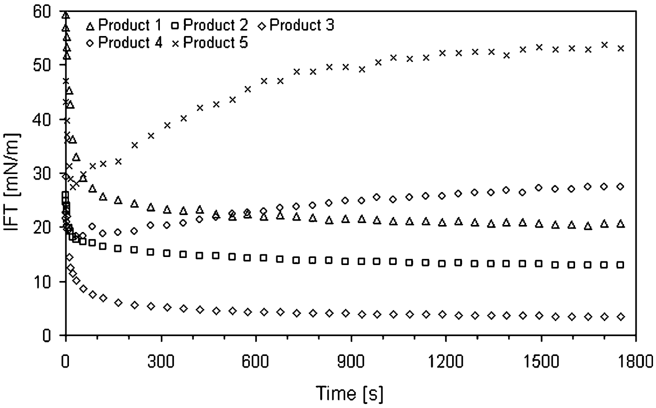


Fig. 7 Interfacial activity of oil-soluble non-ionic surfactant mixtures (products 1–5)

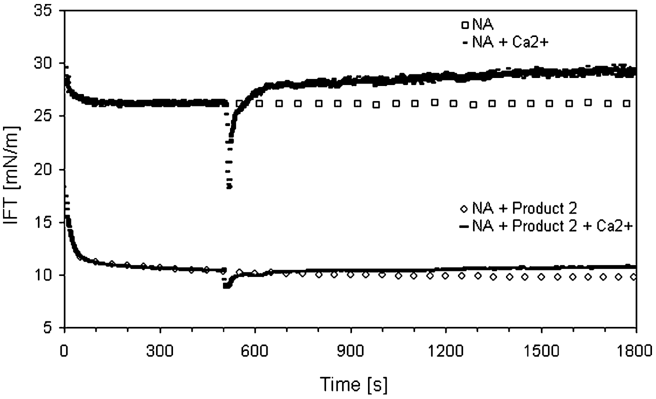


Fig. 8 Dynamic IFT upon addition of $CaCl_2$ in the case of only naphthenic acid and in the case of naphthenic acid combined with non-ionic surfactants of product 2

interfaces. The results show that the dynamic IFT strongly depends on the naphthenic acid structure and type and concentration of divalent cation. Before introducing divalent cations, the naphthenic acids containing aromatic rings seem to be more interfacially active than the corresponding saturated structures. This is due to a twofold effect caused by the π-bonds, which to start with enable the monomers to penetrate deeper into the interfacial layer and, moreover, bring along a higher monomer density at the interface. In combination with divalent cations, the solubility behaviour is changed, either due to reaction to form 2:1 stoichiometric complexes or by forming 1:1 positively charged monoacid complexes residing mainly at the o/w interface. The mechanism which dominates is depending on degree of cation hydration, which affects the cation affinity towards the interface and thus the distance between the interacting compounds.

Saturated naphthenic acid structures, including model as well as indigenous compounds, seem mainly to cause a permanent lowering of IFT in interaction with all the divalent cations. This condition is probably a result of the hydrophobic acid structures, which penetrate less into the interfacial layer when compared to the unsaturated model acids and hence form more well-defined o/w interfaces. Consequently, this causes longer interfacial distances between the acid and the divalent cation which hinder 2:1 stoichiometric complexes to form. In addition, steric hindrance caused by bulky monomers might also counteract a 2:1 binding of monomers as the lateral distance between the acid headgroups increases.

When oil-soluble non-ionic surfactants are introduced to systems containing the aromatic C12 acid and Ca^{2+}, two main effects are generally observed; the initial decline in IFT can be substantially reduced and the rate of the following increase in IFT is lowered. The first is a result interfacial coverage of highly active and non-reactive surfactant molecules, which hinder the less active naphthenic acid monomers to react at the interface with the divalent cations. The second observation likely reflects interfacial dilution of the acid monomers, causing a lower converting into 2:1 complexes.

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References

1. Brient JA, Wessner PJ, Doyle MN (1995) In: Kirk-Othmer Encyclopedia of Chemical Technology, Wiley, New York, pp 1017–1029
2. Seifert WK (1975) Fortschr Chem Org Naturst 32:1–49
3. Tomczyk NA, Winans RE, Shinn JH, Robinson RC (2001) Energy Fuels 15:1498–1504
4. Fan T-P (1991) Energy Fuels 5:371–375
5. Koike L, Reboucas LMC, Reis FdA, Marsaioli AJ, Richnow HH, Michaelis W (1992) Org Geochem 18:851–860
6. Pathak AK, Kumar T (1995) In: Proceedings of PETROTECH-95, New Dehli, India
7. Màrquez ML (1999) In: AICHE spring national meeting, Session T6005, Houston, TX

8. Acevedo S, Escobar G, Ranaudo MA, Khazen J, Borges B, Pereira JC, Méndez B (1999) Energy Fuels 13:333–335
9. Goldszal A, Bourrel M, Hurtevent C, Volle J-L (2002) In: The 3rd international conference on petroleum phase behavior and fouling, New Orleans, USA
10. Ese M-H, Kilpatrick PK (2004) J Disp Sci Techn 25:253–261
11. Taylor SD, Czarnecki J, Masliyah J (2005) J Colloid Interface Sci 282:499–502
12. Poggesi G, Hurtevent C, Buchart D (2002) In: SPE oilfield scale symposium, SPE74649, Aberdeen, UK
13. Gallup DL, Smith PC, Chipponeri J, Abuyazid A, Mulyono D (2002) In: SPE international conference on health, safety and environment in oil and gas exploration and production, SPE73960, Kuala Lumpur, Malaysia
14. Vindstad JE, Bye AS, Grande KV, Hustad BM, Hustvedt E, Nergård B (2003) In: SPE 5th international symposium on oilfield scale, SPE80375, Aberdeen, UK
15. Albers W, Overbeek JTG (1959) J Colloid Sci 14:501–509
16. McLaughlin S, Mulrine N, Gresalfi T, Vaio G, McLaughlin A (1981) J Gen Phys 77:445–473
17. Jennings HY Jr (1975) Soc Pet Eng J 15:197–202
18. Rousseau G, Zhou H, Hurtevent C (2001) In: SPE oilfield scale symposium, SPE68307, Aberdeen, UK
19. Dyer SJ, Graham GM, Arnott C (2003) In: SPE 5th international symposium on oilfield scale, SPE80395, Aberdeen, UK
20. Goldszal A, Hurtevent C, Rousseau G (2002) In: SPE oilfield scale symposium, SPE74661, Aberdeen, UK
21. Gallup DL (2004) In: SPE 6th international symposium on oilfield scale, SPE87471, Aberdeen, UK
22. Pilpel N (1969) Adv Colloid Interface Sci 2:261–296
23. Chifu E, Sálájan M, Demeter-Vodnár I, Tomoaia-Cotisel M (1987) Revue Roumaine de Chimie 32:683–691
24. Flipsen JAC, van der Hijden HTWM, Egmond MR, Verheij HM (1996) Chem Phys Lip 84:105–115
25. Hoppe A, Theimer RR (1996) Phytochem 42:973–978
26. Demeter-Vodnár J, Sálájan M, Lowy DA (1996) J Colloid Interface Sci 183:424–430
27. Touhami Y, Hornof V, Neale GH (1998) Colloids Surf A 133:211–231
28. Acevedo S, Ranaudo MA, Escobar G, Gutierrez X (1999) Fuel 78:309–317
29. Trujillo EM (1983) Soc Pet Eng J 23:645–656
30. McCaffery FG (1976) J Can Pet Tech 15:71–74
31. Sharma MM, Jang LK, Yen TF (1989) In: SPE reservoir engineering, SPE12669, pp 228–236
32. Brandal Ø, Sjöblom J, Øye G (2004) J Disp Sci Techn 25:367–374
33. Mediaas H, Grande KV, Hustad BM, Rasch A, Rueslåtten HG, Vindstad JE (2003) In: SPE 5th international symposium on oilfield scale, SPE80404, Aberdeen, UK
34. Andreas JM, Hauser EA, Tucker WB (1938) J Phys Chem 42:1001–1019
35. Winkel D (1965) J Phys Chem 69:348–350
36. Ambwani DS, Fort T Jr (1979) Surf Colloid Sci 11:93–119
37. Rotenberg Y, Boruvka L, Neumann AW (1983) J Colloid Interface Sci 93:169–183
38. Boucher EA, Evans MJB, Jones TGJ (1987) Adv Colloid Interface Sci 27:43–79
39. Marra J, Israelachvili J (1985) Biochem 24:4608–4618
40. Yazdanian M, Yu H, Zografi G (1990) Langmuir 6:1093–1098
41. Ederth T, Claesson PM (2000) J Colloid Interface Sci 229:123–128
42. Brandal Ø, Sjöblom J (2005) J Disp Sci Techn 26:53–58