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Langmuir films of naphthenic acids at different pH and electrolyte concentrations

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Abstract Langmuir films of naphthenic acids at different pH and electrolyte concentrations are reported. The polydisperse naphthenic acids were commercially available, while two single-component naphthenic acids [5*β*(*H*)-cholanoic acid and 1-naphthalenepentanoic acid, decahydro- (9CI)] were synthesized. 1-naphthalenepentanoic acid, decahydro- is too water-soluble to form stable monolayers. 5*β*(*H*)-Cholanoic acid and Fluka naphthenic acid form stable films when cations are present in the aqueous subphase. At lower pH the cations are less influential since the naphthenic acids are not protolysed and metal naphthenates cannot be formed. pK_a^s for 5*β*(*H*)-cholanoic acid is determined to 5.65. The micellisation of the naphthenates at high pH is described.

Keywords Langmuir films · Naphthenic acid · Critical micelle concentration · Micellisation

Introduction

Interest in the chemical properties of naphthenic acid derivatives originates from an ever-accelerating co-production with crude oils as acidic crudes. It is well known that these naphthenic acids show polydispersity in size and structure [1]. The smallest molecules readily dissolve in the aqueous phase at pH~5, while the larger molecules are preferably oil-soluble. These homologues dissolve in an aqueous phase at pH~10–11 [2, 3, 4].

There are some immense crude oil production problems related to the occurrence of naphthenic acids. They cause corrosion problems at the refineries when being processed. The mechanism of this process has not been clarified in detail, since it takes place in an oil environment [5]. Since the naphthenic acids and their soaps are surface-\interfacial-active they will accumulate at water/oil interfaces and stabilise colloidal structures [1, 2, 6, 7]. The worst scenario from an operational point of view is the stabilisation of water-in-oil emulsions which will cause problems in topside and subside separators [8]. If calcium or magnesium soaps are formed, the precipitation of the corresponding particulate soaps with low water solubility will be a consequence. The metal soaps tend to accumulate as nuclei at water/oil interfaces, where they undergo both nucleation and growth to form large particles. The agglomeration of these particles to voluminous precipitates will cause operational problems in the separation process with shutdown periods, during which thorough cleaning must take place. The formation of naphthenate mixed-scale particles in deep offshore fields has recently been studied by Rousseau et al [9].

In contrast, the low-molecular-weight and water-soluble derivatives will cause quality problems for the wastewater. The total amount of organic compounds in the wastewater must be adjusted to a tolerable level before the discharge takes place.

With this background, it is evident that there is a need to gain better understanding of the chemistry of naphthenic acids and their derivatives. Although the corresponding paraffinic fatty acids are very well characterized with regard to association and micellisation in water, phase equilibria, formation of lyotropic liquid crystals and microemulsions, monomolecular film properties, etc. [10, 11, 12, 13, 14, 15, 16, 17, 18], very little information is available for naphthenic acids.

In this first article we report Langmuir film properties of commercially available polydisperse naphthenic acids together with two synthesized well-defined homologues. The micellisation at high pH is also described.

Experimental

Chemicals

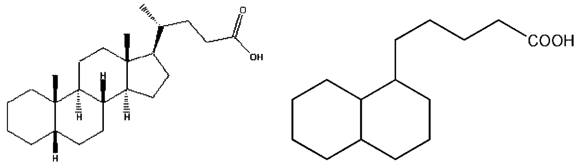
All the chemicals were used as supplied. Naphthenic acid (Fluka), 5*β*(*H*)-cholanoic acid and 1-naphthalenepentanoic acid, decahydro- (9CI) (Chiron AS) were used as film materials (Scheme 1).

$CaCl_2{\cdot}2H_2O$ (above 99.5%, Fluka) and NaCl (p.a. Merck) were used as addtitives to the aqueous subphase. Na_2HPO_4, NaH_2PO_4, (p.a. Merck), NaOH (99%, Riedel-de Haën) and HCl (Baker Chemicals) were used to adjust the pH of the bulk phase. Toluene (p.a., Merck, Darmstadt, Germany) was used as a spreading solvent for the naphthenic acids. For the critical micelle concentration (cmc) study Merck Titrisol buffer solution, pH 11.00 ± 0.05, boric acid/potassium chloride/sodium hydroxide, traceable to SRM of NIST and PTB, was also used.

Methods

Surface pressure–area isotherms and monolayer stability isotherms were recorded with a KSV 5000 Langmuir through double-barrier system (KSV Instruments, Helsinki, Finland). The temperature was kept at 294 ± 0.5 K. The trough was made of Teflon and the barriers of Delrin.

The purity of the surface was monitored before each run by moving the barriers across the pure liquid subphase. The measurement was continued if the surface pressure was less than 0.25 mN/m. The experiments were performed with a subphase consisting of pure water or solutions of Na_2HPO_4, NaH_2PO_4, $CaCl_2$, NaCl, NaOH or HCl. The naphthenic acid/toluene solution had a concentration of 2.0 g/l for Fluka naphthenic acid and 1.0 g/l for 5*β*(*H*)-cholanoic acid. The isotherms were measured on freshly spread monolayers, 50 μl per film, after allowing the spreading solvent (toluene) to evaporate for 15 min.



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Scheme 1. Structures of 5*β*(*H*)-cholanoic acid (*1*) and 1-naphthalenepentanoic acid, decahydro- (9CI) (*2*)

Compression of the monolayers was carried out with a barrier speed of 5 mm/min (1.9 $Å^2$/molecule/min) for 5*β*(*H*)-cholanoic acid and 10 mm/min (1.3 $Å^2$/molecule/min) for Fluka naphthenic acid. If the increase in the surface pressure exceeded 1 mN/m/min, the computer automatically adjusted the barrier speed to 1 mN/m/min.

Surface tension measurements were performed by the ring method using a Du Noüy ring connected to a KSV Sigma 701 computer-controlled tensiometer. The surface tension could be determined to within 1 mN/m. The pH for the water solutions in the cmc study was controlled by addition of NaOH, Na_2HPO_4, NaH_2PO_4 and Merck Titrisol buffer solution pH 11.

Results and discussion

Barrier speed

The comparison of the isotherms obtained with high barrier speed (10 mm/min) with the ones obtained with slow compression (1 mm/min), shows that reduced barrier speed gives rise to increased pressure at large areas and to reduced pressure at small areas. The reduced final pressure is a consequence of the dissolution of the film material into the bulk. While the increased pressure at larger areas may be explained as a result of formation of calcium naphthenate, which gives rise to increased pressure compared to the pure naphthenic acid film. The film is in contact with the Ca^{2+} ions long enough to form the naphthenate at larger areas than would be possible with an increased compression rate. For 5*β*(*H*)-cholanoic acid monolayers the barrier speed was kept at 5 mm/min (1.9 $Å^2$/molecule/min). This barrier speed is used earlier in Langmuir film studies by Ese and Sjöblom [19]. For the polydisperse Fluka naphthenic acid a barrier speed of 10 mm/min (1.3 $Å^2$/molecule/min) was found to give the best results. The reason for the higher speed in the latter is that the smallest of the acid molecules in the Fluka naphthenic acid mixture is more water-soluble than 5*β*(*H*)-cholanoic acid.

Influence of pH

1-Naphthalenepentanoic acid, decahydro

The stability isotherms for 1-naphthalenepentanoic acid, decahydro- (9CI) are given in Fig. 1. The results are expressed as A/A_0 versus time, t, where A_0 is the area of the monolayer after compression to constant surface pressure (10 mN/m) and A is the area of the monolayer at time t. This naphthenic acid rapidly dissolves into the bulk phase and, hence, no stable films are formed. Acidifying the subphase or addition of cations does not influence this situation.

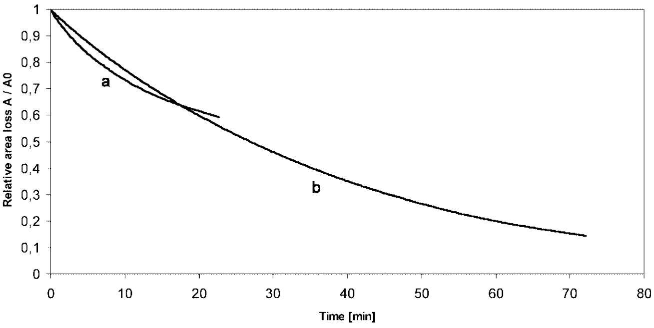

Fig. 1. Stability isotherms (surface pressure of 10 mN/m) for 1-naphthalenepentanoic acid, decahydro- at *a* pH 3.0, $[Na^+]=0.1$ M and *b* pH 5.6, pure water

5β(H)-Cholanoic acid

Pressure–area isotherms for different pH values, at a fixed sodium ion concentration of 0.1 M, are given in Fig. 2. As the pH increases, the film tends to tolerate a higher pressure before collapse. This is an indication of stabler films owing to naphthenate formation. The figure shows that the pressure increase sets in at different areas per molecule at the different pH values. At pH 3.0 the film properties are dominated by the fact that this film has a low long-term stability (Fig. 6, curve c). The reason for this is that the molecules are in an undissociated form and will not be stabilized by Na^+ ions. Figure 2 shows that the pH effects are rather small with regard to changes in area/molecule when the pressure starts to increase.

Joos [20, 21] has suggested that the collapse pressure, $\pi_{c,m}$, of a mixed miscible monolayer may be evaluated from the collapse pressures, $\pi_{c,1}$ and $\pi_{c,2}$, of the separate components according to Eq. (1):

$$X_1 \exp\left(\frac{(\pi_{c,m}-\pi_{c,1})\omega_1}{kT}\right)+X_2\exp\left(\frac{(\pi_{c,m}-\pi_{c,2})\omega_2}{kT}\right)=1, \tag{1}$$

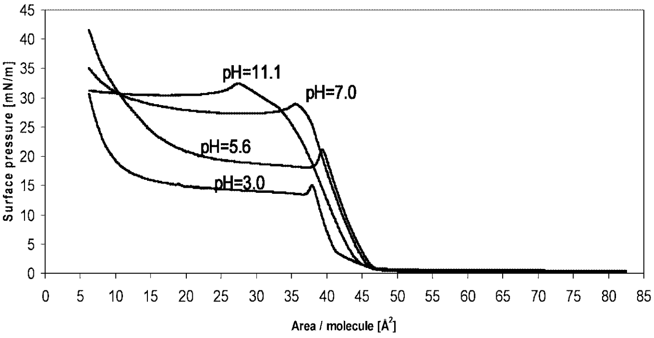

Fig. 2. Pressure–area isotherms for 5β(*H*)-cholanoic acid at $[Na^+]=0.1$ and pH 11.1, 7.0, 5.6 and 3.0

where X_1 and X_2 are the mole fractions in the monolayer of components 1 and 2, respectively, and ω_1 and ω_2 are their partial molecular areas. The activity coefficients are neglected, and it is assumed that equilibrium exist between the molecules in the monolayer and in the collapsed phase.

The acidity constant, K_a^s, in the monolayer can be defined according to Eq. (2):

$$K_a^s=\frac{X_{ZH}}{X_{ZNa}[H^+]}. \tag{2}$$

Here X_{ZH} and X_{ZNa} represent the mole fractions in the monolayer of naphthenic acid and sodium naphthenate, respectively. $[H^+]$ refers to the bulk concentration of H^+ ions.

If it is assumed that the partial molecular area of the undissociated and the soap form of the acid is the same ($\omega_{ZH}=\omega_{ZNa}=\omega$), Eqs. (1) and (2) can be rewritten as

$$\pi_{c,m}=-\frac{kT}{\omega}\ln\left(\frac{[H^+]}{K_a^s+[H^+]}\right)\exp\left(\frac{-\pi_{c,ZH}\omega}{kT}\right)+\frac{K_a^s}{K_a^s+[H^+]}\times\exp\left[\left(\frac{-\pi_{c,ZNa}\omega}{kT}\right)\right]. \tag{3}$$

This equation relates the collapse pressure of the monolayer as a function of the H^+ concentration or the pH of the bulk phase, provided the collapse pressures of the acid form and the soap form are known. It is seen that the surface dissociation constant, K_a^s, can be evaluated from such experiments.

A plot of a curve according to Eq. (3) and the experimental points from Fig. 2 are shown in 3. The fitting of the theoretical curve to the experimental values gives a pK_a^s of 5.65 for 5β(*H*)-cholanoic acid. Joos obtained $pK_a^s=7.5$ for cholic acid. The barrier speed and the composition of the subphase will probably influence the determination of pK_a^s.

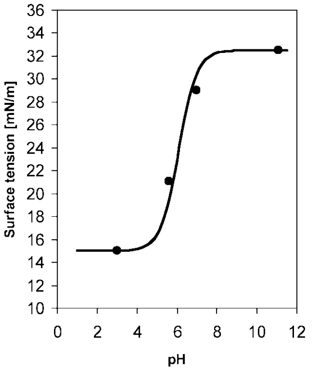

Fig. 3. Collapse pressure of a 5β(*H*)-cholanoic acid monolayer as a function of pH. *Points*: experiment; *full line*: calculated according to Eq. (3). $\omega=46$ Å^2, T = 293 K, $pK_a{}^s=5.65$, $\pi_{c,ZH}=15$, $\pi_{c,ZNa}=32.5$

Fluka naphthenic acid

The pH of the bulk phase is of major importance for the properties of the surface film formed. The isotherms in Fig. 4 show the changes in film behaviour when the pH is varied from 3 to 11. The isotherm at pH 3 deviates distinctly from pH 7 and 11. The film on a bulk phase at pH 3 consists basically of a nonprotolysed naphthenic acid and, hence, not of calcium naphthenate that is formed when the pH is higher.

The stability isotherms in Fig. 5 show that the film is most stable during the first 200 min when the pH of the bulk is high. At high pH, the film is highly protolysed, which gives rise to strong interactions between the film material and the Ca^{2+} ions in the bulk, resulting in formation of a relatively stable calcium naphthenate film. When the bulk is acidic (pH 3), the area of the film is reduced quite quickly during the first 100 min until an increase in area is observed. In addition to lack of formation of the quite stable film consisting of the calcium naphthenate complex, other effects may explain the trends found in Fig. 5. There will most likely be hydrogen bonds between the nonprotolysed carboxyl groups, which might pull the molecules in the film closer together. The Ca^{2+} ions might orient towards the acid film and disturb the hydrogen-bond-based network in the film. Hence, the film requires a larger surface and the A/A_0 value increases.

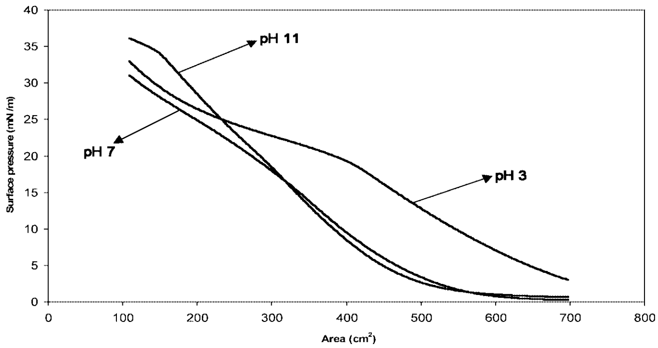

Fig. 4. Pressure–area isotherms for Fluka naphthenic acid at $[Ca^{2+}]=0.2$ M and pH 3, 7 and 11

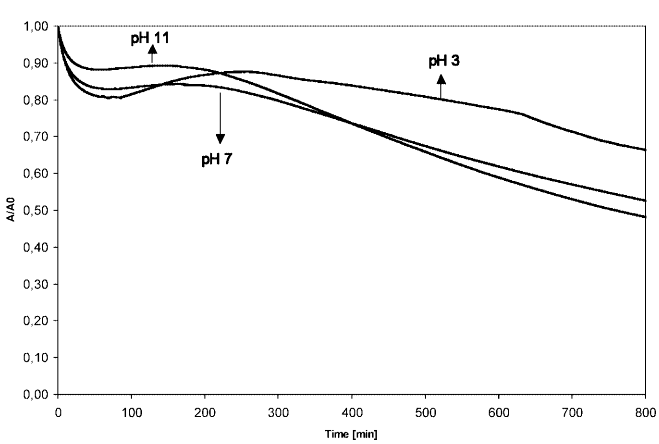

Fig. 5. Stability isotherms (surface pressure of 10 mN/m) for Fluka naphthenic acid at $[Ca^{2+}]=0.2$ M and pH 3, 7 and 11

Influence of sodium and multivalent ions

5β(H)-Cholanoic acid

Figure 6 shows that a film of 5*β*(*H*)-cholanoic acid is stabilised by addition of cations to the bulk solution. The reason for this is most likely the formation of metal naphthenates. At lower pH, the addition of metal ions will have less effect since the naphthenic acid is not protolysed and naphthenates will not be formed. The divalent calcium ions have a more stabilising effect on the film than the sodium ions.

Pressure–area isotherms for different ion concentrations at pH 5.6 are given in Fig. 7. As the concentration of calcium is increased from 0.01 to 0.10 M, each molecule occupies a larger area when the pressure increase sets in. An explanation for this is that with an excess of Ca^{2+} at the interface, each Ca^{2+} ion can attach to one acid molecule, instead of two molecules, at a pH close to pK_a^s and thus creates electrostatic repulsion between the headgroups. The decreased slope of the curve at higher calcium concentration indicates increased compressibility of the monolayer, which means that the film molecules are further apart when the ionic strength in the bulk is high. Hence, the electrostatic repulsion created in the film pulls the molecules apart.

The isotherms for 0 and 0.01 M Ca^{2+} only differ by the value of the collapse pressure. The presence of calcium tends to stabilise the film by naphthenate formation at this pH, but this low bulk concentration of Ca^{2+} does not give a large enough surface concentration to produce the same kind of film interactions as

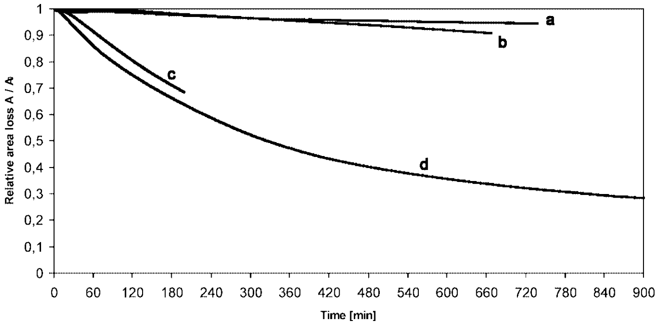

Fig. 6. Stability isotherms (surface pressure of 10 mN/m) for 5*β*(*H*)-cholanoic acid at *a* pH 5.6, $[Ca^{2+}]=0.01$ M, *b* pH 7.0, $[Na^{+}]=0.1$ M, *c* pH 3.1, $[Na^{+}]=0.1$ M and *d* pH 5.6, pure water

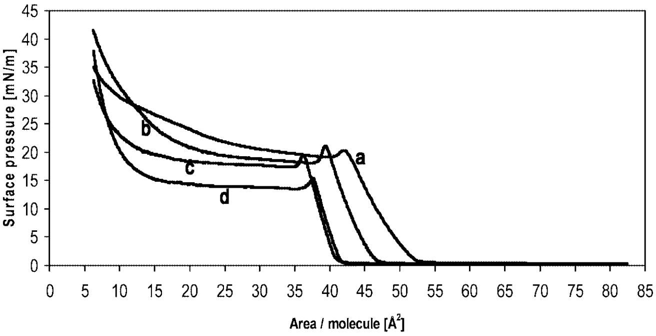

Fig. 7. Pressure–area isotherms for 5*β*(*H*)-cholanoic acid at pH 5.6 and *a* [Ca^{2+}] = 0.1 M, *b* [Na^{+}] = 0.1 M, *c* [Ca^{2+}] = 0.01 M and *d* pure water

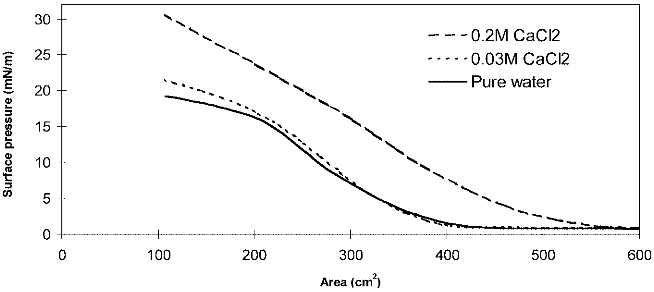

Fig. 8. Pressure–area isotherms for Fluka naphthenic acid on aqueous subphases at pH 5.6 and [Ca^{2+}] = 0.03 and 0.2 M

observed for the larger Ca^{2+} concentration. Hence, at relatively low surface concentrations of Ca^{2+}, there will be a surplus of anionic moieties in the film, thus allowing for one Ca^{2+} to connect with two naphthenates to make a tightly packed film. Owing to this packing structure, the increase in surface area per moiety as a function of the increased surface pressure will be relatively low. The isotherm for 0.1 M Na^{+} is given in Fig. 7, curve b. The set-in of the pressure increase is at a higher area per molecule than for pure water, though distinctly lower than for the same concentration of the divalent Ca^{2+}.

Fluka naphthenic acid

The isotherms of naphthenic acid on an aqueous subphase with and without $CaCl_2$ are shown in Fig. 8. When Ca^{2+} ions are present in the system, the formation of calcium naphthenate on the surface will give rise to a higher surface pressure at the same surface film concentration. Hence, the film of calcium naphthenate has different film properties than pure naphthenic acid. The monolayer stability measurements at constant surface pressure (10 mN/m) shown in Fig. 9, illustrates that Ca^{2+} ions stabilise the film and prevent the dissolution of the film material into the bulk phase.

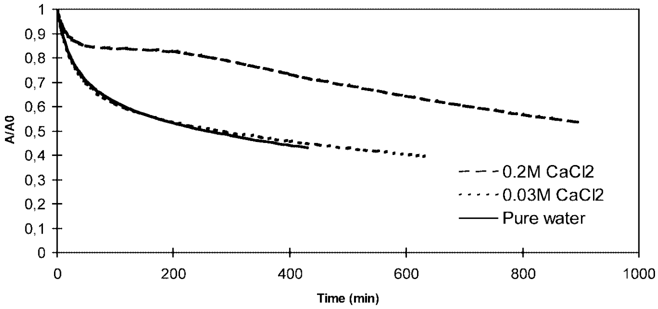

Fig. 9. Stability isotherms (surface pressure of 10 mN/m) for Fluka naphthenic acid on a subphase at pH 5.6 and different $CaCl_2$ concentrations

Micellisation at high pH

Normally the determination of the cmc is the starting point in understanding the inter- and intramolecular interactions in aqueous solutions of surfactants. For paraffinic fatty acid salts with sufficiently long alkyl chains a distinct cmc is normally observed. The driving force is normally considered to be a strong attractive hydrophobic interaction between the hydrocarbon chains. At the same time, the paraffinic alkyl chains do not have any severe packing constraint. On the other hand pharmaceutical surfactants with condensed ring structures are known to have a stepwise association in water and a low cmc results. Obviously these molecules have restrictions in their packing, and ordinary spherical micellar structures do not emerge. The difference in the molecular packing is also reflected in the aggregation numbers. For the paraffinic fatty acid salts, the micelles can contain up to 100 monomers, which is considerably more than for monomers with large condensed ring structures. The interesting thing with naphthenates is to compare the structures and see to what extent they follow an association tendency as ordinary paraffinic homologues, or when a stacking of monomers will set in.

The cmc was determined for the naphthenic acids used in this study. The area per molecule was determined from the Gibbs adsorption equation. The results are given in Table 1. The cmc curve for Fluka naphthenic acid is shown in Fig. 10.

The cmc for the polydisperse Fluka naphthenic acid is rather distinct. The plot of the surface tension versus the logarithm of the concentration for 1-naphthalenepentanoic acid, decahydro- indicates possible contamination. The reason may be due to the presence of aromatic forms of naphthenic acid, i.e. incomplete hydrogenation in the synthesis.

5*β*(*H*)-Cholanoic acid does not have a distinct cmc. The time necessary for achieving an equilibrium value increases for decreasing acid concentration. For a

Table 1. Critical micelle concentration (*cmc*) and area per molecule for the naphthenic acids at high pH

	pH	cmc (mol/dm^3)	Area per molecule (Å^2)
1-Naphthalenepentanoic acid, decahydro (9CI)	11.0	2×10^{-4}	52
Fluka naphthenic acid	11.3	8×10^{-4}	61

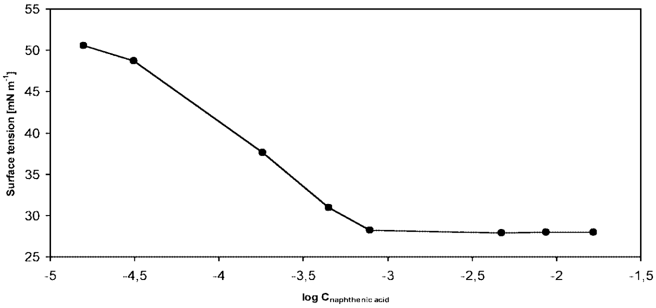

Fig. 10. Critical micelle concentration curve for Fluka naphthenic acid at pH 11.3. Surface tension versus the logarithm of the concentration (mol/dm^3)

concentration of 0.01 g/dm^3, 3 h is required to reach equilibrium. It is uncertain whether this is due to contamination by other surfactants in the chemicals.

The area per molecule for 1-naphthalenepentanoic acid, decahydro- and Fluka naphthenic acid is 52 and 61 Å^2/molecule, respectively. Ovalles et al. [22] have reported values for the area per molecule for naturally occurring naphthenic acids at an interface between water and toluene. They found 113–152 Å^2/molecule for different fractions.

Conclusions

1-Naphthalenepentanoic acid, decahydro- is too water-soluble to form stable monolayers. $5\beta(H)$-Cholanoic acid and Fluka naphthenic acid form stable films when cations are present in the aqueous subphase. At lower pH, the cations will be less influential since the naphthenic acids are not protolysed and metal naphthenates cannot be formed. The pK_a^s for $5\beta(H)$-cholanoic acid is determined to be 5.65.

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References

1. Hsu CS, Dechert GJ, Robbins WK, Fukuda EK (2000) Energy Fuels 14:217–223
2. Sjöblom J, Johnsen EE, Westvik A, Bergflødt L, Auflem IH, Havre TE, Kallevik H (2000) Presented at the 2nd international conference on petroleum and gas phase behaviour and fouling, Copenhagen, Denmark, 27–31 August 2000
3. Rudin J, Wasan DT (1992) Colloids Surf 68:67–79
4. Rudin J, Wasan DT (1992) Colloids Surf 68:81–94
5. Slavcheva E, Shone B, Turnbull A (1999) Br Corros J 34:125–131
6. Márquez ML (1999) AICHE 1999 spring national meeting, Houston, 14–18 March1999. Preprint no 56d, p 7
7. Acevedo S, Escobar G, Ranaudo MA, Khazen J, Borges B, Pereira JC, Méndez B (1999) Energy Fuels 13:333–335
8. Pathak AK, Kumar T (1995) Proceedings of PETROTECH-95, New Delhi. Technology trends in the oil industry
9. Rousseau G, Zhou H, Hurtevent C (2001) SPE oilfield scale symposium, Aberdeen, UK, 30–31 January 2001
10. Ekwall P, Mandell L, Fontell K (1961) Mol Cryst Liq Cryst 8:157
11. Ekwall P (1975) In: Brown GH (ed) Advances in liquid crystals. p 1
12. Ekwall P, Danielsson I, Stenius P (1972) In: Kenken M (ed) Surface chemistry and colloids. MTP Rev Sci Phys Chem Ser 1, vol 7. Butterworths, London, pp 97–145
13. Wennerström H, Lindman B (1979) Phys Rev 52:1
14. Lindman B, Wennerström H (1980) Top Curr Chem 87:1
15. Friberg SE, Mandell L, Ekwall P (1969) Kolloid Z Z Polym 233:955
16. Gillberg G, Lehtinen H, Friberg SE (1970) J Colloid Interface Sci 33:40
17. Skurtveit R, Sjöblom J, Høiland H (1989) J Colloid Interface Sci 133:395–403
18. Sjöblom J, Lindberg R, Friberg SE (1996) Adv Colloid Interface Sci 95:125–287
19. Ese M-H, Sjöblom J (1997) Colloids Surf A 123–124:479–489
20. Joos P (1969) Bull Soc Chim Belg 78:207–217
21. Joos P (1971) Bull Soc Chim Belg 80:277–281
22. Ovalles C, Garcia M, Lujano E, Aular W, Bermúdez R, Cotte E (1998) Fuel 77:121–126