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Interactions between poly(styrene-allyl alcohol) monolayers and surfactants. Correlations to water-in-crude oil emulsion stability

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Abstract: The Π -A isotherms and relaxation behavior of monomolecular films at the air/aqueous solution interface of a copolymer of styrene and allyl alcohol (PSAA, mean molecular weight 1500 g/mol) have been investigated as a function of the subphase surfactant concentration. The surfactants were sodium dodecylsulphate (SDS), cetyltrimethylammonium bromide (CTAB) or cetylpyridinium chloride (CPC). At low surfactant concentrations ($\lesssim 0.3$ CMC), the PSAA film is penetrated by surfactant molecules and undergoes a relaxation consistent with conformation changes of the polymer without dissolution into the subphase. At higher concentrations (\approx CMC) the PSAA film is slowly dissolved into the subphase; Π -A isotherms show a plateau and the films relax by a gradually decreasing surface area. The dissolution of PSAA is probably brought about by adsorption of surfactant molecules onto the polymer chain, giving rise to a water-soluble polymer-surfactant "complex" of poly-electrolyte nature. At medium concentrations, hydrophobic interactions between the neutral polymer and the ionic surfactant increase the hydrophilicity of the film and, thereby, probably lead to the formation of loops of polymer segments into the subphase. All the surfactants seem to interact with the PSAA film in similar ways. PSAA monolayers are good model systems for emulsion-stabilizing monolayers in North Sea crude oils. The monolayers of both the PSAA and the interfacially active crude oil system respond similarly to the presence of ionic surfactants, indicating analogous dissolution mechanisms. Thus, specific surfactant-monolayer interactions of the type observed will be of importance for an understanding of water-in-crude oil emulsion stability.

Key words: Monolayers; air/water interface; polymer; surfactant; interactions; crude oil

Introduction

A prerequisite for predicting coalescence in emulsion systems is to understand the conditions at the water/oil interface. Depending on the type of emulsion, this interface may contain a variety of single constituents or mixtures of surfactants, co-surfactants, particles, and polymers. The water droplets in crude oil based emulsions are generally considered to be surrounded by an interfacial film of asphaltenes, porphyrines, and wax particles [1–5]. The mechanical properties of such films prevent the system from coalescence with a concomitant phase separation.

In a series of articles, studies on water-in-crude oil emulsions from the Norwegian Continental Shelf with regard to formation, characterization, and destabilization have been reported [5–11]. As a part of these studies, a method for separation of the interfacially active (i.e., emulsion stabilizing) fraction in the oils was developed [9]. In order to obtain a fundamental understanding of the film properties of this fraction, a Langmuir study of its monolayer properties on aqueous subphases was undertaken [10]. A correlation between the specific monolayer areas of the fractions and the stability of the corresponding crude oil-based emulsions was found. In order to make further progress with

regard to a basic understanding of interactions in crude oil films, the monolayer behavior of model systems based on poly(styrene-allyl alcohol) was investigated. The film properties of the indigenous crude oil fractions are, to a large extent, reproduced by this system [11].

It has been convincingly shown that surfactants destabilize water-in-crude oil emulsions [7, 12]. Thus, in order to understand the mechanisms behind destabilization, knowledge about the interplay between film constituents and single monomeric surfactant molecules seems crucial. In the present article, the influence of different ionic surfactants in the subphase on monolayers of the water-insoluble, neutral poly(styrene-allyl alcohol) (PSAA) and on monolayers of the interfacially active fractions from a North Sea crude oil are investigated. From the comparison between the data on polymer and crude oil films, information about the mechanisms of emulsion destabilization by surfactants can be inferred.

Previous reports on interactions between polymers and surfactants mainly discuss water-soluble polymers (neutral or ionic) and ionic surfactants [13–16]. The interaction between surfactants and polymers is generally thought to involve the formation of micelle-like clusters adsorbed to the polymer chain. The formation of these clusters generally occurs at a rather well-defined surfactant concentration, denoted the critical aggregation concentration (CAC), which is frequently much lower than the critical micellization concentration (CMC) of the surfactant in bulk. The binding is usually cooperative and the same model has been extended to involve both neutral and charged water-soluble polymers. For polyelectrolytes and an oppositely charged surfactant, there is a large electrostatic contribution to the polymer-surfactant interaction, in addition to the hydrophobic interaction which is common to all polymers.

Only a few articles dealing with water-insoluble, neutral polymers and ionic surfactants have appeared. Isemura et al. have shown that uncharged, water-insoluble polymers such as polyvinylacetate, polyvinylformal, and polyvinylbutyral may be dissolved in highly concentrated solutions of sodium dodecylsulphate (SDS) [17, 18]. The driving force behind the solubilization is most likely nonspecific hydrophobic interactions. It is assumed that the surfactant molecules are adsorbed onto the neutral polymer with the non-polar part interacting with the polymer and with the ionic part directed to the

aqueous phase. This structure, resulting in a negatively charged polymer-surfactant "complex" with polyelectrolyte properties has been verified experimentally [18].

Experimental

Materials

Poly(styrene-allyl alcohol) (PSAA) was supplied by Polyscience Inc. The hydroxy content is 5.7% and the mean molecular weight is 1500 g/mol. Sodium dodecylsulfate (SDS) (> 99% purity) and NaCl (suprapure) were delivered by Merck, whereas cetyltrimethylammonium bromide (CTAB) (> 99% purity) and cetylpyridinium chloride (CPC) (99% purity) were from Janssen Chimica (Geel, Belgium). All these chemicals were used as supplied.

The surface-active fraction in a crude oil from the Norwegian Continental Shelf was separated and treated as described earlier [9]. The molecular weight average of the fraction is 1300 g/mol and the molecular range is 50–10 000 g/mol [10]. The elemental composition is 39.7 mol% carbon, 59.3 mol% hydrogen, 0.20 mol% nitrogen, 0.62 mol% oxygen, and 0.14 mol% sulfur [10]. The fraction was spread from a 1:1 (weight) mixture of redistilled toluene and hexane, both of p.a. quality from Merck. The spreading solvent in all the other experiments was a mixture of redistilled toluene and ethanol (4%).

The pH of the subphase solutions was adjusted by adding HCl (suprapure quality from Merck) to distilled water (pH = 5.6).

The water was first purified by decalcination, prefiltration, and reverse osmosis. Final purification was made by a modified MilliQ-unit which included two mixed bed ion exchangers, an activated charcoal cartridge, a 0.2- μ m in-line filter, an Organex cartridge (all other cartridges were from Millipore), and a final 0.2- μ m filter. All filters were Zetapore products from Cuno, France.

Surface balance experiments

The experiments were performed with a KSV 2200 Langmuir trough system (KSV Chemicals, Helsinki, Finland). The equipment includes automatic recording of Π -A isotherms at pre-deter-

mined compression rates, as well as recording of area losses at constant pressure (relaxation measurements). The temperature was kept at 294.5 ± 0.5 K.

A maximum change in surface pressure of 0.02 mN/m per minute was allowed for as the monolayer components were spread. The amount of material spread and the initial surface area were kept constant in all experiments for each subphase additive. The barrier speed was 10 mm/min and the compression started 30 min after spreading. In area relaxation experiments the films were initially compressed at 10 mm/min and then maintained at a predetermined surface pressure while the change in surface area was recorded as a function of time.

The fracture pressure Π_F is defined as the pressure where the film fractures or collapses at the given experimental conditions [19].

Results

Monolayers of PSAA

Π -A isotherms: The surfactants were added to the subphase prior to spreading the monolayers. The monolayer behavior of PSAA was studied as a function of the concentration of surfactant, as added to distilled water (pH = 5.6) in equilibrium with air, solutions of pH = 2.5 (corresponding to an ionic strength of 0.0032 M) or 0.0032 M NaCl

solutions. This was done in order to separately observe the effect of electrostatic shielding of the ionic surfactant groups and of changes in the pH. The concentration of surfactant was in the range:

$$2.8 \times 10^{-5} \text{ M} - 1.4 \times 10^{-3} \text{ M} \quad \text{for CPC}.$$

$$5.6 \times 10^{-5} \text{ M} - 3.8 \times 10^{-3} \text{ M} \quad \text{for CTAB}.$$

$$1.0 \times 10^{-4} \text{ M} - 1.0 \times 10^{-2} \text{ M} \quad \text{for SDS}.$$

The CMC for CPC, CTAB, and SDS in distilled water at 298 K is 9.0×10^{-4} M, 9.2×10^{-4} M and 8.1×10^{-3} M, respectively [20]. The CMC decreases somewhat as the concentration of electrolyte increases [21].

The monolayer behavior of PSAA on distilled water and on subphases of different pH has been described [11]. PSAA is a completely water-insoluble polymer and forms a stable liquid expanded monolayer at specific surface areas below $0.94 \text{ m}^2/\text{mg}$ on distilled water. At a surface area of about $0.45 \text{ m}^2/\text{mg}$, the isotherm starts to rise more steeply and the film fractures at a surface pressure of 33 mN/m and specific surface area $A = 0.30 \text{ m}^2/\text{mg}$.

Figure 1 shows the Π -A isotherms of PSAA on subphases of CPC in distilled water (pH = 5.6). The characteristic features of the isotherm change dramatically as the concentration of CPC (C_{CPC}) is varied. The surface pressures at $A = 1.4 \text{ m}^2/\text{mg}$ and $0.8 \text{ m}^2/\text{mg}$ and the fracture pressure for the PSAA film are shown in Fig. 2 as a function of the

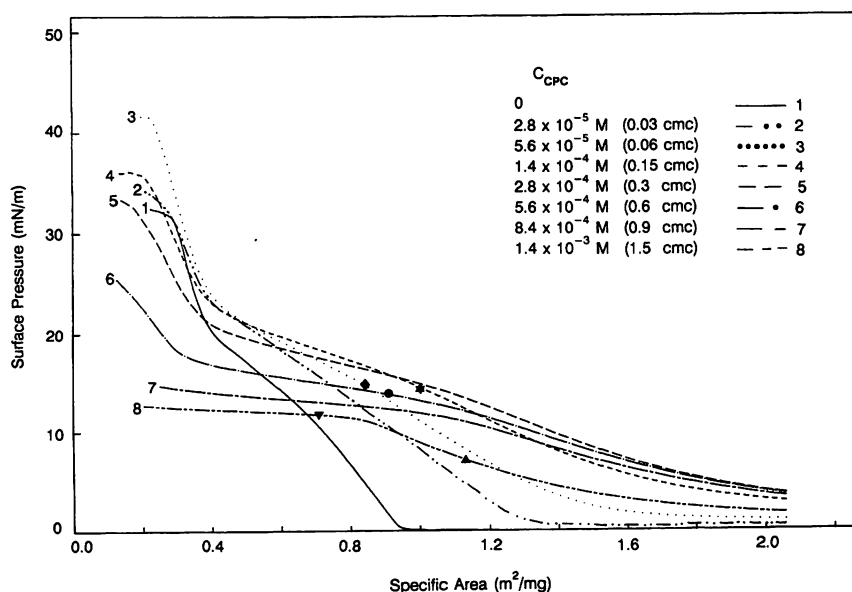


Fig. 1. Π -A isotherms of PSAA on subphases with different concentrations of CPC in distilled water (pH = 5.6). The symbols on the isotherms refer to constant pressure relaxation experiments shown in Fig. 5

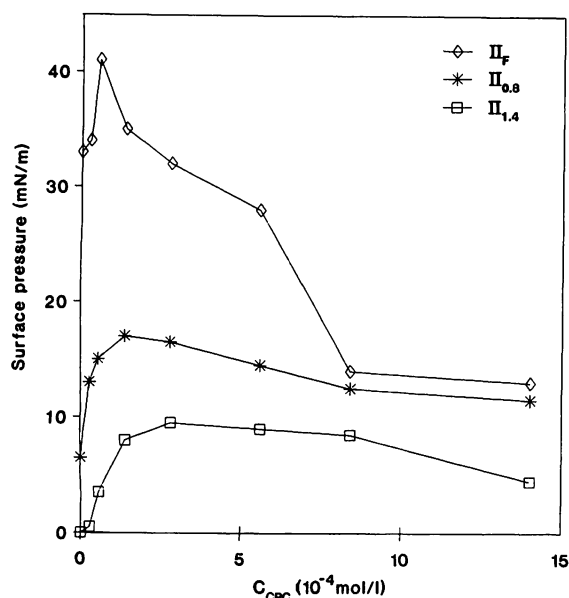


Fig. 2. The surface pressures at $A = 1.4 \text{ m}^2/\text{mg}$ ($\Pi_{1.4}$) and at $A = 0.8 \text{ m}^2/\text{mg}$ ($\Pi_{0.8}$) and the fracture pressure (Π_F) for the PSAA film as a function of the subphase concentration of CPC (C_{CPC}); pH = 5.6

subphase concentration of CPC (the data are also given in Table 1). With increasing C_{CPC} four different concentration regimes may be identified:

- 1) For $C_{\text{CPC}} \leq 1.4 \times 10^{-4} \text{ M}$ ($\approx 0.15 \text{ CMC}$), the surface pressure at large surface areas increases monotonously with increasing concentration. The fracture pressure is higher than on a pure water subphase, and attains a maximum of about 41 mN/m at $C_{\text{CPC}} = 5.6 \times 10^{-5} \text{ M}$ ($\approx 0.06 \text{ CMC}$). The fracture pressure on distilled water is 33 mN/m.
- 2) For $1.4 \times 10^{-4} \text{ M} < C_{\text{CPC}} \leq 2.8 \times 10^{-4} \text{ M}$ ($\approx 0.15 \text{ CMC} - \approx 0.3 \text{ CMC}$), there is still an increasing expansion of the monolayer at large surface areas; the film area at which the film fractures becomes smaller.
- 3) For $2.8 \times 10^{-4} \text{ M} < C_{\text{CPC}} < 8.4 \times 10^{-4} \text{ M}$ ($\approx 0.3 \text{ CMC} - \approx 0.9 \text{ CMC}$) the surface pressure at large areas begins to decrease. The film becomes even more compressible and the fracture pressure decreases.
- 4) For $C_{\text{CPC}} \geq 8.4 \times 10^{-4} \text{ M}$ (close to and above CMC in distilled water), the initial pressure decreases. A distinct plateau (almost constant pressure) is reached upon compression.

Table 1. The surface pressures at $A = 1.4 \text{ m}^2/\text{mg}$ ($\Pi_{1.4}$) and at $A = 0.8 \text{ m}^2/\text{mg}$ ($\Pi_{0.8}$) and the fracture pressure (Π_F) for the PSAA film as a function of the subphase concentration of CPC (C_{CPC}); pH = 5.6

C_{CPC} (10^{-4} mol/l)	$\Pi_{1.4}$ (mN/m)	$\Pi_{0.8}$ mN/m	Π_F (mN/m)
0	0	6.5	33
0.28	0.5	13.0	34
0.56	3.5	15.0	41
1.4	8.0	17.0	35
2.8	9.5	16.5	32
5.6	9.0	14.5	28
8.4	8.5	12.5	14
14.0	4.5	11.5	13

As the pH of the subphase is changed to 2.5, similar regimes for in the Π - A behavior of PSAA occur at lower concentrations of CPC (Fig. 3 and Table 2). The plateau of the isotherm occurs already at $C_{\text{CPC}} = 2.8 \times 10^{-4} \text{ M}$ (in distilled water at $C_{\text{CPC}} \geq 8.4 \times 10^{-4} \text{ M}$). An almost identical effect on the isotherm is obtained by adding 0.032 M NaCl to the water (Fig. 3), resulting in an ionic strength corresponding to pH = 2.5.

The influence of CTAB on the monolayer behavior of PSAA is almost identical to that observed for CPC on all subphases investigated. Therefore, data for CTAB are not given here.

The addition of an anionic surfactant (SDS) to the subphase (Fig. 4 and Table 3) has, to a large extent, a similar effect on the PSAA monolayer as CPC and CTAB. However, higher concentrations of surfactant are required in the case of SDS to obtain the same effects. The effect of changing the pH and adding NaCl to the subphase in which SDS is present, follows the same trend as observed for CPC and CTAB.

Relaxation: Constant pressure relaxation of PSAA was performed on a subphase of CPC added to distilled water. The relaxation process was examined at four different concentrations of CPC; three below and one just above the CPC concentration which gives rise to a plateau on the Π - A curves ($5.6 \times 10^{-5} \text{ M}$, $1.4 \times 10^{-4} \text{ M}$, $5.6 \times 10^{-4} \text{ M}$ and $1.4 \times 10^{-3} \text{ M}$, respectively). At each of the lower concentrations only a single surface pressure was used. At the highest concentration the relaxation

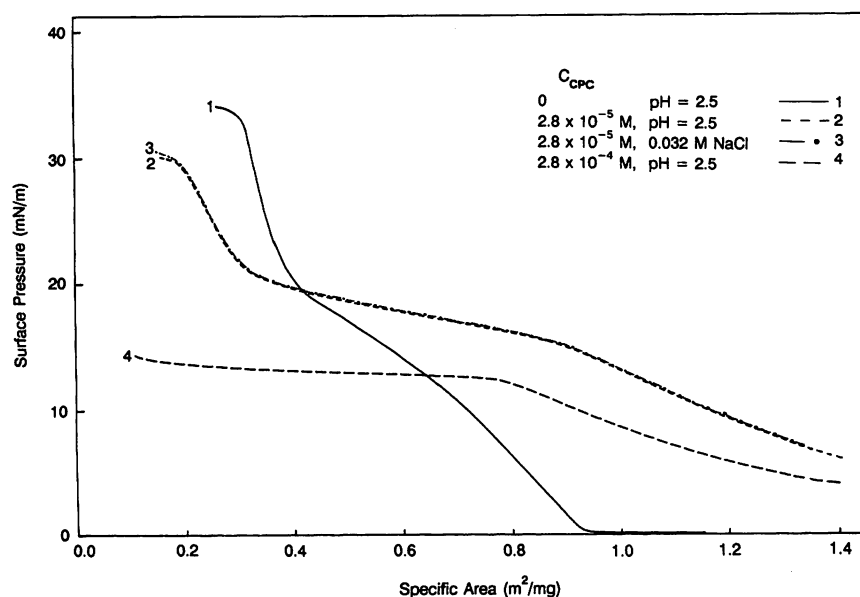


Fig. 3. Π -A isotherms of PSAA on subphases with different concentrations of CPC at pH = 2.5. An isotherm for the case of PSAA on a 0.0032 M NaCl subphase is also included

Table 2. The surface pressures at $A = 1.4 \text{ m}^2/\text{mg}$ ($\Pi_{1.4}$) and at $A = 0.8 \text{ m}^2/\text{mg}$ ($\Pi_{0.8}$) and the fracture pressure (Π_F) for the PSAA film as a function of the subphase concentration of CPC (C_{CPC}). pH = 2.5

C_{CPC} (10^{-4} mol/l)	$\Pi_{1.4}$ (mN/m)	$\Pi_{0.8}$ (mN/m)	Π_F (mN/m)
0	0	6.5	33
0.28	6.0	16.0	30
2.8	4.0	12.0	14

experiment was performed at two pressures, one below and one on the plateau.

The surface pressures for the relaxation experiments are marked on the Π -A curve in Fig. 1.

The relaxation process of PSAA is highly dependent on the concentration of CPC (Fig. 5). For $C_{\text{CPC}} = 5.6 \times 10^{-5} \text{ M}$ and $1.4 \times 10^{-4} \text{ M}$ at $\Pi = 15 \text{ mN/m}$ and for $C_{\text{CPC}} = 5.6 \times 10^{-4} \text{ M}$ at $\Pi = 14 \text{ mN/m}$ the relaxation is characterized by a rapid, initial area loss. The rate of relaxation then

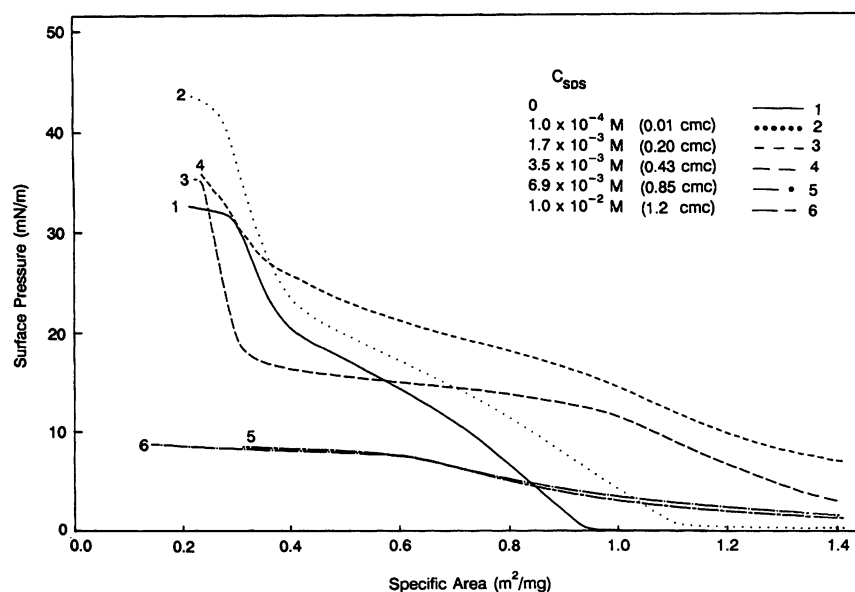


Fig. 4. Π -A isotherms of PSAA on subphases with different concentrations of SDS in distilled water (pH = 5.6)

Table 3. The surface pressures at $A = 1.4 \text{ m}^2/\text{mg}$ ($\Pi_{1.4}$) and at $A = 0.8 \text{ m}^2/\text{mg}$ ($\Pi_{0.8}$) and the fracture pressure (Π_F) for the PSAA film as a function of the subphase concentration of SDS (C_{SDS}). pH = 5.6

C_{SDS} (10^{-3} mol/l)	$\Pi_{1.4}$ (mN/m)	$\Pi_{0.8}$ (mN/m)	Π_F (mN/m)
0	0	6.5	33
0.1	0.5	11.0	42
1.7	7.0	18.0	36
3.5	3.0	13.5	35
6.9	1.6	5.5	8.5
10.4	1.4	5.0	8.5

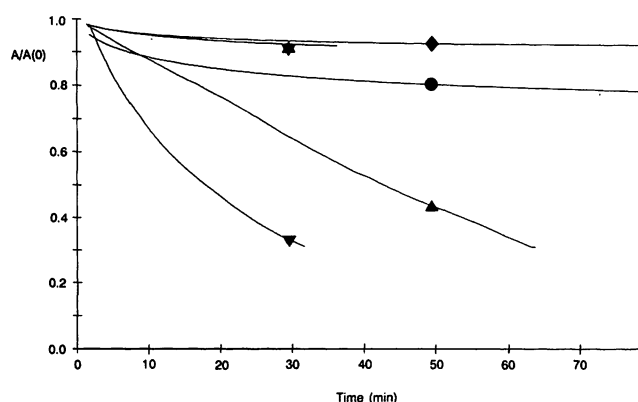


Fig. 5. Constant pressure relaxation of PSAA on subphases with different concentrations of CPC (C_{CPC}) in distilled water (pH = 5.6). \blacklozenge : $C_{\text{CPC}} = 5.6 \times 10^{-5} \text{ M}$ (0.06 CMC), $\Pi = 15.0 \text{ mN/m}$. \star : $C_{\text{CPC}} = 1.4 \times 10^{-4} \text{ M}$ (0.15 CMC), $\Pi = 15.0 \text{ mN/m}$. \bullet : $C_{\text{CPC}} = 5.6 \times 10^{-4} \text{ M}$ (0.6 CMC), $\Pi = 14.0 \text{ mN/m}$. \blacktriangle : $C_{\text{CPC}} = 1.4 \times 10^{-3} \text{ M}$ (1.5 CMC), $\Pi = 7.0 \text{ mN/m}$. \blacktriangledown : $C_{\text{CPC}} = 1.4 \times 10^{-3} \text{ M}$ (1.5 CMC), $\Pi = 11.6 \text{ mN/m}$. The symbols also refer to the markings on the Π - A curves in Fig. 1

slows down and an almost constant surface area is obtained. The area loss is about 10% at $C_{\text{CPC}} = 5.6 \times 10^{-5} \text{ M}$ and $1.4 \times 10^{-4} \text{ M}$, and 20% at $C_{\text{CPC}} = 5.6 \times 10^{-4} \text{ M}$ in a period of 60 min. The relaxation at $C_{\text{CPC}} = 1.4 \times 10^{-4} \text{ M}$ is totally different. At both pressures employed a gradually decreasing surface area is observed with an area loss of about 35% at $\Pi = 7 \text{ mN/m}$ and about 70% at $\Pi = 11.7 \text{ mN/m}$ within 30 min. There is no indication of a flattening out of the relaxation curves.

Because of the very similar effects of CPC, CTAB, and SDS on the Π - A isotherms, relaxation was not investigated for the two latter surfactants.

Monolayers of the interfacially active crude oil fraction

Figure 6 shows the Π - A curves for the interfacially active crude oil fraction on subphases of CPC in distilled water (pH = 5.6). An expansion of the film at large surface areas followed by a gradually increasing compressibility with increasing subphase surfactant concentration is observed, as it is for PSAA.

The crude oil film contains small amounts of alkaline functional groups which become negatively charged at pH = 2.5 [10]. However, no specific effects are observed at pH = 2.5 with ionic surfactants present in the subphase (results not shown).

The effect on the crude oil film by replacing CPC with CTAB or SDS is similar to that observed for the PSAA monolayer (results not shown).

Discussion

Polymer-surfactant interactions

From the Π - A isotherms and the relaxation behavior of the PSAA film on surfactant solutions, it is clear that the concentration of surfactant is the essential parameter determining the properties of the PSAA film at the air/aqueous solution interface and the degree of polymer-surfactant interaction. The influence of surfactant concentration on the PSAA monolayer properties is very similar for CPC and CTAB. Both surfactants are cationic with saturated C_{16} hydrocarbon chains. The structural difference in the cationic part of the molecules does not seem to be of importance for their interactions with the PSAA monolayer. Higher concentrations are required in the case of SDS to obtain the same effects on the PSAA monolayer. This is probably due to the shorter hydrophobic part of SDS, which also results in an increase in the CMC of the surfactant [22]. In relation to the CMC of the surfactants, the concentration effects are almost equal for all surfactants investigated. Both the effect of adding electrolyte to the subphase for one specific surfactant and of increasing the hydrophobicity of the surfactant (the interactions are in both cases initiated at lower concentration of surfactant) are readily understood by considering corresponding effects on micellar systems [21, 22]. Also, in systems of *water-soluble* polymers and

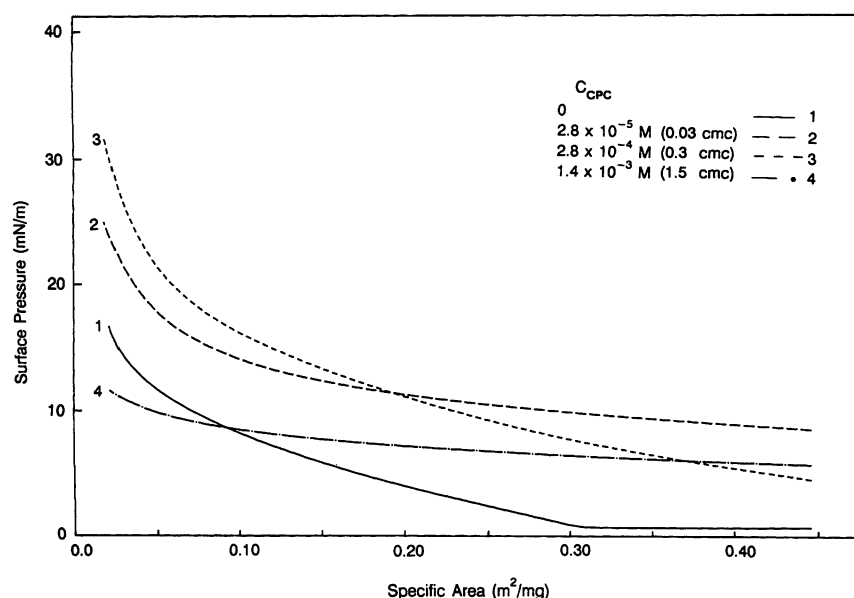


Fig. 6. Π -A isotherms of the interfacially active crude oil fraction on subphases with different concentrations of CPC in distilled water (pH = 5.6)

ionic surfactants similar trends are observed [23–25].

The following discussion concentrates on the monolayer behavior of PSAA on CPC subphase since this is the system we have examined most thoroughly. It is divided into two parts; one discussing CPC concentrations less than and one larger than $C_{\text{CPC}} = 2.8 \times 10^{-4} \text{ M}$ ($\approx 0.3 \text{ CMC}$), since there seems to be different mechanisms of interaction between the polymer monolayer and the subphase surfactant molecules in these intervals.

For $C_{\text{CPC}} \leq 2.8 \times 10^{-4} \text{ M}$ ($\approx 0.3 \text{ CMC}$) penetration of surfactant molecules into the PSAA film at large areas increases with increasing bulk concentration of surfactant (Fig. 1). This results in the formation of a mixed film of polymer and ionic surfactant. Such an expansion at large surface areas has been observed in many systems in which the subphase molecules interact weakly with the film molecules, which may be either polymers and proteins [26] or simpler molecules [27, 28]. The penetrating molecules are usually displaced from the mixed monolayer as the film is compressed and the surface pressure increases, which is similar to the observed behavior of the PSAA film on subphases with low surfactant concentration. The fracture pressure probably increases due to the force needed to completely displace the ionic surfactant from the PSAA monolayer. As the concentration of surfactant is further increased, the intermolecular forces between PSAA molecules in the monolayer will

probably dominate, as seen in the subsequent decrease in fracture pressure and area [27, 28]. Intersections between the isotherms of a polymer on subphases with pure water and added surface-active material have also been observed in systems in which the subphase solute has caused the polymer to assume a more compact conformation [29].

The relaxation curves of the PSAA monolayers are identical at all concentrations of CPC less than $2.8 \times 10^{-4} \text{ M}$ ($\approx 0.3 \text{ CMC}$) and are characterized by a small initial area loss and the rapid establishment of stable films (Fig. 5). The relaxation process is almost identical to that of PSAA on pure water [11] and is consistent with a rearrangement mechanism of the molecules in the film until a stable molecular conformation is reached [30, 31]. Although a stable polymer film is obtained also at $5.6 \times 10^{-4} \text{ M}$ CPC ($\approx 0.6 \text{ CMC}$), the initial relative area loss has increased to about 20% compared to 10% at the lower concentrations. A possible explanation for the larger area loss may be hydrophobic interactions between the neutral polymer and the ionic surfactant. This would lead to adsorption of surfactant molecules onto the neutral polymer in such a way that the non-polar part of the surfactant is directed towards the polymer and the ionic part is directed into the aqueous subphase, giving rise to a polymer with a slight polyelectrolyte character [17, 18]. This will increase the hydrophilicity of the film and, thereby, lead to a formation of loops of polymer segments penetra-

ting into the subphase at high pressures. Partial solubilization of polyelectrolyte molecules into the subphase solution has earlier been observed for systems in which the solute is highly surface active and oppositely charged to the polymer [32].

The surface pressure of the PSAA monolayer at large surface areas increases with increasing surfactant concentration below $C_{CPC} = 2.8 \times 10^{-4}$ M (≈ 0.3 CMC) and then starts to decrease. The onset of decreasing pressure with C_{CPC} coincides with the first signs of a plateau on the Π -A curve. It is not clear why the pressure should start to decrease at this concentration. As seen from Fig. 5, the monolayer is still completely insoluble. A further increase in surfactant concentration gives rise to a very distinct plateau on the isotherm. Similar isotherms are observed at all CPC concentrations close to and above CMC and may be explained by a gradual displacement of the PSAA film into the subphase as the available surface area decreases upon compression.

This conclusion is supported by relaxation at $C_{CPC} = 1.4 \times 10^{-3}$ M (≈ 1.5 CMC) (Fig. 5) which gives additional information about the mechanism of interaction between the PSAA film and the surfactant at high subphase concentrations of the surfactant. The surface area decreases continuously at constant pressure at both pressures investigated. However, the rate of relative area loss is twice as large at the higher surface pressure (on the plateau of the isotherm) as that at the lower pressure (below the plateau). A relaxation behavior with a gradually decreasing surface area is usually observed for films which dissolve into the subphase solution [33]. At high concentrations of surfactant, the adsorption of surfactant onto the polymer probably gives rise to a polymer-surfactant "complex" of hydrophilic character which becomes dissolved in the surfactant bulk solution. This is, of course, entirely compatible with the formation of somewhat fewer hydrophilic and, hence, still insoluble complexes at very low surfactant concentrations.

The displacement of the polymer from the air/water interface first occurs at concentrations somewhat below CMC of the surfactant. Thus, it seems as if the polymer-surfactant interaction involves a gradual adsorption of individual surfactant molecules onto the polymer chain. The data do not allow us to conclude whether the adsorbed surfactant monomers act as sites for further aggregation [34–36], or if there is a continuous adsorption

of monomeric surfactant molecules to the polymer chain [37].

Crude oil systems and emulsion destabilizing mechanisms

The Π -A isotherms of the interfacially active crude oil fraction are, in general, more featureless than those of the PSAA [11]. This is also the case when charged surfactants are introduced to the subphase. Nevertheless, the monolayers of both the crude oil fraction and the synthetic model polymer PSAA respond similarly to the presence of ionic surfactant. This indicates that the main mechanisms of interaction in the system of interfacially active crude oil fraction and ionic surfactant are analogous to those suggested for PSAA. The fact that the dissolution mechanism seems to be similar in the two systems, confirms the conclusion from our earlier paper [11] about PSAA being a good model substance for the crude oil fraction with respect to monolayer properties.

Earlier investigations on destabilizing water-in-crude oil emulsions by means of surfactants have clearly displayed the importance of the surfactant concentration [12, 38]. High concentrations ($>$ CMC) do not give rise to an efficient release of water from the emulsion, while low concentrations do. Thus, concentrations exceeding the CMC in bulk are less efficient in destabilizing the emulsified systems. In the absence of specific interactions this is the way destabilization will be linked to the surfactant activity. The most plausible explanation of the efficiency at low surface concentrations is the lowering of the surface tension γ . Since the indigenous crude oil components are not especially efficient in lowering γ , the surfactant (or amphiphile) will replace these components and form a new interface which does not stabilize the water droplets against coalescence. Such a mechanism is observed, for example, for short-chain alcohols [7, 10, 11]. However, when specific surfactant-oil component interactions occur, the destabilizing mechanisms are different. The destabilizing effects should then not be looked for in the lowering of the surface tension, but in an enhanced surface charge density in the interfacial zone leading to instability [7, 8]. Other mechanisms behind instability may be changed interfacial rheological properties such as elasticity and viscosity [39]. In other cases the surfactants have been shown to change the wett-

ability of stabilizing particles in the interfacial film [40].

On the basis of the present study on interactions between monolayers of polymer/crude oil fraction and ionic surfactants added to the subphase, we suggest a supplementary mechanism for destabilizing water-in-crude oil emulsions. If the water-soluble ionic surfactant adsorbs onto the emulsion-stabilizing polymeric crude oil components, the hydrophilicity of the indigenous polymer is gradually enhanced. This will eventually cause a destabilization of the emulsion as the hydrophilic polymer-surfactant "complex" is displaced from the water/oil interface by dissolution into the water phase. This mechanism is supported by the result from the PSAA model system as well as from the true crude oil system.

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