Colloid Polym Sci 278:1000–1006 (2000)

SHORT COMMUNICATION

I. Grosse
K. Estel

Thin surfactant layers at the solid interface

Received: 11 July 1999
Accepted: 2 May 2000

I. Grosse (✉) · K. Estel
Institut für Polymerforschung Dresden
e.V., Hohe Strasse 6, 01069 Dresden
Germany

Abstract The formation of surfactant layers on solid surfaces is an important process in many industrial applications. The structure of these layers influences the properties of the solid in processing and use. We summarize the literature data on the structure of surfactant layers at the solid/liquid interface and our own results characterizing the interactions between solid surfaces and solutions or emulsions. Ideas are presented for the processes taking place at the solid surface during drying by heat treatment. An outlook is given of how to investigate surfactant layers on dry surfaces.

Key words Solid surface · Adsorption · Surfactant layers · Emulsion layers · Drying

Introduction

Surfactant layers on solid surfaces play an important role in many technological processes and in the use of polymers, especially when the solid has a high surface-to-volume ratio (powders, fibres, textiles). The properties of the solid, for example, hydrophilicity, hydrophobicity, wetting, electrostatics, touch, stick–slip behaviour, are influenced by such layers. Thus, the formation of surfactant layers is an important operation in the surface modification of solids; however, a discrepancy still exists between the practical importance and the theoretical understanding of the different processes involved in the formation of such layers. For instance, the effect of drying on the structure of surfactant layers is not well established.

The investigation of practical systems and the application of the results to usual processes in industry is of great interest; however, some restrictions limit the use of the known methods. One important question is how surfactant layers and deposited emulsions behave during drying and in the dried state.

What is known on surfactant layers on solids?

Formation and structure of layers at the solid/liquid interface

When a solid dips in a solution of a surfactant, wetting, i.e. the replacement of the solid/gas interface by a solid/liquid one, and adsorption occur simultaneously. In contrast to wetting by pure liquids, wetting by solutions of surface-active agents changes the surface energy of the wetted solid by adsorbed molecules: the concentration of the solute is higher at the solid surface than in the bulk.

In the last 8 years work has been done to clarify the structure of these adsorbed surfactant layers. The development of atomic force microscopy (AFM) allowed for the first time direct imaging of surface layers on the submicrometre scale [1–13], mainly using cetyl trimethylammonium bromide (CTAB) as surfactant. The most important result was that surfactants often do not form continuous monolayers or bilayers at the solid/liquid interface but that they form discrete aggregates of different shape and size depending on different factors:

- Surfactant: ionicity, length of the carbon or ethylene oxide chain, headgroup, concentration in solution related to the critical micelle concentration (cmc), phase behaviour.
- Solid: hydrophilic (mica, silica) or hydrophobic (graphite, molybdenum disulfide), surface charges, active centres in the surface region.

Different types of surfactant layers on solids were described depending on the conditions of formation:

- Planar aggregates: monolayers or bilayers [2, 7, 11].
- Spherical aggregates: micelles, hemimicelles [1, 6, 7, 9].
- Cylindrical aggregates: long, parallel-aligned full or hemi-(half) cylinders, or short rodlike aggregates of periodic structure [1–4, 5, 7, 9, 10].

At concentrations below the cmc the surfactant molecules mostly form monolayers or spherical aggregates. The structure on the surface corresponds to that in the bulk phase at much higher concentration [9]. Surfactant concentrations well above the cmc lead to "wormlike" aggregates, i.e. parallel full or half cylinders. There is good correlation between the hydrophilic/hydrophobic behaviour of the solid and the form of the surfactant aggregate (Fig. 1). Hemicylinders dominate on hydrophobic materials because a large contact area between the hydrophobic chains of the surfactant and the solid surface is thermodynamically favourable, whereas structures similar to that in solution (rods, full cylinders) are found on hydrophilic surfaces. The contact between the solid and the hydrophilic headgroups of the surfactant molecules is preferred in this case. The diameter of these aggregates is approximately equal to the diameter of the micelles (twice the length of a surfactant molecule of about 3 nm). These aggregates are aligned parallel in the same direction, owing to micelle–micelle interactions, and are influenced by the symmetry axes of the underlying solid.

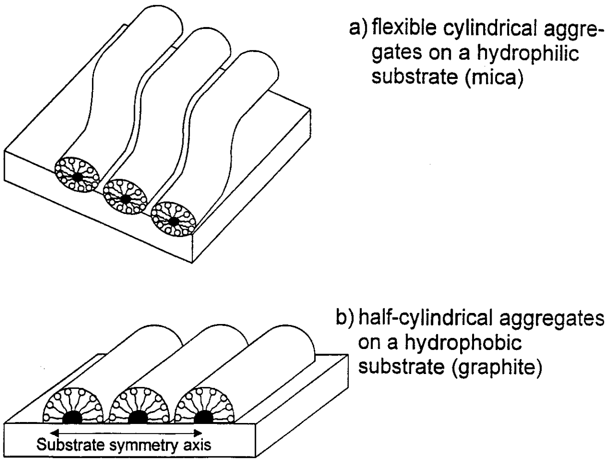


Fig. 1 Model of layers of a cationic surfactant at the solid/liquid interface [1]

The influence of the ionicity of the surfactant on the surface structure is rather small: anionic as well as cationic and nonionic surfactants form similar structures on the solid surface [1, 2, 7]. The effect of the length of the ethylene oxide chain, i.e. of the hydrophilicity of the surfactant is evident: in contrast to the hemicylindrical, parallel-arranged micelles of poly(ethylene oxide) surfactants with short ethylene oxide chains, long ethylene oxide chains lead to featureless layers on the hydrophobic graphite, indicating flat bilayers [11].

In practice mixtures of surfactants and emulsions of oils in surfactant solutions are frequently applied. In these cases the interactions between the solid and the substances in the liquid phase and the formation of surface layers are even more complicated and are not well understood [8].

Changes in the layers during drying

All investigations reported in the literature describe surfactant layers at the solid/liquid interface. In practice the influence of drying on the structure of these layers is very important. In this field only a few publications are known [4, 12, 13]. Dai and Vurens [12] reported the behaviour of perfluorinated nonionic surfactants on carbon surfaces in dry and humid environments. These investigations show the difficulties encountered in such studies.

The drying process involves several steps causing changes in the structure of the surfactant layer [14]. It is difficult to define the dry state. No absolutely dry surface exists under practical conditions. Hydrophilic samples may take up water by diffusion into the matrix (swelling). However, it is necessary to know the structure of such seemingly dry surfactant layers to find out correlations between their structure and the properties of the modified solid.

Different processes take place during drying:

- Separation of the solid and the liquid phase: the adsorbed surfactant remains on the solid, but solution may also adhere. Thus, the amount of surfactant on the solid can be larger than calculated by adsorption measurements.
- At increased temperature the liquid evaporates and the concentration in the residual solution increases up to and above the cmc. The surface tension in this solution drops and different phases may be formed according to the phase diagram of the surfactant.
- On decreasing further the liquid volume, the surface film may rupture and discrete droplets or clusters are formed. In this case the areas dried at the end of evaporation may be covered by higher amounts of

unadsorbed, weakly bound surfactants than the area around.

- The transition of the solid/liquid to the solid/gas interface may be accompanied by restructuring of the layer. Hydrophilic and hydrophobic groups, charge and polarity, residual humidity and hydration of the surfactant molecules are factors influencing the mobility and the alignment of the surfactant molecules or aggregates.

Methods to characterize surfactant layers on solid surfaces

To investigate surface layers, some direct and indirect methods are available and are used in the Institute of Polymer Research, Dresden.

Direct methods

Imaging AFM has been applied for about 10 years as a useful tool for direct imaging of the surface and for characterizing the interaction forces between the solid surface and a cantilever tip in air or aqueous solutions by force–distance plots [1–13]. We used a NanoScope III (Digital Instruments) to investigate surfactant layers on mica using the contact or friction mode in a special liquid cell (solid/liquid interface) or after drying the surface in a nitrogen stream (solid/gas interface). The surfaces of polymers are not suited for these investigations because the surface roughness conceals the structure of thin layers.

Attenuated total reflection Fourier transform IR spectroscopy (ATR-FTIR): a special liquid cell, coupled with an IFS 55 FT spectrometer (Bruker) was developed to observe in situ the kinetics of the formation of surfactant layers and the thickness of the layers obtained [15]. The lateral distribution of the adsorbed substance cannot be derived from these measurements.

Scanning electron microscopy of layers contrasted by osmium tetroxide [16] and X-ray photoelectron spectroscopy (XPS) [19] are other methods available to investigate surfaces. However, it is impossible to get results on the lateral distribution in micrometre or nanometre ranges, so we did not include them in our investigations on surfactant layers.

Indirect methods

The ***amount adsorbed*** was determined by measuring the concentrations before and after the adsorption by potentiometric titration of ionic surfactants (Autochemistry System 960, coupled with an Orion 93–42 surfactant electrode 93–42) and the total organic carbon method (TOC 5000, Shimadzu) to obtain the sum of all organic ingredients. The combination allows the adsorption of an ionic and a nonionic component in a mixture to be calculated separately. We studied the behaviour of different cationic surfactants, alkyl (hexadecyl, octadecyl) trimethylammonium bromides, dialkyl dimethylammonium chloride (DEEDMAC), and of a CTAB-stabilized emulsion on cellulose surfaces. The results were used to calculate the thickness of the layer of the cationic surfactant, assuming a continuous surface film and ignoring other factors such as diffusion.

AFM: force–distance measurements

The change in the forces between the surface and the cantilever tip by adsorbed layers of CTAB allows statements on attractive and repulsive interaction forces indicating the kind of forces and the affinity between the surfactant layer and the surface to be made.

Electrokinetic measurements

Streaming potential measurements of solids in surfactant solutions of increasing concentration are a measure of the electrical interaction forces at the surface and the surface charges of the solid. The concentration where the surface charges are saturated by adsorbed ions is the so-called point of zero charge (PZC) ($\zeta = 0$) and is characteristic for each system. The measurements were carried out using an EKA electrokinetic analysator (A. Paar, Austria).

Heterocoalescence [18]

The interaction of an oil droplet in aqueous surfactant solution and a solid surface is characterized by the time which is needed from the first contact between oil and solid to its spreading on the surface.

Wetting

The results of contact-angle or wetting measurements with water on modified dried solids allow conclusions to be drawn on the alignment of the hydrophilic and hydrophobic parts of the surfactant in the dried state.

The comparison of the results of the different methods is sometimes difficult because each needs special types and shapes of the solids: a very smooth homogeneous surface is required for AFM, ATR-FTIR or contact-angle measurements; a big surface-to-volume ratio is favourable for adsorption or zeta potential measurements. Most of the methods are only suitable for characterizing layers at the solid/liquid interface. Until now only AFM, XPS (X-ray photoelectron spectroscopy) and wetting measurements have been applicable for dry surfaces.

Results

Adsorption of cationic surfactants on hydrophilic surfaces (cellulose, mica)

The adsorption isotherms of different cationic surfactants on cellulose pulp are shown in Fig. 2. It is obvious that the adsorption of CTAB proceeds by another mechanism than for the other cationics investigated. The adsorption isotherms of octadecyl trimethylammonium bromide and the double-chain quaternary ammonium salt DEEDMAC reach a plateau, whereas the adsorption of CTAB increases continuously, even when the concentration in solution exceeds the cmc (up to 1.5 cmc). We explain this behaviour by multilayer adsorption of CTAB, in contrast to the formation of monolayers by octadecyl trimethylammonium bromide or DEEDMAC.

The changes in the force–distance plots between mica and the cantilever tip in CTAB solutions of increasing concentration far below the cmc (350 mg/l) of CTAB are represented in Fig. 3. The results show that the surfactant layer adsorbed at very low concentrations influences the force between mica and the tip: no electrostatic repulsion is measured in a solution of concentration of about 3 mg/l. This result agrees with that of streaming potential measurements on mica plates (Fig. 4): the PZC is also reached at 3 mg/l CTAB. Strong attraction forces act in this solution at small distances ($d < 25$ nm). This is consistent with the hydrophobic interactions between two CTAB monolayers mentioned by Parker [17] because CTAB is adsorbed on the mica plate as well as on the cantilever tip. The surfactant with two long carbon tails (DEEDMAC) needs a noticeably higher concentration to reach the PZC and the region of no electrostatic interactions. The low surfactant concentrations of CTAB used in these experiments are not sufficient to create surface layers, which are visible in AFM images (Fig. 1).

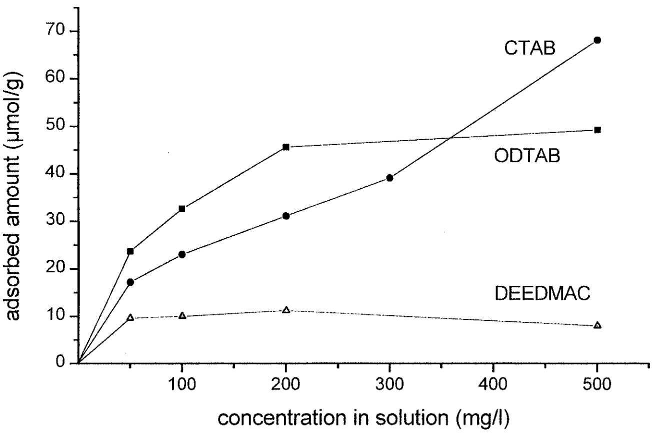


Fig. 2 Adsorption isotherms of cationic surfactants on cellulose: cetyl trimethylammonium bromide (CTAB), octadecyl trimethylammonium bromide (ODTAB), dialkyl dimethylammonium chloride (DEEDMAC)

Deposition of oil and cationic surfactant of an emulsion on hydrophilic surfaces (mica, cellulose)

By heterocoalescence measurements [18] we could show that the deposition of oil from oil-in-water emulsions

Fig. 3 Force–distance plots of mica and an Si_3N_4 cantilever in CTAB solutions of increasing concentration

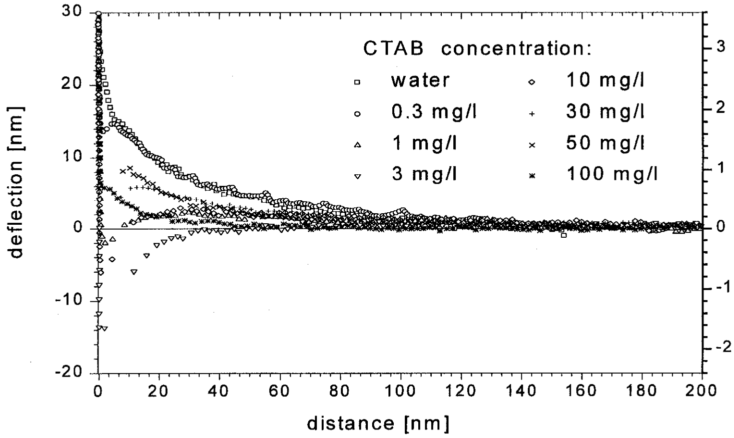
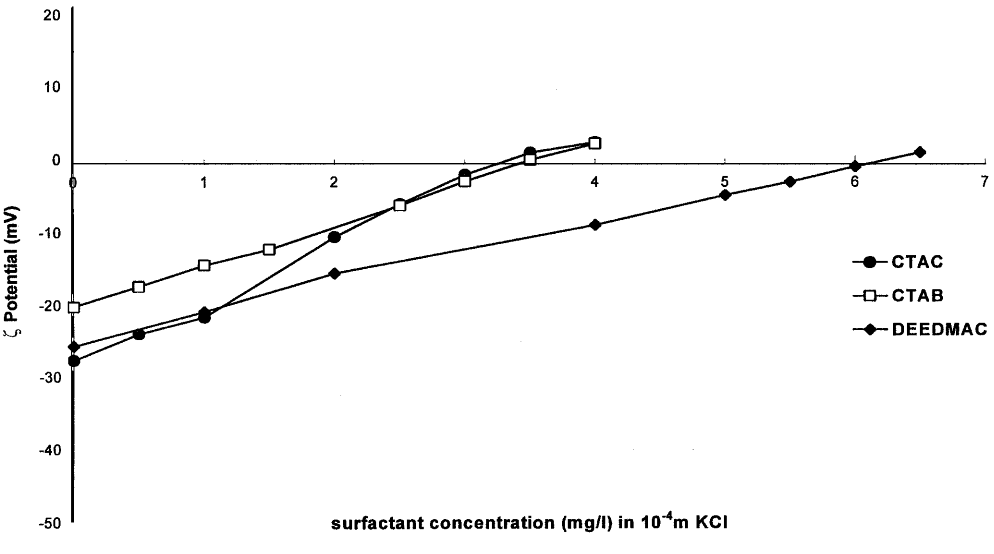


Fig. 4 Zeta potential of mica in surfactant solutions of increasing concentration: cetyl trimethylammonium chloride (CTAC), cetyl trimethylammonium bromide (CTAB), dialkyl diethylammonium chloride (DEEDMAC)



on solids strongly depends on the solid and the kind and the concentration of the surfactant. On exceeding a critical concentration range, which is typical for the chosen surfactant, no wetting of the solid by the oil droplet and consequently no formation of a surface layer of oil took place. This critical concentration slightly corresponds with the cmc of the surfactant. In Ref. [18] a correlation between the heterocoalescence and the behaviour of an emulsified oil in contact with a solid is postulated.

In further experiments we corroborated these results by determining separately the amounts of the surfactant cetyl trimethylammonium chloride (CTAC) and a commercial ester oil adsorbed on cellulose from a very diluted oil-in-water emulsion. The sum of the concentrations of the substances was 200 mg/l (maximum CTAC 75 mg/l) or 500 mg/l (minimum CTAC 75 mg/l). The percentage of the deposited oil calculated from the total amount of oil in the emulsion and the adsorption isotherm of CTAC is shown in Fig. 5. It can be seen that increasing the surfactant-to-oil ratio in the mixture decreases the deposition of the oil up to a value of about 10%. The adsorption of CTAC is not influenced by the presence of the oil.

We performed AFM experiments to show the structure of the emulsion deposited on mica after its drying in a nitrogen stream. In these experiments we investigated the influence of increasing concentration of the emulsion (between 0.3 and 50 mg/l), containing 10% CTAC and 90% oil. We did not change the oil-to-surfactant ratio. Different structures are created with increasing concentration (Fig. 6). Discrete particles with diameters between 30 and 200 nm are formed for $c < 5$ mg/l. If the concentration exceeds 10 mg/l, aggregates are generated which cover a continuously increasing area. The results of the AFM measurements in the force–volume mode (i.e. force–distance curves at different parts of the image) showed that the apparently empty areas are also covered by a surfactant layer. On the patches of the oil droplets on the dried (solid/gas) surface the adhesion between mica and the cantilever is low, expressed by the jump-out distance (36 ± 3 nm). The adhesion strongly increases after the "rehydration" of the surface: a jump-out distance of 160 ± 18 nm is measured on the patches at the solid/water interface. On rehydration, the profile of the droplet's longitudinal view becomes smaller and higher. Probably the contact angle increases due to the decrease in the contact area between the hydrophobic oil droplet and the surroundings when the oil/air interface changes to the oil/water interface. This observation may also be related to the partial removal of the oil ("rolling-up mechanism" in detergency), seen by heterocoalescence. An explanation of the different phenomena cannot be given and further work is necessary.

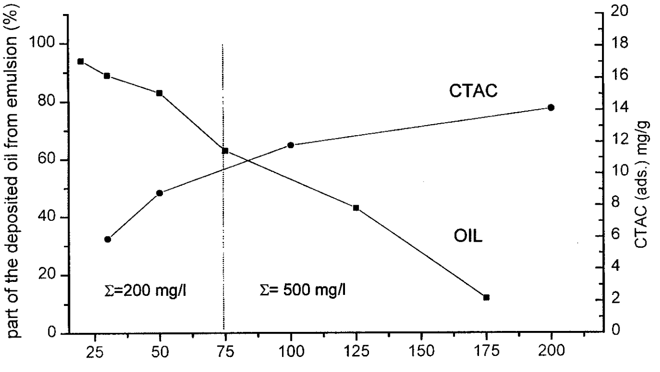


Fig. 5 Deposition of oil and surfactant on cellulose out of emulsions with an increasing portion of the cationic surfactant CTAC

Discussion

The existence of regular self-assembled structures (full or half cylinders, spheres or spheroids) at the solid/liquid interface for concentrations above the cmc has been proved recently by AFM imaging [1–13] in contrast to the monolayers or bilayers postulated in the past. The alignment depends on the concentration and the constitution of the surfactant's headgroup and on the hydrophilic or hydrophobic properties of the solid. CTAB was the most frequently investigated surfactant. The results of other authors are supported by our investigations: the amount of the cationic CTAB adsorbed on cellulose increases to values well above the amount calculated for a monolayer, indicating the formation of multilayers or just cylindrical structures above the cmc. However, CTAB forms layers on solids even at very small concentrations, recognizable by the change in the surface forces of mica in dilute surfactant solutions. The other cationic surfactants investigated tend to form monolayers even at higher concentrations because their adsorption isotherms are of the Langmuir type. So our and other published results [1–4] indicate the special behaviour of CTAB compared with other cationic surfactants: the reason is unknown.

Some of the methods described in the literature to investigate thin layers on solid surfaces are suitable to characterize surfactant layers at the solid/liquid interface: AFM topographic methods and direct-force measurements, determination of the amount adsorbed and assessment of the layer thickness, change in the surface charges (zeta potential) and heterocoalescence. However, the application to dry surfaces has so far only been successful using special conditions and restrictions. Knowledge of the changes which happen in the adsorbed layer during drying is poor. These changes

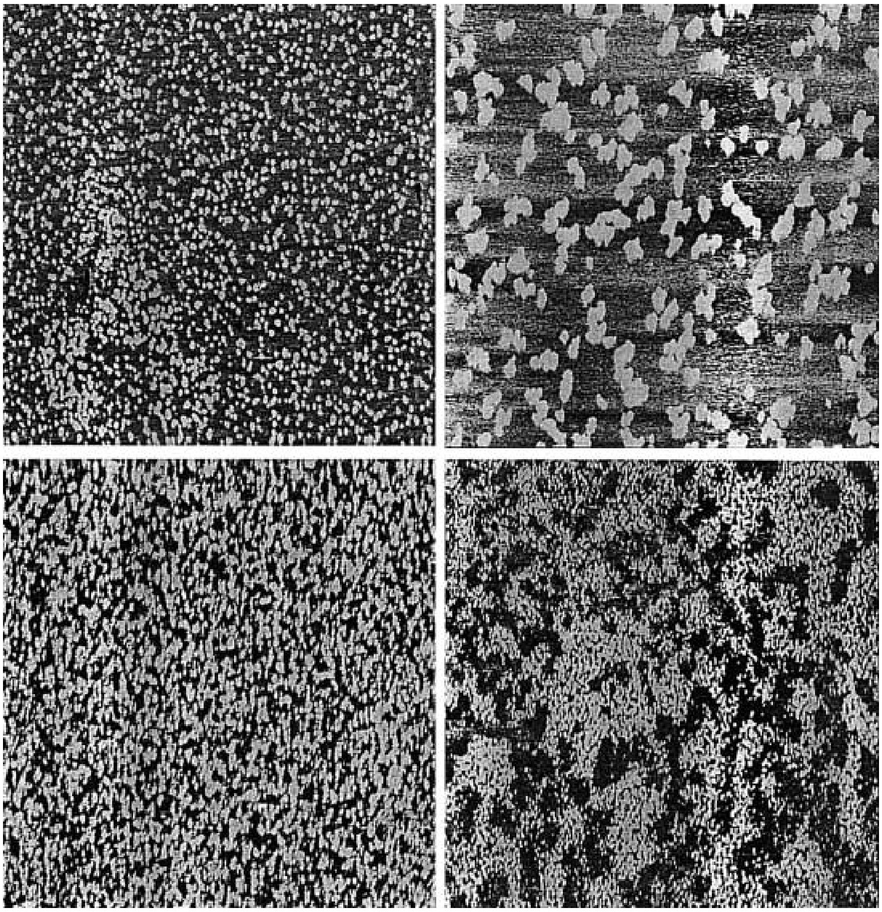


Fig. 6 Distribution of an oil-in-water emulsion of different concentration on mica after drying (atomic force microscope images, friction mode, scan size 5 μm^2)

include the formation of different phases corresponding to the phase diagram of the particular surfactant caused by the increasing concentration during evaporation of the retained water and the inhomogeneous distribution of the deposit on the surface as a result of the rupturing of the film when the volume of the liquid decreases.

The distribution of emulsion droplets on the smooth mica surface became visible by AFM investigations. An important result is that in wet and dried states the low-concentrated cationic surfactant as a part of the emulsion forms a layer, probably a continuous monolayer, on the whole mica surface, whereas the oil deposits in discrete droplets. Their profile alters when the solid/air interface changes to the solid/water one. It is assumed that hydrophilic/hydrophobic properties of the solid and surfactant adsorption and desorption on the solid and the droplet's surface influence this process. Adsorption and heterocoalescence measurements prove the thesis that increasing amounts of surfactant in the emulsion decrease the deposition of the oil on a surface. This may have consequences for practical lubrication processes.

Conclusion

A literature review is given on the present knowledge of surfactant layers on solid surfaces. The existence of self-assembled layers in the form of micelles and hemimicelles, often regularly arranged as cylinders or hemicylinders, has been proved for concentrations above the cmc.

Different methods are available and used to investigate layers at the solid/liquid interface. Until now only AFM measurements have been suitable to characterize the structure of surfactant layers and emulsions at the solid/gas interface.

CTAB behaves differently to other cationic surfactants. It forms multilayers on solid surfaces when the concentration exceeds the cmc.

Results were obtained to characterize the behaviour of emulsions on solid surfaces. They show the influence of the concentration of both surfactant and oil on the amount and droplet structure of the deposited oil and their changes during drying.

A scientific consideration of the technological process of surfactant treatment requires to the knowledge of what happens during adsorption and drying and of how the dried structures are arranged. This knowledge permits the properties of “real”, i.e. rough and chemically inhomogeneous bodies such as polymeric materials or fibres to be influenced in the desired way. The results presented here may be the basis for further investigations.

Acknowledgement The authors wish to express their thanks to the Deutsche Forschungsgemeinschaft for the financial support of the work described here.

References

1. Manne S, Gaub HE (1995) Science 270:1480–1482
2. Manne S (1997) J Prog Colloid Polym Sci 103:226–233
3. Ducker WA, Wanless EJ (1999) Langmuir 15:160–168
4. Sharma BG, Basu S, Sharma MM (1996) Langmuir 12:6506–6512
5. Patrick HN, Warr GG, Manne S, Aksay IA (1999) Langmuir 15:1685–1692
6. Grant LM, Tiberg F, Ducker WA (1998) J Phys Chem B 102:4288–4294
7. Rutland MW, Senden TJ (1993) Langmuir 9:412–418
8. Giasson S, Kuhl TL, Israelachvili JN (1998) Langmuir 14:891–898
9. Ducker WA, Grant LM (1996) J Phys Chem 100:11507–11511
10. Wanless EJ, Ducker WA (1996) J Phys Chem 100:3207–3214
11. Patrick HN, Warr GG, Manne S, Aksay IA (1997) Langmuir 13:4349–4356
12. Dai Q, Vurens G (1997) Langmuir 12:4401–4406
13. Liu Y, Evans FD, Song Q, Grainger DW (1996) Langmuir 12:1235–1244
14. Grosse I (1999) Melliand Textilberichte 6:532–535
15. Müller M, Grosse I, Sams Ph (1998) Tenside Surfactants Detery 35:354–359
16. Grosse I, Müller U (1981) Acta Polym 32:353
17. Parker JL (1994) Prog Surf Sci 47:254–259
18. Grosse I, Müller H-J (1998) Tenside Surfactants Detery 35:65–70
19. Gerenser LJ, Pochan JM (1985) Langmuir 1:305–312