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Surface tension isotherms, adsorption dynamics and dilational visco-elasticity of sodium dodecyl sulphate solutions

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ABSTRACT

The adsorption kinetics, adsorption isotherm and the dilational surface rheology at low oscillation frequencies of sodium dodecyl sulphate (SDS) were studied by drop and bubble profile, and bubble pressure tensiometry. The effect of the inevitably present dodecanol in any SDS solution is taken into account by interpreting the experimental data with theoretical models valid for mixed surfactant solutions. In particular the dilational rheology method appears to be very suitable for demonstrating the continuously on-going hydrolysis reaction in a SDS solution, as the resulting dilational elasticities and viscosities change from a frequency dependencies characteristic to SDS to those expected for dodecanol adsorption layers. For surfactants as active as dodecanol, it turns out that all adsorption and rheological quantities depend significantly on the use of drop or bubble profile tensiometry, i.e. the small reservoir of available surface active molecules in a single droplet has to be considered quantitatively to obtain reliable data.

1. Introduction

Among the ionic surfactants, the adsorption behaviour of sodium dodecyl sulphate, SDS, is the most extensively studied. This is due to important role of SDS (and also its mixtures with non-ionic surfactants, polymers and proteins) in a number of industrial and commercial applications. SDS and mixed systems are widely used in modern technologies. In particular, SDS is a surfactant used for the purpose of solubilization, dispersion, and stabilization of drugs.

There are hundreds of scientific papers in which the dynamic and equilibrium surface and interfacial tensions, adsorption and dilational rheology of SDS solutions are studied. Therefore, we can indicate here only the most important for the present study. The surface tension data obtained for SDS until 1965 were summarised and reviewed critically by Elworthy and Mysels [1]. In a recent book chapter [2] the equilibrium surface tensions of SDS solutions from different references [3–12] were generalised both in presence and absence of NaCl, and it was shown that these data can be represented in dependence on the average activity of ions [13] as a single curve. Some of recent publications [14,15] presented surface tension data of SDS solutions in good agreement with those presented in [2]. Direct measurements of SDS adsorption at the air/water surface were based on radiotracer techniques [9–12] or neutron reflection [16–18]. Also the dilational rheological characteristics of SDS solutions were studied in the frequency range between 1 and 500 Hz [14,19].

Similar to other synthetic surfactants, SDS contains surface active contaminants. In addition to more surface active homologues, the SDS samples also contain dodecanol. Caused by the synthesis or hydrolysis, *n*-dodecanol is the most frequent contaminant of SDS and the hardest to remove. This fact is of general importance as SDS represents the most frequently used model surfactant in colloid and interface science. The problems concerning the criteria of purity of SDS solutions were dealt with in a number of publications, reviewed briefly in [20]. The concept of 'surface chemical purity' was introduced by Lunkenheimer and Miller [21–24]; the purity criterion corresponds to the conditions when the contribution of the impurity component is negligible in the adsorbed layer. To achieve the quality of surface chemical purity, special techniques were proposed. The principle of a device proposed by Lunkenheimer et al. [20,25–27] consists in a repeated aspiration of the surface layer to remove the adsorbed contaminant. The surfactant solution is kept in a flat glass container of relatively large surface area. The container is maintained in this position until

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the solution has almost reached adsorption equilibrium. Then the adsorbed layer at the air/water interface is drastically compressed and aspirated. This cyclic process is repeated until the grade of surface chemical purity is reached. Usually 50–300 of such cycles are required. Other physicochemical methods were also proposed and used by many authors to remove dodecanol from the SDS solution. For example, in [28,29] foam fractionation was used, and in [15] the solutions were poured in the measuring vessel through several clean plastic pipettes, in order to remove the disturbing dodecanol.

The permanent interest in the characterization of the SDS/dodecanol system is due to the large effect of dodecanol traces on the surface properties of the main component SDS [30–32]. The use of well-defined and pure SDS samples is a precondition for the interpretation of model experiments [33–35]. Even though procedures and criteria for surfactant purification have been developed [25–29] there are controversial arguments in the evaluation of the purity of SDS samples. The dominant effect of dodecanol, even in trace amounts, on the co-adsorption of SDS/dodecanol mixtures from aqueous solutions has been corroborated [18,36,37]. The results presented by Vollhardt and Emrich [38] are based on comparative studies of pure and mixed surfactants by equilibrium surface pressure measurements, surface pressure transients and Brewster angle microscopy (BAM). Fundamental differences in the adsorption properties and phase behaviour of the main surfactant SDS and the contamination dodecanol have been obvious. Adsorbed layers of surface chemical pure SDS do not show a phase transition, even at bulk concentrations above the CMC and low temperatures, so that condensed phase domains cannot be formed. On the other hand, the adsorbed dodecanol monolayers can have a first-order LE-LC phase transition with a subsequent growth of condensed phase domains, as it has been evidenced in [39,40]. Due to the dominant influence of the dodecanol adsorption, co-adsorption of SDS/dodecanol mixtures from aqueous solution is mainly investigated for trace amounts of dodecanol [40]. Two limiting cases are of interest for such mixing ratios, namely where a phase transition occurs or cannot occur. In the case where a phase transition cannot occur and consequently the state of the adsorbed layer is fluid, both components (SDS and dodecanol) are adsorbed in comparable amounts. The presence of SDS in the adsorbed layer can remarkably decrease (about two time) the critical adsorption value of dodecanol where the LE-LC phase transition occurs [40]. While in adsorption layers of pure dodecanol the LE–LC phase transition at 20 °C occurs at a bulk concentration of about 4 μmol/l [41], the influence of SDS can decrease this concentration. Therefore, even the presence of traces of dodecanol in an SDS solution (say 0.05–0.1 mol %) could lead to a dodecanol adsorption exceeding the critical value characteristic for a phase transition at a SDS concentrations essentially lower than the critical micellisation concentration (CMC ≈ 8 mmol/l in aqueous solutions without electrolyte [1–12]).

However, even via the application of the adsorption–aspiration, foam fractionation or any other method it is unlikely to remove completely the dodecanol from SDS solution. This is caused by the hydrolysis of SDS in aqueous solution, which was studied in a number of publications [42–47]. In particular, it was shown that increase in both temperature and SDS concentration (especially above the CMC) increases the hydrolysis reaction rate. Complete hydrolysis usually occurs in about 12 h at 80 °C. Vollhardt has shown that the stability of SDS solutions depends on different conditions [47]. In particular the process of SDS hydrolysis is autocatalytic, and the catalysts of this process can be materials like glass, quartz or Al_2O_3. His experiments have shown impressively that the quality of SDS solution, i.e. the contents of dodecanol, can be stable at room temperature over 1 year, if it is kept in a hydrophobic vessel. These results are in line with our experiments: in a glass container the process of SDS hydrolysis is much faster than in a plastic container. In [48] further effects on the rate of hydrolysis were studied.

The present investigation addresses essentially the adsorption and rheological behaviour of SDS solutions at the water/air interface using the bubble and drop profile, ring and maximum bubble pressure tensiometry. It also shows effects caused by dodecanol as hydrolysis product and discusses how these effects can be considered in order to separate the properties of the main component SDS.

2. Experimental

The experiments were performed with ring (TE-1, Lauda, Germany) and bubble/drop profile analysis tensiometers (PAT-1 and PAT-2P, SINTERFACE Technologies, Germany), the principles of which were described in detail elsewhere [49,50]. The temperature of the measuring glass cell (volume $V = 20$ ml) was kept constant at 25 °C. In this study we used a buoyant bubble formed at a Teflon capillary with a tip diameter of 3 mm. We also used the pendant drop method in combination with the so-called coaxial double capillary [51]. The drop of the solution of a certain volume was formed at the capillary tip by supplying the solution through the external channel. As evaporation of solvent could result in a decrease of the drop volume during the experiment, the losses were compensated by supply of pure solvent through the inner channel of the coaxial capillary. Another technique applied was the maximum bubble pressure tensiometry (BPA-1S, SINTERFACE Technologies, Germany), described in [52–55]. To extend the accessible lifetime to values below 1 ms, steel capillaries of 0.25 mm in diameter coupled with a special bubble deflector have been used [53]. In this way, the method provides experimental data in the time range from 0.1 ms to 50 s, so that the time range between 5 and 50 s for the dynamic surface tensions was covered by two experimental techniques, PAT and BPA.

The substances studied were the sodium dodecyl sulphate, SDS, with a purity higher than 99% (SigmaUltra, Sigma–Aldrich), and used without further purification. The SDS used in some experiments was additionally purified by re-crystallisation from a solution in ethanol/benzene. This additional purification had almost no effect on the dynamic surface tension in the short time range 0.001–10000 s for SDS solutions $\leq$1 mmol/l. We did not make any purification of the SDS solutions using the adsorption [15], adsorption–aspiration [20] or foam [29] technique. This is because the present studies of the individual SDS solutions are, similarly to those reported in [56], prior to studies of the adsorption and rheological behaviour of SDS mixtures with non-ionic surfactants (Tritons and oxyethylated alcohols C_nEO_m). As the adsorption activity of these non-ionic surfactants (e.g., $C_{14}EO_8$ and Triton X-45) is comparable with that of the dodecanol [2,57], the adsorption purification process would result in the change of the concentrations of these surfactants in the solution bulk. All solutions were prepared with Milli-Q water, having a surface tension of 72.0 ± 0.2 mN/m at 25 °C over a time interval of up to 10^5 s. The SDS solutions were prepared in 0.01 M NaCl aqueous solution. The presence of this NaCl concentration in the SDS solutions partially diminishes the adsorption of dodecanol [15] due to a significant increase in the SDS adsorption activity and decrease of the CMC down to 4 mmol/l.

3. Theory

The experimental data for equilibrium surface tension and adsorption of SDS were processed using a Frumkin type model generalised to account for the so called internal compressibility, described in detail elsewhere [58,59]. In this model we assume that the molar area of an adsorbed surfactant molecule ω depends on surface pressure $\Pi = \gamma_0 - \gamma$ and surface coverage $\theta = \omega\Gamma$ according