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A disjoining pressure study of foam films stabilized by mixtures of a nonionic ($C_{12}DMPO$) and an ionic surfactant ($C_{12}TAB$)

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ABSTRACT

This work is a continuation of a previous study [*Langmuir* 23 (2007) 5315–5323] of aqueous foam films stabilized by surfactant mixtures consisting of a cationic and a nonionic surfactant. In both studies a *thin film pressure balance* was used to investigate the disjoining pressure Π as a function of the film thickness h. With the resulting Π–h curves the surface charge densities q_0 of the foam films were determined by fitting them with the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. Our previous study demonstrated that mixing the nonionic surfactant β-dodecylmaltoside (β-$C_{12}G_2$) and the cationic dodecyl trimethylammonium bromide ($C_{12}TAB$) allows one to tune q_0 and thus the type of foam film. In the present study the nonionic surfactant dodecyldimethyl phosphineoxide ($C_{12}DMPO$) instead of β-$C_{12}G_2$ was used and $C_{12}DMPO/C_{12}TAB$ mixtures in a concentration range from 0.1 to 2.0 cmc were studied at mixing ratios of $C_{12}DMPO:C_{12}TAB = 1:0, 50:1, 1:1, 1:50, 0:1$. The results are compared with those of the β-$C_{12}G_2/C_{12}TAB$ mixture and are discussed in terms of surface charge densities.

1. Introduction

In order to investigate the properties of dry foams, *i.e.* well drained foams, it is generally accepted as good practice to examine the corresponding foam films which can be regarded as the main building blocks of the foam [1–3]. In dry foams with foam film thicknesses of $h < 100$ nm the film's surfaces interact which, in turn, leads to the origin of the disjoining pressure Π. The disjoining pressure is the sum of long range repulsive electrostatic (Π_{elec}), attractive van der Waals (Π_{vdW}) and short range repulsive steric (Π_{sr}) forces [3–5]. *Common Black Films* (CBF) are stabilized by Π_{elec}, whilst *Newton Black Films* are stabilized by Π_{sr}. The formation of a CBF or an NBF can be controlled by the type of surfactant, the surfactant and/or electrolyte concentration, surface-active additives, and the pH (reviewed elsewhere) [2,6]. Previous investigations of Π–h curves reveal that the surface charge density q_0 of films stabilized by ionic surfactants increases with increasing surfactant concentration, while the opposite holds true for nonionic surfactants [6–9]. This observation automatically raises the question of how a surfactant mixture would behave. In order to fill this gap we studied foam films stabilized by surfactant mixture [10]. The current foam film study complements a recent work where a well-defined surfactant mixture was used, namely the cationic surfactant dodecyl trimethylammonium bromide ($C_{12}TAB$) and the nonionic surfactant *n*-dodecyl-β-D-maltoside (β-$C_{12}G_2$) [10].

Our previous study revealed that one can tune the surface charge density and thus the type of foam film by mixing $C_{12}TAB$ and β-$C_{12}G_2$. While this result could have been expected, another observation was rather surprising. At a mixing ratio of β-$C_{12}G_2:C_{12}TAB = 1:50$ an unexpected steep increase of the Π–h curve was measured, which was interpretated as an increase in q_0. To find out whether this is a special feature of this particular mixture or a general behaviour of nonionic/ionic surfactant mixtures an extensive study with a different nonionic surfactant, namely dodecyldimethyl phosphineoxide ($C_{12}DMPO$), but the same ionic surfactant was performed. Thus the present study forms part of a systematic approach of examining foam films stabilized by nonionic/cationic surfactant mixtures. Both mixtures may appear similar but are structurally quite different due to the head group size of the nonionic surfactant. In the case of β-$C_{12}G_2$ the head group is composed of a maltoside unit which behaves like a hard disc [11] and which is considerably larger in size compared to both $C_{12}DMPO$ and $C_{12}TAB$. This may have a significant influence on the Π–h curves of the two different nonionic/cationic surfactant mixtures. As speculative it may be the much larger head group of β-$C_{12}G_2$ compared to $C_{12}TAB$ may be one reason for the steep increase of q_0 at a mixing ratio of β-$C_{12}G_2:C_{12}TAB = 1:50$ – the increase could be explained if β-$C_{12}G_2$ was displaced/squeezed from the water–air interface during the approach of the two interfaces and replaced by $C_{12}TAB$. To address this point we exchanged

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β-$C_{12}G_2$ by C_{12}DMPO, which has a similar head group size as C_{12}TAB. We have chosen the same experimental approach as before and studied C_{12}DMPO/C_{12}TAB mixtures at different concentrations (c = 0.1–2.0 cmc) and mixing ratios (C_{12}DMPO:C_{12}TAB = 1:0, 50:1, 1:1, 1:50 and 0:1).

Phosphineoxide surfactants are ideal candidates for fundamental research as they are pH- and temperature stable and as they can easily be synthesized and purified [12–14]. There is considerable knowledge regarding the surface and bulk properties of C_{12}DMPO with extensive surface tension [14–21] and surface rheology [22–29] studies in the past. Moreover, studies of adsorption layers and foam films of C_{12}DMPO/protein mixtures were performed [30,31]. However, to our knowledge there exists no study on the properties of foam films or foams stabilized by C_{12}DMPO. Dodecyl trimethylammonium bromide (C_{12}TAB) is also seen as a good candidate for a fundamental study as it is cheap and can be easily purified. Furthermore, there exists a vast amount of work on the adsorption of C_{12}TAB at the water–air interface, namely studies of dynamic [32–35] and static [10,36–40] surface tensions, surface elasticity [34,41,42], foam films [10,38,39] and foams [39,43].

In this study a hydrophobic chain length of C_{12} was chosen to allow for optimum solubility of both the nonionic and the ionic surfactant. An extensive study was carried out on the adsorption of C_{12}DMPO/C_{12}TAB mixtures at the water–air interface by measuring static surface tensions. From the experimental data the critical micellar concentration (cmc), adsorption properties at the water–air interface, and finally both the micellar and the surface composition were determined. The regular solution theory was employed to calculate the interaction parameters and the mole fractions of the individual surfactants in the mixed water–air monolayer as well as in the mixed micelles. Our previous study demonstrated that it is possible to tune the surface charge density of aqueous foam films by mixtures of nonionic and cationic surfactants. Here we have used another nonionic surfactant of equal hydrophobic chain length and have extended the concentration range and the mixing ratios. The current work deals with mixtures over a concentration range from c = 0.1 to 2.0 cmc at mixing ratios of C_{12}DMPO:C_{12}TAB = 1:0, 50:1, 1:1, 1:50 and 0:1.

2. Materials and methods

2.1. Materials

The nonionic surfactant dodecyldimethyl phosphineoxide (C_{12}DMPO) was synthesised and purified as described elsewhere [14]. The cationic dodecyl trimethylammonium bromide (C_{12}TAB) (purity > 98% AT) was purchased from *Fluka* and purified by recrystallizing it three times with pure acetone to which traces of ethanol were added. Acetone (p.a.) and ethanol (p.a.) were purchased from *Aldrich*. Sodium chloride (NaCl) was obtained from *Merck* and roasted at 500 °C over night to drive off organic contaminants. The solutions were prepared with Milli-Q® water. All glassware (except the film holders) was cleaned with *deconex*® UNIVERSAL 11 from *Borer Chemie* and rinsed thoroughly with water before use. Film holders were cleaned with hot distilled water, boiled in hot hydrochloric acid (HCl), again heated in hot distilled water, and then heated at 450–500 °C for 2 h, allowed to cool and eventually, at least 0.5 l of hot Milli-Q® water was sucked through each disc. This process was seen as an ideal cleaning procedure for cationic surfactant contaminated film holders.

2.2. Surface tension measurements

The surface tension isotherms were measured by the Du Noüy ring method, using a Sinterface STA-1 tensiometer. For each surfactant (or surfactant mixture) a 200 ml flask of a stock solution at a concentration above the cmc was prepared. Each time 20 ml solution for washing the glassware and 20 ml solution for a measurement was used. After each measurement the flask was filled up with Milli-Q® water, the platinum ring was washed with water and annealed. The diluted solution was used for the next measurement.

Measuring the surface tension σ as a function of the total surfactant concentration c for a binary surfactant mixture enables the calculation of the total adsorbed amount of the mixture (Γ_{total}) at the surface. Measuring the surface tension as a function of the concentration of surfactant 2 keeping the concentration of surfactant 1 constant allows us to calculate the adsorbed amount of surfactant 2 at the surface (see Fig. 1 (right)). Hence the amount of surfactant 1 adsorbed at the surface can simply be calculated by subtracting the amount of surfactant 2 adsorbed at the surface from the total adsorbed amount of the mixture (Γ_{total}). This approach has been used in previous studies to determine the surface composition for two different binary surfactant mixtures (see Refs. [10,40] for further details).

In addition we plotted the experimentally determined cmc values versus the composition and compared these data with those calculated theoretically (see Fig. S1 in the Supporting material section). The comparison reveals that the interactions between the two surfactants are negligible or at least very weak. In order to confirm that these interactions are indeed negligible we used the regular solution theory, which simultaneously allows for an independent determination of the micelle and surface composition (see Table S1 in the Supporting material section).

2.3. Thin film pressure balance

A Π–h curve for a thin free-standing foam film can be measured with a *Thin Film Pressure Balance* (TFPB). The Π–h curve is obtained by subjecting a free-standing horizontal liquid foam film to a defined gas pressure and measuring its equilibrium thickness h interferometrically. This method is a unique technique to measure interaction forces, thickness (5–100 nm), drainage and stability of thin foam films. Experimental details have been published elsewhere [44]. Briefly, foam films are formed in a special film holder, which is placed in a gastight measuring cell in such a way that the film is exposed to the gas pressure P_g and the free end of the glass tube to the reference pressure P_r. The pressure difference $\Delta P = P_g - P_r$ can be adjusted via two syringes and measured by a high sensitive difference pressure transducer. The Π–h curves are generated by interferometrically measuring the equivalent film thickness h_{eq} after applying a fixed pressure in the cell. The "true film thickness" h can be obtained according to the three-layer model where the film is considered as a water core of refractive index n_s surrounded by two surfactant layers of different refractive index (see Ref. [44] for details). Before measuring the Π–h curves the film holder was kept in the surfactant solution overnight in order to establish equilibrium. To make sure that the film holder did not pollute the solution the surface tension of the solution was measured over a period of 2 h before each experiment. Prior to the measurements the lid of the cell was treated with a commercial anti-fogging agent (Antibeschlag-Intensio from *Silbo*). The cell was filled with excess solution, and the experimental set-up was assembled and left for at least 3 h to ensure vapour-liquid equilibrium. All Π–h curves were reproduced at least once. All measurements were carried out at room temperature.

The measured Π–h curves were compared with the interaction curves calculated within the framework of the DLVO theory in order to determine the surface charge densities q_0. The van der Waals component of the disjoining pressure was calculated with the Hamaker constant ($A = 3.7 \times 10^{-20}$ J) for the air/water/air system [4].