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Drainage of foam films stabilized with mixtures of non-ionic surfactants

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Abstract

The drainage of single foam films stabilized with a mixture of the non-ionic surfactants *n*-dodecyl-β-D-maltoside (β-$C_{12}G_2$) and hexaethyleneglycol monododecyl ether ($C_{12}E_6$) was studied at two different mixing ratios (β-$C_{12}G_2$:$C_{12}E_6$ = 1:1 and 50:1) as a function of the electrolyte and the total surfactant concentration, respectively. The electrolyte concentration was varied from 10^{-3} to 10^{-1} M NaCl and the total surfactant concentration ranged from 0.01 to 10 CMC. Moreover, the influence which the film radius has on the drainage of the foam films was investigated. From the *h* (film thickness) *versus t* (time) dependence the values of the drainage coefficients (α) were determined for all films according to the equation derived by Manev et al. [E. Manev, R. Tsekov, B. Radoev, J. Disper. Sci. Tech. 18 (1997) 769]. It was found that the drainage of these foam films is generally in line with the theory. First, at concentrations below the CMC the value of α decreases with an increase in the total surfactant concentration and levels off at $C_{\mathrm{surf}} \sim$ CMC in all cases except one. Second, increasing the ionic strength increases the rate of drainage at $C_{\mathrm{surf}} <$ CMC, while it does not significantly affect α at $C_{\mathrm{surf}} =$ CMC of the respective solution. Last but not least, films of smaller radius drain faster regardless of their composition. However, the results obtained for the 1:1 and the 50:1 mixture differ quantitatively. These differences are discussed and some of the results are compared with those obtained for the pure surfactants.

Keywords: Foam films; Drainage; *n*-Dodecyl-β-D-maltoside; Hexaethyleneglycol monododecyl ether; Surfactant mixtures

1. Introduction

The properties of thin liquid foam films are of great importance to colloidal science as well as to technological applications. Research has always focused on the effects surfactants have on the properties of these films, like their hydrodynamics and stability. A good introduction to this subject can be found in the comprehensive works of Mysels et al. [1], Scheludko [2], Ivanov [3], and Exerowa and Kruglyakov [4], to name just a few. The presence of a surfactant is the necessary condition for the formation of stable foam. Surfactant adsorption at the water–air surface provides the films with the ability to resist the local thinning during the process of drainage. It is well known that the nature of the surfactant (ionic or non-ionic) as well as its molecular structure strongly affect the properties of the films (reviewed in [5,6]). However, there are only few studies about the properties of films stabilized by surfactant mixtures although nearly all stabilizers for colloidal systems are surfactant mixtures because of their superior surface properties as compared to single surfactants. To our knowledge, the only foam film studies with surfactant mixtures are those in which technical grade surfactants were used [7–9]. Studies with well-defined surfactant mixtures, however, have not been carried out yet.[1]

The present study is part of a more complex project[2] dealing with mixtures of the two non-ionic surfactants *n*-dodecyl-β-D-maltoside (β-$C_{12}G_2$) and hexaethyleneglycol-monododecyl-ether ($C_{12}E_6$). The reason for studying mixtures of ethylene oxide (C_iE_j) and sugar (C_nG_m)-based surfactants is

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[1] For the sake of completeness it has to be mentioned that studies with well-defined mixtures of surfactant + alcohol do exist [10b–13]. Contrary to our work, in these studies the alcohol is an additive rather than a second surfactant.

[2] In this comprehensive European project, funded by the European Commission, interaction forces, adsorption properties, surface rheology, and bulk properties of these mixtures are investigated.

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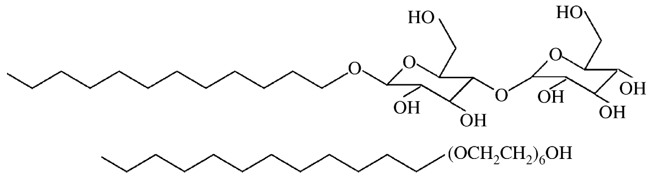

Fig. 1. Molecular structures of the surfactants *n*-dodecyl-β-D-maltoside (β-$C_{12}G_2$) and hexaethyleneglycol monododecyl ether ($C_{12}E_6$).

that these surfactants behave quite differently in spite of both being non-ionic (see Fig. 1).

To illustrate how differently they behave five examples will be given. The first example of how different their properties can be is the adsorption of $C_{12}E_6$ and β-$C_{12}G_2$, respectively, on hydrophilic silica. At first sight, one would not expect a big difference as both surfactants are uncharged, *i.e.*, that the interactions between the silica surface and the non-ionic surfactants cannot differ very much. In fact, quite the opposite was observed. While $C_{12}E_6$ adsorbs strongly on silica, β-$C_{12}G_2$ does not adsorb at all. This is surprising and still not understood [14,15]. A second prominent difference lies in their temperature-sensitivity: while the physico-chemical properties of aqueous solutions of sugar surfactants are not very temperature-sensitive, those of the corresponding ethylene oxide solutions are. The temperature-insensitivity of sugar surfactants in aqueous solution results from the strength of the hydrogen bonds between the hydroxyl groups of the sugar unit and water, which prevents any significant dehydration of the head group in the experimentally relevant temperature range. In contrast to the strong hydrogen bonds between water and sugar units, the hydration water of the corresponding ethylene oxide units is attached only via weak dipole–dipole interactions, which leads to an easy dehydration of the head group (see for example [16] where the temperature-sensitivity of microemulsions formulated with these different surfactants is discussed). Thirdly, it is not only the strength of hydration but also the hydration number that is completely different. It was found that under similar conditions and for similar head group sizes (a glucose unit is comparable to four ethylene oxide units) the hydration of ethylene oxide-based surfactants is one order of magnitude higher than that of sugar-based surfactants [17]. Fourthly, the flexibility of the head groups is different. While a maltoside unit behaves like a hard disc, the ethylene oxide units behave more like short polymer chains, which, in turn, means that they are much more flexible [18]. Last but not least, the surface charge density q_0 of foam films stabilized by sugar surfactants is pH insensitive down to the so-called isoelectric point, while that of ethylene oxide-based surfactants changes linearly with the pH. It is argued in [19] that this difference is a consequence of the fact that an ethylene oxide unit is able to “react” to pH-changes by changing either its hydration degree (easy uptake and release of water) or its conformation (high flexibility). As both processes are very unlikely in the case of a sugar unit, the uptake of OH^- ions is given by the total surfactant concentration rather than by the pH, which results in the observed pH insensitivity.

The mentioned differences automatically lead to the question of how mixtures of C_iE_j and C_nG_m surfactants would behave. The final goal is to tune the behaviour of the system by mixing surfactants and thus making use of their different behaviour. The following general questions need to be answered: (1) Which properties do a 1:1 mixture have? Is it the ethylene oxide or the sugar-based surfactant that dominates the behaviour? (2) How do small traces of the second surfactant (C_iE_j traces in C_nG_m or vice versa) influence the overall properties? In the study at hand we approach these questions by studying the drainage of foam films stabilized by two different mixtures of β-$C_{12}G_2$ and $C_{12}E_6$. The ratios studied are β-$C_{12}G_2$:$C_{12}E_6$ = 1:1 and 50:1. The drainage of foam films stabilized by these mixtures was studied as a function of the electrolyte (10^{-3} to 10^{-1} M NaCl) and the total surfactant (0.01–10 CMC) concentration, respectively. Moreover, the influence which the film radius has on the drainage of the foam films was investigated. From the *h* (film thickness) *versus t* (time) dependence, the values of the drainage coefficients (α) were determined for all films according to the equation derived by Manev et al. [20]. These data were used not only to describe the effect of the film size and the surfactant composition on the hydrodynamic characteristics of the films but also to compare the results with theoretical predictions.

2. Theoretical background

2.1. Film drainage

The properties of foam films are determined by the properties of the adsorption layers, which, in turn, depend on various parameters, such as the surfactant type, molecular structure and concentration, and the electrolyte concentration. The surfactant adsorption provides the films with the ability to resist local deformations and thus to prevent film rupturing e.g., in the process of drainage. This ability is believed to be correlated with the surface elasticity of the monolayer [21] (reviewed in [6,22]). However, the exact relationship between them is still unclear and certainly there is no direct proportionality. The drainage in the presence of surfactants at the film surfaces may be substantially reduced by an opposing gradient of the surface tension, the so-called ‘dynamic elasticity’ or ‘Marangoni effect’ [23]. Drainage behaviour of thin liquid films – primarily of foam films – has been reviewed only recently by Manev and Nguyen [24,25]. In the following, we will focus on the aspects of the film drainage which we consider significant for the present investigation. Briefly, the microscopic horizontal foam films are considered to be of cylindrical shape. They comprise radii in the range of tenths of a millimeter, while their thickness is always much smaller (micrometer range at the moment of film formation and nanometer range at the end of the drainage process). For the velocity of drainage of a free, microscopic horizontal liquid film Scheludko [2] has proposed an equation analogous to that describing the outflow of liquid from a gap between two parallel solid discs of equal radii (the “Reynolds Law”). It holds

$$V_{Re} = -\frac{dh}{dt} = \frac{2h^3}{3\mu r^2}\Delta P, \tag{1}$$

where $\Delta P = P_\sigma - \Pi$ is the driving pressure of drainage with P_σ being the capillary and Π the disjoining pressure, *h* is the film