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The dependence of the interactions in foam films on surfactant concentration

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Abstract

The interaction free energy in foam films is investigated depending on surfactant concentration, to prove the differences between the adsorption density of the stabilizing surfactant at the film surfaces and the surface of the bulk phase of the film forming solution. A change of the adsorption density at the film surface compared to the surface of the bulk phase has been indicated by earlier measurements of the gas permeation through foam films. The film interaction free energy was determined from measurements of the contact angles between free foam films and the surrounding bulk phase meniscus. Also, the disjoining pressure isotherms of foam films were measured and used to estimate the film interaction free energy. The foam films were stabilized with the anionic surfactant sodium dodecyl sulphate (SDS). At the surface of Newton black films, the adsorption density is higher than at a normal surface. The disjoining pressure isotherms measured at constant salt concentration but at different surfactant concentrations, reflect the influence of the surfactant concentration on the total electrolyte concentration. The disjoining pressure is always larger than that predicted from the Derjaguin–Landau–Verwey–Overbeek theory (DLVO theory). The investigation of common black films gives some indication that the adsorption density at the common black film surfaces is smaller than at the normal solution surface. Deviations of the measured interaction free energy from the values expected from the DLVO theory found in our measurements as well as reported in the literature can be explained by this change of adsorption.

Keywords: Foam films; Film interaction free energy; DLVO theory; Disjoining pressure; Contact angle; Adsorption density

1. Introduction

Foam films are a well-investigated model system for the study of the interactions between interfaces [1]. They consist of a thin aqueous layer covered by monolayers of adsorbed surfactant molecules, which stabilize the film (see Fig. 1a and b). The thickness (h) of the film results from the equilibrium between external forces and the interactions between the film surfaces, which cause an additional pressure in the film, known as the disjoining pressure Π. In many cases, the interactions in the film can be described by two forces, the repulsion of electrical double layers at the film surfaces and the van der Waals forces of attraction (Derjaguin–Landau–Verwey–Overbeek theory, DLVO) [2]. In presence of double layer repulsion, the equilibrium thickness of the films decreases from several hundredths of nanometres to a few nanometres with increasing electrolyte concentration. Generally, films with a thickness below 50 nm appear grey or black on observation in reflected light and are called common black films (CBF, see Fig. 1a). If the external pressure on the film is varied at constant temperature, surfactant-concentration and salt-concentration, the so-called disjoining pressure isotherm ($\Pi = f(h)$) can be measured. At very high salt concentration (in the order of 10^{-1} mol/dm^3 of 1:1 electrolyte) the electrical double layers are totally screened, and the van der Waals attraction is the only long-range interaction between the film interfaces. Under these conditions, the film thins until the steric repulsion of the two surfactant adsorption layers become active at film thicknesses of around 3–6 nm, depending on the dimensions of the surfactant molecules (see Fig. 1b). These equilibrium films are called Newton black films (NBF). The surface tension of the surfaces of a NBF is smaller than the surface tension of the liquid bulk phase surrounding the film. Therefore, a contact angle θ is formed between the film surfaces and the surfaces

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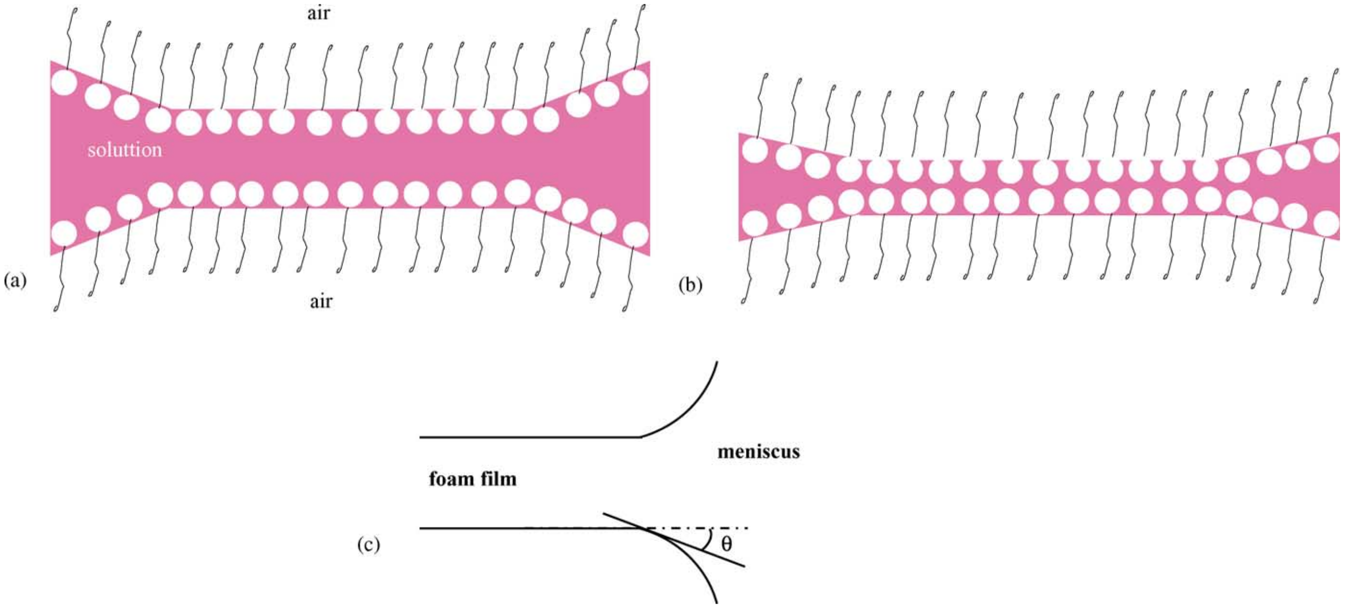

Fig. 1. Schematic cross-section of (a) a common black film (CBF), (b) a Newton black film (NBF) and (c) view of the contact angle between film and meniscus.

of the surrounding liquid meniscus (see Fig. 1b) to establish mechanical equilibrium. In the case of adsorption of a surfactant at a liquid surface it cannot be presupposed that the adsorption remains constant on formation of the film, due to the thermodynamic equilibrium of the film with the bulk phases. Nevertheless, in the earlier works [3,4] constant adsorption has been assumed or presupposed without discussion. The results of measurements of the permeation of gas through foam films indicate that the adsorption density of the stabilizing surfactant depends on the film thickness as well as on the strength and sign of the interfacial interaction in the film [5,6]. Deviations of the measured disjoining pressure isotherms or the measured film interaction free energy from the values expected from the DLVO theory have been observed in some cases [7–9]. Measurements of the disjoining pressure of foam films prepared from solutions of the anionic surfactant sodium dodecyle sulphate [7] and with a non-ionic sugar surfactant [8] deliver higher values than that predicted by the DLVO theory. On the other hand, the film interaction free energy of NBF stabilized with sodium dodecyl sulphate is more negative than expected from the DLVO theory [9]. Until now, these deviations have not been discussed from a common point of view. Such deviations may be a consequence of a change of the adsorption density of the surfactant with film thickness. A variation of the adsorption with film thickness will contribute to a change of the total free energy on formation of a thin film, as well as to a change in the disjoining pressure. It can be assumed that the observed deviations from the DLVO behavior in foam films stabilized by surfactants are related to such variations of the adsorption density in the film.

The aim of this work is to check the adsorption density on transition from a normal surface to a surface of a film, and to prove the hypothesis that the above mentioned discrepancies between experiment and DLVO theory can be explained by changes of adsorption density. Therefore, the film interaction free energy was determined by measurements of the contact angle between the NBF and the surrounding liquid meniscus on variation of the surfactant (SDS) concentration. Besides, the disjoining pressure isotherms of films stabilized by the same surfactant were measured by differing surfactant concentration. The salt (NaCl) concentration in the disjoining pressure experiments was 5×10^{-4} mol/dm^3. This results in a strong double layer repulsion and produces films with a thickness from around 10–30 nm, depending on the external pressure.

It has been shown by Ash et al. [10], Hall [11], and de Feijter and Vrij [12] that the measurement of the disjoining pressure or the interaction free energy depending upon surfactant concentration, can deliver information about the possible variation of the adsorption density of the surfactant on the formation of a film.

In this study, changes in the adsorption density on film formation are investigated, and also its relation to the observed discrepancies between experimental results on foam film interactions and the DLVO predictions is discussed.

2. Experimental

2.1. Materials

The sodium dodecyl sulphate (SDS) used for the preparation of the solutions for film formation has been prepared and purified with special care to remove traces of highly surface active contaminations by Dr. G. Czickocki (MPIKG). The