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Journal of Colloid and Interface Science 312 (2007) 47–51
Journal of Colloid and Interface Science
www.elsevier.com/locate/jcis

Electrostatic effects in films stabilised by non-ionic surfactants

César Márquez-Beltrán [1], Dominique Langevin *

Laboratoire de Physique des Solides, Bâtiment 510, Université Paris-Sud, 91405 Orsay cedex, France

Received 24 July 2006; accepted 2 October 2006

Abstract

The disjoining pressure Π of films of aqueous octyl-β-glucoside (β-C_8G_1) solutions with and without salt was measured as a function of the film thickness by means of a thin film pressure balance. The analysis of the experiments confirms the presence of an electrostatic double layer which dominates the long-range interactions as found in previous experiments with other non-ionic surfactants in the presence of added salt. In the absence of salt, we find a local ion concentration much higher than that of the residual ionic impurities present in the bulk solution.

Keywords: Thin liquid films; Disjoining pressure; Non-ionic surfactants

1. Introduction

The research on foams is presently very active, as their properties are of both technical and fundamental interest [1]. So far there is no satisfactory theory explaining their stability. Liquid foams are dispersions of gas bubbles into a continuous liquid phase. When the amount of liquid is small (less than about 30%), the bubbles are distorted into polyhedra separated by thin liquid films stabilised by surface active species. Foam lifetime is related to film rupture and/or to inter-bubble gas diffusion across the films. The fundamental understanding of foam stability therefore relies on the detailed knowledge of the films between bubbles.

The film rupture process begins by liquid drainage out the film. At very small thicknesses, molecular interactions, frequently electrostatic, create repulsive forces between film surfaces and slow down or completely arrest drainage. The classical description of electrostatic interactions is based in the Poisson–Boltzmann equation (PB) [2–4]. Attractive forces are also present (i.e., van der Waals forces), they accelerate drainage and cause film rupture. The DLVO theory uses both interactions (electrostatic and van der Waals), and is helpful to explain the stability of colloidal systems [5–7]. Let us mention that the DLVO theory has some limitations, since features not taken into account include correlations between ions (important for multivalent ions), finite size of the ions and discrete nature of surface charges (playing important roles at small distances between surfaces). The DLVO theory has been used to model experimental data for the forces between surfaces of films stabilised by ionic surfactants, in a thickness range $h > 10$ nm (common black films). Thinner films (Newton black films) are stabilised by short-range steric repulsive interactions, not taken into account in the DLVO theory. Confinement of micelles or macromolecules lead to stratification phenomena and to additional oscillatory forces [8,9]. Film stability ultimately depends on the properties of the surface active species adsorbed at film surfaces.

Electrostatic forces are surprisingly present in some cases in liquid films stabilised by non-ionic surfactants. This has been attributed to the existence of negative surface charges due to OH^- ions adsorbed at the surface [10,11]. Similar negative surface charges were inferred from measurements of the zeta potential at the water/air [12,13] and the water/oil [14,15] interfaces, even in the absence of any surfactant.

The thin films measurements reported in the literature were all performed in the presence of added salt, with concentrations higher than those of the residual ionic impurities, in order to have reliable values of the Debye length. We present here measurements of the disjoining pressure (force per unit area) of thin

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* Corresponding author.
E-mail address: langevin@lps.u-psud.fr (D. Langevin).

[1] Present address: Institut Français du Pétrole, 92502 Rueil Malmaison, France.

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doi:10.1016/j.jcis.2006.10.015

films stabilised by non-ionic surfactants in the absence of salt, where electrostatic forces were also found. For this purpose, we have used the "thin film balance" method, complemented by electrical conductivity measurements. We will discuss the possible origin of the residual bulk charges.

2. Theoretical background

In the DLVO theory, the disjoining pressure is the sum of electrostatic repulsive and van der Waals attractive force contributions. In the case of the electrostatic contribution (Π_{el}) many numerical solutions have been developed. Analytical solutions can be obtained for weak surface potentials ($e\phi_0 < kT$). For a 1:1 electrolyte between identical, charged, plane–parallel interfaces, the disjoining pressure as function of film thickness h for constant surface potential and for constant surface charge are given respectively by

$$\Pi_{\text{el}} = \frac{\varepsilon\varphi_0^2}{8\pi}\left(\sec h^2(\kappa h)\right) \tag{1}$$

and

$$\Pi_{\text{el}} = \frac{2\pi\sigma_0^2}{\varepsilon}\left[\frac{1+\sec h((\kappa h)/2)}{\tanh((\kappa h)/2)}\right], \tag{2}$$

where σ_0 and φ_0 are the surface charge and the surface potential respectively, ε is the dielectric constant of the solution and κ is the Debye length:

$$\kappa^{-1} = \sqrt{\frac{\varepsilon\varepsilon_0 kT}{2e^2C}}, \tag{3}$$

where ε_0 is the dielectric constant of the vacuum, k the Boltzmann constant, T the absolute temperature, e the electron charge and C the ions concentration. Expressions for higher surface potentials can be obtained in the case of big separation between the surfaces ($\kappa h > 1$). For constant surface potential:

$$\Pi_{\text{el}} = 64CkT\tanh^2\left(\frac{e\varphi_0}{4kT}\right)\exp(-\kappa h). \tag{4}$$

The surface charge is then given by the Grahame equation:

$$\sigma = \sqrt{8\varepsilon\varepsilon_0 CkT}\sinh\left(\frac{e\varphi_0}{2kT}\right). \tag{5}$$

The attractive van der Waals force is given by

$$\Pi_{\text{vdw}} = -\frac{A_{\text{H}}}{6\pi h^3}, \tag{6}$$

where A_{H} is the Hamaker constant, which for air/water/air films is about 3.7×10^{-20} J.

3. Experimental

3.1. Materials

Octyl-β-glucoside, C_8G_1 (n-octyl-β-glucopyranoside), was obtained from Sigma (purity >98%) and used as supplied (Fig. 1). Sodium chloride was also purchased from Sigma (purity >99.5%) and used as supplied. All the solutions were prepared with Milli-Q water. The experiments were made at room temperature, 22 ± 1 °C.

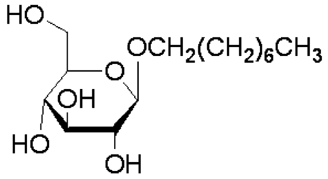

Fig. 1. β-C_8G_1 formula (source: http://www.sigmaaldrich.com/catalog/search/ProductDetail/SIAL/O8001).

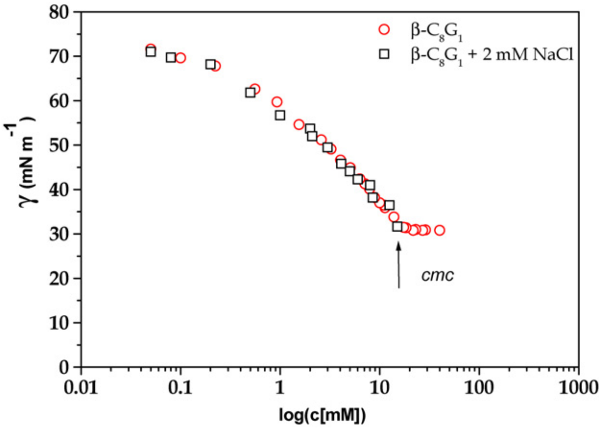

Fig. 2. Surface tension versus surfactant concentration for β-C_8G_1 solutions with and without NaCl.

In order to check for the presence of possible surface active impurities coming from surfactant and/or salt batches, the surface tension was measured with the Wilhelmy method as a function of surfactant concentration. As can be seen in Fig. 2, no minimum is observed around the critical micellar concentration (cmc), confirming the absence of surface active impurities. Indeed, if such impurities were present, they would start to incorporate into the micelles and leave the interface, leading to a surface tension increase in the cmc region. Note that the surface tension is not affected by the addition of 2 mM NaCl, confirming the well know absence of influence of ionic strength on the surfactant monolayer at the surface of the solution. This result also shows that added salt does not introduce additional surface impurities. The results are also in agreement with those of Bergeron et al. on the same surfactant [16].

3.2. Methods

3.2.1. Conductivity

Conductivity measurements have been performed with a Cyberscan Con 100 meter. The volume of the samples was about 50 cm^3.

3.2.2. Thin film balance

Disjoining pressures were measured with a modified version of the porous-plate technique (Fig. 3). This setup is fully described elsewhere [17–19]: single thin-liquid foam films are