



Elasticity of foam bubbles measured by profile analysis tensiometry

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ABSTRACT

Elastic modulus of foam bubbles, stabilized with tetraethylene glycol octyl ether (C₈E₄) and 1 × 10⁻⁵ M NaCl, was determined by cyclic expansion and shrinking of foam bubbles with frequency of 0.1 Hz and volumetric amplitude of 2 mm³. The film tension was monitored by a commercial profile analysis tensiometer (Sinterface Technologies, GmbH). The elastic moduli of foam bubbles were obtained as a function of surfactant concentration in the range of 2 × 10⁻³–1 × 10⁻² M. The theory of Lucassen and van den Tempel [1] for the elastic modulus of a single liquid/air interface at a given frequency was employed. In the theoretical analysis the bulk diffusion coefficient of surfactant molecules was considered as a unknown model parameter which was obtained by matching the theory with the experimental data. Hence, the dependence of the bulk diffusion coefficient of C₈E₄ molecules upon the C₈E₄ concentration was obtained. The diffusion coefficient reached a maximum at 5 × 10⁻³ M C₈E₄ (D = 8.5 × 10⁻¹¹ m²/s). In the experimental surfactant concentration range (2 × 10⁻³–1 × 10⁻² M, CMC = 7.5 × 10⁻³ M) the foam bubbles were relatively dry, with visible interferometric fringes corresponding to thin films stabilized by repulsion of the electrostatic disjoining pressure. Hence, the overall dynamics of periodical expansion and shrinking of the foam bubbles occurred within the thin film state.

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1. Background

The Gibbs elasticity of thin liquid films (TLF) has been defined by Gibbs in 1876 in his famous work “On the equilibrium of the heterogeneous substances” [2]:

$$E_G = \frac{2d\sigma}{d \ln A} \quad (1)$$

where σ is the surface tension of each film surface with area A of the film. He assumed that the solution in the foam lamella becomes depleted of surfactant as a result of the adsorption on the surfaces, and hence the surface tension increases with the expansion of the lamella (film). The film volume and the total number of surfactant molecules were assumed constant during the film expansion. The first experimental determination of the elastic moduli of foam films was conducted by Mysels et al. [3,4] in rectangular vertical frames, adopted later by Prins et al. [5,6] as well. The method consists of measuring the increased tension of a foam lamella stretched it to a measured extent, with concurrently determining the local film thickness of the lamella from the interference pattern. These first attempts to determine the elastic moduli were critically evaluated in the literature [3,7,8]. The arguments [3] were focused on the

dynamic nature of the film elasticity showing that the film dynamics effects should last for milliseconds, while the time-scale of the stretching was of the order of seconds, and this was accompanied by increased values of the film tension. Hence, a different limiting factor – presumably the depletion of surfactant in the intra-lamellar liquid – had to be critical the film [3]. According to Kitchener [8] the latter effect corresponded to the exact definition of the Gibbs elasticity as defined in [2]. This should be valid for thin films in which the electrostatic disjoining pressure was significant, but in many cases the thickness of the foam lamella was of the order of microns, for which the electrostatic disjoining pressure was negligibly weak. The methodology of Mysels et al. [3,4] was limited to relatively stable foam lamellae with high level of surfactant adsorption in the surface layers. In addition, the expanding of the film surfaces was related only to dilatational (not shear) visco-elasticity. The surface shear viscosity of insoluble surfactant monolayers was studied earlier in a series of work [9–11]. In order to study the surface elastic moduli at lower adsorption levels Lucassen and van den Tempel employed the theory of capillary waves on visco-elastic surface adsorption layers [12,13] and introduced a new methodology [1,14], operating with longitudinal surface waves and stress relaxation. The elastic modulus was regarded as a complex value, however the surface viscosity was not considered. The elasticities of the monolayers in Langmuir through [15,16] have been measured directly by determining the changes in surface tension caused by small amplitude sinusoidal compression/expansion cycles. This

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approach was first applied to insoluble protein monolayers [14] and later to slightly soluble surfactants [17]. The authors derived the following expression for the elastic modulus of the surface monolayer:

$$\varepsilon = \frac{\varepsilon_0}{\sqrt{1 + 2\sqrt{\omega_0/\omega} + 2\omega_0/\omega}} \quad (2)$$

where $\varepsilon_0 = -d\sigma/d\ln\Gamma$, σ is the surface tension and Γ is the surfactant molar surface concentration, ω is the cyclic frequency of compression/expansion, while ω_0 is called the adsorption frequency of the surfactant and is expressed by:

$$\omega_0 = \frac{D}{2(d\Gamma/dc)^2} \quad (3)$$

In Eq. (3) D is the bulk diffusion coefficient, while $d\Gamma/dc$ is the so-called adsorption length. It can be determined from the surfactant surface tension isotherm, processed with an appropriate adsorption model (e.g. the Szyskowski–Langmuir model). Eq. (2) shows that the compression and expansion of the surface layer compete with adsorption and desorption of the surfactant molecules. Hence, the elastic modulus depends on the frequency of the compression and expansion. Loglio et al. [18] used the approach of Lucassen and van den Tempel [1] and determined the visco-elastic modulus as a complex value consisting of the real (elastic) and imaginary (loss) components. In addition, they introduced the Fourier transform operator for relating the time domain behavior of $\varepsilon(\sigma, A)$ to the frequency domain $\varepsilon(\omega)$. They advanced later their theory [19–21] by devising a computational procedure allowing accurate evaluation of the spectra of the visco-elastic modulus from the observed transient surface tension decay. The numerical simulations [19,20] showed a maximum of the loss modulus at a given frequency, while the elastic modulus reached a plateau but unfortunately this numerical procedure was very complicated. The methodology of Lucassen and van den Tempel was adopted in the literature as a successful tool to study the elasticity of surfactant monolayers and their adsorption–desorption kinetics [22–41]. Meanwhile, new ways for determining the visco-elastic modulus were sought and developed [42–44]. For example, Hard and Lofgren [42] exploited laser light scattering techniques to determine the surface elastic modulus and surface viscosity. Hühnerfuss et al. [43] developed further an experimental approach for measuring the surface potential variations over propagating water waves covered with monolayers. Vogel and Mobius [44] determined the surface dilatational elasticity by a resonance of longitudinal and transverse surface waves.

Hajiloo and Slattery [45] used the approach of Lucassen and van den Tempel [1,46] and performed a first order perturbation analysis for longitudinal and transverse waves between air and aqueous surfactant solution. They exploited the linear model of Boussinesq [47] to describe the surface adsorption layer (called the Maxwell model) and hence the shear and dilatational viscosities were considered theoretically. Unfortunately, their model was very complicated and difficult to use. All these works were focused on studying the visco-elasticity of adsorption layers on flat liquid/air interface (in the Langmuir trough).

Concurrently with the approach of Lucassen and van den Tempel for determining the visco-elastic moduli in Langmuir trough, Lunkenheimer et al. [48–54] developed independently the oscillating bubble method for the determination of the elasticity (called by them the Marangoni elastic modulus) of adsorption layers. The two approaches agreed theoretically. A good review on the basic methods for studying the rheology of adsorption layers can be found in Ref. [55]. The oscillating bubble method a small bubble fixed at the tip of a capillary. The bubble is submerged in the surfactant solution and connected to a gas compartment, which is

excited to harmonic oscillations by a piezo-drive vibrating with a given frequency and a small amplitude. The pressure in the gas compartment, the cross-sectional area and the amplitude of the bubble (the variation of bubble length) are measured as a function of the excitation frequency. Hence, the phase shift between the excitation signal and the bubble response is measured at different frequencies. The elastic and loss moduli can be determined by this procedure.

The theory and the experiment of the oscillation bubble method have been advanced by the others [56–62]. Wantke and Fruhner applied this method to determine the dilatational viscosity of the surfactant adsorption layer [63]. Kovalchuk et al. [64] performed detailed analysis and showed that the frequency–amplitude relationship depends on the bubble volume and the surfactant concentration up to frequency of 400 Hz. Stubenrauch and Miller [65] applied profile analysis tensiometry (PAT) to study the rheology of adsorption layers at low frequencies (up to 0.1 Hz). A good analysis of the Gibbs elasticity and the visco-elastic modulus can be found in Ref. [66]. Leser et al. [67] reported that the frequency limit of PAT for determining the visco-elastic modulus is 1 Hz. A good review on the both methods can be found in Ref. [68].

Wantke and Fruhner [63] and Ortegren et al. [69] exploited the oscillation bubble method at high frequencies, at which the adsorption–desorption mechanism had no contribution to the elastic modulus, and showed that the model of Lucassen and van den Tempel [1] produced values of the elastic modulus deviating substantially from the data for $d\sigma/d\ln\Gamma$ as determined using the experimental data for surface tension and the surface excess predicted by the surface tension isotherm. This would be true especially at high levels of surface coverage. Kovalchuk et al. [70] reported that this deviation would be due to the existence of two-dimensional intrinsic compressibility of the surfactant layer, which should be correctly accounted for by an appropriate adsorption model. In addition, Wantke et al. [71] showed that subsurface adsorption layer contributed to the surface elastic modulus as well. Yeung and Zhang [72] performed numerical simulations indicating that when the surfactant molecules entangled, the rheology of the expanding/shrinking surface could be described successfully by the Maxwell model of visco-elasticity, although they acknowledged this result as unphysical.

The experimental technique based on the bubble/drop oscillating method underwent significant advance in the last decade [60,73]. For example, the second harmonic generation spectroscopy was combined with the oscillating bubble method [74]. Meanwhile Bianco and Marmur [75] developed a new experimental approach for measuring the Gibbs elasticity of oscillating soap bubble. This methodology was based on the determination of the film tension upon the expansion and shrinking of the soap bubble surface at a given low frequency. The methodology was advanced by Kovalchuk et al. [76]. The inhomogeneous distribution of the soap bubble liquid due to gravity was accounted for. In contrast to the numerous works on the visco-elastic moduli of single gas/liquid surface layers, the literature data on elasticity of soap bubbles has remained scarce. In addition, the questions on the origin of the Gibbs elasticity of foam films remained unanswered. For example, it is not clear why the tension of thick foam films ($\sim 2\text{--}3\ \mu\text{m}$) varies upon the change of the film surface area with speed much lower than the speed of relaxation of the adsorption layer. Obviously, the electrostatic disjoining pressure should not be relevant for those thick films. Hence, it should not be any depletion of surfactant molecules in such kind of foam films. Consequently, the approach of Lucassen and van den Tempel could be applied.

The present work is devoted to studying the elastic modulus of soap bubbles in a wide range of surfactant concentrations. The applicability of Lucassen and van den Tempel approach is critically evaluated.

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