

SOAP BUBBLE ELASTICITY: ANALYSIS AND CORRELATION WITH FOAM STABILITY

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ABSTRACT

A correlation between the elastic modulus of soap bubble and the foam stability was found. A model system was chosen – a soap bubble stabilized by simple nonionic surfactant tetraethylene glycol octyl ether (C₈E₄) and 10⁻⁵ M NaCl.

The Elastic moduli were determined by periodical expansion and shrinking of foam bubbles with frequency of 0.1 Hz and volumetric amplitude of 2 mm³. The film tension was monitored via commercial profile analysis tensiometer (Sinterface Technologies, GmbH). The elastic moduli of foam bubbles versus surfactant concentration in the range of 2x10⁻³ – 10⁻² M were obtained. In addition, the theory of Lucassen and van den Tempel [1] for the elastic modulus of single liquid/air interface at given frequency was exploited as well. The bulk diffusion coefficient of the surfactant molecules is unknown parameter through the adsorption frequency in this theory. Hence, a fitting procedure (with one free parameter) was conducted matching experimental and theoretical data. The value of the bulk diffusion coefficient of C₈E₄ obtained was 5.1x10⁻¹¹ m²/s, which is an order of magnitude lower value than what is expected for. The foam was generated by shaking method and left to decay. A correlation between the elastic modulus and foam life time upon surfactant concentration was found.

Key words: elastic modulus, Gibbs elasticity, foam films, soap bubble, adsorption frequency

INTRODUCTION

The studies on elastic moduli of adsorption layers on Air/Water interface originate from the pioneering works of Lucassen and van den Tempel [2, 3] (in Langmuir through), and Lunkenheimer et al. [4-10] (oscillating bubble method). The two approaches are in theoretical agreement. A good review on the basic methods for studying the rheology of adsorption layers can be found in Ref. [11]. The oscillating bubble method consists in the following: A small bubble is fixed at the tip of capillary, which is immersed in the surfactant solution and connected to a gas compartment. The latter is excited to harmonic oscillations by piezo-drive vibrating

with a given frequency and small amplitudes. The pressure in the gas compartment, the cross-sectional area and the amplitude of the bubble (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 the loss moduli can be determined by this procedure.

Other authors contributed later for advancing the theory and the experiment of the oscillation bubble method as well [12-18]. Wantke and Fruhner applied this method to determine the dilatational viscosity of the surfactant adsorption layer [19]. Kovalchuk et al. [20] performed detailed analysis indicating that the shape of the frequency – amplitude characteristics depends on the bubble volume and the surfactant concentration up to frequency of 400 Hz.

Meanwhile Bianco and Marmur [21] developed new experimental approach for measuring the Gibbs elasticity of oscillating soap bubble. This methodology is based on the determination of the film tension upon the expansion and shrinking of the soap bubble surface with a given low frequency. The methodology was advanced by Kovalchuk et al. [22]. 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 remained scarced. In addition, open questions on the origin of the Gibbs elasticity of foam films remained as well. For example, it is not clear why the tension of thick foam films (~2–3 microns) 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 have any contribution at such high thickness. 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 given surfactant concentration range and to study any possible correlation with the foam lifetime. The applicability of Lucassen and van den Tempel approach was critically evaluated.

EXPERIMENTAL

The elasticity of soap bubbles produced by aqueous solutions of C_8E_4 (produced by Sigma-Aldrich Ltd) in the concentration range of $2 \times 10^{-3} - 10^{-2}$ M and in the presence 10^{-5} M NaCl (produced by Sigma-Aldrich Ltd), was measured. The temperature during the experiment was kept constant at 25°C.

The surface tension isotherm was determined by the Harkins-Brown method [23].

All the measurements were obtained using a commercially available profile analysis tensiometer, (PAT 1 D module of Sinterface Technologies, Ltd., Germany) with a frequency of 0.1 Hz and amplitude of 2 mm³. The tensiometer consists of (1) a *mechanical unit* for creating and controlling the test fluid–liquid interface in a 2 cm x 2 cm x 2 cm cuvette made of optical grade silica, (2) an *optical unit* for monitoring the evolution of the interface profile and (3) a *computer* with the Sinterface software, PAT-1D and a data acquisition system for operating the instrument, storing the raw data for the interface profiles, and processing the data off-line. The mechanical unit has a water bath for controlling the temperature. The soap bubble is produced (see Fig.1) by a dual

tube – a narrower internal tube situated in a wider external tube. A syringe controls the surfactant solution flowing in the external tube, while air flows through the internal tube, controlled by another syringe. The two syringes are mounted on the panel of a motorized pump, controlled by the computer. Once formed, the soap bubble was illuminated, equilibrated and its image was captured by the CCD video camera, stored, and processed by the computer software. The edge (the interface profile) of the bubble was digitally identified with sub-pixel resolution and fitted with the numerical solution of the Young–Laplace equation, allowing the determination of the film tension, volume and area of the bubble. The cyclic time dependence of film tension was determined by changing the bubble volume as a sinusoidal function of time.

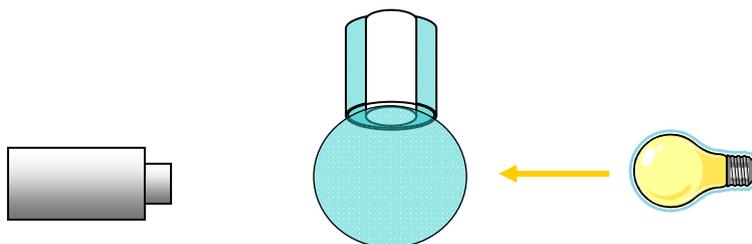


Figure 1. Sketch of the Profile analysis tensiometer system for studying elastic modulus of soap bubble (not to scale).

The shaking test method was used to determine the foam stability. It includes standardized (10-fold) shaking of flask of 50 ml volume, containing 20 ml of the studied solution. The time interval from the formation of foam to the appearance of free water surface is measured. This operation is repeated 10-times, and an average value of the foam decay time is obtained. This method is very simple to use and gives sufficiently good reproducibility. The surface tension isotherm was determined by the Harkins-Brown method [23].

RESULTS AND DISCUSSION

The surface tension isotherm (see Fig.2) of C_8E_4 was measured by Wilhelmi plate method.

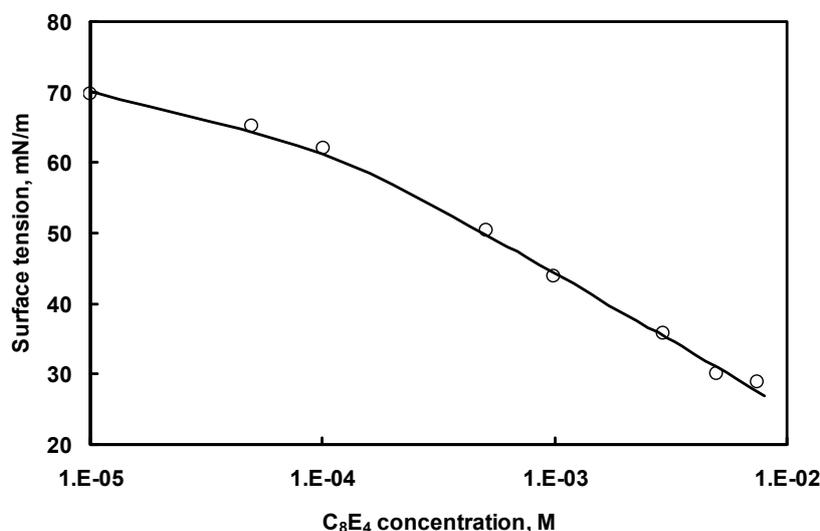


Figure 2. Surface tension isotherm of C_8E_4 – experimental (circles) and computed.

The experiments on expanding a soap bubble were conducted in the concentration range of $2 \times 10^{-3} - 10^{-2}$ M C_8E_4 . At lower surfactant concentrations the data were either or the soap bubbles were not stable. The film tension and the doubled surface tension values are presented in Fig.3.

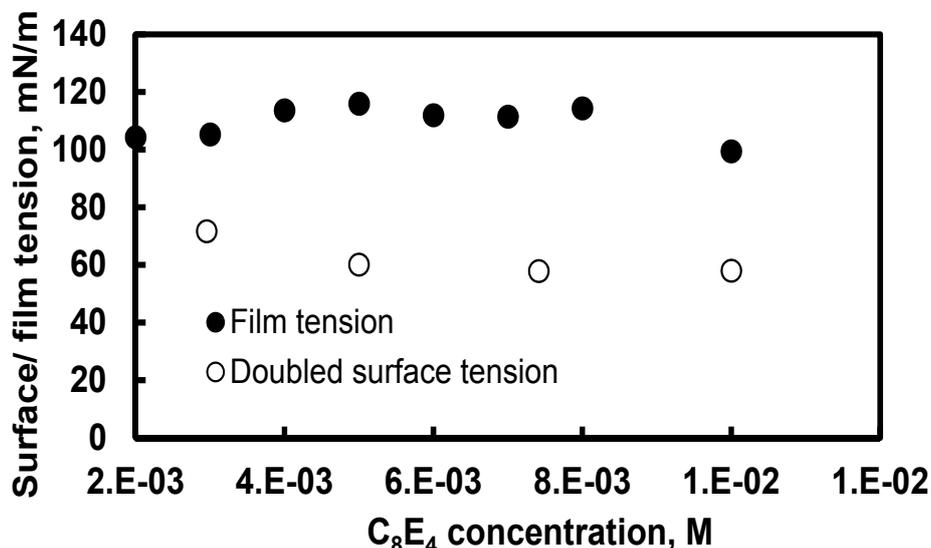


Figure 3. Film tension and surface tension (doubled value) isotherms of C_8E_4 aqueous solutions.

One can see that values of the film tension are larger than the doubled values of the surface tension. According to Refs. [21] and [22] the film tension is a function of the total area of the soap bubble. By the present experimental procedure conducted with the commercial Profile Analysis Tensiometer (PAT 1 D module of Sinterface Technologies, Ltd., Germany), expressed in periodical expansion and contraction of the soap bubble with frequency of 0.1 Hz, an average value of the film tension and Gibbs elasticity is produced.

These experimental data were processed with the Szyskowski-Langmuir equation of state:

$$\sigma = \sigma_0 - \Gamma_{\infty} RT \ln(1 + kc) \quad (1)$$

Fitting procedure with two matching parameters Γ_{∞} and k was conducted via „Solver” option of Microsoft Excel. The theoretical curve is situated in Fig.1. The obtained values of the fitting parameters are $\Gamma_{\infty} = 3.42 \times 10^{-6}$ mol/m² and $k = 25$ m³/mol. Equation (1) is equivalent to the following equation of state:

$$\sigma = \sigma_0 + \Gamma_{\infty} RT \ln \left(1 - \frac{\Gamma}{\Gamma_{\infty}} \right) \quad (2)$$

where Γ_{∞} is the surfactant adsorption at CMC. Hence the Gibbs elasticity of the soap bubble can be calculated by the expression:

$$E_G = 2\varepsilon_0 = -2\Gamma \frac{d\sigma}{d\Gamma} = \frac{2RT\Gamma_{\infty}\Gamma}{\Gamma_{\infty} - \Gamma} \quad (3)$$

Eq.(2)) can be transformed in the following expression:

$$\frac{2\varepsilon}{E_G} = \frac{1}{\sqrt{1 + 2\sqrt{\omega_0 / \omega} + 2\omega_0 / \omega}} \quad (4)$$

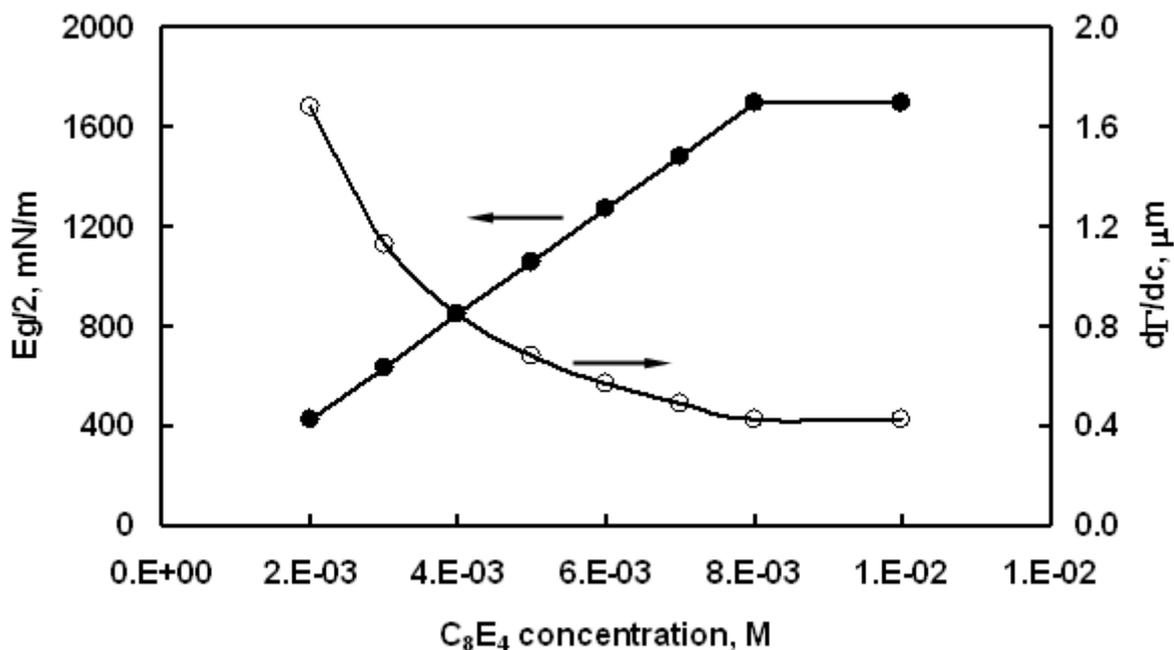


Figure 4. Gibbs elasticity of the single air/water surface $E_g / 2$ and the adsorption length $d\Gamma / dc$ as a function of the surfactant concentration.

The values of the Gibbs elasticity of single air/liquid interface and the adsorption length, calculated from the surface tension isotherm using the model of Szyskowski-Langmuir are presented in Fig. 4. These values are utilized further in Eqs. (2) and (3) to calculate $2\varepsilon / E_G$.

The diffusion coefficient D (see Eq.(3)) of C_8E_4 molecules in the soap bubble is unknown parameter in Eq.(4). Hence the ratio $2\varepsilon / E_G$ and experimental data E_{exp} / E_G can be adjusted by fitting of the unknown parameter the diffusion coefficient D .

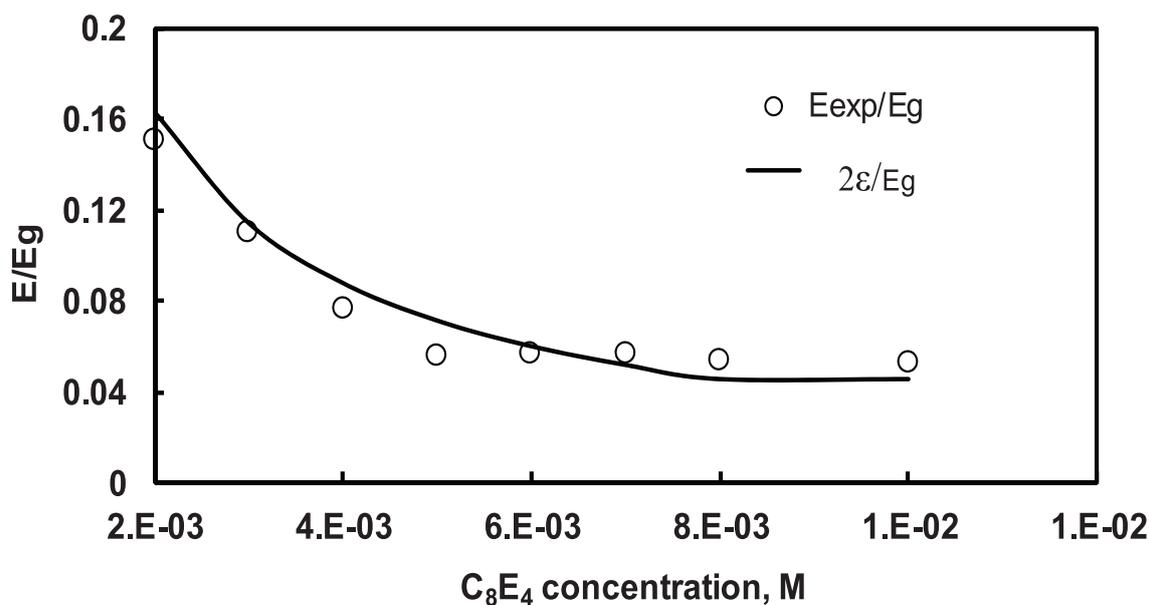


Figure 5. Experimental E_{exp} / E_G and theoretical $2\varepsilon / E_G$ (obtained by adjusting D) ratios versus C_8E_4 concentration.

The experimental E_{exp}/E_G and the theoretical $2\varepsilon/E_G$ ratios versus the surfactant concentration are presented in Fig.5. The fitting procedure gave a value of the bulk diffusion coefficient of $C_8E_4 D = 5.1 \times 10^{-11} \text{ m}^2/\text{s}$, which is an order of magnitude lower, than what was expected for. Fig. 4 shows that the values of the elastic moduli are substantially lower than the values of the Gibbs elasticity obtained by the surface tension isotherm. In addition, the ratio E_{exp}/E_G decreases upon the increase of the C_8E_4 concentration until reaching plateau before the CMC. This result is in accord with Refs.[19, 24], reporting deviations of the values of elastic moduli from these ones of the Gibbs elasticity, when the model of Lucassen and van den Tempel is applied to bubbles oscillating with high frequency.

The values of the Gibbs elasticity and the Foam life-time versus C_8E_4 concentration is presented in Fig. 6.

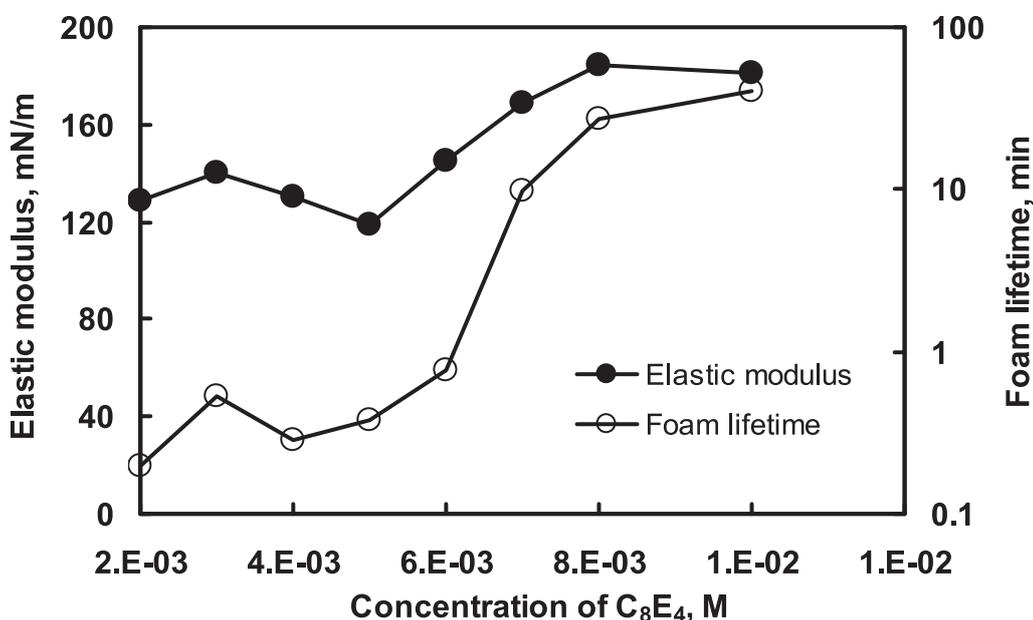


Figure 6. Gibbs elasticity and foam life-time as a function of C_8E_4 concentration

One can see clear correlation between the foam lifetime and the elastic modulus curves. It should be noted here that the elastic modulus values obtained by this method are averaged, due to the variable in time film thickness inhomogeneity over the soap bubble during its expansion and shrinking.

CONCLUSIONS

This paper is dedicated on studying the elasticity of soap bubbles. Although numerous works have been devoted to investigation the rheology of the surface adsorption layers, there are still obscure sides of their behavior. For example, it is not clear the origin of the surfactant depletion in thick foam films (in order of several microns), causing variation of the film tension at slow expansion or shrinking of the film surface. In addition, according to the literature data (e.g. Ref. [24]) the elastic modulus at high frequency of bubble oscillation is not equivalent to the Gibbs elasticity, calculated from the surfactant surface tension isotherm. In addition, the literature data on soap bubble surface rheology are very scarce. Our study showed

that the film tension values of soap bubbles prepared from C_8E_4 aqueous solutions are larger than the doubled values of the surface tension. The elastic moduli values were significantly lower than the values of the Gibbs elasticity, calculated by the surface tension isotherm. Our fit of the ratio $2\varepsilon/E_G$, calculated with the model of Lucassen and van den Tempel (Eqs. (2) and (3)), and experimental data E_{exp}/E_G gave value of the bulk diffusion coefficient of the surfactant molecules $D = 5.1 \times 10^{-11} \text{ m}^2/\text{s}$, which significantly lower than what is expected for C_8E_4 molecules. All this indicates that there is an exchange of the surfactant molecules ($2\varepsilon < E_G$) between the film surfaces and the and bulk of the film, but it is impeded by some unknown factor. In addition, it is very possible increased viscous dissipation of the film liquid during the oscillation soap bubble oscillation as compared to the case of the surface of semi-infinite bulk phase (e.g. bubbles or drop). In addition, a strong correlation was found between the foam lifetime and the elastic modulus of soap bubbles. In short, the higher the elastic modulus, the longer living foam is.

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