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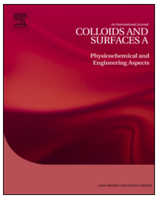

Adsorption and surface dilational visco-elasticity of C_nEO_m solutions as studied by drop profile analysis tensiometry

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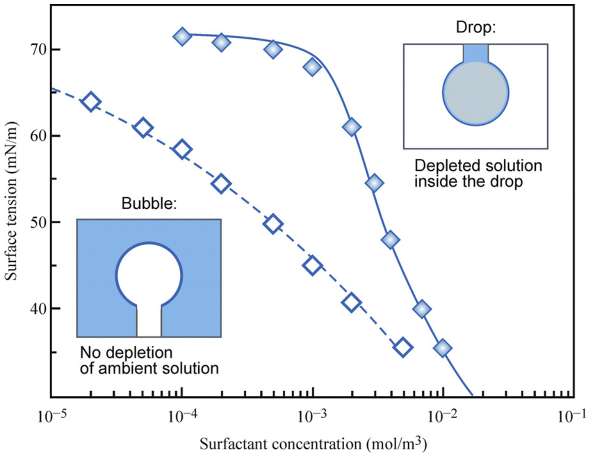
GRAPHICAL ABSTRACT



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ABSTRACT

The surface tension isotherms and dilational visco-elasticity for three nonionic surfactants ($C_{10}EO_8$, $C_{12}EO_5$ and $C_{14}EO_8$) were comparatively studied using the bubble and drop profile analysis tensiometry. The experiments based on drop profiles were analysed assuming the depletion of surfactant molecules from the bulk of the drop due to adsorption. To process the experimental results, two theoretical adsorption layer models (Frumkin and reorientation) were applied, while the reorientation model provides a better description of the experimental results. In addition, the visco-elasticity moduli obtained from drop and bubble profile experiments were compared. It was shown that at higher surfactant concentrations the drop profile method provides visco-elasticities systematically larger than those obtained from bubble profile experiments, even though the adsorption-related depletion has been correctly considered. The proposed correction protocol provides the option for direct comparison between data obtained by the drop profile analysis method with those from other methods.

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1. Introduction

The dynamics of wetting of solid and liquid surfaces by surfactant solutions is a quite complex process because all relevant quantities depend on time due to the adsorption of the surfactant molecules at all involved interfaces [1]. The adsorption processes at the solution/air interface are comparatively easily measured via surface tensiometry, while those at solution/solid interfaces require much more sophisticated methods, such as neutron reflection [2], quartz crystal microbalance (QCM) [3] or indirectly via contact angle investigations using certain surface energy models [4].

The methods of drop and bubble profile analysis tensiometry are widely used by many authors [5–26] to study dynamic contact angles [4], surface tension [5,7,8,11] and dilation visco-elasticity of various systems [24], such as aqueous solutions of surfactants [14,16,21], lipids [9,10,13,18], proteins [19,20,23] or their mixtures [6,12,15,17,22]. These methods provide relatively simple procedures to obtain experimental data.

It should be noted that the drop profile method is characterized by one specific feature which prevents the experimental data obtained by this method to be immediately used in theoretical analysis; this is especially true for surfactants of high surface activity. The adsorption of surfactant on the drop surface results in a decrease of its concentration within the drop bulk as compared to that in the initial solution; this difference of concentrations should be accounted for in any theoretical analysis. On the other hand, this depletion could provide certain advantages of the method, as the drop profile analysis method could be used in combination with the bubble profile (or du Noüy ring, or Wilhelmy plate method), where the volume of the studied solution is large, and therefore any surfactant depletion due to adsorption does not occur [25]. Then, this combination allows to estimate the adsorbed amount at the interface [27].

In our previous studies, the drop profile and bubble profile methods were used complementarily: (i) for the analysis of the surface and interface tension in various systems, in particular, the biologic liquids in medical applications [26]; (ii) for a comparative processing of the results from drop and bubble profile analysis tensiometry, the adsorbed amount for surfactants and proteins can be directly determined [27–29]; and (iii) for the dilation rheological studies using the bubble and drop profile tensiometry [30–32]. In [30] the same elasticity modulus values were obtained with the bubble and drop method only when the equilibrium surface pressure Π was lower than 15 mN/m. For larger surface pressures, the visco-elasticity moduli determined from drop profile experiments become larger than those obtained from bubble profile measurements. In [30] also the stress deformations of bubbles and drops were studied. It was shown that variations in the bulk concentration caused by surface expansions and compressions of the surfactant solution drops result in an increased visco-elasticity modulus. Results of dilational rheology studies of surfactants by various techniques were reported in [33–42].

The non-ionic ethoxylated alcohol surfactants C_nEO_m are widely used in practice, mostly as detergents. In [22,27–32,42–44] the adsorption and rheologic characteristics of C_nEO_m solutions at the air/water interface have been studied.

In the present work, the drop profile method was used to measure the visco-elasticity modulus of $C_{10}EO_8$, $C_{12}EO_5$ and $C_{14}EO_8$ solutions. To analyse the experimental results, a special software was developed recently which takes into account the adsorption-related depletion of the solution to determine the equilibrium concentration within the drop [44]. This software is further refined here. Two thermodynamic models were applied to calculate the adsorption and rheologic dependencies of the surface layers: the Frumkin adsorption model, and the reorientation model [28,29,32]. The comparison of the model calculations with the experimental data has shown that the reorientation model provides much better description of the visco-elasticity results. It is to be noted that the method used in the present study is quite different from that employed in [27–32]. In these earlier publications the surface tension of the same surfactant was also measured by the bubble profile method, to determine the actual concentration of the solution within the drop which was assumed to be equal to the solution concentration for the bubble profile method (where adsorption-related losses do not exist) at the same surface tension. In the procedure proposed here this combination of the two methods is not required because the surfactant concentration within the drop is calculated directly by taking the depletion quantitatively into account.

2. Materials and methods

The three ethoxylated alcohols ($C_{10}EO_8$, $C_{12}EO_5$ and $C_{14}EO_8$) were purchased from Sigma Chemical and used without further purification. The surface tension measurements were performed with the bubble/drop profile analysis tensiometers PAT-1 and PAT-2P (SINTERFACE Technologies, Germany) following the protocols given in [28].

After having reached the adsorption equilibrium, the dilational elasticity was measured via harmonic oscillations of the drop surface area at a fixed frequency of f = 0.1 Hz and surface area amplitudes of 7 ÷ 8%. The drops of initial volumes of 21 mm^3 and a surface area of 33 mm^2 were formed at the tip of a steel capillary with internal diameter of 2 mm. The drop surface area was kept constant during the equilibration process. The results of oscillation experiments were analysed using the Fourier transformation [31].

3. Theory

When using the drop profile analysis tensiometry it should be kept in mind that some amount of the surfactant is adsorbed at the interface. This results in a depletion of the surfactant solution inside the drop [44]. To account for this depletion, one should note that the mass M of the surfactant in the volume V of the initial solution with concentration c_0 is equal to the sum of its amount in the drop volume V with the concentration c, and the amount adsorbed at the drop surface of area S after equilibration: $M = c_0 V = cV + \Gamma S$ (Γ is the adsorbed amount per unit area). Thus, the actual concentration c of the surfactant in the drop is $c = c_0 - (S/V) \times \Gamma$.

To increase the accuracy of the estimated surfactant concentration at equilibrium, a correction should be made for the decrease of the solution drop volume (caused by the drop elongation due to the decreased surface tension) in experiments with a constant drop surface area S_0. It was assumed in this study that the drop volume V could be approximated by the relation $V = V_0 \times (1 - \beta\Pi)$; here V_0 is the pure solvent (water) drop volume, β is a coefficient which was estimated to be 0.001–0.002 m/mN, and Π is the equilibrium surface pressure, $\Pi = \gamma_0 - \gamma$, where γ_0 and γ are the surface tension of pure solvent and the surface tension of the solution, respectively. Therefore, the volume dependence of the concentration becomes:

$$c = c_0 - \frac{S_0}{V_0(1-\beta\Pi)}\Gamma \tag{1}$$

This dependence was taken into account in the simultaneous solution of the surface layer equation of state and adsorption isotherm equation to fit the relevant model of the surface layer to the experimental data. For the Frumkin model these equations are as follows [28]:

$$-\frac{\Pi\omega_0}{RT} = \ln(1-\theta)+a\theta^2 \tag{2}$$

$$bc = \frac{\theta}{1-\theta}\exp(-2a\theta) \tag{3}$$

$$\omega = \omega_0(1-\varepsilon\Pi\theta) \tag{4}$$

Here R is the gas law constant, T is the absolute temperature, θ is the surface coverage (θ = Γω), b is the adsorption activity coefficient, a is the intermolecular interaction coefficient, ω is the surfactant molar area