



Dynamic surface tension of mixed oxyethylated surfactant solutions

E.V. Aksenenko^a, V.B. Fainerman^b, J.T. Petkov^c, R. Miller^{d,*}

^a Institute of Colloid Chemistry and Chemistry of Water, 42 Vernadsky Avenue, 03680 Kyiv (Kiev), Ukraine

^b Donetsk Medical University, 16 Ilych Avenue, 83003 Donetsk, Ukraine

^c Unilever R&D Port Sunlight, Quarry Road East, Bebington CH63 3JW, UK

^d Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Am Mühlenberg 1, 14424 Potsdam, Germany

ARTICLE INFO

Article history:

Received 19 December 2009

Received in revised form 29 January 2010

Accepted 1 February 2010

Available online 6 February 2010

Keywords:

Adsorption kinetics

Mixed adsorption layers

Non-ionic surfactant mixtures

Drop and bubble profile tensiometry

Diffusion controlled adsorption model

ABSTRACT

The adsorption kinetics of mixed non-ionic surfactants can be described by a diffusion controlled adsorption when the correct model is used, i.e. when for each adsorbing species the corresponding thermodynamic model for the adsorption equilibrium is applied. For non-ionic surfactants, such as oxyethylated alcohols $C_{12}EO_5$ and $C_{14}EO_8$ and Tritons X-*n*, the reorientation model is the appropriate model. The dynamic surface tensions measured by bubble profile tensiometry are described very well by an efficient diffusion coefficient decreasing with the total surfactant bulk concentration. The physical reason for the change in D_{eff} is the effect of convection in the system becoming more pronounced with the increasing in adsorption time. Equimolar mixtures of Triton X-45 and X-165 mimic the adsorption behaviour of Triton X-100.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The adsorption behaviour of surfactant mixtures under dynamic conditions is of significant scientific and practical interest. Experimental and theoretical studies of the dynamic surface tension and adsorption kinetics of surfactant mixtures at liquid/fluid interface were presented in [1–17]. In particular, theoretical models capable for the prediction of the equilibrium and dynamic surface tension of the surfactant mixture from the molecular structure of individual components were developed and supported experimentally in [9,10]. Moreover, if we know the parameters needed to describe the equilibrium and dynamic surface tensions of individual surfactant solutions, then the theoretical models developed in [8,12,14,17] allow to calculate the dynamic surface tensions of corresponding mixtures, provided the adsorption is governed by the diffusion mechanism.

In [17] the bubble profile analysis tensiometry was used to study dynamic and equilibrium surface tensions of mixed sodium dodecyl sulphate (SDS)/ C_nEO_m solutions. For the analysis of these experimental data, a new theoretical model was employed which assumes different adsorption mechanisms for each surfactant. The adsorption behaviour of the non-ionic C_nEO_m surfactants was described by the reorientation model which assumes two states of adsorbed surfactant molecules with different molar areas in the surface layer, and an intrinsic compressibility close interfacial pack-

ing. For the ionic SDS, the adsorption was assumed to be governed by a Frumkin-type model, which also accounts for the intrinsic compressibility. For the analysis of the dynamic surface tensions, the developed model was based on the numerical solution of Fick's equations for the actual geometry of the experimental system, i.e. diffusion to the surface of a spherical bubble surface. In [18] the theoretical model given in [17] was generalised for the case of mixtures of two surfactants, both of which exhibit reorientation and intrinsic compressibility in the surface layer, and it was shown that this model agrees well with the measured equilibrium surface tension and dilational rheological characteristics mixed oxyethylated surfactant adsorption layers.

The present work summarises studies of dynamic surface tensions of mixtures of oxyethylated surfactants (oxyethylated alcohols $C_{14}EO_8/C_{12}EO_5$ and the mixtures of Tritons with different degree of oxyethylation). The theoretical treatment of the experimental data is based on the equation of state and adsorption isotherms for reorientable surfactants derived in [18], and the numerical method for the solution of Fick's diffusion equations as proposed in [17]. It is shown that this model provides a sound description of the adsorption dynamics behaviour of the studied non-ionic surfactant mixtures.

2. Theory

The equation of state and adsorption isotherms for mixture of reorientable surfactants were discussed in detail elsewhere [18]. Therefore, we only briefly repeat here the main equations. For

* Corresponding author. Tel.: +49 331 5679252; fax: +49 331 5679202.
E-mail address: miller@mpikg.mpg.de (R. Miller).

reorientable surfactants 1 and 2, the equation of state reads [18]:

$$-\frac{\Pi\omega_0^*}{RT} = \ln(1 - \theta_1 - \theta_2) + \theta_1 \left(1 - \frac{\omega_{10}}{\omega_1}\right) + \theta_2 \left(1 - \frac{\omega_{20}}{\omega_2}\right) + 2a\theta_1\theta_2, \quad (1)$$

with

$$\omega_0^* = \frac{\omega_{10}\theta_1 + \omega_{20}\theta_2}{\theta_1 + \theta_2} \quad (2)$$

Here $\Pi = \gamma_0 - \gamma$ is the surface pressure, γ_0 and γ are the surface tension of solvent and solution, respectively, R is the gas law constant, T is the temperature, ω_i is the molar area, $\theta_i = \omega_i\Gamma_i$ is the surface coverage by surfactant molecules of component i ($i = 1$ or 2), Γ_i is the adsorption, ω_{i0} is the molar area in the states of minimum area at zero surface pressure, and a is the constant of interaction between surfactant molecules 1 and 2. The total adsorption of the reorientable surfactants Γ_i ($i = 1$ or 2) consists of the amounts of surfactants adsorbed in two states: $\Gamma_i = \Gamma_{i1} + \Gamma_{i2}$. Here the first subscript refers to the surfactant, and the second one to the state of the surfactant in the surface layer. The molar areas of surfactants adsorbed in states 1 and 2 are denoted by ω_{i1} and ω_{i2} (for definiteness we assume $\omega_{i2} > \omega_{i1}$), hence the surface coverage of the monolayer by the molecules of the i th surfactant is $\theta_i = \omega_i\Gamma_i = \omega_{i1}\Gamma_{i1} + \omega_{i2}\Gamma_{i2}$.

The molar areas of the surfactants (in the states of minimum area) are approximated by a linear dependence on surface pressure Π and total surface coverage $\theta = \theta_1 + \theta_2$:

$$\omega_{i1} = \omega_{i0}(1 - \varepsilon_i\Pi\theta), \quad (i = 1, 2) \quad (3)$$

where ε_i are the two-dimensional relative surface layer compressibility coefficients.

For the states $i1$ and $i2$ of the surfactant i the respective adsorption isotherms read [18]:

$$b_i c_i = \frac{\Gamma_{i1}\omega_{i0}}{(1 - \theta)^{\omega_{i1}/\omega_{i0}}} \exp(-2a\theta_j), \quad (i, j = 1, 2; i \neq j) \quad (4)$$

$$b_i c_i = \frac{\Gamma_{i2}\omega_{i0}}{(\omega_{i2}/\omega_{i1})^{\alpha_i}(1 - \theta)^{\omega_{i2}/\omega_{i0}}} \exp(-2a\theta_j), \quad (i, j = 1, 2; i \neq j) \quad (5)$$

Here b_i are the adsorption equilibrium constants, c_i are the surfactant bulk concentrations, α_i are the power law exponents. The ratio of the adsorptions in states 1 and 2 is given by:

$$\frac{\Gamma_{i1}}{\Gamma_{i2}} = \frac{1}{(\omega_{i2}/\omega_{i1})^{\alpha_i}(1 - \theta)^{(\omega_{i2}-\omega_{i1})/\omega_{i0}}}, \quad (i = 1, 2) \quad (6)$$

Then, the only additional model parameter for the mixture is the constant a which describes the intermolecular interaction between the molecules of different species, while all other model parameters refer to the individual solutions. If only one of the two components of the mixture is present in the solution, the equations listed above become identical to those developed earlier for the individual solutions of reorientable surfactants assuming the non-ideality of entropy of the surface layer and the intrinsic compressibility of the adsorbed surfactant molecules [19].

To simulate the concurrent adsorption at the bubble surface for a system containing two surfactants in the solution, the method was used as described in [17], and therefore here we outline only those features which are specific to the case considered here. The Eqs. (9)–(12) given in [17] and those presented in the Appendix thereto apply completely to the case presented here. To implement them for the system of two reorientable surfactants, the adsorptions Γ_i in the boundary conditions, namely Eq. (12) in [17] (and hence Eq. (A16) in [17] which are the finite difference representations of Eq. (12)) should be expressed via the subsurface concentrations of the

surfactants c_i using the Eqs. (1)–(5). It is convenient to introduce dimensionless quantities:

$$k_p = \frac{RT}{\omega_{10}}, \quad \Omega_{i2} = \frac{\omega_{i2}}{\omega_{i0}} \quad (i = 1, 2) \quad (7)$$

and

$$\Omega_i = \frac{\omega_i}{\omega_{i0}}, \quad p = \frac{\Pi\omega_{10}}{RT},$$

$$\Omega_{i1} = \frac{\omega_{i1}}{\omega_{i0}} = 1 - \varepsilon_i \cdot k_p \cdot p \cdot (\theta_1 + \theta_2) \quad (i = 1, 2) \quad (8)$$

In this dimensionless formulation, the model Eqs. (4) and (6) become:

$$b_i c_i - \frac{\theta_i}{\Omega_i} \frac{\Omega_{i2} - \Omega_i}{\Omega_{i2} - \Omega_{i1}} (1 - \theta_1 - \theta_2)^{-\Omega_{i1}} \exp(-2a\theta_j) = 0$$

$$(i, j = 1, 2; i \neq j) \quad (9)$$

$$\frac{\Omega_i - \Omega_{i1}}{\Omega_{i2} - \Omega_i} - \left(\frac{\Omega_{i2}}{\Omega_{i1}}\right)^{\alpha_i} (1 - \theta_1 - \theta_2)^{\Omega_{i2} - \Omega_{i1}} = 0 \quad (i = 1, 2) \quad (10)$$

and from Eqs. (1) and (2) it follows:

$$p = -\frac{\theta_1 + \theta_2}{\theta_1 + (\omega_{20}/\omega_{10})\theta_2} \times \left[\ln(1 - \theta_1 - \theta_2) + \theta_1 \left(1 - \frac{1}{\Omega_1}\right) + \theta_2 \left(1 - \frac{1}{\Omega_2}\right) + 2a\theta_1\theta_2 \right] \quad (11)$$

Note that the dimensionless quantities Ω_{i1} introduced by expressions (8) depend now on θ_i and Ω_i via Eq. (11). Therefore Eqs. (9) and (10) constitute the set of four equations which can be solved for any pair (c_1, c_2) with respect to θ_i and Ω_i to obtain the adsorption values:

$$\Gamma_i(c_1, c_2) = \left(\frac{\theta_i/\Omega_i}{\omega_{i0}}\right) \quad (i = 1, 2) \quad (12)$$

Thus, to perform the Crank–Nicolson procedure defined by Eqs. (A12)–(A16) in [17], in each temporal node the set of two equations (A16) in [17] are to be solved. Note that the dimensionless quantities G_i and U_i introduced in [17] are directly related to Γ_i and c_i , respectively. At any iteration step, the solution of the set of Eqs. (9) and (10) should be calculated for each pair of trial values c_1 and c_2 until convergence is achieved. The software package described in [17] was extended to include the present case of mixture of two reorientable surfactants. As the structure of the package is modular, only the segment which implements the solution of Eqs. (9) and (10) had to be developed, while the core of the package which involves the solution of Fick's equations with the respective boundary and initial conditions, the input/output modules, and the visual interface remained essentially the same. Again, in all the cases studied, the mass balance deviation (A17 in reference [17]) did not exceed 1%.

3. Experimental

The experiments were performed with the bubble/drop profile analysis tensiometers PAT (SINTERFACE Technologies, Germany), the principle of which was described in detail elsewhere [20]. The temperature of the measuring cell with a volume of $V = 20$ ml was kept constant at 25 °C. In this study we used a buoyant (oblate) bubble formed at the bottom tip of a vertical Teflon capillary with a diameter of 3 mm.

Download English Version:

<https://daneshyari.com/en/article/595298>

Download Persian Version:

<https://daneshyari.com/article/595298>

[Daneshyari.com](https://daneshyari.com)