The surface profile of aqueous solutions of an amphiphile $(C_{10}E_4)$ near liquid/liquid phase

separation probed by ellipsometry

The surface profile of aqueous solutions of an amphiphile (C$_{10}$E$_4$) near liquid/liquid phase separation probed by ellipsometry

Andrea Hirtz and Gerhard H Findenegg

I-N-Stranski-Institut für Physikalische und Theoretische Chemie, Technische Universität Berlin, Straße des 17 Juni 112, D-10623 Berlin, Germany

Abstract. The free liquid surface of the binary system C$_{10}$E$_4$ + water has been studied by reflection ellipsometry in the temperature range below and near the upper miscibility gap. The ellipticity $\bar{\rho}$ of samples of concentrations below and above the critical composition w_c was measured as a function of temperature T and compared with calculations of $\bar{\rho}$ based on model refractive-index profiles. The pronounced increase of $\bar{\rho}$ with T at concentrations $w \geqslant w_c$ is consistent with a model profile that entails there being a water-enriched layer just below the surface. The thickness of this water-rich layer increases as one approaches the phase-separation temperature, as is to be expected for preferential wetting of the surface of the concentrated micellar solution by the coexistent dilute micellar solution.

1. Introduction

Amphiphilic compounds such as straight-chain oxyethylene monoalkyl ethers, with the formula C$_n$H$_{2n+1}$(OCH$_2$CH$_2$)$_m$OH (abbreviated as C$_m$E$_n$), tend to form an adsorbed monolayer at the surface of their aqueous solutions, oriented with the hydrophobic chains toward the gas phase and the hydrophilic oligo(oxyethylene) chain toward the aqueous phase. Aqueous systems of C$_m$E$_n$ amphiphiles commonly exhibit incomplete miscibility at temperatures above a lower critical solution temperature T_c, due to the hydrophobic aggregation of the amphiphilic molecules in the solution. For higher members of the C$_m$E$_n$ family, like C$_{10}$E$_4$, this hydrophobic aggregation leads to micelles of spherical and/or ellipsoidal shape. It is of interest to study how the adsorption and aggregation of the amphiphile affects the global structure of the surface of these systems. Pertinent information can be derived from ellipsometric measurements [1].

The ellipticity $\bar{\rho}$ of light reflected from a flat interface is a measure of the width d of the inhomogeneous region and, to first order in d/λ, it can be estimated by the approximated Drude equation [2]:

$$\bar{\rho}_i = \frac{\pi\sqrt{n_b^2 + 1}}{\lambda(n_b^2 - 1)} \int_{-\infty}^{+\infty} \frac{(n_b^2 - n_z^2)(n_z^2 - 1)}{n_z^2} \, \mathrm{d}z. \tag{1}$$

Here, n_b is the refractive index of the bulk liquid ($z \to +\infty$) at the given wavelength λ of light (incident through the gas phase, $n_g = 1$), and $n_z \equiv n(z)$ is the refractive-index profile. For a monotonic profile, $1 \leqslant n_z \leqslant n_b$, equation (1) yields a *positive* $\bar{\rho}_i$-value. On the other hand, if $n(z)$ passes through a maximum in the inhomogeneous surface region,

such that $n_z > n_b$ for $z_0 < z < +\infty$, this inner region of the interface will cause a *negative* contribution to the Drude integral. Such a situation is expected in systems exhibiting multilayer adsorption of an organic solute at the surface of aqueous solutions, if the solute has a higher refractive index than water.

Formation of multilayer adsorbed films may occur, generally, at interfaces between phases α and γ when the system approaches a point at which α and γ coexist with a third phase β. In the present context, α and β represent the coexistent liquid phases of the C_mE_n + water system, and γ is the gas phase. In the regime of complete wetting of the α/γ interface by phase β one expects a film of β-like composition at the surface of the (weakly undersaturated) α-like phase, growing in thickness as bulk coexistence of α and β is approached. At bulk coexistence, the interfacial tensions σ_{ij} between the three constituent phases ($i, j = \alpha, \beta, \gamma$) are interrelated by the general relation $\sigma_{\alpha\gamma} \leqslant \sigma_{\alpha\beta} + \sigma_{\beta\gamma}$, where the equality applies to the case of complete wetting and the inequality to incomplete wetting. If α is defined as the phase with higher surface tension ($\sigma_{\alpha\gamma} > \sigma_{\beta\gamma}$), multilayer adsorption (incipient formation of a β-phase) will occur at the surface of phase α in the region near bulk coexistence of α and β. Now, for aqueous systems of amphiphilic compounds one anticipates that the amphiphile tends to lower the surface tension. Accordingly, the amphiphile-rich phase is expected to have a lower surface tension than the water-rich phase and, therefore, should wet the water-rich phase. This behaviour has indeed been observed in the case of a weak amphiphile (*sec/tert*-butanol + water): in this system a pronounced decrease of the ellipticity $\bar{\rho}$ of the water-rich phase was observed as the $\alpha\beta$-coexistence curve was approached, indicating the formation of an alcohol-rich layer at the surface of the water-rich phase [1]. However, the opposite behaviour, i.e. a pronounced *increase* of $\bar{\rho}$ for the surface of the amphiphile-rich phase on approaching liquid/liquid coexistence, was observed in the case of the stronger amphiphile C_4E_1. On the basis of equation (1), this finding hints at the formation of a water-rich layer (i.e. a layer having a lower refractive index than the bulk phase) at the surface of concentrated solutions of the amphiphile [1].

This paper presents an ellipsometric study of the surface of aqueous solutions of the surfactant $C_{10}E_4$ in a temperature range below (and up to) the upper miscibility gap. The ellipticity data are analysed in terms of refractive-index profiles based on a theoretical model for the order parameter profile of semicritical interfaces, and an *ad hoc* model for the incipient β-phase. Such an analysis requires complementary data on the refractive index n and correlation length ξ as a function of temperature and composition. These data were also measured or derived from measured quantities in this work. A review of the underlying theories and preliminary results have been presented elsewhere [1].

2. Results

Ellipsometric measurements were made using the phase-modulation technique. Sample cells with glass windows (0.3 mm) were placed in a three-stage thermostat. The temperature could be controlled to within ± 3 mK [3]. Figure 1(a) shows results for the ellipticity $\bar{\rho}$ of the free surface of aqueous solutions of $C_{10}E_4$ for a series of fixed concentrations in the range from 0.1 wt% to 4.2 wt% $C_{10}E_4$, i.e. from concentrations just above the critical micelle concentration (cmc = 0.05 wt% at 25 °C) up to about twice the critical concentration ($w_c = 2.3$ wt%). In the single-phase region up to nearly T_c ($T_c = 293.53$ K) the ellipticity increases with temperature. At low concentrations ($w < w_c$) this temperature dependence is rather weak; at higher concentrations ($w \geqslant w_c$), however, a pronounced increase of $\bar{\rho}$ with T is seen near the corresponding phase separation temperature T_b (which is close to T_c for all samples except that with 0.1 wt%). For these samples $\bar{\rho}$ exhibits a maximum just
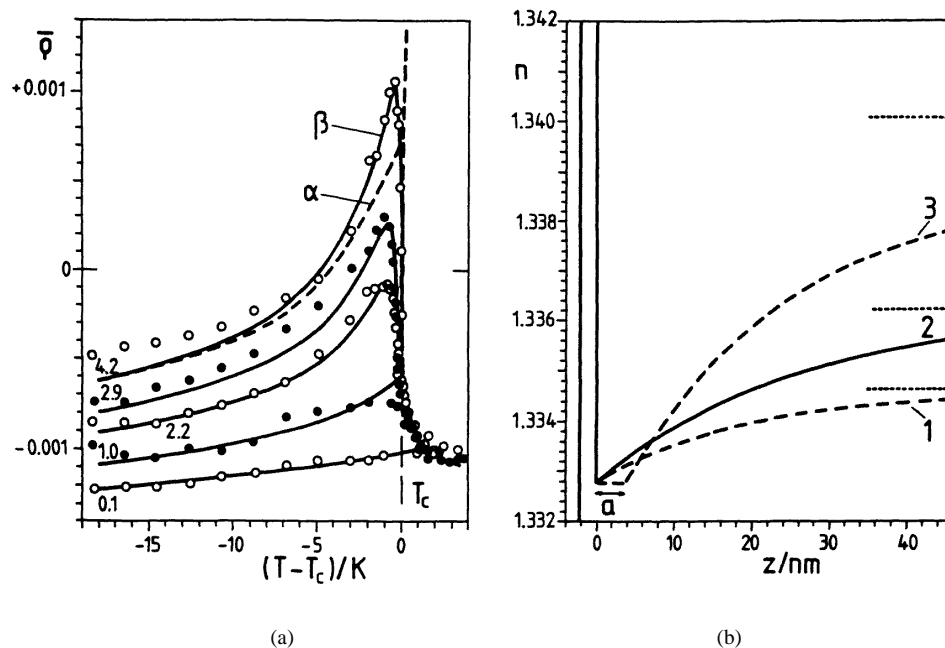
Figure 1. (a) The temperature dependence of the ellipticity $\bar{\rho}$ for samples of increasing concentration (0.1, 1.0, 2.2, 2.9 and 4.2 wt% $C_{10}E_4$): experimental data ($\bigcirc$, $\bullet$) and results of calculations based on model refractive-index profiles plus the capillary-wave contribution (curves). The vertical line marks the critical temperature T_c. (b) Model refractive-index profiles for the samples with 1.0 wt% $C_{10}E_4$ (1), 2.2 wt% $C_{10}E_4$ (2) and 4.2 wt% $C_{10}E_4$ (3) at a temperature $T_c - T = 2$ K. Note the region of thickness a in curve (3) corresponding to the incipient β-phase. The dashed curve in (a) marked α is obtained if this region is omitted in the model refractive-index profile.

below T_b and falls off steeply beyond the maximum. The ellipticity data for the two-phase region above T_c pertain to the surface of the surfactant-rich phase (which has a somewhat lower mass density than the water-rich phase and thus forms the *upper* phase); here, the $\bar{\rho}$-values for samples of different compositions must join a common curve, as is indeed observed within experimental accuracy. In the two-phase region, a slow upward drift of $\bar{\rho}$ was generally observed for the thermostated samples over periods of days, from the values given in figure 1(a) toward less negative values. Gentle shaking caused $\bar{\rho}$ to return to the original value, and small droplets were seen to form just below the free surface and falling through the upper phase. Similar phenomena have been observed previously for a different system (cyclohexane + methanol) by Beaglehole [4] and by Bonn *et al* [5]. These observations indicate that a macroscopically thick layer of the water-rich phase is forming at the surface of the surfactant-rich phase, as is to be expected if the surfactant-rich phase has a higher surface tension than the water-rich phase. In this case a water-rich film (the incipient β-phase) of mesoscopic thickness a will form at the surface of the undersaturated surfactant-rich solution on approaching bulk coexistence ($T \rightarrow T_b$). This conjecture is supported by model calculations for $\bar{\rho}$ based on model refractive-index profiles $n(z)$ of the surface region, as outlined below.

The refractive-index profile is modelled by assuming a surfactant monolayer at the outer surface, followed by a water-enriched region which decays slowly to the composition of the bulk phase (see figure 1(b)). For near-critical compositions near T_c one expects that this

slow decay will scale with ξ, the correlation length of the critical fluctuations in the bulk phase. The following model profile was chosen for the liquid side of the interface ($z > 0$):

$$n(z) = n_b - (n_b - n_w) \exp(-z/\xi) \qquad (2)$$

where n_w is the refractive index of water. The correlation length $\xi = \xi(T, w)$ was derived from complementary measurements of the turbidity in the relevant temperature and concentration range. At the critical composition for $T < T_c$ the turbidity data were analysed using the formalism given by Calmettes *et al* [6], which is based on the power law

$$\xi(t) = \xi_0^+ t^{-\nu} \qquad (3)$$

with $t = (T_c - T)/T_c$ and $\nu = 0.63$. This analysis yields $\xi_0^+ = 1.03 \pm 0.05$ nm, in agreement with the value 1.07 ± 0.05 nm reported by Hamano *et al* [7]. Values of ξ at non-critical compositions (where ξ remains finite for $T \to T_b$) were also derived from turbidity measurements and are given elsewhere [3]. Due to the slow decay of the refractive-index profile (2) near the critical point, the approximated Drude equation (1) is no longer applicable in this regime. A numerical algorithm for calculating $\bar{\rho}_i$ for arbitrary refractive-index profiles based on the full optical theory has been used [8]. The appearance of a maximum in $\bar{\rho}$ below T_c at near-critical and supercritical concentrations w (see figure 1(a)) is a signature of such a slow decay of $n(z)$ for $z \to \infty$ in the critical region, as is $\bar{\rho}_i$ being no longer a linear function of the width of the inhomogeneous region when the width d of the interface approaches the wavelength of light ($d/\lambda \to 1$). The outer region of the liquid/gas interface ($z < 0$) with the oriented monolayer of $C_{10}E_4$ was modelled by a refractive-index profile exhibiting a step from $n(z) = 1$ at $z \leqslant -z_m$ to a 'box' consisting of a hydrocarbon-like layer (thickness $l_C = 0.6$ nm, refractive index $n_C = 1.405$) and an inner layer ($l_E = 1.50$ nm, $n_E = 1.374$) accounting for the hydrated oligo(oxyethylene) chains ($l_C + l_E = |z_m|$). Furthermore, it was assumed that the ellipticity of the interface is a sum of the term $\bar{\rho}_i$ resulting from the intrinsic profile and a capillary-wave contribution $\bar{\rho}_{cw}$ [9]:

$$\bar{\rho}_{cw} = \frac{3\pi kT(n_b^2 - 1)}{8\lambda(n_b^2 + 1)^{1/2}} \frac{1}{\sqrt{\sigma K}} \qquad (4)$$

where σ is the surface tension and K the bending elastic modulus of the surfactant monolayer; both quantities were taken to be independent of composition: $\sigma/\text{mN m}^{-1} = 32.3 - 0.172(T/\text{K} - 273)$, $K = 0.76$ kT [10].

Results for the calculated ellipticity $\bar{\rho} = \bar{\rho}_i + \bar{\rho}_{cw}$ are shown in figure 1(a) (full and dashed curves). Note that all relevant temperature-dependent and concentration-dependent quantities needed in the calculation of $\bar{\rho}$ (namely, the correlation length ξ and the refractive indices of the bulk phases) were already known from complementary measurements. The parameters needed to model the (nearly) constant background ($\bar{\rho}_{cw}$ and the short-range part of $\bar{\rho}$) are based on reasonable estimates and only a single parameter (n_E) was adjusted to obtain a good fit of the experimental ellipticity for the most dilute solution ($w = 0.1$ wt% $C_{10}E_4$) at a temperature well below T_b. On this basis a reasonably good fit of the experimental ellipticities at higher concentrations including the critical concentrations is achieved, as is to be seen in figure 1(a). However, the very pronounced temperature dependence of $\bar{\rho}$ at the highest concentration ($w = 4.2$ wt%) near T_b is underestimated by this model (the dashed curve marked α). As outlined in the introduction, it is this region in which one expects a water-rich film of growing thickness a to form as T approaches T_b. This *incipient β-phase* was modelled by assuming a layer of refractive index $n_w = 1.333$ and a temperature-dependent thickness a:

$$a = a_0 \exp[2(T_b - T)^{1/2}] \qquad (5)$$

with $a_0 = 25$ nm. With this *ad hoc* assumption a good fit of the $\bar{\rho}$-data for the concentrated sample is achieved (the full curve marked β in figure 1(a)).

3. Discussion

A remarkable qualitative result of this study emerges immediately from the observation of a positive temperature dependence of $\bar{\rho}$. This finding can be traced back to the appearance of a water-enriched layer near the surface of the surfactant solution, growing in thickness as temperature increases. We conjecture that this water-enriched layer is induced by an *autophobic effect* caused by the oriented monolayer of surfactant molecules at the surface, which makes the inner side of this monolayer strongly hydrophilic. This autophobic effect is expected to prevail generally for surfactant monolayers at the water surface. However, in the proximity to a liquid/liquid phase separation of the surfactant solution it will be amplified by the generic features of wetting phenomena. Generally one expects at compositions and temperatures near the coexistence of two liquid phases (α and β) that a β-like layer will grow at the surface of the α-like phase, when α has a higher surface tension than β. In the present case we have identified α as the surfactant-rich phase and β as the water-rich phase, and the pronounced temperature dependence of $\bar{\rho}$ on the surfactant-rich side is shown to be a signature of the growing thickness of the β-like layer at the surface of the α-phase as T approaches T_b. This interpretation of the ellipticity data in the one-phase region near the two-phase coexistence is consistent with direct observations of the wetting behaviour reported by Kahlweit and Busse [11] who studied the system C_8E_3 + water and observed wetting of the surface of the surfactant-rich phase by the water-rich phase at two-phase coexistence. Such a behaviour implies a positive relative adsorption of water and thus a negative relative surface excess amount of the surfactant ($\Gamma_2^{(1)} < 0$) at the surface of surfactant-rich solutions, which means that the positive surface excess arising from the surfactant monolayer must be outweighed by the surfactant depletion in the water-rich layer underneath the monolayer. This situation arises generally as the thickness of the water-rich layer increases on approaching bulk coexistence of the surfactant-rich phase with the water-rich phase.

The present work also shows that the ellipticity data can be fitted quantitatively by modelling $\bar{\rho}$ as a sum of a nearly temperature-independent and concentration-independent background terms (accounting for surface roughness and the surfactant monolayer) and a term accounting for the slow decay of the refractive-index profile on the liquid side of the interface. This long-ranged tail of the profile is shown to scale with the correlation length ξ and can be represented by equation (2) without adjustable parameters. The ellipticity data $\bar{\rho}(T)$ at near-critical compositions are also consistent with a profile function based on the Liu–Fisher scaling function for critical adsorption [12, 13], $P(x) = (x^{-1} + c)^{\beta/\nu} \exp(-x)$, with $x = z/\xi$. However, a good fit of the experimental data with this profile function is achieved only when one adopts an unreasonably large value of the c-parameter ($c \approx 10$), which suppresses the algebraic $z^{-\beta/\nu}$-dependence of the profile which is a signature of critical adsorption. Thus the present analysis suggests that the slowly decaying part of the composition profile in samples of near-critical composition is dominated by effects other than critical adsorption, possibly due to the existence of micellar aggregates [14]. The very pronounced increase of $\bar{\rho}$ seen at concentrations $w > w_c$ for $T \rightarrow T_b$ is compatible with the expected formation of a water-rich layer. This has been shown in an *ad hoc* manner by inserting into the model refractive-index profile a layer of constant refractive index $n = n_w$ and thickness a which is an increasing function of $T_b - T$. For the pure wetting regime well away from the critical composition, one expects the thickness of the wetting layer to

grow as $(T_b - T)^{-1/3}$, as $T_b - T$ is proportional to the distance from two-phase coexistence in terms of the chemical potential difference of the two species [15]. Further measurements are required to gain a better understanding of the crossover region from critical adsorption, where the interface width is determined by the correlation length ξ, to the pure wetting regime.

Acknowledgments

References

[1] Hirtz A, Bonkhoff K and Findenegg G H 1993 *Adv. Colloid Interface Sci.* **44** 241
[2] Drude P 1959 *The Theory of Optics* (New York: Dover)
[3] Hirtz A 1993 *PhD Thesis* Technische Universität Berlin
[4] Beaglehole D 1983 *J. Phys. Chem.* **87** 4749
[5] Bonn D, Kellay H and Wegdam G H 1992 *Phys. Rev. Lett.* **69** 1975; 1993 *J. Chem. Phys.* **99** 7115
[6] Calmettes P, Lagues I and Laj C 1972 *Phys. Rev. Lett.* **28** 478
[7] Hamano K, Kuwahara N, Mitsushima I, Kubota K and Kamura T 1991 *J. Chem. Phys.* **94** 2172
[8] Süssmann R and Findenegg G H 1989 *Physica* A **156** 114
[9] Meunier J 1987 *J. Physique* **48** 1819
[10] Meunier J and Lee L T 1991 *Langmuir* **7** 1855
[11] Kahlweit M and Busse G 1989 *J. Chem. Phys.* **91** 1339
[12] Liu A J and Fisher M E 1989 *Phys. Rev.* A **40** 7202
    Flöter G and Dietrich S 1995 *Z. Phys.* B **97** 213
[13] Hirtz A, Lawnik W and Findenegg G H 1990 *Colloids Surf.* **51** 405
[14] Strunk H, Lang P and Findenegg G H 1994 *J. Phys. Chem.* **98** 11 557
[15] Dietrich S 1991 *Phase Transitions in Surface Films 2 (Nato ASI Series B, vol 267)* ed H Taub, G Torzo, H J Lauter and S C Fain (New York: Plenum) p 391