Unequivocal Evidence for a Liquid−Gas Phase Transition in Monolayers of Decanol Adsorbed at the Air/Water Interface

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The rich phase behavior of insoluble monolayers spread at the air/water interface is well documented.[1−3] The pioneering surface tensiometry work of Pockels[4] and Langmuir[5] has advanced over the past century as more phases have been identified and their structures elucidated in ever greater detail with techniques such as grazing incidence X-ray diffraction.[6] The simplest two-dimensional (2D) phase transition, from a gas to a liquid, occurs when an insoluble monolayer below its critical temperature is compressed from zero surface pressure. It is now generally accepted that the liquid−gas transition in insoluble monolayers is first order in nature.[7] In this paper, we provide unequivocal evidence for a first-order liquid−gas phase transition in monolayers of soluble surfactants.

For practical applications, soluble surfactants are much more widely used than insoluble monolayers. Soluble surfactants adsorb at the air/water interface to form monolayers in equilibrium with the bulk solution. A change in phase in an adsorbed monolayer can lead to a dramatic change in interfacial properties, such as surface viscosity[8] and foam drainage,[9] but until recently few phase transitions had been observed in adsorbed, equilibrium monolayers at the air/water interface. There is now firm evidence for transitions between condensed phases in a number of systems.[10−13] The most detailed studies have been on monolayers of medium-chain alcohols (C_9−C_{14}) on water, which show a clear first-order phase transition from a crystalline solid to a liquid at well-defined temperatures.[10,11]

Historically, there were good reasons for suspecting that monolayers of common soluble amphiphiles would be above their 2D critical point at room temperature and hence would not exhibit a liquid−gas phase transition. Early measurements on lauric acid [$CH_3(CH_2)_{10}CO_2H$] monolayers suggested that they were super-critical at 15 °C,[14] and careful measurements by Pallas and Pethica showed that the critical temperature of insoluble monolayers of the longer chain homologue, pentadecanoic acid, was only 50−60 °C.[15] Furthermore, theoretical models of 2D van der Waals fluids yield a critical temperature that is $^1/_2$ that of the analogous
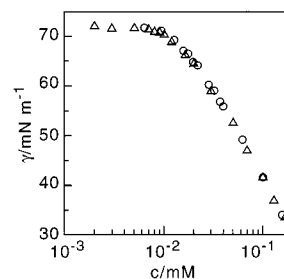

Figure 1. Equilibrium surface tension for decanol solutions at 22.7 °C reprinted from Lin, S. Y.; Hwang, W. B.; Lu, T. L. Adsorption kinetics of soluble surfactants and the phase transition model 2. Experimental demonstration of 1-decanol. *Colloids Surf., A* **1996**, *114*, 143 with permission from Elsevier Science.

3D fluid.[16] In 1984 however, Motomura reported surface tension measurements on a number of soluble surfactants that apparently showed a kink in the surface tension−concentration (γ−c) isotherm at low concentrations.[17] This kink was interpreted as evidence for a first-order phase transition in the monolayer, although other workers disputed these results.[18] More recently, Lin and co-workers have shown that the equilibrium and dynamic adsorption behavior of decanol at the air/water interface is better described by a phase-transition model than by a Frumkin isotherm,[19−21] though definitive proof of a phase transition is lacking.

There is a fundamental problem in the use of equilibrium surface tension measurements to observe a first-order liquid−gas phase transition. A first-order transition requires a discontinuity in $d\gamma/dc$ (or equivalently $d\gamma/d \ln c$), or a change in slope (a kink) in the γ−c isotherm. It is difficult to demonstrate the existence of a kink convincingly in a region where $d\gamma/dc$ is changing rapidly with concentration. Figure 1 shows the equilibrium surface tension obtained by Lin and co-workers for decanol solutions at the air/water interface.[21,22] From these data, it is impossible to decide whether the data show a phase transition at $c = 0.01$ mM or simply a rapid change in slope without an actual discontinuity. In this paper, we use ellipsometry to show unequivocally that decanol monolayers do indeed exhibit a first-order liquid−gas phase transition.

Ellipsometry is a highly sensitive technique for the measurement of the optical properties of thin films.[23] We have carried out measurements on decanol solutions using light incident at the Brewster angle, θ_B, which is defined as the angle where $\text{Re}(r_p/r_s) = 0$ (r_p and r_s are the reflection coefficients for p- and s-polarized light, respectively). We report the coefficient of ellipticity, $\bar{\rho} = \text{Im}(r_p/r_s)$ at θ_B. For thin films, $\bar{\rho}$ depends on a single parameter, η

$$\bar{\rho} = \frac{\pi}{\lambda} \frac{\sqrt{\epsilon_1 + \epsilon_2}}{\epsilon_1 - \epsilon_2} \eta \tag{1}$$

The ellipsometric thickness, η, characterizes the profile of the

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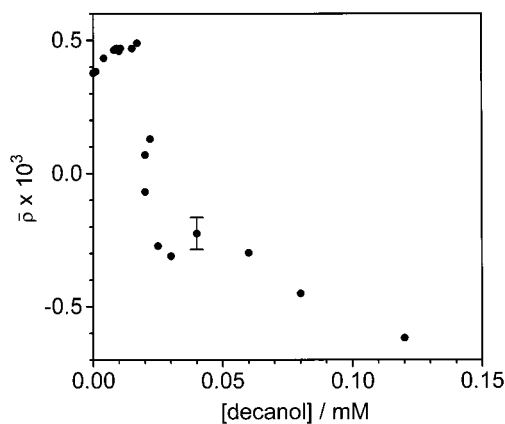(22) Lin, S. Y.; Lu, T. L.; Hwang, W. B. *Langmuir* **1995**, *11*, 555.

Figure 2. The coefficient of ellipticity of monolayers of decanol as a function of the bulk concentration at 25 °C. The error bars in the gas phase lie within the symbols. A representative error bar obtained from repeated measurements on freshly prepared solutions in the liquid phase is shown.

dielectric constant, ϵ, through the interface

$$\eta = \int \frac{(\epsilon - \epsilon_1)(\epsilon - \epsilon_2)}{\epsilon}\,dz \qquad (2)$$

where ϵ_1 and ϵ_2 are the dielectric constants of air and water, respectively.[24] As ϵ is determined by the density of the monolayer,[25] a first-order phase transition is manifested by a discontinuous change in $\bar{\rho}$. It is thus much easier to detect phase transitions by ellipsometry than by surface tensiometry.

Figure 2 shows $\bar{\rho}$ as a function of the bulk decanol concentration at a temperature of 25 °C.[26] At low concentrations of decanol, $\bar{\rho}$ rises above the value obtained for pure water ($\bar{\rho}_{H_2O} = +0.38 \times 10^{-3}$). This change implies that the surface layer has a dielectric constant intermediate between that of the air and water, as would be expected for a gaseous phase.[27] At a concentration of 0.018 mM there is a discontinuous change in $\bar{\rho}$, which falls to a negative value, indicating that the surface layer now has a dielectric constant greater than that of water, as would be predicted for a liquid hydrocarbon. As the bulk concentration of decanol is increased further, $\bar{\rho}$ continues to decrease slowly, indicating a gradual increase in surface coverage in the liquid phase, as would be expected. The concentration at which we observe the liquid−gas phase transition is slightly higher than the value of 0.01 mM, estimated by Lin and co-workers from surface tension data at 22.7 °C.[21]

Slightly above the concentration at which the phase transition occurs (at 0.020 and 0.022 mM), the ellipsometric readings appear

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(24) There is a contribution to $\bar{\rho}$ from the roughness of the interface. This contribution scales as $\gamma^{-1/2}$ and does not change across the liquid−gas phase transition since γ itself is continuous.

(25) The Clausius−Mossotti equation expresses ϵ in terms of the number density of molecules, N, and the molecular polarisability, α: $(\epsilon - 1)/(\epsilon + 2) = N\alpha/3\epsilon_0$ (Atkins, P. W. *Physical Chemistry*, 4th ed.; Oxford University Press: Oxford, 1990; p 650).

(26) The *n*-decanol (>99%, Larodan) was used as received. The water was ultrahigh purity (Elga UHQ). The temperature was controlled to ±0.5 °C. A phase-modulation ellipsometer (Beaglehole Instruments) was employed.

(27) To model $\bar{\rho}$ in the gas phase, we have treated the decanol molecules as cylinders of diameter 5 Å lying flat on the water surface and used the Clausius−Mossotti equation to calculate ϵ as a function of coverage, Γ. Isotropic and anisotropic models of the polarisability give values of $\bar{\rho}$ due to the monolayer that differ by less than 10%. The calculated curve, $\bar{\rho}(\Gamma)$, reproduces the form of the experimental data with the phase transition occurring at a gas density of ∼2000 Å^2 molecule^{-1}. Lin and co-workers suggest an area per molecule of ∼345 Å^2 at the phase transition. This difference may arise because the decanol molecules are partially immersed in the water phase, which would have the effect of decreasing the value of $\bar{\rho}$ for a given surface coverage.
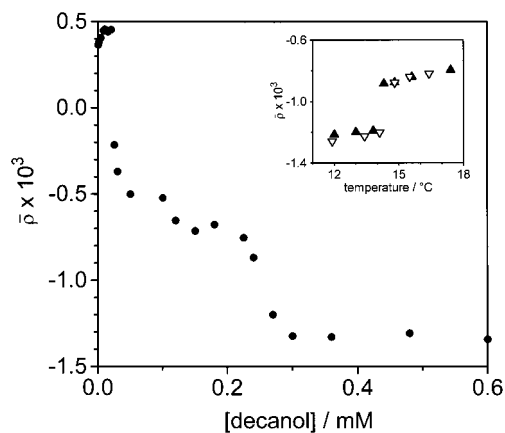

Figure 3. The coefficient of ellipticity of monolayers of decanol as a function of the bulk concentration at 10 °C. The inset shows the coefficient of ellipticity of a saturated solution of decanol as a function of temperature to demonstrate the solid−liquid phase transition at 14.5 °C. The closed triangles represent a heating cycle, and the open triangles a cooling cycle.

to indicate an intermediate value between the liquid and gaseous phases. These readings were stable over a 20-minute period. At the phase transition the transfer of decanol molecules to the monolayer from the dilute solution causes a significant change in the bulk concentration. The bulk solution becomes depleted until the concentration reaches the value at which the two phases are in equilibrium. The monolayer is then composed of domains of both 2D gas and liquid, and the measured value of $\bar{\rho}$ is intermediate between that of the pure gaseous and liquid monolayers. At such low concentrations, slow diffusion kinetics mean that the time required to reach true equilibrium would be very long, even in the presence of an infinite reservoir of bulk solution.[28] We did not detect sharp fluctuations in $\bar{\rho}$, indicating that any domains were much smaller than the size of the laser beam on the surface (∼1 mm^2).

It is well-known that saturated solutions of decanol show a first-order liquid−solid phase transition when the temperature is lowered past 14.5 °C (inset in Figure 3).[10,11] We would therefore expect to see two phase transitions in adsorption isotherms below 14.5 °C. Figure 3 shows $\bar{\rho}$ as a function of concentration for decanol solutions at 10 °C. As expected, two phase transitions are observed: the gas−liquid transition at a concentration of 0.022 mM and the liquid−solid transition at 0.25 mM. The values of $\bar{\rho}$ above and below the liquid−solid phase transition are in good agreement with those observed in the thermal transition.

In summary, we have used ellipsometry to demonstrate the existence of a 2D first-order liquid−gas phase transition at the surface of decanol solutions. The change in $\bar{\rho}$ across the gas−liquid phase transition was comparable at the two temperatures studied, suggesting that the two-dimensional critical temperature for decanol monolayers is well above room temperature. A very recent study by Riegler and co-workers has shown that monolayers of volatile hydrocarbons (such as heptane) condensed onto water show a liquid−gas-phase transition during the growth of the film.[29] This work gives powerful support to the notion that liquid−gas-phase transitions may be widespread in monolayers of soluble surfactants.

(28) For planar diffusion to the interface, the characteristic diffusion time, t_D, is given by: $t_D = [(\Delta\Gamma/\Delta c)^2]/2D$, where $\Delta\Gamma$ is the change in surface excess at the phase transition, Δc the supersaturation of the bulk solution and D is the diffusion coefficient. For $\Delta\Gamma \approx 5 \times 10^{-6}$ mol m^{-2}, $\Delta c \approx 2 \times 10^{-3}$ mol m^{-3} and $2D = 10^{-9}$ m^2 s^{-1}, we find $t_D \approx 2$ h.

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