

Observation of G–LE and LE–LC Phase Transitions of Adsorbed 1-Dodecanol Monolayer from Dynamic Surface-Tension Profiles

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Two phase transitions, G–LE and LE–LC, of the adsorbed monolayer of the soluble surfactant 1-dodecanol at the air–water interface were observed from the dynamic surface tension measurement by using a pendant bubble tensiometer. Two constant surface-tension (γ) regions were detected in the dynamic surface-tension $\gamma(t)$ profiles of different surfactant concentrations at 20 °C. They are at $\pi = 0.75$ and 17.9 mN/m. A constant γ region in dynamic $\gamma(t)$ profiles indicates the existence of a 2D phase transition. These 2D phase transitions of adsorbed layer are presumed to be the coexistence of the gas (G) and liquid-expanded (LE) phases and that of the LE and liquid-condensed (LC) phases. A new phase-transition isotherm, which is possible to describe the 1-dodecanol adsorbed monolayer, is also proposed.

1. Introduction

Phase transitions of a spreading (Langmuir) monolayer of insoluble surfactants are well known. Recently, theoretical and experimental studies have provided evidence that the adsorbed layer (Gibbs monolayer) of surfactants dissolved in the aqueous phase can have a first-order transition. The adsorbed monolayer of soluble surfactants can exist in gaseous (G), liquid-expanded (LE), liquid-condensed (LC), and solid (S) states. The possible phase transition, therefore, includes G–LE, LE–LC, LC–S, G–LC, G–S, and LE–S transitions.

Pollard et al.¹ presented evidence for $G \rightarrow LE \rightarrow LC$ monolayer phase transitions, using fluorescence microscopy and tensiometry, for the slightly water-soluble poly(ethylene glycol) alkyl ether surfactants $C_{14}E_1$ and $C_{16}E_2$. They confirmed the LE–LC coexistence at π near 20 mN/m and revealed the G–LE coexistence at low π for $C_{14}E_1$. The transition leads to a plateau in the dynamic surface-tension $\gamma(t)$ profiles.

Subramanyam and Maldarelli² presented fluorescence images verifying the G–LE phase transition for $C_{14}E_6$ during a clean interface adsorption. An induction period in the surface-tension relaxation was observed that as the adsorption begins the tension remains near the clean interface value for an extended period of time before decreasing rapidly to the equilibrium value.

Motschmann and Lunkenheimer³ measured the equilibrium surface tension of an anionic, water-soluble sulfonate surfactant at the air–water interface. They presented that a Frumkin adsorption isotherm with a critical interaction parameter could fit the equilibrium γ data well; therefore, a G–LE phase transition at π near 2 mN/m was concluded. It was concluded that the major structural difference between the two phases is the amphiphile's molecular orientation.

Casson and Bain⁴ observed a discontinuous change in the coefficient of ellipticity on the adsorbed 1-decanol monolayer at $C = 0.018$ mM at 25 °C. It was concluded that a liquid–gas phase transition exists at the air–water interface at 25 °C; furthermore, they proposed two phase transitions at 10 °C from the ellipticity data: a gas–liquid transition at $C = 0.022$ mM and a liquid–solid transition at 0.25 mM.

Tomassone et al.⁵ theoretically predicted the G–LE transition of an adsorbed monolayer using molecular dynamic (MD) simulations. A plateau exists in the surface-tension profile as a function of surface coverage from the theoretical simulation.

Braun et al.⁶ had observed a first-order transition of the Langmuir monolayer of 1-undecanol using sum-frequency vibrational spectra and an ellipsometer.⁶ Melzer et al.⁷ reported that the adsorbed Gibbs monolayer and the spread Langmuir monolayer show similar crystal structures, morphological textures, and thermodynamic properties.

Vollhardt et al.⁸ measured the dynamic surface tension of a 1-dodecanol aqueous solution. A characteristic break point in the $\pi(t)$ curve was observed at π around 4–10 mN/m, depending upon solution concentration and the temperature. It was concluded that this characteristic break point indicates a phase transition for the adsorbed monolayer. The BAM (Brewster angle microscope) image confirmed the formation and the growth of a condensed 2D phase domain after the surface transition point.^{8,9} After the break point, a slow surface pressure increase, not a constant π region, was observed.

However, no equilibrium surface-tension data has been reported in the literature for 1-dodecanol solutions; furthermore, two open questions are still left: Does a constant surface-tension (pressure) region at the phase transition exist, especially at the G–LE transition, in the dynamic surface tension profile, and, is there an abrupt slope change in the equilibrium surface-tension (π vs $\log C$) curve at the corresponding bulk concentrations where the phase transition (G–LE or LE–LC) takes place.

The aim of this work is to study the above two questions. 1-Dodecanol is chosen as the model compound for investigating

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the phase transitions of the Gibbs monolayer. A pendant bubble tensiometer¹⁰ was utilized for the dynamic and equilibrium surface-tension measurement because it is capable for the measurement of 0.5 s to several hours.

2. Experimental Measurements

Materials. The nonionic surfactant 1-dodecanol $\text{CH}_3(\text{CH}_2)_{11}\text{OH}$ purchased from Fluka (purity >99.5%) was used without further modification. The aqueous solutions were prepared with clean water purified via a Barnstead NANOpure water purification system with the output water having a specific conductance of $<0.057 \mu\Omega^{-1}/\text{cm}$.

Tensiometer. A pendant bubble tensiometer that was enhanced by video digitization was employed for the measurement of the dynamic surface tension $\gamma(t)$ and the equilibrium surface tension $\gamma(C)$ of 1-dodecanol. The apparatus and the edge detection routine have been described in detail in previous studies.^{10,11} The temperature variation of aqueous solution was $<\pm 0.05 \text{ K}$.¹¹ A 17-gauge stainless steel inverted needle (1.07-mm i.d.; 1.47-mm o.d.) was used for the bubble generation. The value of the surface tension of the air–water interface, using the pendant bubble technique, was 72.75 mN/m at $20.0 \pm 0.1^\circ\text{C}$.

Surface Tension. A pendant bubble of air with a diameter of ca. 2 mm was formed in a 1-dodecanol aqueous solution, which was put in a quartz cell of size $2.6 \times 4.1 \times 4.3$ (height = 4.3) cm inside. Digital images of the bubble were taken sequentially and then processed to determine the surface tension. The time required to create an air bubble in this work was about 1.46 s; therefore, 0.73 s (half of the formation time) was added to evaluate a more accurate surface age. Note that Taylor et al. had proposed that the choice of $t = 0$ to correct for the adsorption of the surfactant to the growing bubble is $2/3$ of the bubble growth time.¹²

The edge coordinates of pendant bubble are best fit with the theoretical shape generated from the classical Laplace equation. The accuracy and reproducibility of the γ measurements are ca. 0.1 mN/m .¹³

The measurement was performed at 20°C for different bulk concentrations (5.0×10^{-10} to $1.06 \times 10^{-8} \text{ mol/cm}^3$), and each sample was repeated 2 to 5 times. The bubbles were measured up to around 3 to 10 h, depending on the 1-dodecanol concentration, until the adsorption reached the equilibrium state. The equilibrium surface tension was then extracted from the long-time asymptotes¹⁰ of the dynamic surface-pressure $\pi(t)$ curves.

3. Adsorption Isotherm

Surfactant molecules with long, slender hydrocarbon chains and small polar groups are subject to strong, attractive van der Waals forces when surface crowding causes interchain contact. To account for this cohesion, the well-known Frumkin isotherm and a phase-transition model are utilized for describing the molecular interaction and/or the phase transition behavior between the adsorbed 1-dodecanol molecules. The phase-transition model consists of a Henry isotherm, working at dilute concentrations, and a Frumkin isotherm, working at more elevated concentrations.

Frumkin Isotherm. The Frumkin model utilizes the Langmuir formalism and assumes that the rate of mass transport across the interface depends on the activation energies of the adsorption and desorption processes.^{10,14} The activation energies are proportional to surface concentration Γ . When the adsorption

process reaches equilibrium, the surface concentration and bulk concentration are related by

$$\frac{\Gamma}{\Gamma_\infty} = x = \frac{C}{C + a \exp(Kx)} \quad (1)$$

where C denotes the bulk concentration, Γ is the surface concentration, Γ_∞ is the maximum surface concentration, K takes into account the molecular interaction between the adsorbed 1-dodecanols, and a indicates the surfactant activity. The presence of cohesive intermolecular forces, which lower the desorption rate at increasing Γ , is described by $K < 0$.^{14–16} Alcohols with long hydrocarbon chains are found to have a cooperative adsorption.

For an ideal solution, the Gibbs adsorption equation $d\gamma = -\Gamma RT \ln C$ and the equilibrium isotherm (eq 1) allow for the calculation of the surface tension

$$\gamma - \gamma_0 = \Gamma_\infty RT \left[\ln(1 - x) - \frac{Kx^2}{2} \right] \quad (2)$$

where γ_0 is the surface tension of pure water. By fitting the data of $\gamma(C)$, the model constants (K , a , and Γ_∞) result. When the parameter of molecular interaction K equals to its critical value ($K_C = -4$) from the fit with the data, the Frumkin adsorption isotherm predicts a phase transition of the adsorbed monolayer.

Phase-Transition Model. To account for the strong, attractive van der Waals forces between the long, slender hydrocarbon chains of 1-dodecanol, a phase-transition model was constructed.¹⁷ In this model, intermolecular attraction among the slender hydrocarbon chains of the adsorbed 1-dodecanol existing in the gaseous state (G) leads to the formation of a separate liquid-type phase, a liquid-expanded (LE) phase. Prior to the critical surface coverage (Γ_{gc}), intermolecular attraction is not significant, except for coverage in the immediate vicinity of Γ_{gc} ; therefore, the adsorbed state is essentially gaseous. Two Langmuir models, with different surfactant activity, were used to describe the behavior of the G and LE phases, respectively.¹⁸

In this work, the two isotherms used are Henry and Frumkin for the G and LE phases, respectively. In the gaseous phase, surfactant molecules are far away from each other. It is reasonable to apply the Henry isotherm for the G phase. When surfactant molecules crowd the air–water interface, the Frumkin isotherm, instead of the Langmuir one, is applied to predict its behavior because the molecular interaction of the adsorbed 1-dodecanol is very significant.

For the adsorbed 1-dodecanol monolayer, the surface pressure (π_C) that corresponds to Γ_{gc} is only 0.75 mN/m ; therefore, at dilute surface concentration, where $\Gamma < \Gamma_{gc}$, the adsorption rate may be approximately described by a Henry model

$$\frac{d\Gamma_G}{dt} = \beta_G C_S \Gamma_\infty - \alpha_G \Gamma_G \quad (3)$$

$$\Gamma_G = HC \quad (4)$$

where Γ_G is the surface monomer concentration in gaseous phase, C_S is the subsurface concentration, and $H (= \beta_G \Gamma_\infty / \alpha_G)$ is the Henry constant, which takes into account the surfactant activity of the gaseous 1-dodecanol monomer.

At the critical surface coverage (Γ_{gc}), aggregation commences, and a liquid-expanded-type phase (LE) begins to develop at the air–water interface and coexists with the gaseous monomer phase. It is assumed that as more surfactants are added to the

system in a quasistatic series of equilibrium states the liquid-expanded phase grows at the expense of the gaseous phase with the surface tension and bulk sublayer concentration remaining fixed. It is a first-order phase transition for the formation of the LE phase because the surface tension remains fixed. With continuing addition of surfactant, the gaseous phase disappears completely (where $\Gamma = \Gamma_{lc}$), and the surface coverage is uniform and of the liquid-expanded type.

The liquid-expanded phase is presumed compressible, and the attractive van der Waals forces are significant between the adsorbed 1-dodecanol molecules. To describe molecule exchange between this phase and the subsurface of the bulk, we used a Frumkin model with the same limiting area per molecule, $(N\Gamma_\infty)^{-1}$, as the gaseous phase; thus,

$$\frac{d\Gamma_L}{dt} = \beta_L \exp\left(\frac{-\nu_{aL}\Gamma_L}{RT}\right) C_s (\Gamma_\infty - \Gamma_L) - \alpha_L \exp\left(\frac{-\nu_{dL}\Gamma_L}{RT}\right) \Gamma_L \quad (5)$$

$$\frac{\Gamma_L}{\Gamma_\infty} = x_L = \frac{C}{C + a_L \exp(K_L x_L)} \quad (6)$$

where β_L and α_L are the rate constant of adsorption and desorption processes, $K_L = (\nu_{aL} - \nu_{dL})\Gamma_\infty/RT$, and $a_L (= \alpha_L/\beta_L)$ is the surfactant activity of the liquid-expanded type of 1-dodecanol.

In the phase-transition model, the equilibrium dependence of the surface tension on the bulk concentration may be obtained from the Gibbs adsorption equation ($d\gamma = -\Gamma RT \ln C$) and is summarized below

$$(i) C < C_C \quad (\Gamma < \Gamma_{gc}) \quad \gamma(C) = \gamma_0 - RTHC \quad (7)$$

$$(ii) C = C_C \quad (\Gamma_{gc} \leq \Gamma \leq \Gamma_{lc}) \\ \gamma(C_C) = \gamma_C = \gamma_0 - RTHC_C \quad (8)$$

$$(iii) C > C_C \quad (\Gamma > \Gamma_{lc})$$

$$\gamma(\Gamma) = \gamma_0 - RTHC_C - \Gamma_\infty RT \left[\ln\left(\frac{1-x}{1-x_{lc}}\right) - K \frac{x^2 - x_{lc}^2}{2} \right] \quad (9)$$

where $x_{lc} = \Gamma_{lc}/\Gamma_\infty$ and C_C is the bulk concentration corresponding to the critical surface coverage and is given by

$$\Gamma_{gc} = HC_C \quad (10)$$

$$\frac{\Gamma_{lc}}{\Gamma_\infty} = \frac{C_C}{C_C + a_L \exp(K_L x_{lc})} \quad (11)$$

where Γ_{gc} and Γ_{lc} are the critical surface coverage at which the liquid-expanded phase begins to develop and the gaseous phase disappears completely, respectively, at the surface.

There are five parameters in this Henry-Frumkin phase transition model: Γ_∞ (maximum surface concentration), H (Henry constant), C_C (critical bulk concentration), a_L (surfactant activity of 1-dodecanol at LE phase), and K (intermolecular interaction between the adsorbed 1-dodecanol). The bulk concentration applied for this phase-transition model is $< 4 \times 10^{-9}$ mol/cm³; therefore, the Gibbs adsorption equation (for ideal solutions), $d\gamma = -\Gamma RT \ln C$, is presumed to work. By fitting the data of $\gamma(C)$, the equilibrium constants (H , C_C , K , a , and Γ_∞) result.

4. Experimental Results

Surface Tension. Pendant bubbles of air were formed suddenly in 1-dodecanol solutions with different bulk concentra-

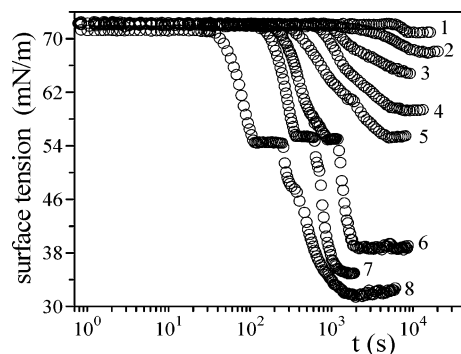


Figure 1. Representative dynamic surface tensions for the adsorption of 1-dodecanol onto a clean air-water interface for $C_0 =$ (1) 1.6, (2) 2.0, (3) 2.3, (4) 3.3, (5) 4.0, (6) 8.0, (7) 9.18, and (8) 10.6 (10^{-9} mol/cm³).

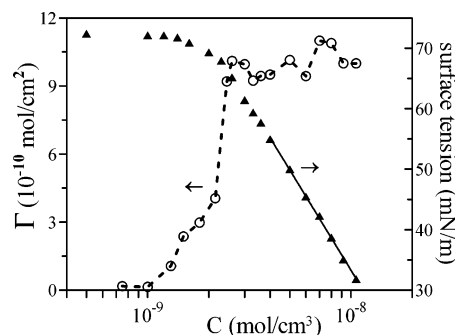


Figure 2. Experimental data of equilibrium surface tension measured by the pendant bubble tensiometer and the surface concentration Γ evaluated from the Gibbs adsorption equation.

tions. Bubble profiles were taken sequentially and processed to obtain the relaxation of the surface tension. Dynamic surface tension for the adsorption of 1-dodecanol onto a clean air-water interface was measured up to several hours. Shown in Figure 1 are representative dynamic surface-tension profiles (for one selected bubble at each bulk concentration) of solutions at eight different concentrations, $C = 1.6 \times 10^{-9}$ to 1.06×10^{-8} mol/cm³. The equilibrium surface tension was extracted from the long-time asymptotes for each concentration and is shown in Figure 2.

Constant Tension I. Curves 1 and 2 in Figure 1 were replotted in Figure 3 to detail the relaxation of the surface tension of 1-dodecanol solutions. A constant surface-tension region exists in the dynamic $\gamma(t)$ profiles. The constant γ region lasts for several thousands of seconds in the $\gamma(t)$ profiles shown in Figure 3 for $C = 1.6 \times 10^{-9}$ and 2.0×10^{-9} mol/cm³. A similar constant γ phenomenon was also observed for other $\gamma(t)$ profiles at $C = 1.4, 2.3, 2.6, 3.0, 3.3$, and 3.6×10^{-9} mol/cm³. At a higher bulk concentration, a shorter, constant γ region results, and the constant γ region starts early also; for example, the constant γ region starts at 20 s and ends at around 400 s for $C = 3.6 \times 10^{-9}$ mol/cm³.

The constant surface tension is 72.00 ± 0.10 mN/m (i.e., $\pi = 0.75$ mN/m) at 20 °C for 1-dodecanol aqueous solutions. A constant surface pressure in the dynamic $\gamma(t)$ profile represents a phase transition of the Gibbs monolayer at the air-water interface.^{1,2,7} At $\pi < 0.75$ mN/m, it is reasonable to assume that the 1-dodecanol at air-water interface is dilute and molecular interaction among them is insignificant; therefore, the adsorbed molecules behavior is similar to that of a 2D gas (G). At increasing surface coverage, $\pi \rightarrow 0.75$ mN/m, the surface coverage in the immediate vicinity of Γ_{gc} , intermolecular attraction among the slender hydrocarbon chains of the adsorbed

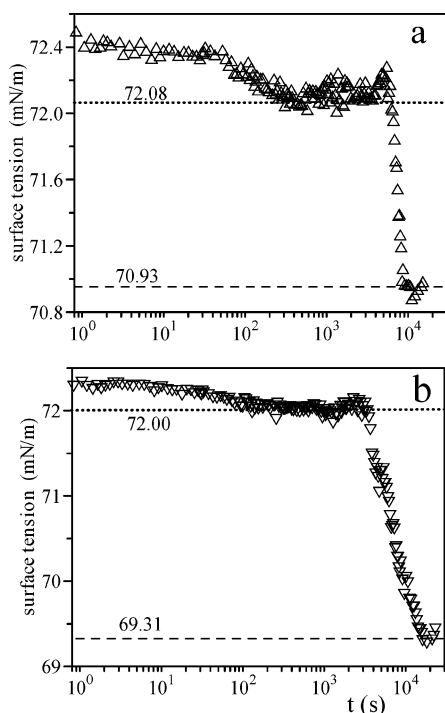


Figure 3. Dynamic surface tensions of 1-dodecanol for $C_0 =$ (a) 1.6 and (b) 2.0 (10^{-9} mol/cm^3) showing a region of the G–LE coexistence with constant surface tension.

1-dodecanol becomes significant and leads to the formation of a separate loose aggregation phase, a liquid-expanded (LE) phase.

In a regular γ relaxation profile, γ decreases from γ_0 (fresh surface tension) to γ_e (equilibrium surface tension) monotonically and smoothly without passing any constant γ region.¹⁰ The decrease of γ indicates an increase in surface concentration of small surfactant molecules adsorbing from bulk phase onto the air–water interface. Note that for a polymer surfactant the intramolecular interaction may cause a significant decrease in γ with a fixed surface concentration.¹⁹

The mass transport of small surfactant molecules from a uniform aqueous bulk phase to a suddenly created fresh air–water interface consists of two consecutive steps: diffusion in bulk phase and the adsorption/desorption between sublayer and interface. For a diffusion-limited process, the surface tension is uniquely dependent upon the surface concentration of surface-active agent because sublayer and interface are in thermodynamic equilibrium. Before reaching the equilibrium adsorption, the number of surfactant molecules at air–water interface will increase monotonically with time because of the continuous mass transport process of adsorption and bulk diffusion.

Only phase-transition behavior can allow for the existence of a constant surface-tension region at increasing surface concentration; furthermore, it lasts for several hundreds or thousands of seconds in this work. At the critical surface coverage (Γ_{gc}), aggregation commences, and the LE phase begins to develop at the air–water interface and coexists with the gaseous monomer phase. As more surfactants adsorb onto the interface, the LE phase grows at the expense of the G phase, with the surface tension and bulk sublayer concentration remaining fixed. With continuing addition of surfactant, the G phase disappears completely (where $\Gamma = \Gamma_{lc}$, another critical surface coverage), and the surface is uniform and of the LE type.

The equilibrium surface tension γ_e for $C = 1.2 \times 10^{-9} \text{ mol/cm}^3$ is 72.12 mN/m, and no constant γ region is detected in the

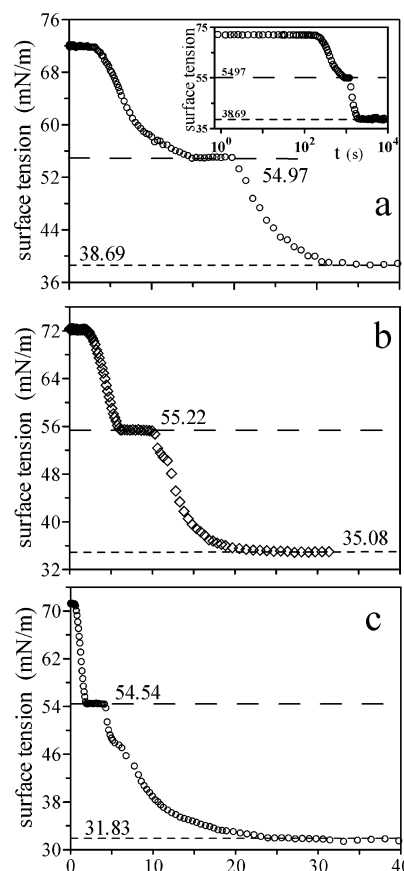


Figure 4. Dynamic surface tensions of 1-dodecanol for $C_0 =$ (a) 8.0, (b) 9.18, and (c) 10.6 (10^{-9} mol/cm^3) showing a region of the LE–LC coexistence with constant surface tension. X-axis is time in min.

dynamic $\gamma(t)$ profile. At $C = 1.4 \times 10^{-9} \text{ mol/cm}^3$, equilibrium, $\gamma_e = 71.78 \text{ mN/m}$, and a clear constant γ region, at $t = 500 \text{ s}$ to ca. 10^4 s , are observed in the $\gamma(t)$ profile. Figure 2 shows that the slope of the equilibrium surface-tension profile (γ_e vs $\log C$) begins to increase significantly at C of approximately $1.4 \times 10^{-9} \text{ mol/cm}^3$; however, the slope increase is not very significant because the surface concentration is still pretty low at this stage.

Constant Tension II. At more elevated bulk concentrations, the relaxation profiles of surface tension for 1-dodecanol adsorption onto a freshly created air–water interface show a second constant surface tension region at $\gamma = 54.8 \pm 0.2 \text{ mN/m}$. Three representative dynamic surface-tension profiles are plotted in Figures 1 and 4. All of the dynamic data for $C > 4 \times 10^{-9} \text{ mol/cm}^3$ possess such a constant γ region. It lasts for a few hundred to a few thousand of seconds. Similar to the first constant γ region, a higher bulk concentration has a shorter constant γ region in the $\gamma(t)$ profile and it starts early also. The data in Figure 4 demonstrate this trend clearly.

The second constant surface tension takes place at $\pi = 17.9 \text{ mN/m}$ for the Gibbs monolayer of 1-dodecanol at 20°C . It is highly possible the LE–LC phase transition. The π value is very close to those reported in the literature: $\pi = 16$ and 21 mN/m at 15 and 20°C , respectively, for 1-dodecanol, $\pi = 21.2 \text{ mN/m}$ at 23.4°C for $C_{14}E_1$, and $\pi = 24.5 \text{ mN/m}$ at 22.5°C for $C_{16}E_2$.^{1,20}

The equilibrium surface tension (Figure 2) shows a nearly linear decrease in the γ_e vs $\log C$ plot at $C > 3 \times 10^{-9} \text{ mol/cm}^3$. Because the bulk concentration is very dilute at C between 3×10^{-9} and $1 \times 10^{-8} \text{ mol/cm}^3$, it is presumed that the Gibbs adsorption equation works in this concentration region. The

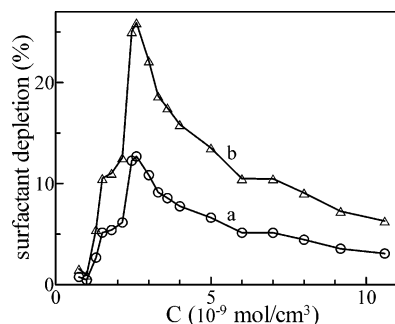


Figure 5. Examples of the percentage of depletion of surfactants in the bulk phase for aqueous 1-dodecanol solutions. The height of solution in cell is (a) 3.1 and (b) 1.5 cm. Surface concentrations are evaluated from the Gibbs adsorption equation according to the data in Figure 2.

surface concentration Γ calculated from Gibbs adsorption equation and the equilibrium data is plotted in Figure 2. A nearly constant slope in the γ_e vs $\log C$ plot at $C > 3 \times 10^{-9}$ mol/cm³ results a slight increase only on Γ at $C > 3 \times 10^{-9}$ mol/cm³. A value of $\Gamma = 9.7 \times 10^{-10}$ mol/cm² resulted from the Gibbs adsorption equation for the equilibrium data of $C > 4 \times 10^{-9}$ mol/cm³, as shown by the straight line in Figure 2. Note that Legrand et al. had reported $\Gamma = 8.0 \times 10^{-10}$ mol/cm² for the 1-dodecanol monolayer by X-ray diffraction.²¹

Note that a phase transition occurs at subsurface concentration C_s around 4×10^{-9} mol/cm³ for the adsorbed 1-dodecanol, according to the dynamic surface-tension data. It is a coexistence of the of the liquid-expanded (LE) and liquid-condensed (LC) phases.¹ The Γ increase for the LE-LC phase transition is not significant according to the Gibbs adsorption equation.

For $C > 4 \times 10^{-9}$ mol/cm³, $\gamma = 72.00 \pm 0.05$ mN/m since $t = 1$ s, as shown in the inset of Figure 4a. In other words, it is in the G-LE coexistence state. For 1-dodecanol, we are not able to observe a dynamic surface-tension profile with three completely different phases, including the $G \rightarrow LE \rightarrow LC$ transitions, by using this pendant bubble system.

The equilibrium γ data show an abrupt decrease at C around 2.2×10^{-9} mol/cm³. The Gibbs adsorption equation, therefore, predicts a significant and continuous increase in Γ . This steep increase in surface concentration at a very short range of bulk concentration indicates a nearly phase-transition phenomenon at C around 2.2×10^{-9} mol/cm³ due to the significant intermolecular interaction between the adsorbed 1-dodecanol molecules. More interpretation is given later when the data are fit with the phase-transition isotherm.

Depletion in Bulk. To model successfully the dynamic and equilibrium surface tension of aqueous 1-dodecanol solutions, one must take much care on the exactness of bulk concentration. The surface concentration has been very high, as show in Figure 2, at extremely dilute concentrations, for example, $\Gamma = 9.2 \times 10^{-10}$ mol/cm² at $C = 2.45 \times 10^{-9}$ mol/cm³. Therefore, the amount or the percentage of 1-dodecanol transports from bulk onto the air-water interface is significant and depletes the bulk concentration even when the bubble is small and the quartz cell is fairly large, $2.6 \times 4.1 \times 4.3$ (height = 4.3) cm inside.

The surfactant solution is usually filled up to ca. 3.1 cm high in this work. The percentage of surfactant molecules adsorbed onto the air-water interface (the planar free surface plus the bubble surface) ranges ca. 0.5 to 13%, depending on the bulk concentration. The shallower of the solution in cell, the higher the percentage of surfactants that go up to the interface. Figure 5 shows two examples of the percentage of surfactant depletion in bulk phase on the basis of the Γ data evaluated from the Gibbs adsorption equation, as shown in Figure 2. Note that the

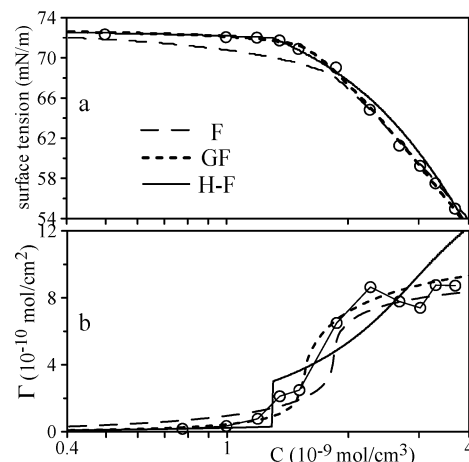


Figure 6. Comparison between the experimental equilibrium γ data and the theoretical $\gamma(C)$ (a) and $\Gamma(C)$ (b) profiles predicted from the Frumkin (---), generalized-Frumkin (···), and Henry-Frumkin phase transition (—) models. The $\Gamma(C)$ data (○ in b) are surface concentrations that were evaluated from the Gibbs adsorption equation and the $\gamma(C)$ data. Bulk concentrations have been corrected for the surfactant depletion.

concentration reported above is the original bulk concentration, that is, before correction.

The number of 1-dodecanol molecules that adsorbed onto the air-water interface is estimated as ΓA , where Γ is the surface concentration at this bulk concentration evaluated from the Gibbs adsorption equation and A is the total air-water surface area. In this work, A consists of the surface area of the pendant bubble, ca. 0.13 cm², and the free surface, 2.6×4.1 cm², in the quartz cell. The bulk concentrations are, therefore, modified by taking out the adsorbed 1-dodecanol from the bulk phase: $C_0 V = C_1 V + \Gamma A$, where V is the volume of the solution (33.1 cm³) in the quartz cell, C_0 is the original concentration, and C_1 is the corrected concentration after depletion. The corrected data are plotted in Figure 6a. The surfactant concentrations in Figure 1, illustrating the dynamic $\gamma(t)$ profiles, becomes 1.51 (1), 1.87 (2), 2.08 (3), 3.02 (4), 3.69 (5), 7.64 (6), 8.84 (7), and 10.3 (8) (10^{-9} mol/cm³).

Adsorption Isotherm. The well-known adsorption isotherms, Frumkin and generalized-Frumkin models, were used to fit the equilibrium γ data. Here, consider only the equilibrium surface tension at $C < 3.69 \times 10^{-9}$ mol/cm³ because it is highly impossible that the Langmuir or Frumkin isotherm can describe the data at the liquid-condensed state. Figure 6 shows the model predictions and the comparison with the experimental data of equilibrium surface tension.

The most popular Frumkin isotherm describes the equilibrium γ data reasonably well. However, the Frumkin model predicts a lower surface tension at dilute concentrations, especially at $C < 2 \times 10^{-9}$ mol/cm³, for example, an error with 1.5 mN/m results at $C = 1.2 \times 10^{-9}$ mol/cm³. Note that the value of K (model parameter, indicating the molecular interaction), resulting from best fitting the equilibrium $\gamma(C)$ data, is very close to its critical value ($K_C = -4$). This model predicts an abrupt Γ increase at C around 1.8×10^{-9} mol/cm³ (Figure 6b) instead of ca. 1.29×10^{-9} and 3.69×10^{-9} mol/cm³ that were predicted from the constant γ region in the dynamic $\gamma(t)$ curves. Therefore, the Frumkin model fails to predict the existence of G-LE coexistence in the dynamic γ data.

The generalized-Frumkin isotherm, possessing one more parameter than the Frumkin model, predicts the equilibrium γ data perfectly with a K value that is very close to its K_C (Table 1). Similar to the Frumkin isotherm, this model fails to

TABLE 1: Model Constants of Optimal Fit of 1-Dodecanol Aqueous Solution

model ^a	H (1/cm)	$C_C \times 10^9$ (mol/cm ³)	$\Gamma_\infty \times 10^{10}$ (mol/cm ²)	$A_L \times 10^8$ (mol/cm ³)	K_L	n	K_L/K_C^b
F			9.12	1.29	-3.89	1	0.97
GF			10.7	10.3	-5.48	0.41	0.96
H-F ^c	0.0235	1.294	18.1	0.969	-2.40	1	0.60

^a F = Frumkin, GF = generalized Frumkin, and H-F = Henry-Frumkin phase-transition model. ^b K_C = critical value of $K_L = -(1 + 1/n)^{1+n}$; at $K_L = K_C$, the model predicts phase-transition behavior. ^c H-F isotherm predicts critical surface coverage $\Gamma_{gc} = 3.04 \times 10^{-11}$ mol/cm², $\Gamma_{lc} = 3.0 \times 10^{-10}$ mol/cm².

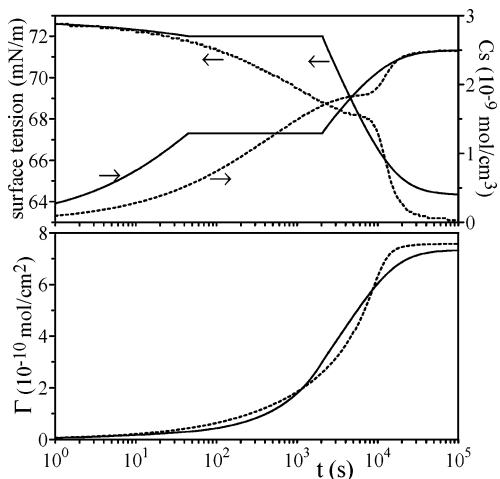


Figure 7. An example illustrating the model prediction on the relaxations of surface tension, subsurface concentration C_s , and surface concentration Γ due to the G-LE phase transition from the H-F phase-transition model for $C = 2.5 \times 10^{-9}$ mol/cm³. The theoretical profiles from Frumkin model are also shown as the dashed curves for comparison. $D = 6.0 \times 10^{-6}$ cm²/s was assumed.

predict the coexistence of the G and LE phases. An abrupt Γ increase at C around 1.6×10^{-9} mol/cm³ (Figure 6b) is predicted by the GF model, which is not consistent with the constant γ region in the dynamic $\gamma(t)$ curves.

Figure 6b shows the relaxation of surface concentration predicted from these two isotherms. Both models predict a continuous increase on Γ , especially at $C = (1 - 2) \times 10^{-9}$ mol/cm³.

A phase-transition (H-F) model with Henry and Frumkin isotherms is introduced to describe the G and LE states, respectively. The H-F isotherm describes the equilibrium γ data well and predicts a coexistence of G-LE phase at $C = 1.29 \times 10^{-9}$ mol/cm³. This G-LE coexistence is demonstrated by a vertical jump (between Γ_{gc} and Γ_{lc}) in the surface-concentration profile (the solid curve in Figure 6b) at $C = 1.29 \times 10^{-9}$ mol/cm³. For a diffusion-limited process at bulk concentration $C > 1.29 \times 10^{-9}$ mol/cm³, the surface tension will remain at 72.0 mN/m constant tension in the dynamic $\gamma(t)$ curve when the surface excess is between Γ_{gc} and Γ_{lc} . During this constant γ region, the subsurface concentration remains at constant, 1.29×10^{-9} mol/cm³. Figure 7 demonstrates an example of the theoretical prediction for the relaxations of surface tension, subsurface concentration, and surface excess.

Desorption. If we compress the preequilibrium air-water interface, which had already reached its equilibrium state, the surface coverage of 1-dodecanol will become overcrowded and result in a lower surface tension. 1-Dodecanol molecules will desorb out of the surface, and the surface tension will increase with time. After a certain amount of time, the surface will come back to its previous equilibrium state.

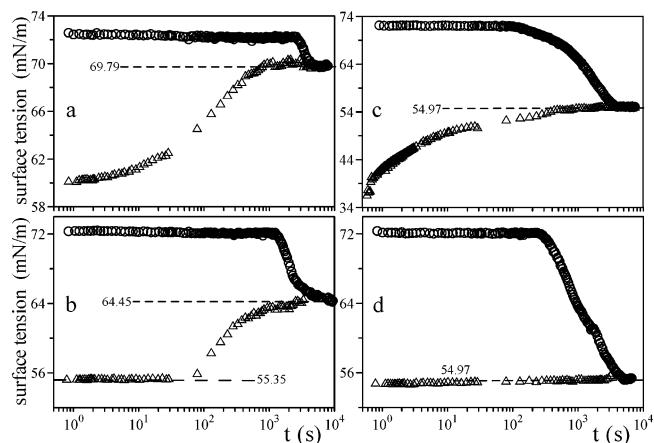


Figure 8. Representative examples of the re-equilibration of surface tension for pendant bubbles via a sudden compression for $C_0 = 1.87$ (a), 2.68 (b), and 3.69 (c and d) (10^{-9} mol/cm³).

Figure 8 shows the relaxation of $\gamma(t)$ data for 1-dodecanol for a process consisting of a sudden creation of a fresh surface of the pendant bubble and a sudden compression of the surface when it had reached equilibrium adsorption. Surface tension relaxes from fresh value γ_o and reaches its equilibrium value γ_e . When the surface is suddenly compressed, γ has a tension lower than γ_e , and then it relaxes back to its previous γ_e .

At dilute concentrations (Figure 8a), the $\gamma(t)$ profile due to a sudden compression is similar to that of other small surfactants such as 1-decanol²² or C_mE_n .^{23,24} As the concentration increases, the surface tension after surface compression may reach the γ_{LE-LC} , where the LE and LC phases coexist. Figure 8b shows one of the cases that is kept at this γ_{LE-LC} ($= 54.8$ mN/m) for ca. 50 s right after surface compression before γ starts to increase. This indicates that the increase in surface coverage due to a compression of a 23% decrease in surface area does not exceed the Γ_{lc2} (the critical surface concentration in which all the liquid-expanded phase at the surface disappears at increasing surface concentration).

The equilibrium surface tension for $C = 3.69 \times 10^{-9}$ mol/cm³ equals the critical surface tension γ_{LE-LC} at which the LE and LC coexist at the surface. (See curve 5 in Figure 1.) When we compress the bubble surface at $C = 3.69 \times 10^{-9}$ mol/cm³, two different types of behavior were observed. Figure 8c shows that the surface tension decreases suddenly to a number lower than γ_{LE-LC} after compression. However, Figure 8d shows another different type of relaxation where the γ does not change at all via a compression of a 23% decrease in the surface area. The reason for these different relaxations is not yet clear.

5. Discussions and Conclusion

In this study, two constant surface-pressure regions were observed at 20 °C in the dynamic surface-tension profile of the adsorbed 1-dodecanol monolayer. The constant γ region in the dynamic $\gamma(t)$ curve indicates a phase transition for the adsorbed monolayer at the air-water interface. This behavior is similar to the L_1-L_2 transition that Pollard et al.¹ reported for $C_{14}E_1$ and the G-LE transition that Subramanyam and Maldarelli² observed for $C_{14}E_6$. Note that Vollhardt et al.⁷ observed a characteristic break point instead of a constant γ region in the $\gamma(t)$ curve of 1-dodecanol for the formation of a condensed phase.

The first constant γ region occurs at $\pi = 0.75$ mN/m and implies a coexistence of gaseous and liquid-expanded phases. The second one takes place at $\pi = 17.9$ mN/m, corresponding

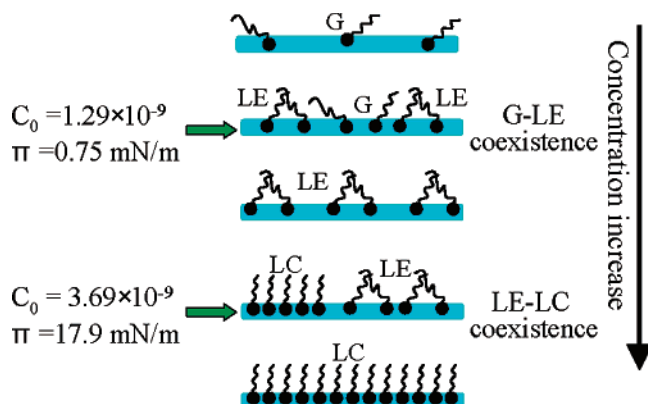


Figure 9. Cartoon showing three different phases of the adsorbed 1-dodecanol monolayer at the air-water interface.

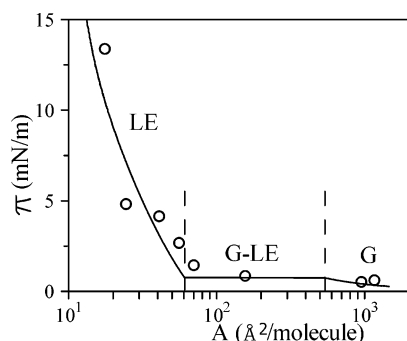


Figure 10. π - A profile (surface pressure vs area occupied by each molecule) predicted from the Henry-Frumkin phase-transition model.

to the coexistence of liquid-expanded and liquid-condensed phases. A cartoon describing these three different phases of the Gibbs monolayer of 1-dodecanol at the air-water interface is presented in Figure 9.

To the best of our knowledge, it is the first time that (i) a complete profile of dynamic surface tension is presented showing the G-LE coexistence and that (ii) a complete set of equilibrium surface tension of 1-dodecanol is reported. Furthermore, it was observed that no abrupt slope change exist in the γ vs $\log C$ curve of 1-dodecanol at the corresponding bulk concentration where the LE-LC phase transition takes place. The success of these new observations relies on a wide time range, from a tenth of second to several hours, of continuously monitoring the relaxation of surface tension using the pendant bubble tensiometer.

The three-phase behavior, with G-LE and LE-LC coexistence, provides evidence for what Vollhardt et al. proposed:⁷ the assumption that small aggregates can form fits better, compared with that for monomer/aggregate model, with the experimental results for both the equilibrium and dynamic surface tension. It has been also proposed that three types of entities (monomers, average dimmers, and large aggregates) are present in the transcritical adsorbed monolayer.⁷

A comparison between the calculated π - A data (the circles) and the theoretical π - A curve predicted by the H-F phase-transition model (the solid curve) was shown in Figure 10. The data are calculated from the equilibrium tension data and the Gibbs adsorption equation. The π - A curve from the model shows a constant surface-pressure region of G-LE coexistence

at $61 < A < 540 \text{ Å}^2/\text{molecule}$, which is close to that for the Langmuir monolayer of pentadecanoic acid. A constant π region for the G-LE coexistence was observed at $42 < A < 1500 \text{ Å}^2/\text{molecule}$ at 20 °C for pentadecanoic acid.²⁵

At C around $1.7 \times 10^{-9} \text{ mol/cm}^3$, equilibrium tension decreases abruptly; therefore, a big increase in surface coverage exists. There is a good possibility of phase transition at this concentration. However, neither a constant γ behavior nor a characteristic break in dynamic $\gamma(t)$ curve was observed in this study. Unless there is a kind of transition with no break in the dynamic surface-tension profile, it is hard to conclude that there is a 2D transition.

The H-F phase-transition model proposed in this study can describe the equilibrium surface tension reasonably well with K_L/K_C of 0.60. The parameter $K_L/K_C = 0.60$ indicates a significant molecular interaction but is still far away from its critical value, where the phase transition takes place. The increase in Γ in a short range of bulk concentration may have resulted from the enhanced effect in surface tension decrease due to the molecular interaction of the LE phase at increasing surface coverage.

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