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Surface Equation of State of Nonionic C_mE_n Surfactants

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The surface equation of state (γ vs $\Gamma/\Gamma_{\text{ref}}$), based on the experimental data from rapid expansion of a pendant bubble, has been used on studying the adsorption kinetics for $C_{12}E_6$ (Pan et al. *J. Colloid Interface Sci.* **1998**, 205, 213) and $C_{14}E_8$ (Lin et al. *J. Colloid Interface Sci.* **2001**, 244, 372). In those studies, the relationship between surface tension γ and relative surface concentration $\Gamma/\Gamma_{\text{ref}}$ was applied, and the $\gamma(\Gamma/\Gamma_{\text{ref}})$ data profiles were found very useful for the determination of the adsorption isotherm and its parameters. In this work, the value of Γ_{ref} was evaluated from the equilibrium surface tension data $\gamma(C)$ and the Gibbs adsorption equation. It was found that the dependence of γ vs Γ is more sensitive than $\gamma(\Gamma/\Gamma_{\text{ref}})$ and brings more help to studying the adsorption kinetics. The role of $\gamma(\Gamma)$ data was examined using the equilibrium $\gamma(C)$ and dynamic $\gamma(t)$ data of six nonionic polyoxyethylene surfactants C_mE_n and two alcohols. The $\gamma(\Gamma)$ data play an important role on the determination of the adsorption isotherm, model parameters, and controlling mechanism, and also on the evaluation of surfactant diffusivity. Applying $\gamma(\Gamma)$ data with $\gamma(\ln C)$ data does bring a much better result on studying the adsorption behavior. According to the $\gamma(\Gamma)$ data, (i) the Langmuir isotherm clearly fails to describe the above nonionic surfactants, and (ii) the interaction between the adsorbed surfactant molecules is significant.

1. Introduction

On studying the adsorption kinetics of a surfactant, one would like to know the surfactant activity, dynamic property, controlling mechanism, diffusivity, and enhancement of surfactant activity due to the molecular interaction or mixed surfactants. Surfactant activity includes the decrease in surface tension, the amount of surfactant needed to add into solution, and the temperature effect. The dynamic property considers how fast the surface tension changes or oscillates.^{1,2} Regarding the controlling mechanism, there are three possibilities: diffusion-control, kinetic-control, and diffusive-kinetic mixed control processes.

Hsu et al.³ proposed that using only a limited range of equilibrium surface tension $\gamma(C)$ data to determine the adsorption isotherm can cause a mistake on the determination of the adsorption mechanism and on the evaluation of surfactant diffusivity. Applying only the $\gamma(C)$ data with high surface pressure to determine the adsorption isotherm and model parameters, one may find that the $\gamma(t)$ data (i) show agreement with a diffusion-controlled process, but in fact the surfactant diffusivity is incorrect, or (ii) show agreement with a mixed controlled process, but in fact the mass transport is diffusion-controlled. In the first case for the adsorption of surfactant onto a clean water–fluid interface, one may underestimate the diffusivities for surfactants with cohesive forces between the adsorbed molecules and overestimate them for those with anticooperative adsorption behavior.

Lee et al.⁴ reported that even though an adsorption isotherm describes the equilibrium $\gamma(\ln C)$ data profile

excellently, it may describe the dynamic surface tension data $\gamma(t)$ incorrectly. An incorrect controlling mechanism and/or a surfactant diffusivity with a significant error may result. These mistakes are simply due to the fact that an excellent model prediction on $\gamma(C)$ data does not imply a correct prediction on $\Gamma(C)$ dependency, the slope of γ vs $\ln(C)$.

Pan et al.⁵ and Lin et al.⁶ expanded rapidly a pendant bubble, with the air–water interface having reached the equilibrium adsorption of surfactant, and found out the experimental relationship of γ vs A/A_{ref} . With the assumption that the amount of surfactant molecules adsorbing onto the air–water interface during the expansion process (in about 1 s) is negligible, a unique relationship of γ vs $\Gamma/\Gamma_{\text{ref}}$ (relative surface concentration) was then obtained from the $\gamma(A/A_{\text{ref}})$ data profile. Therefore, they introduced a second set of equilibrium data, $\gamma(\Gamma/\Gamma_{\text{ref}})$, on studying the surfactant adsorption kinetics. It was concluded that the experimental $\gamma(\Gamma/\Gamma_{\text{ref}})$ data profile is very useful for the determination of adsorption isotherm and model parameters.

The role of surface equation of state, $\gamma(\Gamma/\Gamma_{\text{ref}})$, on studying surfactant adsorption kinetics has been examined theoretically recently.⁴ The theoretical simulation indicated that an adsorption isotherm which fitted $\gamma(C)$ data well may have a significant deviation on predicting the $\gamma(\Gamma/\Gamma_{\text{ref}})$ profile. A larger diffusivity resulted for the surfactants with cohesive forces, and a smaller diffusivity was obtained for the anticooperative surfactants from best-fitting the dynamic surface tension data.

In this work, the experimental dependency of γ vs $\Gamma/\Gamma_{\text{ref}}$ was expanded to γ vs Γ by introducing the Gibbs adsorption equation ($d\gamma = -\Gamma RT d \ln C$) to evaluate the value of Γ_{ref} from the equilibrium surface tension data $\gamma(\ln C)$. It was found that the $\gamma(\Gamma)$ data profile is more sensitive than $\gamma(\Gamma/\Gamma_{\text{ref}})$ and brings more help to studying the adsorption

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Figure 1. Equilibrium data of surface tension vs relative surface concentration and surface tension vs bulk concentration (the inset) and model predictions from the Langmuir (L), Frumkin (F), and generalized Frumkin (GF) models for $C_{12}E_4$. The solid curve in the inset is the best-fit of a polynomial equation, and the dashed line represents the slope at reference point $\gamma = 54$ mN/m.

kinetics. This idea is illustrated in this work using the experimental $\gamma(\Gamma)$ data of six nonionic C_mE_n surfactants and two alcohols.

2. Experimental Measurements

Materials. Nonionic polyoxyethylene glycol alkyl ether surfactants C_mE_n ($C_mH_{2m+1}O(CH_2CH_2O)_nH$) purchased from Nikko (Tokyo, Japan) were used without further modification. The nonionic surfactants 1-nonanol and 1-decanol ($C_mH_{2m+1}OH$, $m = 9$ or 10 , >99% purity) purchased from Aldrich were used without modification. Aqueous solutions are prepared with clean water purified via a Barnstead NANOpure water purification system, with the output water having a specific conductance of less than $0.057 \mu\Omega^{-1}/\text{cm}$.

Adsorption. A pendant bubble tensiometer enhanced by video digitization was used to measure the relaxation of surface tension. The apparatus and the edge detection routine have been described in detail in a previous study.⁷ The temperature variation of the aqueous solution was less than ± 0.05 K.⁸ A 17-gauge stainless steel inverted needle (1.07 mm i.d.; 1.47 mm o.d.) was used for the bubble generation.

A pendant bubble of air with a diameter of ~ 1.5 – 2 mm was formed in a surfactant solution, which was put in a quartz cell of $26 \text{ mm} \times 41 \text{ mm} \times 43 \text{ mm}$ i.d. Digital images of the bubble were taken sequentially and then processed to determine the surface area and surface tension. The bubbles were measured up to a few hours, depending on the bulk concentration. The equilibrium surface tension was then extracted from the long-time asymptote of $\gamma(t)$.

Surface Expansion. The pendant bubble tensiometer was also used as a Langmuir trough for measuring the dependency of surface tension γ vs surface concentration Γ . A pendant bubble of air was formed first in surfactant solution. When the adsorption reached the equilibrium state, the air–water interface was expanded rapidly till the bubble dropped off. Digital images of the bubble were taken sequentially and then processed to determine the surface area $A(t)$ and surface tension $\gamma(t)$. Usually, two or three different surfactant concentrations were picked for surface expansion measurements. At each working concentration, the expansion measurement was repeated for about 10 times with different expansion rates, dA/dt . An average rate of surface expansion was evaluated from the relaxation data of surface area $A(t)$.

Data of $\gamma(t)$ were plotted with $A(t)/A_{\text{ref}}$, the relative surface area at time t , and a unique relationship between γ and A/A_{ref} resulted for those runs with a large expansion rate dA/dt . An illustration has been given in Figure 9b in ref 23. The $\gamma(A/A_{\text{ref}})$ curve with a lower expansion rate deviated clearly from the unique curve. This implies there was nearly no surfactant molecule adsorbing onto the expanding air–water surface during the surface expansion process at a large expansion rate. A unique curve relating γ and $\Gamma/\Gamma_{\text{ref}}$ (relative surface concentration = A_{ref}/A)

A) was then obtained (Figure 1). By introducing the Gibbs adsorption equation, $d\gamma = -\Gamma RT d \ln C$, the value of Γ_{ref} was evaluated from the equilibrium surface tension data profile $\gamma(\ln C)$. A unique relationship between surface tension γ and surface concentration Γ then resulted for each surfactant.

3. Theoretical Framework

The adsorption model used here assumes that adsorption and desorption are activated processes,^{7,9–12} and the activation energies for adsorption (E_a) and desorption (E_d) are dependent on surface concentration Γ by a power law ($E_a = E_a^\circ + RT\nu_a^*(\Gamma/\Gamma_\infty)^n$ and $E_d = E_d^\circ + RT\nu_d^*(\Gamma/\Gamma_\infty)^n$ with constants E_a° , E_d° , ν_a^* , and ν_d^*).^{13,14} Here T is the temperature and R is the gas constant. Intermolecular interactions were assumed to alter the rate of desorption but leave the rate of adsorption unaffected, so ν_a^* was assumed to be zero. With these assumptions, the adsorption flux to the interface was assumed to obey

$$d\Gamma/dt = \beta_1 C_s (\Gamma_\infty - \Gamma) - \alpha_1 \exp(-\nu_d^*(\Gamma/\Gamma_\infty)^n) \Gamma \quad (1)$$

where Γ_∞ is the maximum packing at the interface and C_s is the sublayer concentration or the surfactant concentration immediately adjacent to the interface that has yet to adsorb. At equilibrium, the surface concentration, which reduces to the isotherm

$$\frac{\Gamma_{\text{eq}}}{\Gamma_\infty} = x = \frac{C_\infty}{C_\infty + a \exp(Kx^n)} \quad (2)$$

where $1/a = \beta_1/\alpha_1$ is a measure of the surface activity at the interface, C_∞ is the bulk concentration far from the interface and the interaction parameter $K = \nu_a^* - \nu_d^*$.

Attractive intermolecular forces, such as van der Waals attractions among the hydrocarbon chains of the surfactant, are described by $K < 0$.^{12,15,16} For this case, the greater is the surface concentration, the slower is the desorption rate. A positive K indicates an anticooperative adsorption, in which the adsorption becomes more difficult at increasing Γ compared with the desorption process. Equation 2 becomes the Frumkin isotherm^{7,17–20} when a linear dependence between $E_{a/d}$ and Γ is assumed. The Langmuir adsorption isotherm results when $E_{a/d}$ is independent of Γ .

For an ideal solution, the Gibbs adsorption equation, $d\gamma = -\Gamma RT d \ln C$, allows the derivation of the surface equation of state relating the surface tension γ to the surface concentration:

$$\gamma - \gamma_0 = \Gamma_\infty RT [\ln(1 - x) - Knx^{n+1}/(n + 1)] \quad (3)$$

where γ_0 is the surface tension when the interface is in the absence of surfactants.

The bubble deformation and associated fluid flow were assumed to die out rapidly compared to the time required for surfactant to restore its equilibrium distribution.

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Deviations of the bubble shape from a spherical geometry were slight and were neglected in the theoretical analysis. Therefore, surfactant is assumed to diffuse through a quiescent fluid and to adsorb on the bubble interface. The solution to Fick's equations for this geometry is a Ward and Tordai equation modified to account for the spherical shape of the bubble.^{21,22}

$$\Gamma(t) = \Gamma_b + 2(D/\pi)^{1/2} [C_\infty t^{1/2} - \int_0^t C_s(t-\tau) d\tau^{1/2}] + (D/b)[C_\infty t - \int_0^t C_s(\tau) d\tau] \quad (4)$$

where D denotes the diffusion coefficient, Γ_b is the initial surface concentration, and b is the bubble radius.

When the diffusion between the bulk and the sublayer is slow compared to the rates of adsorption and desorption, diffusion is the rate-limiting process. Diffusion supplies the sublayer, and surfactant rapidly establishes equilibrium between the sublayer and the interface. The surface concentration therefore evolves according to eq 4 and the isotherm requiring equilibrium between Γ and C_s :

$$\frac{\Gamma(t)}{\Gamma_\infty} = \frac{C_s(t)}{C_s(t) + a \exp\left(K \frac{\Gamma(t)^n}{\Gamma_\infty^n}\right)} \quad (5)$$

When the rate at which surfactant diffuses to the sublayer is comparable to the rates of adsorption/desorption, the mass transfer is of mixed control, and $\Gamma(t)$ is found by solving eqs 1 and 4 simultaneously. The surface tension is assumed to instantaneously reflect the adsorbed concentration in all cases, so $\gamma(\Gamma(t))$ is found from eq 3.

Intermolecular interactions among the adsorbed surfactants $C_m E_n$ and alcohols play an important role in the equilibrium and dynamic data. Data were analyzed in terms of the Frumkin (F) and the Langmuir (L) models. If the Frumkin model cannot describe the data well, the generalized Frumkin (GF) model was then used.

4. Results

A surface expansion experiment was performed using a pendant bubble tensiometer to obtain the relaxations of surface tension and surface area. In general, a unique profile of surface tension γ vs relative surface area (A/A_{ref}) was obtained when the expansion rate was high enough, and this profile indicates a unique dependency between $\gamma(t)$ and relative surface concentration $\Gamma(t)/\Gamma_{\text{ref}}$. Here, $\Gamma/\Gamma_{\text{ref}} = (A/A_{\text{ref}})^{-1}$. A unique profile at high but different expansion rates implied that the amount of surfactants adsorbing onto the air–water interface was negligible during surface expansion.

For $C_m E_n$, a surface expansion experiment was usually performed at two or three different bulk concentrations in order to cover a wide range of working surface tension. Unique $\gamma-A/A_{\text{ref}}$ data profiles at different concentrations were then merged into a final unique curve by choosing the same reference point. Shown in Figure 1 is the unique $\gamma-\Gamma/\Gamma_{\gamma=54}$ data profile for $C_{12}E_4$, adopted from ref 23.

Data of the surface equation of state, $\gamma(\Gamma)$, was found to be more sensitive than the $\gamma(\Gamma/\Gamma_{\text{ref}})$ data for determining

Figure 2. Experimental data of (a) surface equation of state and (b) equilibrium surface tension and model predictions from the Langmuir (L), Frumkin (F), and generalized Frumkin (GF) isotherms for $C_{12}E_4$.

the adsorption isotherm in this work. The equilibrium surface tension, $\gamma(\ln C)$, coupled with the Gibbs adsorption equation, $d\gamma = -\Gamma RT d \ln C$, was used to evaluate the surface concentration at the reference point (Γ_{ref}). The inset of Figure 1 shows the fit using a polymeric equation (solid curve, $-d\gamma/dz = 1924.6 + 263.73z + 11.871z^2 + 0.18179z^3$; $z = \ln C$) on the $\gamma(\ln C)$ data around the reference point with $\gamma = 54$ mN/m. Surface coverage at γ_{ref} was then calculated from the slope of $d\gamma/d \ln C$ (the dashed straight line). The experimental data of the surface equation of state $\gamma(\Gamma)$ of $C_{12}E_4$ then resulted from Figure 1 and are shown in Figure 2a.

Model predictions from the Langmuir (L) and Frumkin (F) isotherms fit $C_{12}E_4$ data profiles differently, as shown in Figures 1 and 2a of $\gamma(\Gamma/\Gamma_{\text{ref}})$ and $\gamma(\Gamma)$, but the deviation from experimental data for the Frumkin model is not significant for $C_{12}E_4$. This is due to a good evaluation of Γ , the slope of γ vs $\ln(C)$, at γ_{ref} from equilibrium $\gamma(C)$ data. Note that a large deviation may result for other surfactants. More illustrations are given later in this work.

Figure 2b shows that the model predictions from all L, F, and GF isotherms agree excellently with the equilibrium surface tension data of $C_{12}E_4$. Therefore, it is hard to tell which isotherm can predict the adsorption behavior better if one has only $\gamma(\ln C)$ data. However, when one examines the model predictions using the $\gamma(\Gamma)$ data, it is clear that the Frumkin isotherm predicts the experimental data much better than the Langmuir one, as shown in Figure 2a. Note that the generalized Frumkin isotherm predicts the $\gamma(\Gamma)$ data better than the Frumkin model, since it predicts a more accurate Γ at γ_{ref} from the $\gamma(\ln C)$ data.

Shown in Figure 3a–c are the equilibrium data of $C_{10}E_4$. Dashed curves (L for Langmuir isotherm and F_1 for Frumkin isotherm) were from the best-fit with the $\gamma(\ln C)$ data, and solid curves (F_2 for Frumkin isotherm) considered both sets of equilibrium data, $\gamma(\ln C)$ and $\gamma(\Gamma)$. Data in Figure 3a indicate that F_1 and F_2 predict $\gamma(\ln C)$ data perfectly and L also does a good job. However, a larger deviation between the experimental $\gamma(\Gamma/\Gamma_{\text{ref}})$ data and the model prediction from the Langmuir model (Figure 3b) was observed. This indicates clearly that $\gamma(\Gamma/\Gamma_{\text{ref}})$ data do bring more useful information for the determination of the adsorption isotherm. Both F_1 and F_2 are able to predict well the $\gamma(\Gamma/\Gamma_{\text{ref}})$ data. This is because we are lucky to obtain a set of model parameters of the Frumkin isotherm

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Figure 3. (a) Equilibrium surface tension $\gamma(C)$, (b) relationship between surface tension and relative surface concentration, (c) experimental data of surface equation of state $\gamma(\Gamma)$, (d) representative dynamic surface tension for the adsorption onto a clean interface for $C_0 = 1.3 \times 10^{-8}$ mol/cm³, and model predictions using Langmuir (L) and Frumkin (F_1 and F_2) models for $C_{10}E_4$. F_1 best-fits the $\gamma(\ln C)$ data, and F_2 was from the best-fit on both $\gamma(\ln C)$ and $\gamma(\Gamma)$ data.

by using only the $\gamma(\ln C)$ data. Such good results are not always found for the model parameters using only the $\gamma(\ln C)$ data.

If we examine the model predictions using the $\gamma(\Gamma)$ data, as shown in Figure 3c, a significant deviation resulted for F_1 and that from L deviates far away from the $\gamma(\Gamma)$ data. Nevertheless, F_2 predicts both sets of equilibrium data $\gamma(\ln C)$ and $\gamma(\Gamma)$ excellently. This is an illustration that $\gamma(\Gamma)$ data are more sensitive than the $\gamma(\Gamma/\Gamma_{\text{ref}})$ data for the determination of the adsorption isotherm and model parameters.

The data in Figure 3d show that both F_1 and F_2 predict the dynamic surface tension profiles $\gamma(t)$ well; however, different diffusivities resulted from F_1 ($D_{1,\text{avg}} = 7.9 \times 10^{-6}$ cm²/s) and F_2 ($D_{2,\text{avg}} = 7.2 \times 10^{-6}$ cm²/s) for $C_{10}E_4$. D_{avg} is the averaged diffusivity resulted from the $\gamma(t)$ profiles at seven different concentrations of $C_{10}E_4$. Note that the

difference between $D_{1,\text{avg}}$ and $D_{2,\text{avg}}$ may be significant for some surfactants. More illustrations are given later.

Similar behavior was observed for $C_{10}E_8$, $C_{12}E_8$, $C_{14}E_8$, and $C_{12}E_6$ for their equilibrium data (shown in Figures 4 and 5). In general, the Langmuir isotherm fits the $\gamma(\ln C)$ data well for those compounds having an insignificant molecular interaction (for example, $C_{12}E_4$ with $K = 1.88$ and $C_{12}E_6$ with $K = 3.31$ using the Frumkin model, as listed in Table 1); nevertheless, a worse fit resulted for those surfactants having a K far from zero (for example, $C_{10}E_8$ with $K = 12.5$ and $C_{12}E_8$ with $K = 10.2$). Recall that a larger K represents more significant molecular interaction forces between the adsorbed surfactant molecules. The Langmuir model fits well also $C_{14}E_8$, which has a K of 6.0. This is because the range of available equilibrium γ data is narrow, that is, due to the lack of low surface pressure data at $\gamma > 62$ mN/m.

The Langmuir isotherm always fits poorly the $\gamma(\Gamma)$ data profiles of C_mE_n (Figures 2–5). The Frumkin isotherm could predict the $\gamma(\Gamma)$ data pretty well if one considered both sets of equilibrium data, $\gamma(\Gamma)$ and $\gamma(\ln C)$, for determining the model parameters. For C_mE_8 surfactants, which have long EO groups, it was found that the generalized Frumkin (GF) isotherm describes better the $\gamma(\Gamma)$ data profiles. In addition, a better prediction on dynamic $\gamma(t)$ data was observed using the GF model and a lower diffusivity resulted for C_mE_8 (Table 1).

Recall that the Langmuir model describes the $\gamma(\ln C)$ well and $\gamma(\Gamma)$ reasonably well (Figure 2) for $C_{12}E_4$, which has a small K of 1.88. Therefore, the Langmuir model predicts satisfactorily the dynamic $\gamma(t)$ profiles of $C_{12}E_4$. Figure 6a shows an example for $C = 1.5 \times 10^{-8}$ mol/cm³. Although the Langmuir isotherm fits $\gamma(\ln C)$ data well for the whole range of surface tension, there exists a significant deviation for surface concentration Γ evaluated from the slope of γ vs $\ln(C)$ data. Figure 2a indicates clearly that the Langmuir model overestimates Γ at $50 < \gamma < 65$ mN/m and underestimates Γ at $\gamma < 50$ mN/m. In other words, at $50 < \gamma < 65$ mN/m, the Langmuir model predicts a higher γ and a lower γ is predicted at $\gamma < 50$ mN/m. This overestimation of γ at $50 < \gamma < 65$ mN/m reflects an overestimation of γ on the dynamic surface tension profile (at the beginning $t < 50$ s or $\gamma > 53$ mN/m for the run shown in Figure 6a). The underestimation of γ at $\gamma < 50$

Figure 4. Experimental data of (a and c) equilibrium surface tension $\gamma(C)$, (b and d) surface equation of state $\gamma(\Gamma)$, and model predictions using Langmuir (L), Frumkin (F_1 and F_2), and generalized Frumkin (GF) isotherms. L and F_1 were from the best-fit on $\gamma(\ln C)$ data; F_2 and GF were from the best-fit on both $\gamma(\ln C)$ and $\gamma(\Gamma)$ data. Parts a and b are for $C_{10}E_8$, and c and d are for $C_{12}E_8$.

Figure 5. Experimental data of (a and c) equilibrium surface tension $\gamma(C)$, (b and d) surface equation of state $\gamma(\Gamma)$, and model predictions using Langmuir (L), Frumkin (F), and generalized Frumkin (GF) isotherms. L was from the best-fit on $\gamma(\ln C)$ data; F and GF were from the best-fit on both $\gamma(\ln C)$ and $\gamma(\Gamma)$ data. Parts a and b are for $C_{12}E_6$, and c and d are for $C_{14}E_8$.

Table 1. Model Parameters, Diffusivity, and Bubble Radius for C_mE_n and Alcohols at 25 °C

	model ^a	Γ_∞ (10^{-10} mol/cm ²)	a (mol/cm ³)	K	n	D (10^{-6} cm ² /s)	b (cm)
$C_{10}E_4$	L	3.020	2.682×10^{-9}				0.10
	F ₁	3.801	1.750×10^{-9}	2.862	1	7.9	0.10
	F ₂	4.577	1.690×10^{-9}	4.647	1	7.2	0.10
$C_{10}E_8$	L	1.804	5.437×10^{-10}				0.10
	F ₂	3.470	1.046×10^{-10}	12.52	1	7.3	0.10
	GF	3.424	2.132×10^{-11}	10.88	0.556	6.5	0.10
$C_{12}E_4$	L	3.905	4.660×10^{-10}			7.3	0.10
	F ₂	4.633	3.521×10^{-10}	1.875	1	6.5	0.10
	GF	6.585	2.942×10^{-10}	4.105	0.717	6.4	0.10
$C_{12}E_6$	L	3.103	2.765×10^{-10}			11.2	0.10
	F ₂	4.039	1.610×10^{-10}	3.314	1	7.3	0.10
$C_{12}E_8$	L	2.043	7.676×10^{-11}				0.13
	F ₁	2.668	2.501×10^{-11}	5.186	1	11.0	0.13
	F ₂	3.506	1.475×10^{-11}	10.21	1	7.8	0.10
$C_{14}E_8$	GF	5.282	2.329×10^{-12}	13.23	0.503	7.3	0.125
	L	2.547	2.429×10^{-11}			14.1	0.10
	F ₂	3.544	6.915×10^{-12}	6.019	1	9.8	0.10
C_9OH	GF	4.229	7.644×10^{-13}	8.971	0.490	7.6	0.10
	L	19.03	4.310×10^{-7}				
	F	5.915	3.137×10^{-7}	-3.410	1		
$C_{10}OH^b$	GF	6.786	2.717×10^{-6}	-4.634	0.268	6.3	0.10
	L	15.38	8.37×10^{-8}				
	F	6.334	9.18×10^{-8}	-3.717	1	7.5	0.13
	GF	6.946	9.703×10^{-8}	-5.031	0.259	6.6	0.13

^a L: Langmuir isotherm. F, F₁, and F₂: Frumkin isotherm. GF: generalized Frumkin isotherm. L and F₁: best-fit $\gamma(\ln C)$ data. F₂ and GF: best-fit both $\gamma(\ln C)$ and $\gamma(\Gamma)$ data. ^b $T = 22.7$ °C.

mN/m reflects an underestimation of γ on the $\gamma(t)$ profile (at $50 < t < 150$ s or $41 < \gamma < 53$ mN/m for the run in Figure 6a).

The Frumkin isotherm fits $\gamma(\ln C)$ and $\gamma(\Gamma)$ data profiles much better than the Langmuir isotherm (Figure 2); therefore, it predicts much better the $\gamma(t)$ profile of $C_{12}E_4$ also (Figure 6a). However, the diffusivities resulting from both models, F and L, are nearly the same even though the fit on dynamic $\gamma(t)$ of $C_{12}E_4$ using the Langmuir model is worse. This nearly same diffusivity is due to the nearly same fits on equilibrium data profiles using either the L or F model. Note that a quite different diffusivity may result when different models are used for other surfactants.

Another illustration is given in Figure 7 for $C_{12}E_8$ using two Frumkin models F₁ and F₂. F₁ best-fitted the $\gamma(\ln C)$ data, and F₂ was from the best-fit with both sets of equilibrium data, $\gamma(\ln C)$ and $\gamma(\Gamma)$, as shown in Figure 4c

and d and listed in Table 1 of the model parameters. Both F₁ and F₂ fit $\gamma(\ln C)$ and $\gamma(\Gamma/\Gamma_{ref})$ data profiles very well (Figure 4c and the inset of Figure 4d); however, F₂ predicts $\gamma(\Gamma)$ data much better than F₁ (Figure 4d). Therefore, F₂ predicts the dynamic $\gamma(t)$ data much better than F₁ (Figure 7a). In addition, the diffusivities resulted from F₁ and F₂ are quite different ($D = 11 \times 10^{-6}$ cm²/s from F₁ and 7.0×10^{-6} cm²/s from F₂ for the run shown in Figure 7a). Note that the generalized Frumkin model fits equilibrium and dynamic data profiles better than the F₂ model, and an averaged diffusivity of 7.3×10^{-6} cm²/s was evaluated using the GF model for $C_{12}E_8$. The decrease of diffusivity with surfactant concentration (Figure 7b) is due to a shift of controlling mechanism from diffusion-control to mixed-control, that has been discussed in previous articles.^{24–26}

Figure 6. (a) Representative dynamic surface tension profiles of $C_{12}E_4$ and the model predictions from the Langmuir (L) and Frumkin (F) models with $D = 6.5 \times 10^{-6} \text{ cm}^2/\text{s}$ for $C_0 = 1.5 \times 10^{-8} \text{ mol/cm}^3$. (b) Diffusivities resulting from dynamic $\gamma(t)$ data at different concentrations using the Langmuir and Frumkin models for $C_{12}E_4$.

Figure 7. (a) Representative dynamic surface tension profiles of $C_{12}E_8$ and the model predictions from the Frumkin (F_1 and F_2) model for $C_0 = 1.5 \times 10^{-10} \text{ mol/cm}^3$. (b) Diffusivities resulting from dynamic $\gamma(t)$ data at different concentrations using F_1 and F_2 . F_1 best-fits only the $\gamma(\ln C)$ data, and F_2 was from the best-fit on both $\gamma(\ln C)$ and $\gamma(\Gamma)$ data. In part a, $D = 11.0 \times 10^{-6} \text{ cm}^2/\text{s}$ for F_1 and $7.0 \times 10^{-6} \text{ cm}^2/\text{s}$ for F_2 .

Alcohols. The equilibrium and dynamic data profiles of two alcohols (1-nonanol and 1-decanol) were also investigated to examine the role of the surface equation of state. Shown in Figures 8 and 9 are the equilibrium data of $\gamma(\ln C)$ and $\gamma(\Gamma)$. Unlike the case of C_mE_n , the Langmuir isotherm fits poorly the $\gamma(\ln C)$ data of 1-nonanol and 1-decanol. This is because we have complete $\gamma(\ln C)$ data sets and the molecular interaction is significant for these two alcohols, having long hydrocarbon chains. The interaction parameters, $K = -3.4$ for nonanol and $K = -3.7$ for decanol using the Frumkin model,^{13,27} are listed

Figure 8. (a) Equilibrium surface tension $\gamma(C)$ and (the inset) experimental data of the surface equation of state $\gamma(\Gamma)$, (b) relationship between surface tension and relative surface concentration, and model predictions using Langmuir (L), Frumkin (F), and generalized Frumkin (GF) isotherms for 1-nonanol. L best-fits the $\gamma(\ln C)$ data, F is from the best-fit on both $\gamma(\ln C)$ and $\gamma(\Gamma/\Gamma_{\text{ref}})$ data, and GF is from the best-fit on both $\gamma(\ln C)$ and $\gamma(\Gamma)$ data.

Figure 9. (a) Equilibrium surface tension $\gamma(C)$, (b) relationship between surface tension and relative surface concentration and (the inset) experimental data of the surface equation of state $\gamma(\Gamma)$, and model predictions using Langmuir (L), Frumkin (F), and generalized Frumkin (GF) isotherms for 1-decanol. L best-fits the $\gamma(\ln C)$ data, and F and GF are from the best-fit on both $\gamma(\ln C)$ and $\gamma(\Gamma/\Gamma_{\text{ref}})$ data. $T = 22.7^\circ\text{C}$

in Table 1. Recall that the critical value for K is -4 for the Frumkin isotherm.⁷

The Frumkin model fits the $\gamma(\ln C)$ data nearly perfectly but predicts the $\gamma(\Gamma/\Gamma_{\text{ref}})$ data profile only satisfactorily (Figures 8b and 9b). A significant deviation was observed between the model prediction from the Frumkin isotherm and the $\gamma(\Gamma)$ data profile for nonanol (the inset of Figure 8a). Similar behavior was also observed for decanol, as shown in the inset of Figure 9b. This gives another illustration that the $\gamma(\Gamma)$ dependency is more sensitive than $\gamma(\Gamma/\Gamma_{\text{ref}})$ and brings more help to studying the adsorption behavior of surfactants. It had been reported that the Frumkin model is not good enough for describing the adsorption behavior of nonanol and decanol, and a

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Figure 10. (a) Representative dynamic surface tension profiles of 1-decanol and model predictions from the Langmuir (L), Frumkin (F), and generalized Frumkin (GF) models for $C_0 = 3.95 \times 10^{-8}$ mol/cm³. (b) Diffusivities resulting from dynamic $\gamma(t)$ data at different concentrations using L, F, and GF models for 1-decanol. In part a, $D = 4.2 \times 10^{-6}$ cm²/s for L, 8.6×10^{-6} cm²/s for F, and 7.3×10^{-6} cm²/s for GF.

model (e.g., the generalized Frumkin or phase transition models) with four parameters is needed for these two surfactants.^{13,27–31} The generalized Frumkin isotherm does fit better the $\gamma(\Gamma)$ profiles, as shown in the insets of Figures 8a and 9b for nonanol and decanol, respectively.

If one examines more closely the fits of the dynamic surface tension data of nonanol and decanol, one will observe there always exists a deviation between the theoretical prediction and the $\gamma(t)$ profile of the shoulder region.^{13,27} The model prediction always underestimates the measured $\gamma(t)$ data. An example is shown in Figure 10a for decanol at $C = 3.95 \times 10^{-8}$ mol/cm³. All these three models (L, F, and GF) predict a lower surface tension for the beginning 30 s, at which the $\gamma(t)$ data profile shows nearly cusp or shoulder behavior. This is because all these three isotherms (L, G, and GF) predict a lower surface tension at dilute surface concentration, as shown in the inset of Figure 9b. This underestimation on γ using the Langmuir isotherm has been shown in the equilibrium surface tension $\gamma(\ln C)$ data (Figure 9a). However, this underestimation cannot be observed for the F and GF isotherms from the $\gamma(\ln C)$ data. Therefore, the experimental data of the surface equation of state $\gamma(\Gamma)$ do bring more information on studying surfactant adsorption kinetics.

The $\gamma(\Gamma)$ data also bring help for evaluating the surfactant diffusivity. For example, the Langmuir isotherm underestimates the $\gamma(\Gamma)$ data significantly (ca. 5 mN/m, the inset of Figure 9b). The correct model prediction on $\gamma(t)$ in Figure 10a should be lower than the data profile. However, to best-fit the $\gamma(t)$ data profile, one has to move the theoretical (dashed) curve up to approach the data profile. A lower diffusivity therefore results due to the underestimation of $\gamma(\Gamma)$ data. This is why a lower diffusivity resulted for decanol at dilute concentrations using the Langmuir model. A reverse behavior on D

evaluation resulted at high decanol concentrations, since the Langmuir isotherm overestimates surface tension at high concentration (Figure 9).

A similar, but minor, behavior was observed when the Frumkin and generalized models were used. The underestimation of γ at dilute surface concentrations, $\gamma(\Gamma)$, makes it an impossible mission to fit the $\gamma(t)$ data perfectly. A poor prediction of $\gamma(\Gamma)$ for the Frumkin isotherm, overestimation at $60 \text{ mN/m} < \gamma < 68 \text{ mN/m}$ (the inset of Figure 9b), causes an error on evaluating the diffusivity. An overestimation of diffusivity therefore resulted at dilute concentrations using the Frumkin model. This is because the best-fitting procedure tried to move the theoretical $\gamma(t)$ curve lower by increasing the diffusivity. Since the GF isotherm fits the $\gamma(\Gamma)$ data with the smallest deviation, the diffusivities resulted from the GF model therefore have the smallest variation at different concentrations and also have the highest reliability among these three models (L, F, and GF).

5. Discussion and Conclusions

The experimental data profiles of the surface equation of state, $\gamma(\Gamma)$, of six nonionic C_mE_n surfactants and two alcohols are given in this work. It has been illustrated that the $\gamma(\Gamma)$ data play an important role on studying the surfactant adsorption kinetics. This second equilibrium data profile, $\gamma(\Gamma)$, brings help for the determination of the adsorption isotherm, model parameters, and the controlling mechanism, and also for the evaluation of surfactant diffusivity. The examples in this work have also illustrated that the dependence of γ vs Γ is more sensitive than $\gamma(\Gamma/\Gamma_{\text{ref}})$ and brings more help.

According to the $\gamma(\Gamma)$ data, the Langmuir isotherm clearly fails to describe the adsorption behavior of nonionic C_mE_n surfactants and the alcohols with long hydrocarbon chains. When a nonionic surfactant has a long EO group (e.g., C_mE_8) or a very short EO group (e.g., C_mE_0), the molecular interaction is significant, and the Frumkin model can only describe satisfactorily the equilibrium $\gamma(\Gamma)$ and dynamic $\gamma(t)$ data. A model with four parameters is therefore needed in order to describe better the $\gamma(\Gamma)$ and $\gamma(t)$ data.

The surface equation of state describes the unique $\gamma(\Gamma)$ dependency and the surface tension of the air–water interface at different surfactant surface coverages, and it can be described by eq 3. When the Frumkin isotherm is used, it becomes

$$\gamma - \gamma_0 = \Gamma_{\infty} RT [\ln(1 - x) - Kx^2/2] \quad (6)$$

where x is the surface coverage ($= \Gamma/\Gamma_{\infty}$). There are three model parameters in the Frumkin isotherm (Γ_{∞} , a , and K); however, only two parameters (Γ_{∞} and K) show up in eq 6 to relate the γ vs Γ dependency in the equation of the surface equation of state.

When one applied eq 6 to fit the experimental $\gamma(\Gamma)$ data profile, only two parameters resulted and usually many sets of Γ_{∞} and K could describe the data profile well. However, only one specific set of the parameters with the third parameter (surfactant activity a) can fit the $\gamma(\ln C)$ data profile well simultaneously. Note that it is impossible to determine Γ_{∞} and K independently using the $\gamma(\Gamma)$ data profile alone. In other words, the $\gamma(\Gamma)$ data profile does bring help for the determination of the adsorption isotherm, model parameters, the controlling mechanism, and diffusivity, but there is no way for one to use only the $\gamma(\Gamma)$ data profile to find out a unique set of parameters Γ_{∞} and K .

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The surface equation of state, $\gamma(\Gamma)$, relates the equilibrium dependency between surface tension and surface excess. In this work, the system was not at equilibrium when the $\gamma(\Gamma)$ data profile was obtained from the surface expansion experiment, in which the amount of surfactant molecules adsorbing onto the expanding air–water interface was negligible. The dynamic surface equation of state had been discussed in previous articles.^{12,32–34} Hansen and Wallace³² proposed that the surface tension depends

only on the surface excess, whether the system is at equilibrium or not. Posner et al.³³ reported that the slow orientation process results in negligible, if any, surface tension changes. Therefore, the assumption that the surface tension depends only on the surface concentration and is not affected by the rearrangement or reorientation of molecules was applied in this work for small, simple surfactants.

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