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Role of Equation of State on Studying Surfactant Adsorption Kinetics

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The adsorption kinetics of a surfactant is used to apply the equilibrium surface tension data $\gamma(C)$ for the determination of the adsorption isotherm and then to apply the dynamic surface tension $\gamma(t)$ on determining the controlling mechanism, the diffusivity, and/or the sorption rate constants. A concept for surfactants lacking low surface pressure data has been proposed (Hsu et al. *Langmuir* **1997**, *13*, 6204; **1999**, *15*, 1952): using only a limited range of equilibrium surface tension data to determine the adsorption isotherm can cause a mistake on determining the adsorption mechanism and diffusion coefficient. In this work, the above concept is extended: even though an isotherm describes the $\gamma(C)$ data well, it may describe the dynamic surface tension data incorrectly. An incorrect controlling mechanism and/or a diffusion coefficient with a significant error may result if only the $\gamma(C)$ data are applied on determining the adsorption isotherm and model parameters. A second set of equilibrium data, equation of state $\gamma(\Gamma)$, is useful and necessary for studying the adsorption kinetics. A theoretical simulation and two examples (for surfactants with either cooperative or anticooperative adsorption) are presented in this article to illustrate this concept.

Introduction

A concept on the study of adsorption kinetics of surfactant has been recently proposed by Hsu et al.:[1] using only a limited range of equilibrium surface tension data to determine the adsorption isotherm can cause a mistake on determining the adsorption mechanism and diffusion coefficient (D). A simpler model may be applied, and it may overestimate (for anticooperative surfactants) or underestimate (for cooperative surfactants) the diffusion coefficient at dilute bulk concentrations due to the lack of the data at low surface pressure. At elevated concentrations, the fit between the model predictions and dynamic surface tension profiles may become worse; however, a smaller deviation on D resulted.

For an anticooperative surfactant, the diffusivity, obtained from the best-fit between the dynamic data of surface tension and the model-predicted profiles, varies from a higher value to a lower one and this decrease of D may cause a misjudgment on the controlling mechanism. In other words, one may misjudge a diffusion-controlled adsorption process (for surfactant onto a fresh fluid interface) to be either a mixed kinetic−diffusive process or a shift process.

For $C_{14}E_8$, $C_{12}E_8$, and $C_{12}E_6$, the $\gamma(C)$ data for low surface pressure ($\gamma > 58$, 65, and 66 mN/m, respectively) are unavailable (see Figure 1) due to the extremely low surfactant concentrations and/or the extremely long time needed for the solutions to reach the equilibrium state. It was found that even the simplest model, the Langmuir adsorption isotherm, can describe the $\gamma(C)$, equilibrium surface tension, profiles of $C_{14}E_8$ and $C_{12}E_6$ very well[2−5] and describe $C_{12}E_8$ reasonably well[6] (Figure 1). Therefore, care must be taken on studying the adsorption kinetics
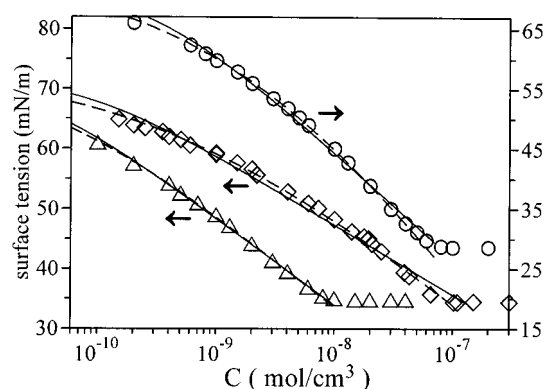

Figure 1. Equilibrium surface tension and theoretical predictions of Langmuir (solid curves) and Frumkin (dashed curves) isotherms for $C_{12}E_6$ (○), $C_{12}E_8$ (◇), and $C_{14}E_8$ (△).

for these surfactants. Another set of equilibrium data, equation of state $\gamma(\Gamma)$, is found to be very helpful on determining the adsorption isotherm and controlling mechanism and on evaluating the diffusion coefficient.[2,5,7−9]

The aim of this work is to extend the above concept: even though an isotherm describes the equilibrium surface tension data $\gamma(C)$ reasonably well (or excellently), it may describe the dynamic surface tension data incorrectly. An incorrect controlling mechanism and/or a diffusion coef-

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ficient with a significant error may be result if only the $\gamma(C)$ data are applied on determining the adsorption isotherm and model parameters.

The second set of equilibrium data, the equation of state $\gamma(\Gamma)$, is therefore useful and necessary for studying the adsorption kinetics. Data of $\gamma(\Gamma)$ are proportional to the slope of γ vs ln C curve. A good job of fitting the $\gamma(\ln C)$ data does not warrant a correct prediction on its slope, the $\gamma(\Gamma)$.

In this work, a theoretical simulation is first performed to illustrate the concept. The second part of this work gives two examples (one surfactant with cooperative adsorption and the other one with anticooperative adsorption) for a demonstration.

Governing Mass Transfer Equation

Bulk Diffusion. The adsorption of surfactant molecules onto a freshly formed spherical liquid/gas interface in a quiescent surfactant solution is modeled. It is assumed that the bulk phase contains initially uniform surfactant molecules and the bulk diffusion of surfactants onto the spherical interface (with curvature b^{-1}) is only r-direction dependent. It is also assumed that surfactant molecules do not dissolve into the gas phase of the bubble and the convection effects are negligible. The diffusion of surfactant in the bulk phase obeys Fick's law[10]

$$\frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right) = \frac{\partial C}{\partial t} \quad r > b; \, t > 0 \quad (1)$$

with the following initial and boundary conditions:

$$C(r, t) = C_0 \quad r > b; \, t = 0$$

$$C(r, t) = C_0 \quad r \rightarrow \infty; \, t > 0$$

$$d\Gamma/dt = D(\partial C/\partial r) \quad r = b; \, t > 0$$

$$\Gamma(t) = 0 \quad t = 0 \quad (2)$$

Here r and t are the spherical radial coordinate and time, D denotes the diffusion coefficient, $C(r, t)$ is the bulk concentration, $\Gamma(t)$ is the surface concentration, b is the bubble radius, and C_0 is the concentration far from the bubble. By using the Laplace transform, the solution of the above set of equations can be formulated in terms of the unknown subsurface concentration $C_s(t) = C(r = b, t)$:

$$\Gamma(t) = (D/b)[C_0 t - \int_0^t C_s(\tau)\,d\tau] + 2(D/\pi)^{1/2}[C_0 t^{1/2} - \int_0^{\sqrt{t}} C_s(t - \tau)\,d\tau^{1/2}] \quad (3)$$

Adsorption Isotherm. The kinetic equation describing the adsorption−desorption process of surfactant molecules between the sublayer and the interface is

$$d\Gamma/dt = \beta(\exp(-E_a/RT))C_s(\Gamma_\infty - \Gamma) - \alpha(\exp(-E_d/RT))\Gamma \quad (4)$$

where β, α, $E_a(\Gamma)$, and $E_d(\Gamma)$ are the preexponential factors and the energies of activation for adsorption and desorption, respectively. Γ_∞ is the maximum surface concentration, T is the temperature, and R is the gas constant. To account for the enhanced molecular interactions at increasing surface coverage, the activation energies are assumed to be the function of surface concentration with

Table 1. Adsorption Isotherms Used in This Work[a]

model/params	Γ_∞	a	K	n	isotherm
Langmuir	P_1	P_2	0	0	$\Gamma/\Gamma_\infty = x = C_s/(C_s + a)$
Frumkin	P_1	P_2	P_3	1	$\Gamma/\Gamma_\infty = x = C_s/(C_s + a\exp(Kx))$
generalized Frumkin	P_1	P_2	P_3	P_4	$\Gamma/\Gamma_\infty = x = C_s/(C_s + a\exp(Kx^n))$

[a] P_i ($i = 1-4$): parameter of the isotherm.

a power law dependence:[11]

$$E_a = E_a{}^0 + \nu_a\Gamma^n$$

$$E_d = E_d{}^0 + \nu_d\Gamma^n \quad (5)$$

where $E_a{}^0$, $E_d{}^0$, ν_a, and ν_d are constants. At equilibrium, the time rate of change of Γ vanishes and the adsorption isotherm that follows is given by

$$\Gamma/\Gamma_\infty = x = C_s/(C_s + a\exp(Kx^n)) \quad (6)$$

where $K = (\nu_a - \nu_d)\Gamma_\infty{}^n/RT$, indicating the molecular interaction between the adsorbed surfactant molecules, and $a = \alpha/\beta\,\exp[(E_a{}^0 - E_d{}^0)/RT]$, representing the surfactant activity.

Equation 6 describes the adsorption isotherm, and it allows one to develop three models including Langmuir, Frumkin, and generalized Frumkin isotherm with 2, 3, and 4 parameters (listed in Table 1), respectively. The Langmuir model assumes there exists no molecular interaction (neither in bulk phase nor at fluid interface); therefore, the activation energies are surface concentration independent and $\nu_a = \nu_d = K = 0$. The Frumkin model considers the molecular interaction, cohesive and repulsive forces, between the surfactant molecules; thus, a nonzero K resulted. A linear dependence between the activation energies and surface concentration is assumed. The Frumkin isotherm can also be obtained by considering the free energy regarding to the entropy of mixing and molecular interaction.[12−15] The generalized Frumkin model considers the molecular interaction and a power law relationship between the activation energies and surface concentration.[16]

Since the surfactant is nonionic and the solution is extremely dilute, the Gibbs adsorption equation $d\gamma = -\Gamma RT\,d\ln C$ can be applied and the equilibrium isotherm (eq 6) allows for the calculation of surface tension explicitly in terms of surface concentration:

$$\gamma - \gamma_0 = \Gamma_\infty RT[\ln(1 - x) - Knx^{n+1}/(n + 1)] \quad (7)$$

Here $x = \Gamma/\Gamma_\infty$ and γ_0 is the surface tension of solvent (pure water in this work).

Numerical Calculation. When the adsorption process is controlled solely by bulk diffusion, the surface concentration can be obtained by solving eq 3, describing the mass transfer between sublayer and bulk, and eq 6, the sorption kinetics between sublayer and interface. If the adsorption process is of mixed control, eq 4 instead of eq 6 is solved coupled with eq 3 to find out the surface concentration. Then the dynamic surface tension $\gamma(t)$ is

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Table 2. Best-Fit Parameters Using the Langmuir Isotherm[a]

Frumkin (data)			Langmuir (fit)	
Γ_∞	a	K	Γ_∞	a
5.0	1.0	−3	6.835	0.5274
5.0	1.0	15	2.030	2.989

[a] Γ_∞: 10^{-10} mol/cm^2. a: 10^{-10} mol/cm^3.

calculated from eq 7. Methods of numerical calculation have been detailed in previous studies.[11,16]

In this study, $\nu_a = 0$ was picked for the simulation when the Frumkin and generalized Frumkin models are applied. The effect of choosing a different ν_a has been discussed in a previous article.[17]

Simulations

Two theoretical simulations are performed below to illustrate a concept: even though one isotherm describes the equilibrium surface tension data $\gamma(C)$ well, it may describe the dynamic surface tension data incorrectly, may result an incorrect controlling mechanism, and may obtain a diffusion coefficient with a significant error. This is caused by utilizing only the $\gamma(C)$ data to determine the adsorption isotherm and model parameters. To simulate the adsorption of surfactant molecules onto a freshly created spherical fluid interface from a bulk phase of uniform concentration, the following parameters are assumed: maximum surface concentration $\Gamma_\infty = 5 \times 10^{-10}$ mol/cm^2; surfactant activity $a = 1 \times 10^{-10}$ mol/cm^3; solution temperature $T = 25$ °C; solvent = water; surface tension of pure water $\gamma_0 = 72.0$ mN/m; fluid interface is spherical with radium of curvature $b = 1$ mm; diffusion coefficient $D = 5 \times 10^{-6}$ cm^2/s.

Case I. The first part of simulations assumes the adsorption kinetics of surfactants follows exactly what the Frumkin model predicts with a significant molecular interaction. Two surfactants with $K = -3$ and 15 (with cooperative and anticooperative adsorption, respectively) are considered (Table 2). Note that a high absolute value of K represents strong intermolecular forces between surfactant molecules. A total of 13−15 data points of equilibrium surface tension (the circles in Figure 2) ranging between 30 and 71 mN/m are generated. The Langmuir isotherm, which assumes an ideal behavior in solution and in the adsorbed layer, is applied to fit the $\gamma(C)$ data (the circles). The fits are not excellent but reasonably good (the solid curves in Figure 2), and the best-fit model parameters (Γ_∞ and a) are listed in Table 2.

Examine the fitting more closely, one can find that the Langmuir isotherm predicts the equilibrium data poorly at dilute concentrations for both cases. Furthermore, there exists an opposite tendency for the surfactants with positive and negative K. The Langmuir isotherm predicts a lower γ than the Frumkin model with $K < 0$ and predicts a higher γ than the Frumkin model with $K > 0$ at dilute concentrations (Figure 2). Nevertheless, at the middle range of surfactant concentration the Langmuir isotherm has a higher γ than the Frumkin model with $K < 0$ and has a lower γ than the Frumkin model with $K = 15$.

A comparison between the data of equation of state (the circles, generated from the Frumkin isotherm) and the model predictions from the Langmuir model (solid curves) is shown in Figure 3 for both cases of $K = -3$ and 15. Note that the data of equation of state can be obtained
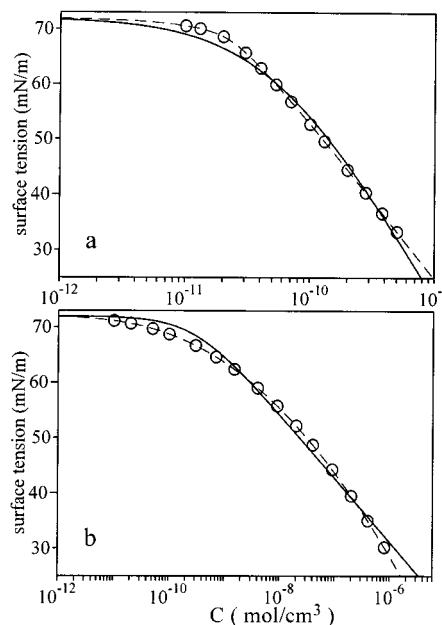
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Figure 2. Equilibrium surface tension predicted from the Frumkin isotherm (dashed curves) for surfactants with $K = -3$ (a) and 15 (b) and the theoretical profiles (solid curves) best-fitting the data (circles) using the Langmuir isotherm.
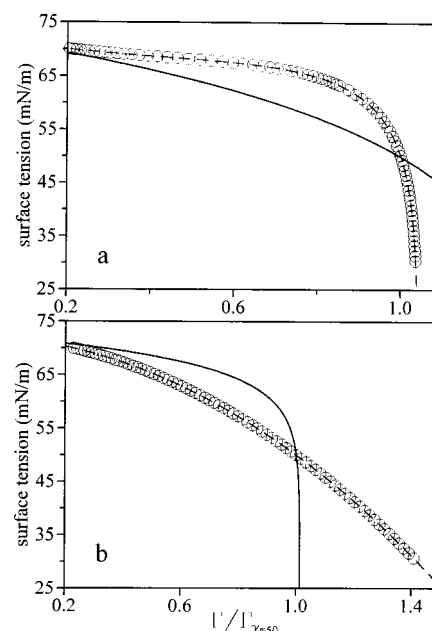

Figure 3. Data for the equation of state predicted from the Frumkin isotherm for surfactants with $K = -3$ (a) and 15 (b) and the model predictions (solid curves) from the Langmuir isotherm that best fits the $\gamma(C)$ data.

experimentally by expanding quickly the air−water interface, in which nearly no surfactant adsorbs onto interface during the expansion.[5,8] It is recalled that the Langmuir isotherm predicts the $\gamma(C)$ data reasonably well. However, the deviations for both cases of $K = -3$ and 15 are very large, especially at high surfactant concentrations. Data in Figure 3 indicate clearly that the Langmuir model describes poorly the $\gamma(\Gamma)$ dependences for surfactants with significant intermolecular forces.

Figure 4 shows some representative relaxation profiles of surface tension generated from the Frumkin model (solid curves) and the dynamic $\gamma(t)$ profiles from the Langmuir model (broken curves). At dilute concentrations, a lower diffusivity is resulted from the best fit for a cooperative
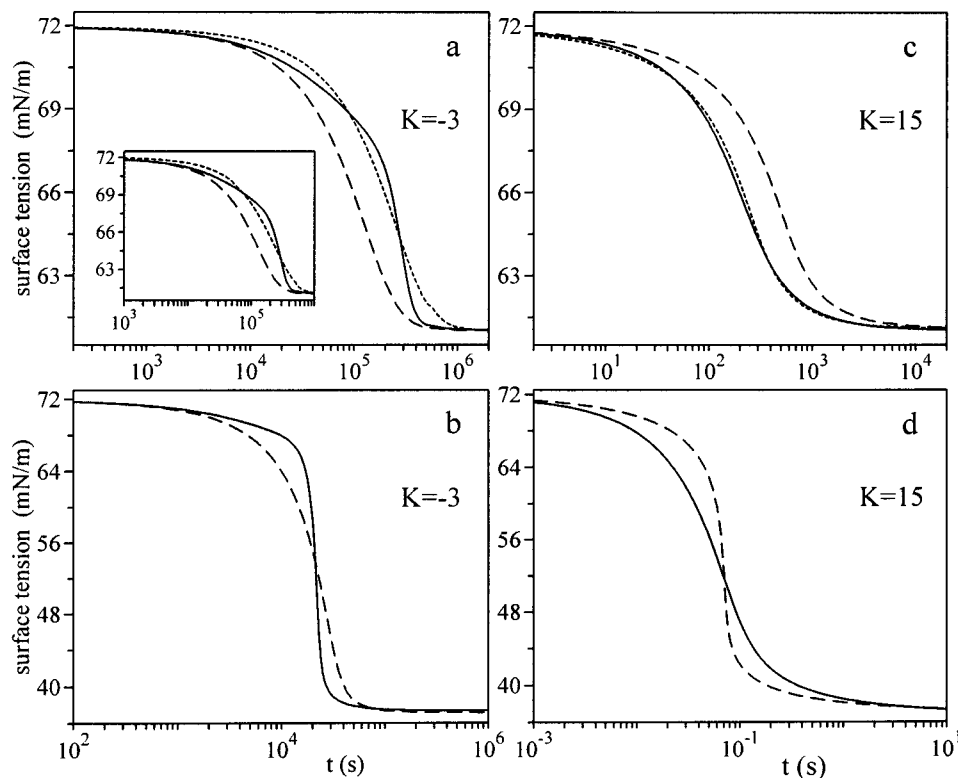
Figure 4. Representative dynamic surface tensions for adsorption onto a clean interface for $C_0 =$ (a) 2.48×10^{-11}, (b) 3.6×10^{-10}, (c) 2.3×10^{-9}, and (d) 3.0×10^{-7} mol/cm^3. The solid curves present the exact data predicted from the Frumkin model with $D = 5.0 \times 10^{-6}$ cm^2/s, and the dashed curves are from the Langmuir model with $D = 5.0 \times 10^{-6}$ cm^2/s. $D = 2.5 \times 10^{-6}$ and 10.0×10^{-6} cm^2/s for the dotted curves in (a) and (c), respectively. The dotted curve in the inset of (a) is the mixed controlled profile with $D = 5.0 \times 10^{-6}$ cm^2/s and $\beta \exp(E_a^0/RT) = 1 \times 10^5$ cm^3/(mol·s).

surfactant. At more elevated concentrations, close to cmc or the solubility in solvent, the deviation in diffusivity becomes small but it predicts a different γ vs ln(t) slope. For example, the curve with $D = 2.5 \times 10^{-6}$ cm^2/s (the dotted curve) generated from the Langmuir model describes the data profile well for $C = 2.48 \times 10^{-11}$ mol/cm^3 (Figure 4a for $K = -3$). For $C = 3.6 \times 10^{-10}$ mol/cm^3, the curve with $D = 5 \times 10^{-6}$ cm^2/s (the dashed curve) of the Langmuir model describes the data profile reasonably well (by considering roughly the relaxation time it needed, Figure 4b) but with different γ(log t) relaxation rate.

Consider next the anticooperative surfactants. At dilute concentrations, a larger diffusivity is obtained from the best fit, and at more elevated concentrations the deviation in diffusivity becomes small. As shown in Figure 4c, the curve with $D = 1.0 \times 10^{-5}$ cm^2/s generated from the Langmuir model describes the data profile excellently for $C = 2.3 \times 10^{-9}$ mol/cm^3. For $C = 3.0 \times 10^{-7}$ mol/cm^3, the curve with $D = 5 \times 10^{-6}$ cm^2/s of the Langmuir model describes the data profile reasonably well (Figure 4d) but with different γ(log t) relaxation rate.

Figure 4b,d shows that, at high surfactant concentration, the Langmuir model predicts a slower and a faster rate of relaxation of surface tension for $K < 0$ and $K > 0$, respectively. This incorrect relaxation rate is due to the poor prediction on the slope of γ vs ln C curve (Figure 2) or the poor data prediction on the γ vs Γ relationship (Figure 3).

Plotted in Figure 4a also is the dynamic $\gamma(t)$ profile from the Langmuir model with $D = 5 \times 10^{-6}$ cm^2/s (the dashed curve). The dashed curve is significantly far away from the solid curve (the imaginary experimental data). If the correct diffusion coefficient is known, for example, obtained from the dynamic $\gamma(t)$ profiles at more elevated concen-

trations, a wrong conclusion may be obtained: the adsorption is of mixed kinetic−diffusive control at dilute concentrations. The inset in Figure 4a demonstrates that a relaxation profile (the dotted curve) with $D = 5 \times 10^{-6}$ cm^2/s and finite adsorption/desorption rate constants ($\beta = 1 \times 10^5$ cm^3/(mol·s) and $\alpha = 5.3 \times 10^{-6}$ s^{-1}) fits the experimental dynamic data (the solid curve) well. Therefore, a conclusion with incorrect controlling mechanism on the adsorption process may result in this case.

Shown in Figure 5 is the consequence from Figure 4, which best-fits the $\gamma(t)$ data using the Langmuir model by adjusting the diffusivity (D). The data clearly indicate that a poor value of D resulted at dilute concentrations even when a full range of equilibrium $\gamma(C)$ data is used. The value of D decreases from 10 to 5×10^{-6} cm^2/s for $K = 15$ and increases from 2.5 to 5×10^{-6} cm^2/s for $K = -3$ with increasing concentration. This shift trend on D is consistent with what reported in ref 6, in which an erroneous shift is induced by the lack of equilibrium $\gamma(C)$ data of high surface tension. In this work the equilibrium $\gamma(C)$ data of high γ have been used. The deviation of D is caused by the inadequacy of adsorption isotherm used for interpreting the $\gamma(C)$ data. The Langmuir isotherm assumes no molecular interaction, so it is hard to predict the behavior of a surfactant with strong intermolecular forces. The error on D is then generated on best-fitting the $\gamma(t)$ data. It can also be predicted that if the Langmuir model is utilized to fit the data generated by a Frumkin model with a smaller absolute K value, the variation on D will still exist but the deviation will become smaller.

Case II. The Frumkin model is not able to predict the adsorption kinetics of some widely used surfactants, for
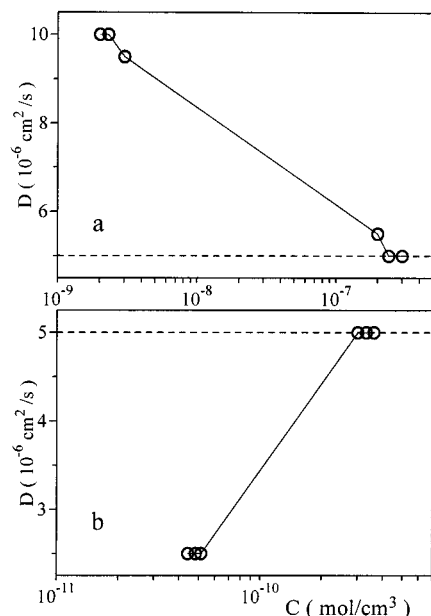
Figure 5. Deviation of diffusivity as a function of concentration obtained by using the Langmuir model for $K = 15$ (a) and -3 (b).

Table 3. Best-Fit Parameters Using the Frumkin Isotherm[a]

generalized Frumkin				Frumkin		
Γ_∞	a	K	n	Γ_∞	a	K
5.0	1.0	−4	0.5	4.905	0.3648	−3.432
5.0	1.0	−3	0.5	4.878	0.4830	−2.697
5.0	1.0	8	0.5	5.630	6.355	9.083
5.0	1.0	15	0.5	5.314	18.89	17.82

^{a} Γ_∞: 10^{-10} mol/cm^2. a: 10^{-10} mol/cm^3.

example 1-decanol, $C_{10}E_8$, and $C_{12}E_8$,[6,18,19] and it was found that the generalized Frumkin model does a much better job. Part two of the simulations assumes the adsorption kinetics of surfactants follows exactly what the generalized Frumkin (GF) model (with $n = 0.5$) predicts; i.e., the molecular interaction is significant and a power law dependence of $E \propto \Gamma^{0.5}$ between the activation energy (E) of adsorption/desorption and surface concentration is assumed. The model parameters (Γ_∞ and a) and experimental conditions (T, b, and D) used for the simulation are the same as case I. Four different molecular interactions ($K = -4$ and -3 for cooperative surfactants and 8 and 15 for anticooperative surfactants) are considered, and the model constants are listed in Table 3. A total of 11−16 data points of equilibrium surface tension (the circles in Figure 6a) ranging between 30 and 71 mN/m are generated. The Frumkin isotherm is applied to fit the equilibrium surface tension data for the whole range of $\gamma(C)$ data. The fits are shown as the solid curves in Figure 6a with best-fit model parameters (Γ_∞, a, and K) listed in Table 3. The fits using the Frumkin isotherm are nearly perfect except a little deviation at dilute concentrations. For $K = 15$, the Frumkin model predicts a little higher γ at $C < 3 \times 10^{-8}$ mol/cm^3 and a slightly smaller γ above 3×10^{-8} mol/cm^3. For $K = -3$, an opposite trend was resulted. Note that the deviation is smaller than the measurement error in both cases.

Although the fits on $\gamma(C)$ data are nearly perfect, the prediction from the Frumkin isotherm on the data of
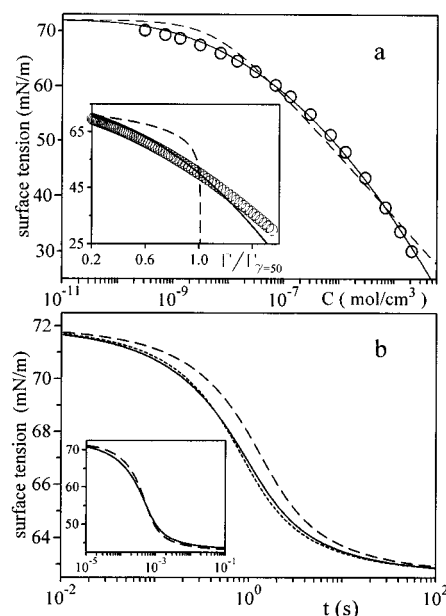
(18) Chang, H. C.; Hsu, C. T.; Lin, S. Y. *Langmuir* **1998**, *14*, 2476.
(19) Lin, S. Y.; Lu, T. L.; Hwang, W. B. *Langmuir* **1995**, *11*, 555.

Figure 6. (a) Equilibrium surface tension and data for the equation of state (the inset, which best-fits the $\gamma(C)$ data), predicted from the generalized Frumkin isotherm, for a surfactant with $K = 15$ and the best-fit profile using the Frumkin (solid curve) and Langmuir (dashed curve) isotherms. (b) Representative dynamic surface tension of adsorption for $C_0 = 7.3 \times 10^{-8}$ and 3.0×10^{-6} (the inset) for $K = 15$: solid curve is the exact data predicted from the generalized Frumkin model with $D = 5.0 \times 10^{-6}$ cm^2/s, and dashed and dotted curves are from the Frumkin model with $D = 5.0 \times 10^{-6}$ and 8.0×10^{-6} cm^2/s, respectively.

equation of state $\gamma(\Gamma)$ is only reasonably good (solid curve in the inset of Figure 6a). The deviation is consistent with what is shown in Figure 6a. At dilute concentrations, a smaller surface concentration is obtained, and a larger Γ is resulted at more elevated concentrations for $K = 15$. However, these deviations are enlarged on the prediction of the dynamic $\gamma(t)$ profiles. In Figure 6b, the model prediction with $D = 5 \times 10^{-6}$ cm^2/s (the dashed curve) does show a significantly slower relaxation. A similar slower relaxation at small time is observed for all concentrations for $K = 15$. When the concentration is high, a faster relaxation at $\gamma < 55$ mN/m is resulted (dashed curve in the inset of Figure 6b), corresponding to the lower γ prediction at higher Γ as shown in Figure 6a.

Shown in Figure 6b (the dotted curve) also is the model prediction from the Frumkin model with $D = 8 \times 10^{-6}$ cm^2/s, which fits the data (the solid curve) nearly perfectly. One will definitely conclude a diffusion-controlled adsorption with $D = 8 \times 10^{-6}$ cm^2/s at this run for $C = 7.3 \times 10^{-8}$ mol/cm^3. A higher D is therefore obtained by using the Frumkin model for anticooperative surfactants ($K > 0$), as shown in Figure 7a. As the concentration increases, the diffusivity best-fitting the dynamic $\gamma(t)$ data decreases and approaches the exact D (5.0×10^{-6} cm^2/s). The effect of molecular interaction (K) and surfactant concentration on the evaluated diffusion coefficient is shown in Figure 7a for $K = 8$ and 15.

An opposite deviation is resulted for a cooperative surfactant ($K < 0$). The deviation on $\gamma(t)$ is similar to what shown in Figures 2b, 3b, and 4a,b. The effect of K and C on the evaluated D is shown in Figure 7b for $K = -3$ and −4.

Shown in Figure 6a also are the model predictions using the Langmuir isotherm (dashed curves). The data indicate that the Langmuir model used to fit the data generated
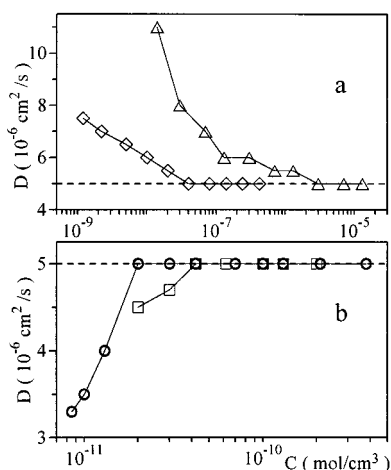
Figure 7. Deviation of diffusivity as a function of concentration obtained by using the Frumkin model for $K = 15$ ($\triangle$), 8 ($\diamond$), -3 ($\bigcirc$), and -4 ($\square$).
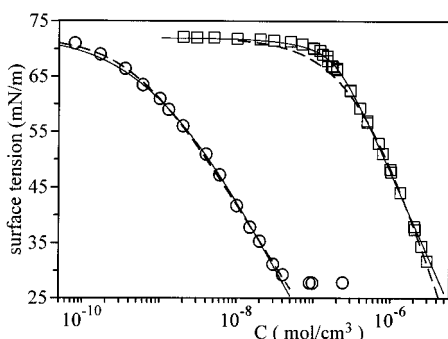

Figure 8. Equilibrium surface tension and the theoretical predictions of the Langmuir (dashed curves) and Frumkin (solid curves) adsorption isotherms: $C_{12}E_4$ ($\bigcirc$); 1-octanol ($\square$).

Table 4. Constants of the Optimal Fit of $C_{12}E_4$ and 1-Octanol Solutions

	model[a]	Γ_∞ $(10^{-10}$ mol/cm$^2)$	a (mol/cm^3)	K
$C_{12}E_4$	L	3.905	4.660×10^{-10}	
$C_{12}E_4$	F	4.663	3.521×10^{-10}	1.875
1-octanol	L	8.958	5.565×10^{-7}	
1-octanol	F	5.910	7.653×10^{-7}	-2.661

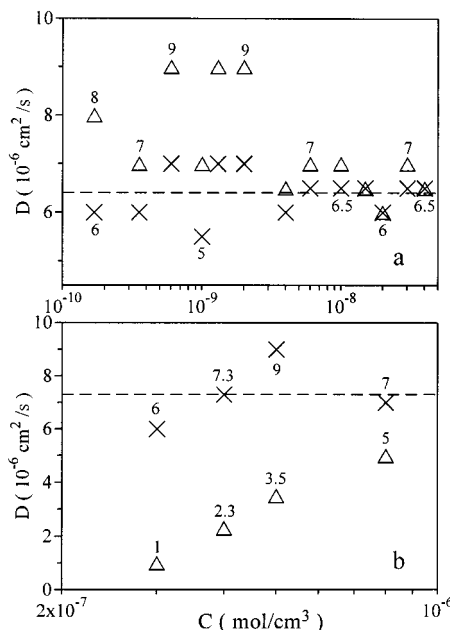[a] L: Langmuir. F: Frumkin.

Figure 9. Variation of diffusion coefficients as a function of surfactant concentration obtained by using the Langmuir ($\triangle$) and Frumkin ($\times$) model for (a) $C_{12}E_4$ and (b) 1-octanol.

from the generalized Frumkin model with $n = 0.5$ is much worse than the Frumkin model. One can therefore expect a larger deviation on the D value and the $\gamma(t)$ profiles if the Langmuir model is applied here.

Illustrations

As mentioned in Introduction, the $\gamma(C)$ data for low surface pressure for $C_{12}E_8$, $C_{14}E_8$, and $C_{12}E_6$ are unavailable (Figure 1); therefore, these surfactants are not the ones that we discuss in this work. The surfactants discussed in this work are those having a pretty complete $\gamma(C)$ data set, for example, 1-decanol, 1-octanol, $C_{12}E_4$, and 7-tetradecyn-6,9-diol.[8,16,20-23] For $C_{12}E_4$ and 1-octanol, the $\gamma(C)$ data are available up to 71 mN/m and the adsorption process (onto a clean air–water interface) is found to be diffusion-controlled. To illustrate the concept proposed in this work, data for $\gamma(\ln C)$, $\gamma(\Gamma)$, and the variation of diffusion coefficient as a function of concentration $D(C)$ for $C_{12}E_4$ and 1-octanol are adapted from the literature[8,23] and discussed below.

The equilibrium $\gamma(C)$ data and the model predictions using the Langmuir and Frumkin isotherms are shown in Figure 8. The model constants best-fitting the $\gamma(C)$ data are listed in Table 4.[8,23] It is clear that the Langmuir isotherm describes the $\gamma(C)$ data of $C_{12}E_4$ as good as the Frumkin model. The fit using the Langmuir model on the

1-octanol data is slightly worse than the Frumkin model, especially at dilute concentrations.

The diffusion coefficients which best fit the dynamic surface tension data for $C_{12}E_4$ and 1-octanol by using the Langmuir and Frumkin model are shown in Figure 9. For anticooperative surfactant $C_{12}E_4$, a nearly constant diffusivity ($D = (6.4 \pm 1.0) \times 10^{-6}$ cm^2/s) resulted using the Frumkin model. However, the D value obtained from the Langmuir model decreases from 8.0 or 9.0 $\times 10^{-6}$ cm^2/s at dilute concentrations to 6.5×10^{-6} cm^2/s at the concentrations close to cmc. Note that the average value of D at high concentrations ($C = 4 \times 10^{-9}–4 \times 10^{-8}$ mol/cm^3) using the Langmuir model is nearly the same as what the Frumkin model predicts. This is exactly what Figure 5a presents: at dilute concentrations, a higher D resulted due to the imperfect model being applied, and it approaches the correct D at elevated concentrations. Figure 10 (adapted from ref 8) shows the comparison between the $\gamma(\Gamma/\Gamma_{ref})$ data and the model predictions, which best fit the $\gamma(C)$ data, of the Langmuir (dashed curve) and the Frumkin (solid curve) isotherm. The Frumkin isotherm does predict the $\gamma(\Gamma/\Gamma_{ref})$ data much better than the Langmuir model. Therefore, it was concluded that the adsorption onto the clean air–water interface is diffusion-controlled with $D = (6.4 \pm 1.0) \times 10^{-6}$ cm^2/s (the dashed line).

For cooperative surfactant 1-octanol, a nearly constant diffusivity ($D = (7.3 \pm 1.2) \times 10^{-6}$ cm^2/s; the dashed line in Figure 9b) resulted using the Frumkin model. The D value obtained from the Langmuir model increases from 1.0×10^{-6} cm^2/s (at $C = 3 \times 10^{-7}$ mol/cm^3) to 5.0×10^{-6} cm^2/s (at $C = 8 \times 10^{-7}$ mol/cm^3) monotonically. This is similar to what Figure 5b presents: at dilute concentra-

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(21) Ferri, J. K.; Stebe, K. J. *J. Colloid Interface Sci.* **1997**, *209*, 1.
(22) Ferri, J. K.; Stebe, K. J. *Adv. Colloid Interface Sci.* **2000**, *85*, 61.
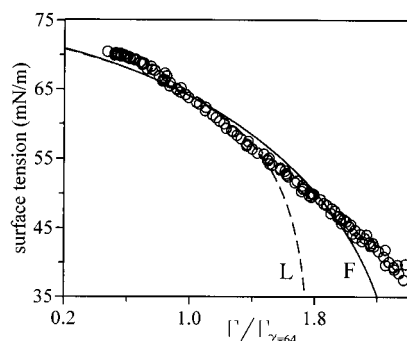(23) Lin, S. Y.; Wang, W. J.; Hsu, C. T. *Langmuir* **1997**, *13*, 6211.

Figure 10. Comparison between the experimental data for the equation of state and the profiles predicted from the Langmuir and Frumkin isotherms.

tions, a lower D resulted due to the imperfect model being applied and it approaches the correct D at elevated concentrations for cooperative surfactants.

Discussion and Conclusions

A new concept was presented in this work: even though an isotherm describes the $\gamma(C)$ data well, it may describe the dynamic surface tension data incorrectly. An incorrect controlling mechanism and/or a diffusion coefficient with a significant error result if only the $\gamma(C)$ data are applied on determining the adsorption isotherm and model parameters.

The above theoretical simulation and illustrations clearly indicate that a second set of equilibrium data, the equation of state $\gamma(\Gamma)$, is necessary for studying the adsorption kinetics. Data for $\gamma(\Gamma)$ are proportional to the slope of γ vs ln C data. A nice fit on the $\gamma(C)$ data does not warrant a correct prediction of its slope.

An ascending (for $K < 0$) or descending (for $K > 0$) trend on evaluating the diffusivity may result by using an inadequate adsorption isotherm. For anticooperative surfactants of $K > 0$, the descending diffusivity, being a judge criterion for a shift in controlling mechanism, may come from three possibilities: (i) Surfactant does have a shift in controlling mechanism. (ii) The adsorption isotherm is inadequate. (iii) The lower diffusivity at elevated concentration is due to the effect of the existence of premicelles or submicelles.

Surfactants of $C_{12}E_6$ and $C_{12}E_8$ have a positive K and a descending diffusivity at increasing concentration. For $C_{12}E_8$,[3] the Langmuir model predicts a diffusivity shifting from 19.0×10^{-6} to 5.0×10^{-6} cm^2/s and the Frumkin model predicts a diffusivity shifting from 12.0×10^{-6} to 5.0×10^{-6} cm^2/s at increasing surfactant concentration. Even the generalized Frumkin model predicts a diffusivity shifting from 9.0×10^{-6} to 4.5×10^{-6} cm^2/s. All theses three Langmuir type models predict a nearly same diffusion coefficient ($D \sim 5.0 \times 10^{-6}$ cm^2/s) at concentrations close to the cmc. Either an inadequate model was applied or there does exist a shift in the controlling mechanism for $C_{12}E_8$. More care is needed on studying the adsorption kinetics. Unless a better model is found and it can result in a constant diffusivity at the whole range of working concentrations, it is concluded for the time being that $C_{12}E_6$ and $C_{12}E_8$ have a shift in the controlling mechanism for their adsorption onto a freshly created air–water interface.[2,3,6]