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ORIGINAL CONTRIBUTION

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A model for simulating the dynamic surface tension behavior of aqueous surfactant dispersions

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Abstract A dynamic adsorption model for surface-active materials at air/liquid interfaces with the consideration of aggregate dissolution effect was developed to investigate the dynamic surface tension behavior of aqueous surfactant dispersions. Two catanionic surfactants, cetylpyridinium dodecylsulfate (CP-DS) and dodecyltrimethylammonium dodecylsulfate (DTMA-DS), with low critical aggregation concentrations were chosen as model systems. Dynamic surface tensions of aqueous CP-DS and DTMA-DS systems were measured by a drop volume tensiometer. A model with diffusion-controlled or mixed-kinetic dynamic adsorption mechanisms considering the dissolution effect of dispersed aggregates was developed to simulate the dynamic surface tension data. An analysis by comparing the model predictions with experimental data demonstrated that the dynamic surface tension behavior of aqueous CP-DS and DTMA-DS dispersions could be described with a diffusion-controlled dynamic adsorption model taking the aggregate dissolution effect into account.

Keywords Air/liquid interface · Catanionic surfactant · Dynamic adsorption · Dynamic surface tension · Aggregate dissolution

Introduction

For a surfactant solution, there is an equilibrium relationship between the bulk concentration and the surface concentration if an adsorption equilibrium is reached at the air/liquid interface. When a new air/liquid interface is created, surfactant molecules in the bulk phase will start adsorbing onto the interface to establish the equilibrium adsorption condition. As a result, the surface tension will decrease with time or with the extent of surfactant adsorption, finally reaching an equilibrium surface tension. The time-dependent surface tension is so-called the dynamic surface tension [1, 2]. To understand the dynamic adsorption or dynamic surface tension behavior is useful for surfactant applications such as foaming [3], laundry process [4], and therapeutic lung surfactant preparation [5, 6].

Some aqueous surfactant or lipid systems may contain an aggregated phase, such as microcrystallites, mainly due to solubility limit. The aggregated phase or particles can be considered as the source of free molecules in the bulk phase. When free surface-active molecules in the bulk phase adsorb onto the air/liquid interface because of the new interface formation, the dispersed particles can dissolute and provide free molecules to resume the original equilibrium condition between free molecules and particles. It has been found that when an aqueous surfactant dispersion was filtered and then the dynamic surface tensions of the remaining solution were measured, the rate of surface tension decreasing with time was significantly reduced, apparently caused by the removal of surfactant particles or the sources for free molecules [7].

For a soluble surfactant, the dynamic surface tension behavior of the aqueous surfactant solutions containing monomers and micelles has been extensively studied and can be described by theoretical models with a reasonable extent [8]. If only surfactant monomers exist in the bulk phase, one usually uses a diffusion-controlled or mixed-

kinetic dynamic adsorption model to simulate the dynamic surface tension behavior of the surfactant solution [9–11]. When micelles are available in the bulk phase, the loss of surfactant monomers in the bulk phase due to the dynamic adsorption at interfaces can be replenished through the micellar dissolution [12–15]. To take micelles into account, Dushkin et al. [16] have used a gradual aggregation–disintegration mechanism of micellar dissolution kinetics to predict the dynamic adsorption behavior of surfactant solutions containing polydispersed micelles. A simplified model with the consideration of micellar dissolution and diffusion effects on surfactant adsorption dynamics has been developed recently [17].

However, there are few studies investigating the dynamic adsorption behavior of aqueous systems containing surfactant particles [18–21]. The present work aims to develop a dynamic adsorption model considering the aggregate dissolution effect to simulate the dynamic surface tension behavior of aqueous surfactant dispersions. Two aqueous systems of catanionic surfactant, cetylpyridinium dodecylsulfate (CP-DS) and dodecyltrimethylammonium dodecylsulfate (DTMA-DS), were chosen as model systems. Catanionic surfactant is usually formed by the precipitation of mixed anionic and cationic surfactant solutions due to the pairing of two oppositely charged surfactant chains. The precipitate or catanionic surfactant is usually highly surface active and is considered as a pseudodouble-chained surfactant [22].

Experimental

The anionic surfactant sodium dodecylsulfate ($C_{12}H_{25}SO_4Na$) was supplied by Sigma, USA with a purity of 99% and was used as received. The cationic surfactants, cetylpyridinium chloride ($C_{16}H_{33}C_5H_5NCl$) (laboratory grade) and dodecyltrimethylammonium chloride [$C_{12}H_{25}N(CH_3)_3Cl$] (99% purity), were purchased from Sigma and TCI, respectively, and were used without further purification. All experiments were conducted with purified water that was passed through a Milli-Q plus purification system (Millipore, USA) with a resistivity of 18.2 MΩ cm. Two catanionic surfactants, CP-DS ($C_{16}H_{33}C_5H_5N$-$C_{12}H_{25}SO_4$) and DTMA-DS [$C_{12}H_{25}N(CH_3)_3$-$C_{12}H_{25}SO_4$], were obtained as precipitates by mixing the corresponding cationic and anionic surfactants in aqueous solutions of sufficiently high concentrations [23]. The precipitates were separated from the solutions by repeated centrifuging and washing. They were then dried for 36 h under vacuum and ground into fine powders for further adsorption studies.

Equilibrium surface tensions were measured at 25 °C with a platinum Wilhelmy plate tensiometer (model CBVP-A3, Kyowa Interface Science, Japan). The dynamic surface tension behavior of the aqueous catanionic surfactant solutions or dispersions was obtained at 25 °C with a drop volume tensiometer (model TVT1, Lauda, Germany). At first, an aqueous drop containing the catanionic surfactant with a definite volume, which was smaller than the critical volume corresponding to the equilibrium surface tension of the aqueous catanionic surfactant sample, was formed very fast at the tip of a capillary surrounded by ambient air. The surface tension decreased with time due to the dynamic adsorption behavior of the surface-active molecules at the interface. The time necessary for the surface tension decreasing to a value that the drop detached from the capillary tip due to gravity force was measured, and the corresponding surface tension value was calculated from the known volume of the drop and the capillary diameter. After the drop detached from the capillary tip, the next drop was formed with a slightly smaller volume and the procedure started again. By repeating this procedure, the dynamic surface tension behavior of the aqueous catanionic surfactant sample was constructed [24].

Dynamic adsorption model

For a one-dimensional dynamic adsorption process at the air/liquid interface without considering the aggregate dissolution effect, the governing equations are well known, and a detailed review had been reported before [9].

$$\frac{\partial C(x,\,t)}{\partial t} = D\frac{\partial^2 C(x,\,t)}{\partial x^2} \tag{1}$$

$$D\frac{\partial C(0,\,t)}{\partial x} = \frac{d\Gamma(t)}{dt} \tag{2}$$

The initial and boundary conditions are

$$C(x,\,0) = C_0 \tag{3}$$

$$\Gamma(0) = 0 \tag{4}$$

$$C(l,\,t) = C_0 \tag{5}$$

Here, C is the surfactant concentration in the domain of finite length l, Γ is the surface concentration of the surfactant, t is the time, D is the diffusivity, x is the distance from the subsurface, and C_0 is the initial uniform bulk concentration.

To solve the above equations, one needs to know the dependence of Γ on $C(0,t)$ (diffusion-controlled case) or the kinetic equation for $d\Gamma/dt$ (mixed-kinetic case). Moreover, because it is much easier to measure $\gamma(t)$ than $\Gamma(t)$, an equation relating $\Gamma(t)$ to $\gamma(t)$ is always applied to obtain the problem solution with an expression of $\gamma(t)$. One usually

assumes that the equation relating $\Gamma(t)$ to $\gamma(t)$ is the same as the equilibrium surface equation of state [25].

If the dynamic adsorption process is diffusion-controlled, the generally accepted approach for solving the problem is to couple Eqs. (1, 2, 3, 4, 5) with an equilibrium isotherm $\Gamma(C)$. Several equilibrium isotherms have been used in the literature [12, 26], and the simplest nonlinear isotherm is the Langmuir isotherm.

$$\Gamma = \Gamma_m \frac{K_L C}{1 + K_L C} \tag{6}$$

where Γ_m is the maximum surface concentration and K_L is the adsorption equilibrium constant. Combining Eq. (6) with the Gibbs adsorption equation, one readily derives the Szyszkowski and Frumkin equations [27]:

$$\gamma = \gamma_0 - nRT\Gamma_m \ln(1 + K_L C) \tag{7}$$

$$\gamma = \gamma_0 + nRT\Gamma_m \ln\left(1 - \frac{\Gamma}{\Gamma_m}\right) \tag{8}$$

Here, γ_0 is the surface tension of pure solvent (water), γ is the surface tension of the solution, R is the gas constant, and T is the temperature. The factor n equals 2 for 1:1 ionic surfactants in the absence of supporting electrolyte, and n=1 for nonionic surfactants.

With Eqs. (1, 2, 3, 4, 5, 6), the problem solution $C(0,t)$ or $\Gamma(t)$ can be obtained by a numerical approach. The problem solution with an expression of $\gamma(t)$ can then be transformed from the $C(0,t)$ or $\Gamma(t)$ expressions by coupling with Eq. (7) or (8) and can be used to compare with experimental dynamic surface tension data.

If the adsorption is not diffusion-controlled and the adsorption/desorption barriers have to be considered, a kinetic equation for $d\Gamma/dt$ is required to solve Eqs. (1, 2, 3, 4, 5). A simple kinetic equation consistent with the Langmuir isotherm at equilibrium is the Langmuir–Hinshelwood equation:

$$\frac{d\Gamma}{dt} = k_a C\left(1 - \frac{\Gamma}{\Gamma_m}\right) - k_d\Gamma \tag{9}$$

where k_a and k_d are the adsorption and desorption rate constants, respectively. Using the Langmuir–Hinshelwood equation at equilibrium, i.e., $d\Gamma/dt$=0, and comparing it to the Langmuir isotherm yield

$$K_L = \frac{k_a}{k_d\Gamma_m} \tag{10}$$

If one considers the aggregate dissolution effect, Eq. (1) may be rewritten as

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2} + q \tag{11}$$

with the corresponding initial and boundary conditions

$$C(x,0) = C_s \tag{12}$$

$$\Gamma(0) = 0 \tag{13}$$

$$C(l,t) = C_s \tag{14}$$

The term q takes account of the aggregate dissolution effect on the intrinsic adsorption rate from the subphase, and C_s is the saturation concentration of the surface-active solute in the monomer form. If one assumes that the aggregate dissolution consists of two processes occurring simultaneously, q may be expressed as [28]

$$q = k_1 - k_2 C \tag{15}$$

Here, the first term in the right-hand side describes a zero-order reaction for the transfer of surface-active molecules from the aggregates into the solution with a rate constant k_1. The second term in the right-hand side describes a first-order reaction for the deposition of surface-active solutes from the bulk solution to the aggregates with a rate constant k_2. When an equilibrium is reached, i.e., a steady state between dissolution and deposition is obtained, then q=k_1–k_2C_s=0. Thus, the relationship between k_1 and k_2 can be expressed as

$$C_s = k_1/k_2 \tag{16}$$

Results and discussion

The numerical method used to solve the problem is similar to the one used before [29] with some modifications to take the aggregate dissolution effect into account. To illustrate the aggregate dissolution effect, sample model calculations are shown first. The parameter values chosen in the computations are Γ_m=8×10^{-6} mol/m^2, K_L=3×10^3 m^3/mol, D=4×10^{-10} m^2/s, l=2.4×10^{-4} m, and C_s=10^{-3} mM.

Figure 1 shows the aggregate dissolution effect on the dynamic surface tension behavior for a diffusion-controlled dynamic adsorption case, in which only the barrier for the diffusion step of surface-active monomers is concerned in the adsorption process. As expected, the higher the dissolution rate constant, the faster the dynamic surface

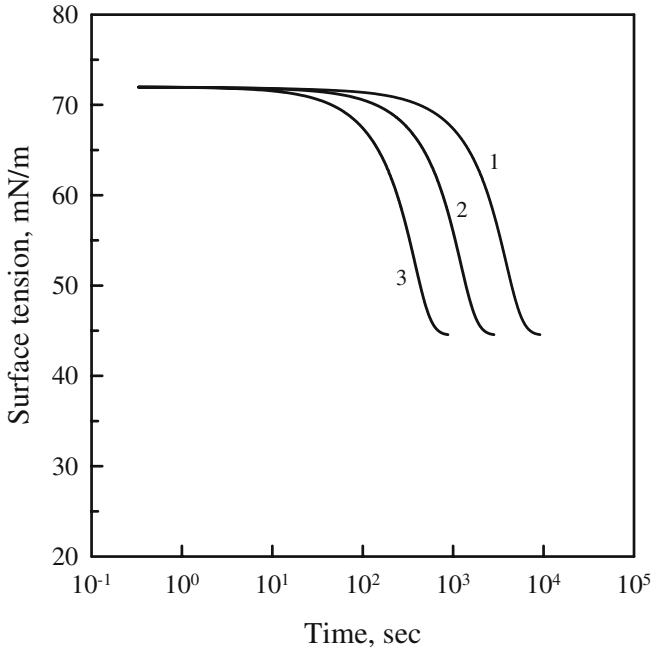

Fig. 1 Dynamic surface tensions calculated by using the diffusion-controlled adsorption model with dissolution rate constants of 0 (*curve 1*), 7×10^{-8} mol/l s (*curve 2*), and 7×10^{-7} mol/l s (*curve 3*). Other parameters are $D=4\times10^{-10}$ m^2/s, $\Gamma_m=8\times10^{-6}$ mol/m^2, $K_L=3\times10^3$ m^3/mol, $l=2.4\times10^{-4}$ m, and $C_s=10^{-3}$ mM

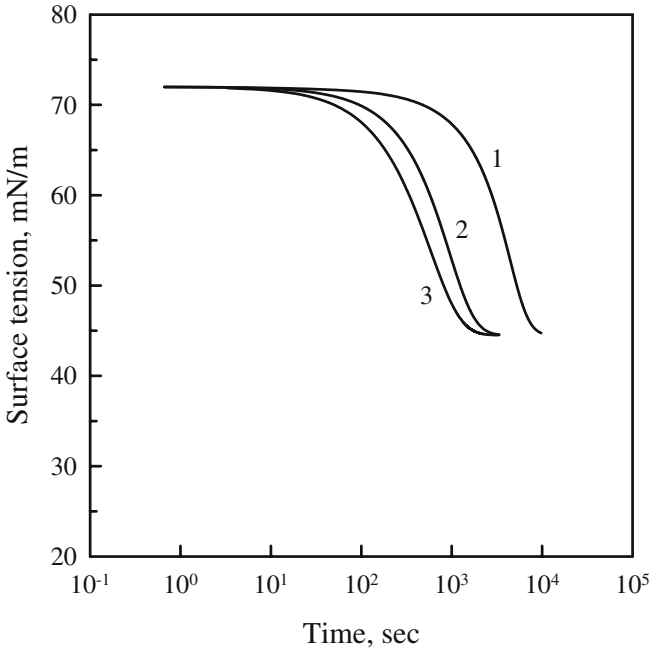

Fig. 2 Dynamic surface tensions calculated by using the mixed-kinetic adsorption model with dissolution rate constants of 0 (*curve 1*), 7×10^{-7} mol/l s (*curve 2*), and 7×10^{-3} mol/l s (*curve 3*). Other parameters are $D=4\times10^{-10}$ m^2/s, $\Gamma_m=8\times10^{-6}$ mol/m^2, $K_L=3\times10^3$ m^3/mol, $l=2.4\times10^{-4}$ m, $k_a=1.66\times10^{-5}$ m/s, and $C_s=10^{-3}$ mM

tension response. With a higher dissolution rate constant, more free surface-active monomers can be provided from the aggregates and thus the increase in surface concentration becomes significant, resulting in faster dynamic tension response and less equilibrating timescale.

A qualitatively similar trend is observed with the case of mixed-kinetic dynamic adsorption, which tends to predict slower dynamic surface tension response than the diffusion-controlled dynamic adsorption due to the existence of additional adsorption/desorption barriers at the interface (Fig. 2). However, if the dissolution rate constant k_1 keeps increasing, then eventually, the concentration of surface-active monomer inside the diffusion length will be close to the saturation concentration and thus the barrier for the diffusion step can be ignored. Under such condition, the dynamic adsorption process will be controlled by the adsorption/desorption step. Indeed, the sample calculations with a much higher k_1 value resulted in a curve, curve 3 in Fig. 2, corresponding to the limiting case predicted by a dynamic adsorption model with adsorption/desorption-controlled mechanism.

To perform a model analysis on the dynamic adsorption behavior of surface-active materials, one usually compares the dynamic surface tension data to the model predictions with adjustable parameters and determines the parameters based on the best-fit condition [9]. For both catanionic surfactants, CP-DS and DTMA-DS, it is reasonable to assume the diffusivity D to be 4×10^{-10} m^2/s as compared to other surfactants with known diffusivities. In addition, it first appears that one may have at most six adjustable parameters, Γ_m, K_L, k_a, k_d, k_1, and k_2, in applying the model. However, because k_a and k_d are related by Eq. (10) and k_1 and k_2 are not independent as suggested by Eq. 16, there are actually only two and four adjustable parameters for the diffusion-controlled and the mixed-kinetic adsorption models, respectively.

To avoid estimating four adjustable parameters, Γ_m, K_L, k_a (or k_d), and k_1(or k_2), simultaneously from the dynamic surface tension data, one can perform the model analysis by determining the equilibrium adsorption parameters, Γ_m and K_L, independently from the equilibrium surface tension vs surfactant concentration data. The dynamic surface tension data for a catanionic surfactant solution with a concentration lower than its saturation concentration (without aggregates), if they are available, are then compared to the predictions by the diffusion-controlled dynamic adsorption model with available D, Γ_m, and K_L values. If the agreement of the comparison is reasonable, one can conclude that the dynamic adsorption behavior of the catanionic surfactant at the air/liquid interface is diffusion-controlled. Thus, the dissolution rate constant or the aggregate dissolution effect can be evaluated by comparing the dynamic surface tension data of the aqueous catanionic surfactant dispersions with model calculations.

If the dynamic surface tension data for a catanionic surfactant solution at a concentration without aggregates

present cannot be described with a reasonable extent by the diffusion-controlled model predictions, it can be concluded that the dynamic adsorption behavior of the catanionic surfactant is mixed-kinetic. Thus, the k_a (or k_d) value can be determined, with the available D, Γ_m, and K_L values, from the dynamic surface tension data by comparing with the mixed-kinetic adsorption model predictions. By the model considering the aggregate dissolution effect with the available Γ_m, K_L, and k_a (or k_d) values, the parameter k_1 (or k_2) can then be estimated from the dynamic surface tension data obtained for an aqueous catanionic surfactant dispersion.

Equilibrium surface tension data obtained by the Wilhelmy plate method for various concentrations of aqueous CP-DS and DTMA-DS systems are shown in Fig. 3. Equilibrium tensions for the aqueous CP-DS system below its critical aggregation concentration are generally lower than those for DTMA-DS solutions. From Fig. 3, it appears that CP-DS is more efficient and DTMA-DS has a higher effectiveness in reducing the surface tension of water [27].

The equilibrium surface tension data below the critical aggregation concentration were then fit to the Szyszkowski equation (Eq. 7), and the best-fit equilibrium parameters, Γ_m and K_L, for CP-DS and DTMA-DS were obtained. In both cases, the calculated surface tensions with the best-fit parameters compare fairly well to the experimental data as shown in Fig. 3. The catanionic surfactant DTMA-DS has a larger Γ_m value than CP-DS. The equilibrium adsorption constant K_L, which is a measure of the surface activity [27], or the ability of the surfactant to reduce the surface tension at a given concentration, is a lot higher for CP-DS than DTMA-DS. Hence, the CP-DS is much more surface active than DTMA-DS. These values, Γ_m and K_L, provide a good basis for calculating $\gamma(t)$ from the adsorbed density or surface concentration $\Gamma(t)$ (surface equation of state) and for calculating the expected dynamic surface tensions at the diffusion-controlled adsorption limit.

Before one applies the mixed-kinetic adsorption model, he has to first establish that the adsorption process is not diffusion-controlled. For typical experiments, the l value in Eq. 5 or 14 can vary from 1,000 μm or more, if there is natural convection and no stirring, to about 10 μm, if there is significant forced convection, which produces a diffusion boundary layer. For the following calculations, l is assumed in the order of 10^2 μm.

The dynamic surface tensions of aqueous CP-DS and DTMA-DS systems are plotted in Figs. 4 and 5, respectively. For CP-DS, the critical aggregation concentration is estimated to be 1.4×10^{-3} mM from the equilibrium surface tension data. As a result, the characteristic adsorption length l_a [30], which is Γ_m/C_0 for the case of the Langmuir isotherm, for an aqueous CP-DS solution with a concentration lower than C_s is larger than 2.7 mm. This characteristic length defines the region of the subphase containing enough material to cover the interface [29], and the surface-active material in farther regions affects the adsorption a little. In view of the extremely large l_a value for an aqueous CP-DS

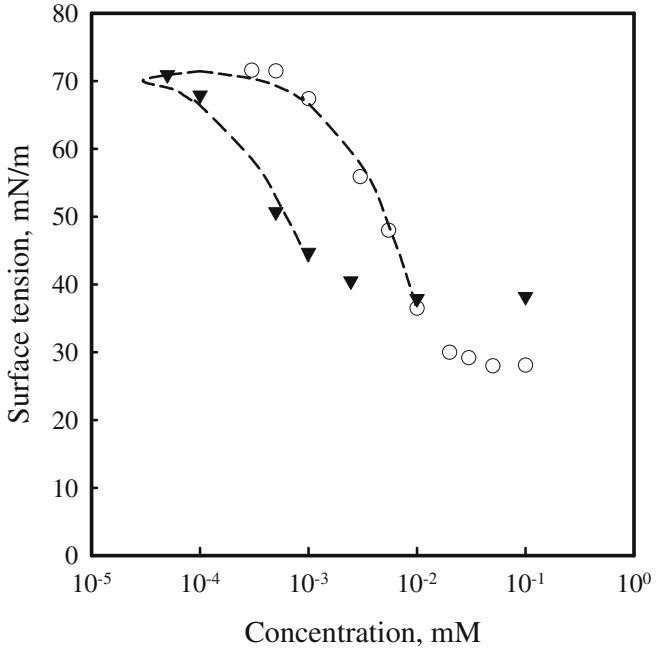

Fig. 3 Equilibrium surface tensions of aqueous CP-DS (▼) and DTMA-DS (○) systems at 25 °C obtained by the Wilhelmy plate method. *Broken lines* Calculated surface tensions by fitting data to the Szyszkowski equation (Eq. 7) with $\Gamma_m=4.0\times10^{-6}$ mol/m^2 and $K_L=3.3\times10^3$ m^3/mol for CP-DS and with $\Gamma_m=8.5\times10^{-6}$ mol/m^2 and $K_L=1.3\times10^2$ m^3/mol for DTMA-DS

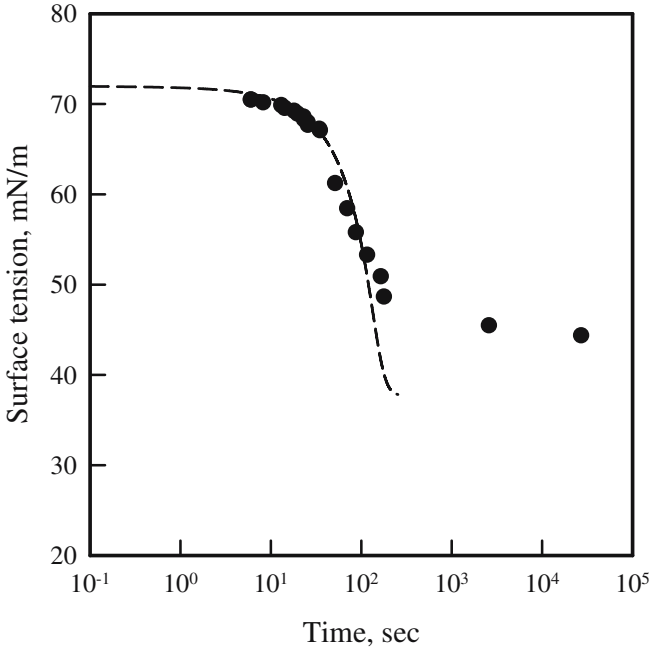

Fig. 4 Dynamic surface tension data of a 0.01-mM CP-DS dispersion (●). The *broken lines* indicate the diffusion-controlled adsorption model predictions with $k_1=1.2\times10^{-6}$ mol/l s

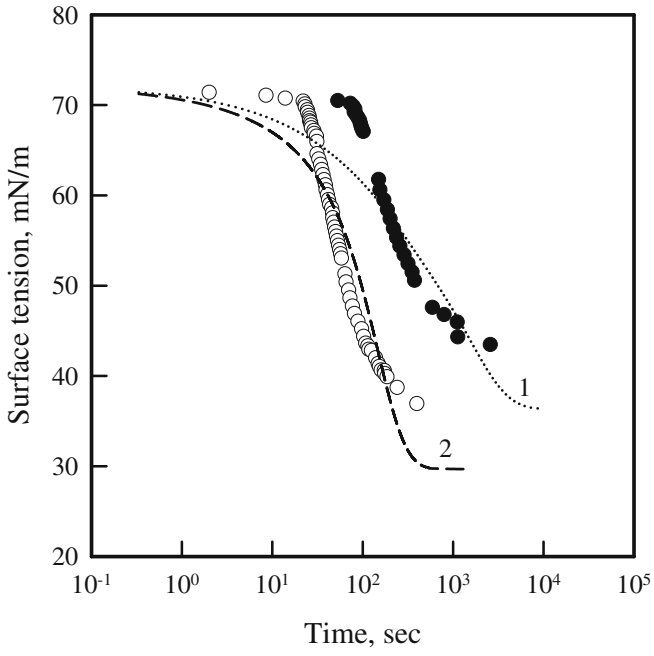

Fig. 5 Dynamic surface tension data of 0.01 mM DTMA-DS solution (○) and 0.02 mM DTMA-DS dispersion (●). *Curve 1* Diffusion-controlled adsorption model predictions. *Curve 2* Diffusion-controlled adsorption model calculations with k_1=2.6×10^{-7} mol/l s

solution, it is unlikely that one can obtain the meaningful dynamic tension response for a CP-DS solution with a concentration lower than C_s. Thus, only the dynamic surface tension data for an aqueous CP-DS dispersion are reported in this study and used to estimate the dissolution rate constant by comparing with the model calculations.

At a CP-DS concentration of 0.01 mM, which is higher than its critical aggregation concentration and with an adsorption characteristic length l_a of about 400 μm, predictions of the diffusion-controlled adsorption model taking the aggregate dissolution effect into account were calculated with a reasonable D=4×10^{-10} m^2/s. Figure 4 shows the comparison between the dynamic tension data for a 0.01-mM CP-DS dispersion and the diffusion-controlled model predictions with the determined k_1 value by the best fit of the data to the model. The agreement is quite reasonable at smaller adsorption times or lower surface coverage. The significant discrepancy between the model predictions and the data at longer adsorption times or higher surface coverage may suggest that a more sophisticated adsorption isotherm than the Langmuir isotherm has to be applied to take account of the higher adsorption density more accurately. In addition, it may also imply that the apparent k_a value (which is extremely large for a diffusion-controlled dynamic adsorption case) decreased significantly as the surface coverage became higher. That is, the role of the adsorption/desorption barriers might become important when the interface became crowded.

The significant influence of dispersed aggregates on the dynamic tension behavior is clearly demonstrated in Fig. 5 for the aqueous DTMA-DS system. In Fig. 5, curve l shows the $\gamma(t)$ predictions of the diffusion-controlled adsorption model with the Langmuir isotherm for a 0.01-mM DTMA-DS solution. With the reasonable diffusivity value of D=4×10^{-10} m^2/s, the dynamic adsorption behavior of DTMA-DS can be described with a reasonable extent by the diffusion-controlled dynamic adsorption model, indicating that the energy barriers for the adsorption/desorption steps can be ignored. The fit may be improved by applying a more sophisticated or realistic adsorption isotherm. For a 0.02-mM DTMA-DS dispersion, the comparisons of the model calculations (for D=4×10^{-10} m^2/s) considering the aggregate dissolution effect with the dynamic tension data are also shown in Fig. 5. With a dissolution rate constant k_1 of 2.6×10^{-7} mol/l s, the curve of model predictions can describe the experimental data in a reasonable extent.

Conclusions

In this study, a dynamic adsorption model of surfactants at the air/liquid interface with the consideration of aggregate dissolution effect was developed and applied to the dynamic surface tension data of two aqueous systems of catanionic surfactant, CP-DS and DTMA-DS. Experimental dynamic tension results first suggested that the dynamic adsorption timescales were significantly influenced by the presence of aggregates. It appears that by taking the aggregate dissolution effect into account, the dynamic surface tension data of both aqueous CP-DS and DTMA-DS dispersions could be described by a dynamic adsorption model with the diffusion-controlled mechanism.

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