Diffusion-controlled adsorption kinetics of aqueous submicellar and micellar solution at air/solution interface in the limit of short time

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Abstract−The equilibrium surface tensions γ_{eq} of aqueous Pentaethylenglycol-monododecylether ($C_{12}E_5$) solutions at temperature 25 °C were measured by means of Wilhelmy plate method and the determined critical micelle concentration (cmc) is 6.8×10^{-2} mol·m^{-3}. To study adsorption kinetics of aqueous submicellar and micellar solutions, the dynamic surface tensions $\gamma(t)$ were measured by means of maximal bubble pressure method. Using the derived equations of adsorption kinetics for submicellar and micellar solutions, the experimental data were analyzed and the adsorption kinetics was studied. For micellar solution ($c_0 >$ cmc) of $C_{12}E_5$, the demicellization constant $\bar{k}$ was calculated.

Key words: Adsorption, Diffusion, Surface Tension, Demicellization Constant, Critical Micelle Concentration

INTRODUCTION

Compared with the adsorption kinetics of aqueous surfactant solutions on a solid surface [Kim et al., 2005], the adsorption kinetics at air/solution interface [Ward and Tordai, 1946; Bendure, 1971; Liggieri et al., 1996; Fainerman and Miller, 1996; Fang et al., 1995; Eastoe et al., 1998; Lin et al., 1996; Liu and Messow, 2000; Lucassen, 1975; Dushkin, 1998; Filippov and Filippova, 1997; Miller, 1981; Rillaerts and Joos, 1982; Geeraerts and Joos, 1994; Iliev and Dushkin, 1992; Joos and Hunsel, 1988; Makievski et al., 1994] has been paid more and more attention because it plays an important role in wetting, foam stability, emulsion stability, fast coating, detergency, surface oscillation, adsorptive bubble separation technique etc. For surfactant solutions, there are micelles if the concentration exceeds the critical micelle concentration (cmc). Therefore, two cases, i.e., the adsorption kinetics as $c_0 <$ cmc and $c_0 >$ cmc, were always studied. For submicellar solution ($c_0 <$ cmc), there are only monomers in the solutions. The adsorption process of monomers consists of two steps (Fig. 1). The first step is the transport of monomers from the bulk phase to the subsurface due to a concentration gradient, i.e., the diffusion step; the second one is the transport of monomers from the subsurface to the surface, i.e., the adsorption step. If the rate of the first step is much slower than that of the second one, then the whole process is controlled by the diffusion. Such kind of diffusion controlled adsorption kinetics for submicellar solution was first treated quantitatively by Ward and Tordai [1946] and the derived equation was always quoted in the literature [Bendure, 1971; Liggieri et al., 1996; Fainerman and Miller, 1996; Fang et al., 1995; Eastoe et al., 1998; Lin et al., 1996; Liu and Messow, 2000].

For micellar solution ($c_0 >$ cmc), there are monomers and micelles in solution. Although micelles are not surface active, they affect the adsorption of monomers. When the local concentration of monomers is smaller than due to diffusion, the equilibrium between monomers and micelles will be disturbed and the micelles will break down to

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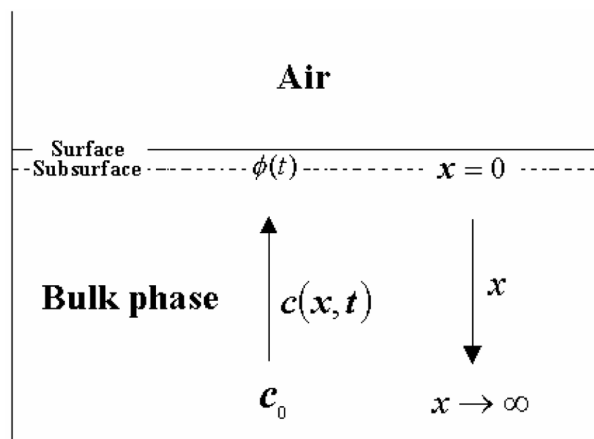E-mail: liujunji@tju.edu.cn

Fig. 1. Schematic of adsorption process from submicellar solution.

supply monomers. This kind of effect of micelles on adsorption kinetics was taken into account in the literature [Lucassen, 1975; Dushkin, 1998; Filippov and Filippova, 1997; Miller, 1981; Rillaerts and Joos, 1982; Geeraerts and Joos, 1994; Iliev and Dushkin, 1992; Joos and Hunsel, 1988; Makievski et al., 1994], but no general equation was given.

In this paper, the diffusion equations for submicellar and micellar solutions were solved by means of Laplace transformation under initial and boundary conditions, and the general adsorption equations were obtained and discussed in the short time limits. Using the derived equations, the adsorption kinetics of aqueous Pentaethylenglycol-monododecylether ($C_{12}E_5$) solution was studied.

THEORY

In this part, the diffusion-controlled adsorption kinetics for submicellar and micellar solutions is discussed.

1. The Adsorption from Submicellar Solution ($c_0 <$ cmc)

For submicellar solution, there are only monomers. When the adsorption is controlled by diffusion, then the diffusion equation

(Fick's second law) is the starting point:

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

where D represents the diffusion coefficient of monomers, $c(x, t)$ is the monomer concentration.

Eq. (1) can be solved under the necessary initial and boundary conditions (Eqs. (2)-(4)):

i.c.: $\qquad\qquad c(x, 0)=c_0 \qquad\qquad\qquad (2)$

1st b.c.: $\qquad\qquad \lim_{x\to\infty} c(x,t) = c_0 \qquad\qquad (3)$

2nd b.c.: $\qquad\qquad c(0, t)=\phi(t) \qquad\qquad\qquad (4)$

c_0 and $\phi(t)$ are the bulk monomer concentration and subsurface concentration, respectively.

The solution of Eq. (1) is

$$c(x,t) = \phi(t) + \frac{2[c_0 - \phi(0)]}{\sqrt{\pi}}\int_0^{\frac{x}{2\sqrt{Dt}}}\exp(-z^2)dz$$
$$- \frac{2}{\sqrt{\pi}}\int_0^t \phi'(u)\left[\int_0^{\frac{x}{2\sqrt{D(t-u)}}}\exp(-z^2)dz\right]du \qquad (5)$$

To derive the dynamic adsorption, the following equation (Fick's first law) was used at subsurface (x=0):

$$\frac{d\Gamma(t)}{dt}\bigg|_{x=0} = D\frac{\partial c(x,t)}{\partial x}\bigg|_{x=0} \qquad (6)$$

By inserting Eq. (5) in Eq. (6) and integrating there is

$$\Gamma(t) = 2\sqrt{\frac{D}{\pi}}\left[c_0\sqrt{t} - \frac{1}{2}\int_0^t \frac{\phi(u)}{\sqrt{t-u}}du\right] \qquad (7)$$

This is Ward-Tordai equation for submicellar solutions [Ward and Tordai, 1946].

In the study of adsorption kinetics, the short time limit will always be discussed. For the short time limit, i.e., at the early stages of diffusion, the backward movement of monomers can be neglected. The surface is empty enough to take up solute molecules as soon as they arrive. Hence there is:

$$\phi(t)=0 \qquad (8)$$

then Eq. (7) reduces to:

$$\Gamma(t) = 2c_0\sqrt{\frac{Dt}{\pi}} \qquad (9)$$

2. The Adsorption from Micellar Solution (c_0>cmc):

Falls the concentration c_0 exceeds the cmc, there are micelles in the surfactant solutions. Due to the diffusion and adsorption of monomers, the equilibrium between monomers and micelle will be disturbed and monomers are supplied by the micelles (Fig. 2). Taking into account this kind of effect, an additional term must be added in diffusion equation of monomers [Rillaerts and Joos, 1982; Geeraerts and Joos, 1994]:

$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c(x,t)}{\partial x^2} + \overline{k}[cmc - c(x,t)] \qquad (10)$$

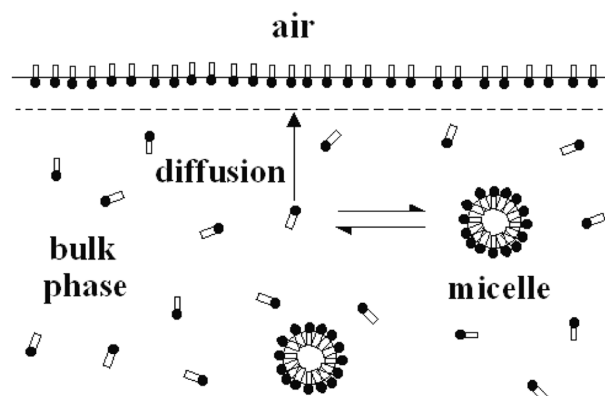**Fig. 2. Schematic of adsorption from micellar solution.**

where $\overline{k}$ is the demicellization constant. Here it is assumed that the demicellization follows a first-order reaction.

This equation can also be solved by means of Laplace transformation under the initial and boundary conditions.

i.c.: $\qquad\qquad c(x, 0)=cmc \qquad\qquad\qquad (11)$

1st b.c.: $\qquad\qquad \lim_{x\to\infty} c(x,t) = cmc \qquad\qquad (12)$

2nd b.c.: $\qquad\qquad c(0, t)=\phi(t) \qquad\qquad\qquad (13)$

The initial condition (Eq. (11)) means that the monomer concentration is cmc everywhere before the new (bubble) surface is created in the micellar solution. The first boundary condition (Eq. (12)) indicates that the monomer concentration far away from subsurface is also cmc. The second boundary condition (Eq. (13)) is the subsurface concentration which should change with time t.

Solving Eq. (10) there is

$$c(x,t) = \phi(t) - \frac{2}{\sqrt{\pi}}\exp(-\overline{k}t)\left\{\int_0^t \phi'(u)\exp(\overline{k}u)\int_0^{\frac{x}{2\sqrt{D(t-u)}}}\exp(-z^2)dz\,du\right.$$
$$\left. + \phi(0)\int_0^{\frac{x}{2\sqrt{Dt}}}\exp(-z^2)dz + \overline{k}\int_0^t \phi(u)\exp(\overline{k}u)\int_0^{\frac{x}{2\sqrt{D(t-u)}}}\exp(-z^2)dz\,du\right\}$$
$$+ \frac{2cmc}{\sqrt{\pi}}\exp(\overline{k}t)\int_0^{\frac{x}{2\sqrt{Dt}}}\exp(-u^2)du$$
$$+ \frac{2\overline{k}\cdot cmc}{\sqrt{\pi}}\int_0^t \exp(-\overline{k}u)\int_0^{\frac{x}{2\sqrt{Du}}}\exp(-z^2)dz\,du. \qquad (14)$$

The first Fick's law (Eq. (6)) should also be used at subsurface (x=0) in order to get the surface adsorption. After integration and rearranging there is the general dynamic surface adsorption for micellar solutions:

$$\Gamma(t) = \left\{\sqrt{\frac{D}{\pi}}\left\{2\sqrt{t}(cmc+\overline{k}\cdot cmc\cdot t - \phi(0))\exp(-\overline{k}t)\right.\right.$$
$$+ [\overline{k}\cdot cmc + 2\overline{k}^2\cdot cmc\cdot t - 4\overline{k}\phi(0) - 2\phi'(0)]\int_0^t \sqrt{u}\exp(-\overline{k}u)du$$
$$- 4\overline{k}\int_0^t \exp(-\overline{k}t)\int_0^t \exp(\overline{k}u)\phi'(u)\sqrt{t-u}du\,dt$$
$$- 2\int_0^t \exp(-\overline{k}t)\int_0^t \exp(\overline{k}u)\phi''(u)\sqrt{t-u}du\,dt$$
$$\left.\left. - 2\overline{k}^2\int_0^t \exp(-\overline{k}t)\int_0^t \exp(\overline{k}u)\phi(u)\sqrt{t-u}du\,dt\right\}\right. \qquad (15)$$

For the short time limit ($\phi(t)=0$), there is

$$\Gamma(t) = 2\,cmc\sqrt{\frac{Dt}{\pi}}(1+\bar{k}t)\exp(-\bar{k}t)$$
$$+\bar{k}\cdot cmc\sqrt{\frac{D}{\pi}}(1+2\bar{k}t)\int_0^t \sqrt{u}\exp(-\bar{k}u)du \qquad (16)$$

3. The Relationship Between $\gamma(t)$ and $\Gamma(t)$

The following relationship between $\gamma(t)$ and $\Gamma(t)$ is already derived [Liu and Messow, 2000]:

$$\gamma(t)=\gamma_0+RT\Gamma_\infty\ln[1-\Gamma(t)/\Gamma_\infty] \qquad (17)$$

where Γ_∞ is the saturation adsorption, γ_0 the surface tension of the solvent (water), T is the temperature, and R the ideal gas constant. Developing the logarithm in Eq. (17) into a power series and breaking off after the first term leads to the following approximation:

$$\gamma(t)=\gamma_0-RT\Gamma(t) \qquad (18)$$

Applying Eq. (9) and Eq. (16) to Eq. (18) there are the expressions of dynamic surface tensions in the short time limit:

for submicellar solution ($c_0<cmc$):

$$\gamma(t) = \gamma_0 - 2RTc_0\sqrt{\frac{Dt}{\pi}} \qquad (19)$$

and for micellar solution ($c_0>cmc$):

$$\gamma(t) = \gamma_0 - RT\left[2\,cmc\sqrt{\frac{Dt}{\pi}}(1+\bar{k}t)\exp(-\bar{k}t)\right.$$
$$\left.+\bar{k}\cdot cmc\sqrt{\frac{D}{\pi}}(1+2\bar{k}t)\int_0^t \sqrt{u}\exp(-\bar{k}u)du\right] \qquad (20)$$

EXPERIMENTAL

The equilibrium surface tensions were measured with Wilhelmy plate tensiometer (K12 from the Company Krüss GmbH Hamburg, Germany). The dynamic surface tensions measurements were carried out by means of a maximum bubble pressure tensiometer (BP-2 made by Krüss GmbH Hamburg, Germany). Pentaethylenglycol-monododecylether ($C_{12}E_5$) was obtained from SIGMA-ALDRICH Chemie GmbH, Fluka, Swiss. The surfactant was used without any further purification. The aqueous surfactant solutions were prepared by using double distilled and deionized water. The final distillation was performed over alkaline $KMnO_4$ so that the effect of surface active impurities was removed. To prepare the solutions of different concentrations, a digital balance was used to weigh the surfactant ($C_{12}E_5$), which was put in empty volumetric flask (500 ml). The solution concentrations are easy to calculate. All measurements of dynamic surface tension were performed at 25±0.1 °C.

RESULTS AND DISCUSSIONS

The critical micelle concentration (cmc) is very important for a surfactant. To determine cmc of surfactant $C_{12}E_5$, the equilibrium surface tensions γ_{eq} of its aqueous solutions for different concentrations are measured with Wilhelmy plate tensiometer. The measured data are plotted in Fig. 3 (γ_{eq} vs $\lg c_0$). One can see that γ_{eq} decreases with the increase of concentration ($\lg c_0$) until 6.8×10^{-2} mol·m^{-3}. It is the determined cmc of surfactant $C_{12}E_5$ at 25 °C.
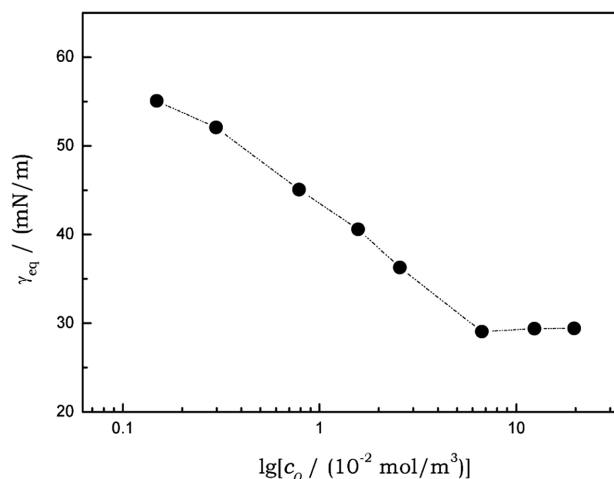

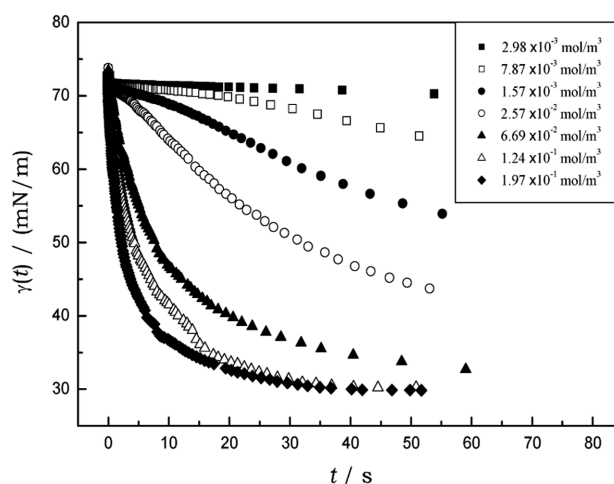Fig. 3. Experimental equilibrium surface tensions of aqueous $C_{12}E_5$ solutions at 25 °C.

Fig. 4. Experimental dynamic surface tensions of aqueous $C_{12}E_5$ solutions at 25 °C.

To study adsorption kinetics of aqueous submicellar and micellar solutions, the dynamic surface tensions $\gamma(t)$ of aqueous $C_{12}E_5$ solutions were measured by means of maximal bubble pressure method. Among seven different concentrations, two of them are micellar solutions. The experimental dynamic surface tensions at 25 °C are shown in Fig. 4. For all seven solutions, the initial values of the surface tensions equal that of pure water. This means that the monomers are not adsorbed at the surface and the surface is empty at the beginning ($t\rightarrow0$) for either submicellar or micellar solutions.

For submicellar solution in the short time limit (Eq. (19)), there should be a linear relationship between $\gamma(t)$ and $\sqrt{t}$ if the adsorption is diffusion controlled. Fig. 5 shows such kind of expected linear relationship and the diffusion-controlled mechanism for submicellar solution is proved in the short time limit. From the slope, the diffusion coefficient D of $C_{12}E_5$ monomers was calculated. The result is 4.01×10^{-10} m^2·s^{-1}.

For micellar solution in the short time limit (Eq. (20)), there is no more linear relationship between $\gamma(t)$ and $\sqrt{t}$. The dynamic surface tensions are function of D and $\bar{k}$. D was already determined
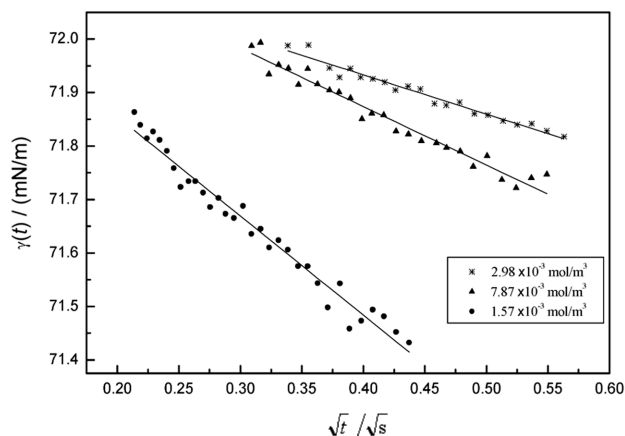
Fig. 5. The linear relation between $\gamma(t)$ and $\sqrt{t}$ for submicellar solutions in the short time range.

from the experimental data in the submicellar region by using Eq. (19). Then the demicellization constant $\bar{k}$ can be numerically calculated from the dynamic surface tensions of micellar solutions by means of Eq. (20) (Fig. 6). The calculated $\bar{k}$ is between 154-160 s^{-1}. For most nonionic surfactants, the demicellization constant $\bar{k}$ is between 70-2,000 s^{-1}. The obtained result falls into this range.

Eq. (15) is the general dynamic surface adsorption equation of
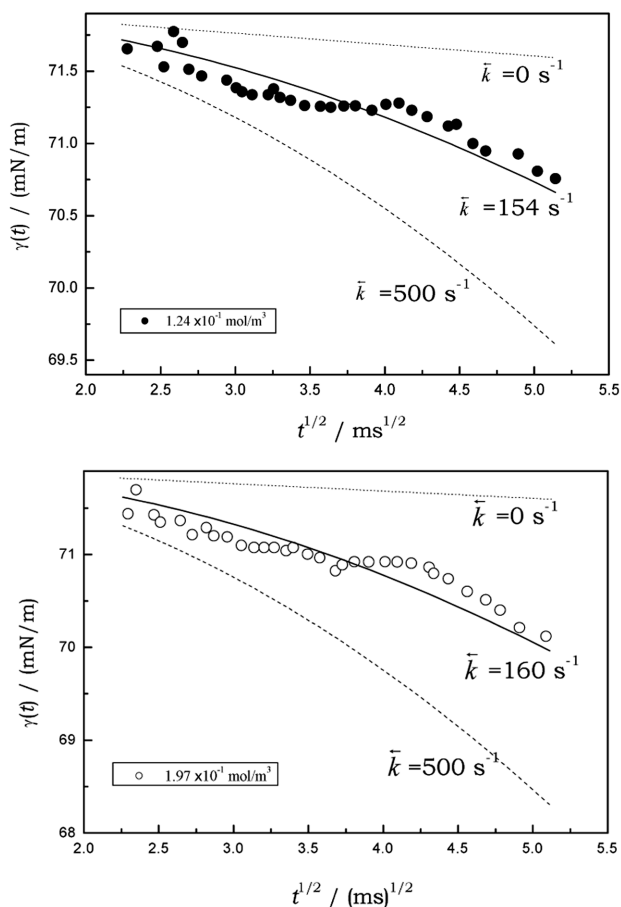

Fig. 6. The relation between $\gamma(t)$ and $\sqrt{t}$ for micellar solutions in the short time range.

$\Gamma(t)$ for micellar solutions. With $\bar{k}=0$ and cmc=c_0, it will reduce to the Ward-Tordai equation (Eq. (7)) as it should be. Hence Eq. (7) can be considered as the special case of Eq. (15).

The same as Eqs. (15) and (7), Eq. (9) is also the simplified form of Eq. (16) as $\bar{k}=0$ and cmc=c_0 in the short time limits. In contrast to the case of submicellar solutions, the dynamic surface adsorption $\Gamma(t)$ for micellar solutions in Eq. (16) is higher due to $\bar{k}>0$ than that of in Eq. (9). Therefore, the dynamic surface tensions of micellar solution should decay stronger than that of submicellar solution. The experimental data (Fig. 4) showed also such kind of results.

SUMMARY

The general dynamic surface adsorptions ($\Gamma(t)$) for submicellar and micellar solutions were derived by solving Fick's diffusion equation under different initial and boundary conditions. In case of $c_0>$ cmc, the demicellization constant appeared in the expression of $\Gamma(t)$. By analyzing the dynamic surface tensions $\gamma(t)$ of aqueous $C_{12}E_5$ ($CH_3(CH_2)_{11}(OC_2H_4)_5OH$) solutions at temperature 25 °C, which were measured by means of maximal bubble pressure method, the adsorption kinetics was studied. For micellar solutions, the determined demicellization constant $\bar{k}$ for $C_{12}E_5$ was about 154-160 s^{-1}.

NOMENCLATURE

c_0 : bulk concentration of monomers [mol·m^{-3}]
$c(x, t)$: concentration of monomers [mol·m^{-3}]
cmc   : critical micelle concentration [mol·m^{-3}]
D   : diffusion coefficient of monomers [m^2·s^{-1}]
$\bar{k}$: demicellization constant [s^{-1}]
x   : distance to subsurface [m]
R   : ideal gas constant, 8.314 J·mol^{-1}·K^{-1}
t   : adsorption time [s]
T   : temperature [K]
$\phi(t)$: subsurface concentration [mol·m^{-3}]
γ_0 : surface tension of the solvent (water) [mN·m^{-1}]
γ_{eq} : equilibrium surface tension [mN·m^{-1}]
$\gamma(t)$: dynamic surface tension [mN·m^{-1}]
$\Gamma(t)$: dynamic surface adsorption [mol·m^{-2}]
Γ_∞ : saturation adsorption [mol·m^{-2}]

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