Adsorption dynamics of homogeneous polyoxypropylene-polyoxyethylene alkyl ether nonionic surfactants at the air/water interface

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ABSTRACT

The dynamic surface tensions of two homogeneous polyoxyethylene (EO) alkyl ether nonionic surfactants with terminal hydroxy group ($C_{12}EO_x$, where C_{12} is a dodecyl chain and x is the length of the EO chain; $x = 6, 8$) and two homogeneous polyoxypropylene-polyoxyethylene (PO-EO) alkyl ether nonionic surfactants ($C_{12}EO_xPO_3$, where PO_3 is a trioxypropylene chain inserted between the EO_x and the terminal hydroxy group) were measured using the maximum bubble pressure method. The effects of EO chain length, the presence or absence of the PO_3 chain, and the surfactant concentration on the maximum rates of surface-tension reduction and diffusion coefficient were investigated. The $C_{12}EO_6PO_3$ surfactant exhibited the fastest rate of surface-tension reduction of the four systems studied, despite its complex hydrophobic-alkyl-chain/hydrophilic-EO-chain/hydrophobic-PO-chain structure that differs from that of conventional EO alkyl ether surfactants. The diffusion coefficients obtained from short and long time analyses indicate that surfactant diffusion to the subsurface is faster for the $C_{12}EO_xPO_3$ surfactants than the $C_{12}EO_x$ surfactants (short time data), while surfactant adsorption from the subsurface to the air/water interface is faster for the $C_{12}EO_x$ surfactants than the $C_{12}EO_xPO_3$ surfactants (long time data).

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1. Introduction

Many interfacial processes, such as the high-speed wetting of textiles, paper, and other substrates, or foaming, do not attain equilibrium conditions. In such cases, the dynamic surface tension, which is the surface tension as a function of time, of a surfactant is more important for determining the performance of the surfactant during interfacial processes than the equilibrium surface tension [1]. Indeed, exchanges between the monomers and micelles of a surfactant in bulk solution occur on the order of milliseconds, and the monomers are repeatedly adsorbed and desorbed at the interface layer [2]. Even if two substances exhibit the same surface tension under equilibrium conditions, differences that can be temporally characterized are observed under a variety of conditions during transition processes. Consequently, understanding the adsorption dynamics of a surfactant at the air/water interface through its dynamic surface tension is very important. Techniques for the measurement of dynamic surface tension include the oscillating jet, maximum bubble pressure, pendent drop, drop volume, and Wilhelmy plate methods; these techniques differ in their timescales. Among them, the maximum bubble pressure method is applicable to relatively short time, from 0.1 ms to 10 s.

Rehbinder was apparently the first to apply the maximum bubble pressure method to the measurement of the dynamic surface tension of a surfactant solution; [3,4] this method was further developed by other researchers [5–11]. There was a revival in dynamic surface tension studies during the 1990s due to the manufacture and availability of commercial instruments for the determination of maximum bubble pressure and the control of the foam drop volumes [12,13]. For example, Kawale et al. reported that the maximum rate of dynamic-surface-tension reduction was related to foam diameter; their studies used conventional surfactants such as sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), and the polyoxyethylene dodecyl ether, Brij30, in which the diameters are small and the maximum rates are large [14]. Gao and Rosen reported that when the interactions between two surfactants in surfactant mixtures are weak, dynamic surface tensions over short times ($<1\,s$) and long times are close to those of the surfactant component with the lower equilibrium surface tension, whereas when the interactions are strong, the dynamic surface tensions over short times are greater than those of either component [15]. Eastoe and Dalton reported that the gradient of the linear relationship obtained by plotting surface tension against $t^{-1/2}$, where t is the surface age, for an anionic surfactant over long times increased significantly with increasing salt concentration [13]. Hua and Rosen reported that the lowest surface tensions in aqueous media at short surface ages are exhibited by surfactants with highly branched hydrophobic groups [16].

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Recently, we reported the syntheses and solution properties of homogeneous polyoxypropylene-polyoxyethylene (PO-EO) alkyl ether nonionic surfactants composed of alkyl, EO, and PO chains with identical chain length distributions [17]. Homogeneous $C_nEO_xPO_y$ surfactants, where n is alkyl chain length, x is the length of the oxyethylene (EO) chain, and y is the length of the oxypropylene (PO) chain inserted between the EO_x and the terminal hydroxy group, were adsorbed efficiently at air/water interfaces, despite their complex hydrophobic-alkyl-chain/hydrophilic-EO-chain/hydrophobic-PO-chain structures; they also exhibited excellent micelle-forming abilities in aqueous solution. Homogeneous $C_nEO_xPO_y$ surfactants with constant EO- and PO-chain distributions were reported for the first time, and this research revealed the usefulness of these surfactants to a variety of industrial fields. However, few studies have reported the adsorption dynamics of homogeneous $C_nEO_xPO_y$ surfactants by dynamic-surface-tension techniques. It is very important to clearly identify the dynamic processes that occur at the air/water interfaces of novel surfactants with new structures that are unlike those of conventional surfactants, from both scientific and industrial viewpoints.

In this study, the adsorption dynamics at the air/water interfaces of $C_{12}EO_xPO_3$ and $C_{12}EO_x$ ($x = 6, 8$) surfactants (Fig. 1) were investigated through the measurements of their dynamic surface tensions using the maximum bubble pressure method. The effects of EO chain length, the presence or absence of the PO chain, and surfactant concentration on the adsorption dynamics were studied using the adsorption model and Rosen's approach, and diffusion coefficients were obtained for short and long times.

2. Experimental and methods

2.1. Materials

Homogeneous EO alkyl ether type nonionic surfactants ($C_{12}EO_x, x = 6, 8$) were supplied by Nikko Chemicals Co., Ltd. (Tokyo, Japan), and used as received. Homogeneous PO–EO alkyl ether type nonionic surfactants ($C_{12}EO_xPO_3, x = 6, 8$) were synthesized as described elsewhere [17].

2.2. Measurements

Solutions of the polyoxypropylene-polyoxyethylene (PO-EO) alkyl ether nonionic surfactants ($C_{12}EO_xPO_3 = C_{12}EO_6PO_3$ and $C_{12}EO_8PO_3$) and polyoxyethylene (EO) alkyl ether surfactants ($C_{12}EO_x = C_{12}EO_6$ and $C_{12}EO_8$) were prepared with Milli-Q Plus water (resistivity = 18.2 MΩ cm), and all measurements were performed at 20.0 ± 0.5 °C for $C_{12}EO_6PO_3$ and $C_{12}EO_6$, and 25.0 ± 0.5 °C for $C_{12}EO_8PO_3$ and $C_{12}EO_8$. The critical micelle concentrations (CMCs) obtained from the equilibrium surface tensions are 0.0854, 0.0422, 0.0930, and 0.102 mmol dm^{-3} for $C_{12}EO_6PO_3$ (20 °C), $C_{12}EO_8PO_3$ (25 °C), $C_{12}EO_6$ (20 °C), and $C_{12}EO_8$ (25 °C), respectively [17]. The concentrations of the surfactant solutions used in these experiments were 1, 5, 10, 20, and 40

times the CMC, and experiments were conducted with surface ages in the 15 to 30,000 ms range.

2.3. Dynamic surface tension

The dynamic surface tensions of the $C_{12}EO_xPO_3$ and $C_{12}EO_x$ surfactants were measured by the maximum bubble pressure method with a Krüss BP2 bubble pressure tensiometer (Hamburg, Germany), which measures changes in gas-discharge times. The dynamic surface tension γ_t is calculated by the Laplace equation (Eq. (1)):

$$\gamma_t = \frac{rp}{2}, \tag{1}$$

where r is the inner radius of the capillary and p is the pressure inside the bubble. The measured-pressure correction for hydrostatic pressure and buoyancy gives Eq. (2): [18].

$$\gamma_t = \frac{r\left[p_{max} - \left(h + \frac{2}{3}r\right)\rho g\right]}{2}, \tag{2}$$

where p_{max} is the maximum pressure inside the bubble when the radius of the bubble's curvature is equal to r, h is the distance from the surface to the capillary nozzle, ρ is the density of the solvent, and g is the acceleration of gravity.

A typical plot of change in surface tension as a function of time contains four regions: an induction region, a rapid-fall region, a meso-equilibrium region, and an equilibrium region [1,19].The first three regions of this plot are fitted to Eq. (3): [1,9].

$$\gamma_t = \gamma_m + \frac{\gamma_0 - \gamma_m}{1 + \left(\frac{t}{t^*}\right)^n}, \tag{3}$$

where γ_t is the surface tension of the surfactant solution at time t, γ_m is the meso-equilibrium surface tension (where γ_t changes little with time), γ_0 is the surface tension of the pure solvent, and t^* is the time required for γ_t to reach the midpoint between γ_0 and γ_m; n is calculated by computer curve fitting. Differentiation of Eq. (3) gives the equation for the rate of change of surface tension, at constant surfactant concentration, with t (Eq. (4)): [20].

$$\frac{-d\gamma_t}{dt} = \frac{(\gamma_0 - \gamma_m)n\left(\frac{t}{t^*}\right)^{n-1}}{t^*\left[1 + \left(\frac{t}{t^*}\right)^n\right]^2}. \tag{4}$$

The partial derivative, $(\partial\gamma_t/\partial t)_{max}$, is expressed by Eq. (5), which is obtained by substituting t^* for t in Eq. (4): [20].

$$\left(\frac{\partial\gamma_t}{\partial t}\right)_{max} = \frac{n(\gamma_0 - \gamma_m)}{4t^*}. \tag{5}$$

An alternative way of analyzing the dynamic surface tension is through the diffusion-controlled model; the Ward and Tordai model is most commonly used for this purpose [21]. This process can be analyzed quantitatively using the following integral equation:

$$\Gamma(t) = \left(\frac{4D}{\pi}\right)^{\frac{1}{2}}\left(C_0 t^{\frac{1}{2}} + \int_0^t C_s(\pi)d\sqrt{t-\tau}\right), \tag{6}$$

where t is the time, $\Gamma(t)$ is the surface concentration, D is the diffusion coefficient of the monomer, C_0 is the bulk concentration, $C_s(t)$ is the concentration at the subsurface, and τ is a dummy time-delay variable. Values of D at short time, which are based on the short-time approximation (Eq. (7)), can be obtained using dynamic short-time surface tension
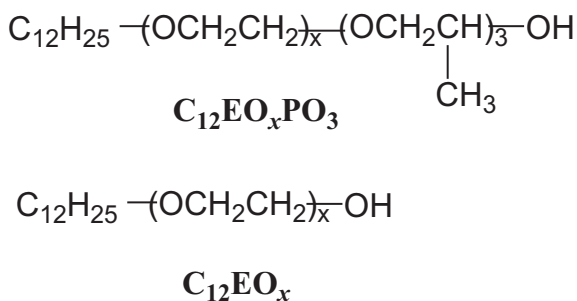
$C_{12}H_{25}-(OCH_2CH_2)_{\overline{x}}(OCH_2CH)_{\overline{3}}-OH$

$| \atop CH_3$

$\mathbf{C_{12}EO_xPO_3}$

$C_{12}H_{25}-(OCH_2CH_2)_{\overline{x}}-OH$

$\mathbf{C_{12}EO_x}$

Fig. 1. Structures of $C_{12}EO_xPO_3$ and $C_{12}EO_x$.