Adsorption Kinetics of Alkyl Polyglucoside at the Air-Solution Interface

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Abstract: The air-solution equilibrium tension γ_e and dynamic surface tension γ_t, of nonionic surfactant alkyl polyglucoside have been studied. γ_e was measured by the Wilhelmy method with Krüss K12 tensiometer.   The CMC and the surface excesses Γ were determined from the surface tension *vs.* concentration curve.   The γ_t decays were measured in the range 0.2～20 s using a maximum bubble pressure instrument and analyzed with the Ward and Tordai equation.

Keywords: Dynamic surface tension, adsorption kinetics, alkyl polyglucoside.

Alkyl polyglucosides (C_iG_j) are an important class of "green" surfactants that are synthesized from renewable raw materials such as fatty alcohols and sugars. They display dermatological safety(safe for skin and eyes), a good biodegradability, and excellent surface — active properties. Their synthesis, interfacial properties, and micellar properties have early been reported[1-3]. But their dynamic surface tensions and adsorption kinetics have not been investigated. From both scientific and industrial perspectives the dynamic surface tension is an important property of surfactant solutions[4-6]. To extend our knowledge about this kind of surfactant, we have studied the adsorption kinetics of alkyl polyglucoside.

Experimental

The technical grade alkyl polyglucoside $C_{9.6}G_{1.3}$ was provided by Jinling research institute of petrochemical corporation, and was purified by recrystallization with alcohol/ propanone.

A maximum bubble pressure instrument was established by our research group, the principle and installation are the same as introduced in some surface chemistry books[7]. Besides, we adopted a special computer software to collect dynamic information, and transform them into dynamic surface tension and the aging time data[8].

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Results and Discussion

The effect of APG concentration on both equilibrium surface tension γ_e at different temperatures and dynamic surface tension γ_t show in **Figure 1** and **Figure 2** respectively. The CMC was determined from the inflexion of **Figure 1** curve to be 0.032 g/L. The equilibrium surface tension data can be interpreted with the Szyszkowski equation[9] and the adsorption isotherm belongs to Langmuir type. The maximum surface excess Γ_m was obtained to be 3.95×10^{-6} mol/ m^2. Γ is an important parameter used to analyze DST data.

Figure 1 Plot of equilibrium surface tension γ_e *vs* APG concentration C(mg/l)
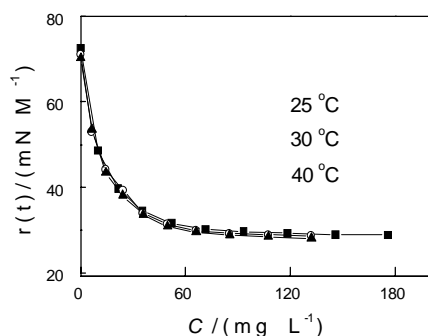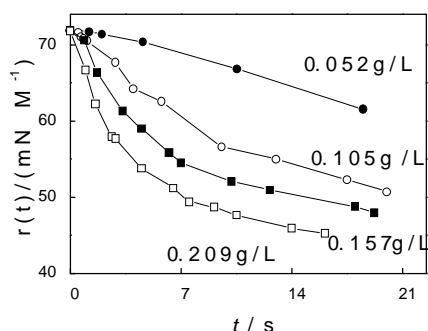
Figure 2 Plot of γ_t *vs* aging time for different APG concentrations

It can be seen from **Figure 2** that at the short measuring time (0~2s), the tensions reduce sharply and after that the curves enter "plateau regions" gradually. The higher the concentration is, the greater the tension reduces.

Ward and Tordai equation[10] describes the diffusion controlled adsorption of surfactants at a fresh interface. At the start and final stages, this equation can be expressed

$$\gamma_{t\,(t \to 0)} = \gamma_0 - 2RTC(Dt/\pi)^{1/2} \tag{1}$$

$$\gamma_{t(t \to \infty)} = \gamma_e + RT\,\Gamma^2/2C\,(\pi/Dt)^{1/2} \tag{2}$$

where c, Γ and D represent the bulk concentration ,equilibrium surface excess and monomer diffusion coefficient of the surfactant respectively. Γ can be obtained from **Figure 1** according to Gibbs' adsorption equation. The D values can be obtained from the slopes of $\gamma_{t(t \to \infty)}$ *vs.* $t^{-1/2}$ linear relation suggested by Eq. (2). For a mixed diffusion-activation adsorption mechanism, it was often necessary to introduce an apparent diffusion coefficient D_a, which was lower than D, thus the application of Ward and Tordai equation has been extended[11], the adsorption barrier is quantified in terms of D_a

$$D_a = D\exp(-E_a/RT) \tag{3}$$

with E_a the activation energy. Since the characteristic monomer lifetime in a micelle is $10^{-5} \sim 10^{-4}$ s much shorter than that of a micellar dissociation rate, the Eqs. (1) and (2) are also applied to the system in which APG concentration is above its CMC[12,13]. These parameters of Γ, D_a and E_a are listed in **Table 1**.

Table 1   The calculated surface excesses Γ, apparent diffusion coefficients D_a and adsorption barriers E_a in different APG concentrations

$C/(\text{mg} \cdot \text{L}^{-1})$	52.32	104.6	157.0	209.3
$\Gamma/(\times 10^{-6} \text{mol} \cdot \text{m}^{-2})$	3.89	3.92		
$D_a/(\times 10^{-12} \text{m}^2 \cdot \text{s}^{-1})$	31.2	5.20	3.93	3.93
$E_a/(\text{KJ} \cdot \text{mol}^{-1})$	0	4.44	2.20	1.94
			6.57	6.88

Effect of temperature on dynamic surface tension γ_t is shown in **Figure 3**.

Figure 3   Effect of temperature on γ_t at fixed APG concentration   (0.157g / L)
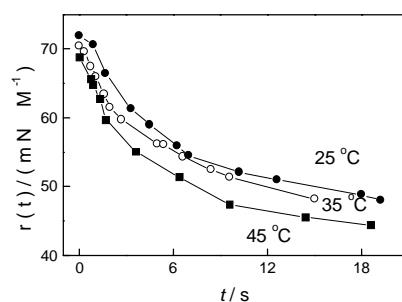
It has been seen from **Figure 1** that temperature has little effect on equilibrium surface tension, but has significant influence on dynamic surface tension (**Figure 3**). The difference in γ_0 (the surface tension of water) at the start is small , as the aging time increases, the difference in γ_t also increases.   So increasing temperature is an effective means to reduce dynamic surface tension.   This may be explained that when temperature increases, more and more surfactant molecules obtain enough energy to be activated, and easily adsorb at the air-solution interface.

Acknowledgment

References

1.   F. A. Hughes, B. W. Lew, *J. Am. Oil Chem. Soc.* ,**1970**, *47*, 162.
2.   K. Shinoda, T. Yamaguchi, R. Hori, *Bull. Chem. Soc. Jpn.* **1961**,*34*,237.
3.   D. Balzer, *Tenside Surfactants Deterg.,* **1991**, *28*, 419
4.   R. Miller, P. Joos, V. Fainermann, *Adv. Colloid Interface Sci.* **1994**, *49*, 249.
5.   G.Z. Li, J.H. Mu , H. Sui, *China Surfactant Detergent & Cosmetics* (in Chinese), **1999**,(4), 1.
6.   L.Q. Zheng, L.L. Shui, Y. You, O. Zheng, Y. Li, J.X. Zhao, G.Z. Li, *Acta Chimica Sinica* (in Chinese), **2001**,*59* (5),637.

7.   B. Y. Zhu, Z. G. Zhao, *Basic Interface Chemistry* (in Chinese), Chemical Industry
     Publication House, Beijing, **1996**, *31* ,46.
8.   Y. Li, Ph.. D. *Thesis, Shandong University* (in Chinese), Jinan, **1999**.
9.   B. Szyszkowski, *Z. Phys. Chem.* ,**1908**, *64*, 385.
10. A. F. H. Ward, L. Tordai, *J. Chem. Phys.* ,**1946**,*14*, 453.
11. F. Ravera , L. Liggieri, A. Steinchen, *J. Colloid Interface Sci*., **1993**, *156*, 109.
12. E. Julian, S. D. James, G. A. Philippe, R. C. Esther, R. P. Alan, A. S. Elizabeth, *J. Colloid*
13. *Interface Sci.*, **1997**, *188*, 423.
14. A. Johner, J. F. Joanny, *Macromolecules*, **1990**, *23*, 5299.