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Adsorption kinetics of the partially protonated cationic surfactant dodecylamine

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ABSTRACT

The adsorption kinetics of the partially protonated cationic surfactant dodecylamine ($C_{12}H_{27}N$) in a 50 mM NaCl solution was examined. The dynamic and equilibrium surface tensions (STs) were measured using a video-enhanced pendant bubble tensiometer with a modified cell system. The equilibrium and complete ST relaxation profiles were compared with the theoretical profiles predicted from the non-ionic, partially ionized and fully ionized ionic models. A quasi-equilibrium approach was used in the ionic model to describe the electric field in the electrical double layer. In the very low surface pressure regime ($\pi < 2$ mN/m), the dynamic ST data were compared with the theoretical ST predicted by the ionic (partially or fully ionized) Frumkin model under a diffusion-controlled condition. The fitted theoretical profiles produced a diffusivity value of 0.6–1.0 $\times 10^{-6}$ cm^2/s, which is much lower than the diffusivity calculated using the Wilke-Chang equation, which was $D = 5.6 \times 10^{-6}$ cm^2/s. Therefore, it could be concluded that in the low surface pressure regime, the controlling mechanism of the adsorption process exhibits a mixed diffusive-kinetic control model.

1. Introduction

The adsorption of a surfactant at a fluid-liquid interface plays an important role in many technological and industrial applications [1]. Thus, much effort has been spent on studying surfactant adsorption kinetics. While earlier studies on the surfactant adsorption kinetics mainly focused on nonionic surfactants, more recently, the focus has turned to the ionic surfactants. However, the adsorption behavior of ionic surfactants involves an additional electric double layer (EDL) due to non-vanishing electrostatic interactions. A surface charge accumulates and a locally non-neutral EDL arises when the ionic surfactant molecules adsorb at the air-water interface. Davies and Rideal [2] proposed an electrostatic correction term in the Langmuir isotherm in 1963, and two decades later, Dukhin et al. [3] introduced a quasi-equilibrium approach that coupled with the Gouy-Chapman model of the EDL [4]. This quasi-equilibrium approach has been widely applied in studying the adsorption kinetics of ionic surfactants [5–9].

Borwankar and Wasan [5] used this quasi-equilibrium approach to describe the dynamic surface tension (ST) of fully dissociated SDS in a NaCl solution. MacLeod and Radke [7] examined the applicability of the quasi-equilibrium approach in 1994. They compared the dynamic ST profiles from either the quasi-equilibrium approach or a full transient model, which involved solving the Nernst-Planck equation and the Poisson equation simultaneously. It was concluded that the ST discrepancies between the quasi-equilibrium model and the full transient model could only be observed at timescales inaccessible to current dynamic ST techniques. In 2001, Datwani and Stebe [8] applied an ionic Langmuir model with the quasi-equilibrium approach to simulate the dynamic ST of the anionic gemini surfactant aerosol-OT.

To simplify the ionic modeling, some studies applied either short-time/long-time asymptote approximations [10–17] or the nonionic model [18–22] to simulate the adsorption behavior of ionic surfactants. In 1994, Bonfillion et al. [10] measured the dynamic ST of SDS in a 100 mM NaCl solution and used a long-time asymptote approximation for studying the adsorption kinetics of SDS. Geeraerts et al. [11] applied a short-time asymptote approximation for evaluating of the adsorption behavior of the cationic surfactant MTAB (myristyl trimethyl ammonium bromide). The dynamic ST data of C_nTAB were best fitted by using the nonionic Frumkin model by Stubenrauch et al. [18] and Mucic et al. [21]. Vlahovska et al. [22] compared the results from the long-time asymptote approximation to the result obtained from the full transient model. More articles in the literature that reported dynamic ST data and the model simulation are detailed in Part A of the Supplementary Material (Table S1).

Since cationic surfactants are essential in sanitation, antiseptic agents, cosmetics and pharmaceutics [23], some studies [15,18–20,24–30] focused on the dynamic STs of cationic surfactants. Several of them [15,19,20,26,27] have provided complete sets of dynamic ST data that decreased from the ST of the solvent to the equilibrium ST. The complete set of dynamic ST data are not easy to obtain because a high bulk

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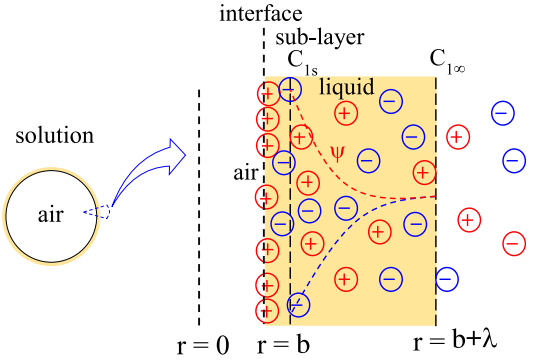

Fig. 1. A schematic diagram of the double layer. λ is the characteristic length of the double layer, C_{1s} is the surfactant concentration at the sublayer, $C_{1\infty}$ is the surfactant concentration at the outer double layer, and b is the radius of the spherical bubble.

concentration is usually needed to produce a significant ST decrease in the ionic solutions. The ST starts to decrease at a very short time for the concentrated surfactant solutions. In addition, the reproducibility of the dynamic ST measurements of cationic surfactant solutions is low due to the probable adsorption of cationic surfactant molecules onto the transparent glass cell [31]. Recently, Casandra et al. [31] have implemented two modifications in the solution cell of the pendant bubble tensiometer, and some complete sets of the dynamic ST of the partially protonated cationic surfactant dodecylamine have been successfully obtained.

In this study, the dynamic ST data of the partially ionized cationic surfactant dodecylamine in a 50 mM NaCl solution were measured, and the adsorption kinetics was examined by comparing these complete sets of dynamic ST data with the theoretical ST profiles generated from the partially ionized ionic model [32].

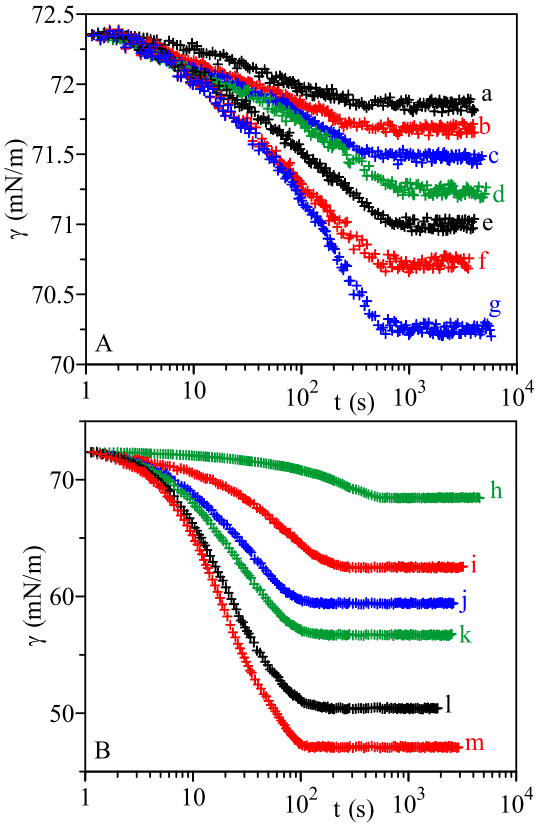

Fig. 2. Relaxations of the ST of DDA in 50 mM NaCl solutions at dilute (A) and middle (B) concentrations: C = 0.502 (a), 0.602 (b), 0.702 (c), 0.801 (d), 0.951 (e), 1.09 (f), 1.31 (g), 1.69 (h), 2.28 (i), 2.64 (j), 3.11 (k), 3.68 (l), and 4.25 (m) (10^{-8} mol/cm^3).

2. Experiment

2.1. Materials

Dodecylamine (DDA, $CH_3(CH_2)_{10}CH_2NH_2$, MW = 185.35 g/mol) was purchased from Fluka (purity > 99.5%) and used without modification. Acetone (HPLC grade), which was used to calibrate the ST measurement, was obtained from Fisher Scientific Co. The water with which the aqueous solutions were prepared was purified via a Barnstead NANOpure water purification system, and the output water had a specific conductance of <0.057 μS/cm. The values of the ST of air-water and air-acetone using the pendant bubble tensiometer were 72.0 mN/m and 23.1 mN/m, respectively, at 25.0 °C.

2.2. Tensiometer

A video-enhanced pendant (emerging) bubble tensiometer with a coated-quartz cell and a continuous solution pumping system was employed for the measurements of the equilibrium [γ(C)] and dynamic [γ(t)] STs of DDA in a 50 mM NaCl aqueous solution at 25.0 ± 0.1 °C. The apparatus and the edge detection routine were described in detail in previous studies [31,33]. The temperature variation of the aqueous solution was less than ±0.1 K during the measurement of γ(t). A 16-gauge stainless steel inverted needle (0.047 in. I.D.; 0.065 in. O.D.) was used to generate bubbles.

2.3. Measurement

The DDA solutions were placed in a coated quartz cell. The pumping system operated for 5–8 h prior to the generation of a pendant bubble. A pendant bubble of air with diameter of approximately 2 mm was

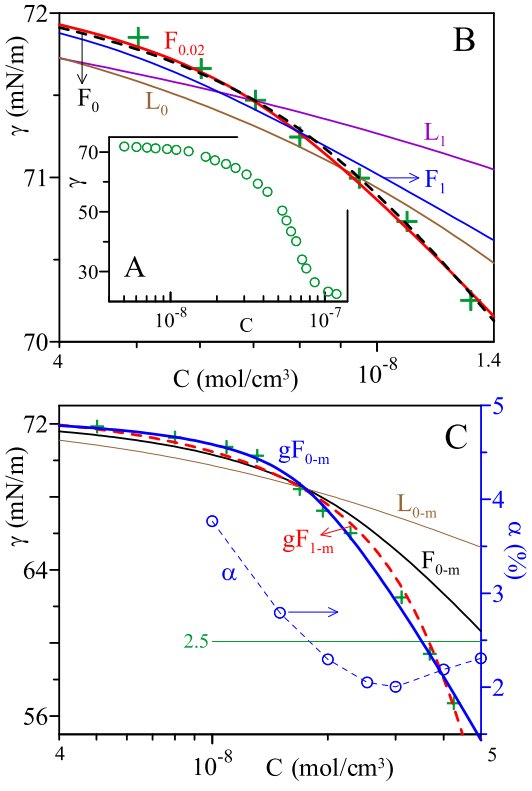

Fig. 3. (A) The equilibrium ST of DDA in a 50 mM NaCl solution. (B and C) The comparisons between the equilibrium ST data (+) and the model predictions (curves, best-fitting the γ(C) data) at low (π < 2 mN/m) and middle (π < 16 mN/m) concentrations; L = Langmuir, F = Frumkin, gF = generalized Frumkin, the subscripts 0, 0.02 and 1 indicate the value of α.