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# Adsorption kinetics of the ionic surfactant decanoic acid

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ABSTRACT

The adsorption kinetics of ionic surfactant decanoic acid was examined. Dynamic and equilibrium surface tensions (ST) were measured using a video-enhanced pendant bubble tensiometer. The equilibrium ST data and the complete ST relaxation profiles were compared with theoretical profiles predicted by both non-ionic and ionic models. The quasi-equilibrium approach was used in the ionic model to describe the electric field in the electrical double layer. Both non-ionic and ionic generalized-Frumkin models predict the equilibrium and dynamic ST data very well. Using the ionic model, a comparison between the dynamic ST data and the theoretical ST profiles gave a diffusivity of $5.5 \times 10^{-6}$ cm$^2$/s. The adsorption of decanoic acid onto the air–water interface was determined to be diffusion controlled. Dynamic surface properties ($\Gamma$ and $\psi_s$), the electrical potential $\psi(r, t)$ in the double layer, and the double layer thickness $\lambda(C, t)$ were also evaluated. It was found that the surface charge density increases very quickly at the early stages ($\sim$1 s) of the surfactant adsorption process. Additionally, the electrical surface potential data implied that the surface charge density becomes significantly stronger at very dilute surfactant concentrations, where $\pi$ is less than 1 mN/m.

## 1. Introduction

Surfactant molecules are commonly used for reducing the surface tension of liquid–gas interfaces in industrial processes [1], including sundry practical applications and products like detergents, inks, adhesives, pesticides, cosmetics, among others [2]. Since the optimal dosage of a surfactant relies on specific knowledge of dynamic adsorption properties [3], it is not surprising that investigations on the kinetics of surfactant adsorption have gained tremendous interest in the past two decades.

Surfactants are amphiphilic molecules that commonly have a simple structure consisting of a hydrocarbon chain bound with a hydrophilic head group. Surfactant monomers are sparingly soluble in an aqueous phase because of the unfavourable interactions between the surfactant hydrocarbon chain and water. These unfavourable interactions make surfactant molecules preferentially adsorb at the air–water interface, which depletes the surfactant concentration in the sublayer and initiates the surfactant adsorption process [4] once a fresh air–water interface has been created. For ionic surfactants, a surface charge density is established as a result of the adsorption of ionic surfactant molecules. This surface-charge density creates a repulsive force in the electrical double layer and significantly affects the mass transport of ionic surfactant molecules. The surfactant adsorption process consists of at least three steps: bulk diffusion, adsorption–desorption between the subsurface, and surface re-arrangement. In this study, a pendant bubble was formed in a static uniform aqueous solution of ionic surfactants with nearly negligible convection [5].

There are approximately ten articles in the literature that have reported dynamic surface tension (ST) data for ionic surfactants in the past decade [6–17]. However, only three of these articles give complete dynamic ST profiles (from the ST of the solvent to its equilibrium value). Datwani and Stebe [6] applied a pendant bubble method to measure an aqueous Aerosol-OT solution with 10–500 mM NaCl and several complete sets of dynamic ST curves were obtained. Then, an ionic Langmuir model was used to simulate the surfactant adsorption process. Stubenrauch et al. [7] and Mucic et al. [8] applied the maximum bubble (or drop) pressure method for C$_n$TAB ($n = 14$ and 16) solutions and 3–5 complete sets of dynamic ST curves for each surfactant were obtained. In this case, the authors applied a Frumkin ionic compressibility model for simulating the adsorption process.

Several other articles have also reported some dynamic ST data [9–17]. Unfortunately, these dynamic ST data excluded the initial portions of the ST curves. This data loss is because of the high

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surfactant concentration and the lack of a suitable instrument for measuring the initial relaxation phase of the ST process (usually at $t < 1$ s). In these studies, the long time approximation model of nonionic surfactants was commonly applied for simulating the surfactant adsorption process.

To the best of our knowledge, there are only three articles in the past decade that have showed the dynamic ST data of ionic surfactants without the addition of salt or buffer [7,9,17]: cationic surfactant $C_n$TAB by Stubenrauch et al. [7], catanionic alkyltrimethylammonium decanoate by Li et al. [9], and anionic oxyethylated surfactant by Miller [17]. However, only one of these reports [7] provided a complete ST relaxation profile.

Davies and Rideal [18] proposed an ionic Langmuir adsorption isotherm in 1963. Dukhin et al. [19–21] introduced the idea of a quasi-equilibrium approach by using Gouy-Chapman theory [22,23], which relates the surface charge density and the surface potential in an electrical double layer. This quasi-equilibrium model was then frequently applied to the study of adsorption kinetics of ionic surfactants [24–27]. In 1994, MacLeod and Radke [28] compared the difference between the quasi-equilibrium approach and the full transient model (i.e., the Nernst-Plank diffusion equation). They concluded that the difference between these models occurs only at times inaccessible to current dynamic surface tension techniques. In 1997, Vlahovska et al. [29] proposed a long time asymptotes approximation and resulted a nearly same DST as the full transient model [28] at long adsorption time.

The aim of this study is to investigate the adsorption kinetics of decanoic acid without salt. A video-enhanced pendant bubble tensiometer was employed for the dynamic/equilibrium ST measurement. A comparison between the experimental data (i.e., a complete set of ST curves) and theoretical ST profiles predicted from an ionic Frumkin model was performed. Moreover, the relationship between the surface properties and the distribution of the ionic surfactant in the electrical double layer were reported. An outline of this paper is as follow: Section 2 describes briefly the pendant bubble experimental method. The theoretical framework for surfactant mass transport is detailed in Section 3. In Section 4, the experimental dynamic ST data are compared with the theoretical ST profiles from the ionic model. The paper concludes in Section 5 with a discussion.

## 2. Experimental measurements

### 2.1. Materials

Decanoic acid ($C_9H_{19}COOH$, M.W. = 172.26 g/mol), purchased from Fluka Chemical (GC grade, purity $\geqslant$ 99.5%), was used without modification. Acetone (HPLC grade), which was used to calibrate the surface tension 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, with the output water having a specific conductance of less than 0.057 μS/cm. The values of the surface tension of air–water and air-acetone using the pendant bubble technique described in the following sections 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 was employed for the measurement of the equilibrium ($\gamma(C)$) and dynamic ($\gamma(t)$) surface tension of the aqueous decanoic acid solutions at 25.0 ± 0.1 °C. The apparatus (shown in Fig. 1) and the edge detection routine have been described in detail in a previous study [5]. The temperature variation of the aqueous solution was less than ±0.1 K during the measurement of $\gamma(t)$. A 16-gauge stainless steel inverted needle (0.047 in. I.D.; 0.065 in. O.D.) was used to generate the bubble.

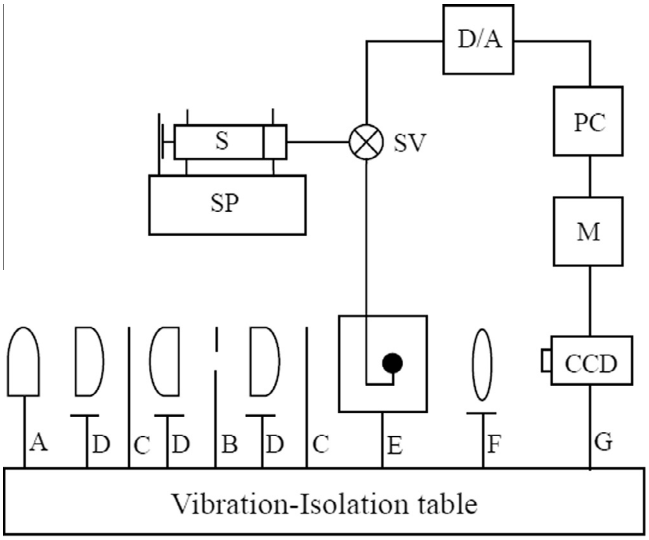

**Fig. 1.** A pendant bubble apparatus and the video image digitization equipment. A: light source; B: pinhole; C: filter; D: planoconvex lens; E: quartz sample cell and inverted needle inside thermostatic air chamber; F: objective lens; G: video camera; M: monitor; PC: personal computer; D/A: data translation card; S: syringe; SP: syringe pump; SV: solenoid valve.

### 2.3. Measurement

A pendant bubble of air with a diameter of approximately 2 mm was formed in a decanoic acid solution, which was put in a quartz cell. Digital images of the bubble were taken sequentially and were processed to determine the edge coordinates. The edge coordinates of the pendant bubble were fitted to the theoretical bubble profiles generated from the classical Young–Laplace equation to obtain the surface tension. In this work, the time required to create an air bubble is approximately 0.72 s.

The measurements were taken for several different bulk concentrations: 2.0–18.0 ($10^{-8}$ mol/cm$^3$). Each sample was performed in duplicate. Bubbles were measured for up to 1 or 2 h, depending on the surfactant concentration, to ensure that $\gamma(t)$ reached its equilibrium value. The accuracy and reproducibility of the surface tension measurements obtained by this procedure are approximately 0.1 mN/m [5]. A pH meter (MP8100, AI-ON Industrial Corp., Taiwan) was used to measure the pH values of the decanoic acid solutions at 25.0 °C

## 3. Theoretical framework

### 3.1. Mass transport

The mass transport of surfactant molecules onto a freshly created surface in a quiescent solution was modeled. Presently, only the case of one-dimensional diffusion and the adsorption onto a spherical interface from a bulk phase containing an initially uniform concentration of decanoic acid was considered. The surfactant molecules were assumed not to dissolve into the gas phase of the pendant bubble.

Dukhin et al. [19–21] developed a quasi-equilibrium approach for the diffusive transport of ionic surfactants with an assumption. That is, the double-layer potential is always in an instantaneous