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Adsorption of alkyltrimethylammonium bromide surfactants at the air/water interface

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ABSTRACT

The dynamic behavior of three trimethylammonium bromide surfactants, C_{14}TAB, C_{15}TAB and C_{16}TAB, was studied by a dynamic modeling framework, which consists of the Ward and Tordai equation and an adsorption isotherm. Three adsorption isotherms, Langmuir, Henry and Freundlich, were used separately. The simplest isotherm, Henry isotherm, could not fit experimental data. Freundlich isotherm can model C_{15}TAB and C_{16}TAB adsorption, but failed to describe C_{14}TAB. On the other hand, Langmuir isotherm was able to model all three surfactants. The results confirmed that the adsorption isotherm is monotonic but non-linear for all surfactants. In the other words, the surfactants have not reached the saturation at the CMC. The results also demonstrated a monotonic correlation between carbon length and adsorption effectiveness of the cationic surfactants. The new insights are important for designing new cationic surfactants.

1. Introduction

Surfactants have been extensively used in various chemical processes to enhance the air/water interface such as foaming, flotation and wetting [1,2]. It is generally agreed that these molecules can significantly concentrate, Γ, at the air/water interface even with very small concentration in bulk, c_b (Fig. 1a). Despite of the numerous investigations, quantification and verification of the relationship between Γ and c_b remains unsatisfactory.

While the surface tension of surfactant solutions can be measured routinely, the surface tension alone (such as Fig. 1b) does not provide sufficient insights into the interface. Consequently, most studies on interfacial adsorption rely on the Gibbs adsorption equation. The Gibbs adsorption equation for ionic surfactants is given as:

$$d\gamma = -2RT\Gamma d\ln c_b \tag{1}$$

where γ is the surface tension, Γ and c_b are surface (mol/m^2) and bulk (mol/m^3) concentration, respectively.

One might combine Eq. (1) with the γ-versus-lnc_b plot to get the corresponding value of Γ [3]. However, the graphical method can produce a significant error [4] and thus is rarely used. Since the direct measurements require expensive equipment and materials, quantifying adsorption by modelling remains the most effective method [5]. Modeling surfactant adsorption is often obtained from equilibrium surface tension by combination of Gibbs adsorption equation and an adsorption isotherm [2]. A number of equations have been proposed for the relationship between Γ to c_b, namely: Henry, Langmuir, Frumkin, Freundlich and Volmer isotherms [6]. In the literature, Langmuir and Frumkin isotherms are the most popular isotherms for surfactants adsorption at air/water interface [7].

Appropriate modelling is critical to quantify the relationship between surfactant structure and adsorption behavior, for surfactant application and design. Typically, surfactant adsorption is quantified in term of *efficiency* and *effectiveness* [7]. While adsorption *efficiency* can be easily obtained from the plot of equilibrium surface tension, *effectiveness* is defined from the saturation surface excess and can only be obtained from modelling. For ionic surfactants, a linear relationship between the efficiency and carbon chain is generally observed [3]. On the other hand, the correlation between adsorption effectiveness and carbon chain is unclear [7]. One of the reasons is that the reported effectiveness is dependent on the model selection, which can be difficult to justify. For instance, Ivanov and coauthors employed six different models to the same surface tension data of ionic surfactants [8]. They found that all models fit equilibrium surface tension and thus the fitting cannot be used to justify nor reject any of them. Recently, we have

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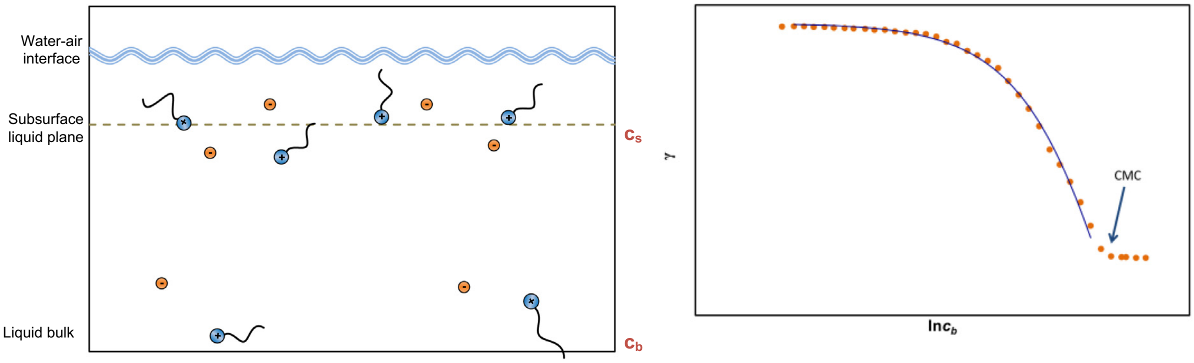

Fig. 1. Sufactant adsorption at the air/water interface: (a) adsorption concentrations (b) equilibrium surface tension.

attempted to find the adsorption parameters from dynamic process [9]. In our modeling, the adsorption parameters were obtained from fitting to dynamic surface tension, instead of equilibrium surface tension. The approach does not require the Gibbs adsorption isotherm [10]. The key advantages of our approach are uniqueness in equilibrium and consistency in dynamic modelling.

This study focuses on a series of three alkyl trimethylammonium bromide, with increasing carbon length. The study aims to (i) verify the adsorption isotherm and (ii) establish the relationship between alkyl chain and adsorption behavior. In addition to fundamental understanding, the relationship can be used to quantify the surfactant effectiveness for applications. It should be highlighted that new cationic surfactants have been synthesized to improve interfacial processes. They include Gemini [11], photo-responsive [12,13], or anti-microbial surfactants [14]. In these synthesis works, the length of the surfactant is often varied to find the optimal structure. Consequently, a correct correlation between hydrocarbon tail and effectiveness will provide important insights for developing new cationic systems.

2. Theoretical model

The dynamic model was similar to the previous framework [9,10]. In summary, the dynamic modeling can be described by Ward and Tordai equation:

$$\Gamma(t) = 2\sqrt{\frac{D}{\pi}}\left\{c_b\sqrt{t} - \int_0^{\sqrt{t}} c_s(\tau)d\left(\sqrt{t-\tau}\right)\right\} \tag{2}$$

where D is the diffusion coefficient, c_b is the bulk concentration, $c_s(t)$ is the transient sub-surface concentration, $\Gamma(t)$ is the transient surface excess and τ is the dummy variable of integration.

The surface tension is then obtained from:

$$\gamma_{eq} = \gamma_0 e^{-\chi c_b} \tag{3}$$

$$\gamma(t) = \gamma_0 e^{-\chi c_s(t)} \tag{4}$$

where γ_0, γ_{eq} and $\gamma(t)$ are the surface tension of pure water, equilibrium surface tension and dynamic surface tension respectively, χ is an adsorption constant (M^{-1}).

The surface concentration, $\Gamma(t)$, is in equilibrium with the concentration of sub-surface, $c_s(t)$, which can be decided by an adsorption isotherm. In addition to Langmuir isotherm (Eq. (5)), Henry isotherm [15] (Eq. (6)) and Freundlich isotherm [16] (Eq. (7)) are used:

$$\Gamma(t) = \Gamma_m \frac{K_L c_s(t)}{1 + K_L c_s(t)} \tag{5}$$

$$\Gamma(t) = K_H c_s(t) \tag{6}$$

$$\Gamma(t) = K_{Fr} c_s(t)^{1/n} \tag{7}$$

where Γ_m, K_L, K_H, K_{Fr} and n are adsorption constants which are defined in the literature [2].

It is noteworthy that the latest neutron reflectometry results on C_nTAB indicated an linear relationship between Γ and c_b over the measurement range [17]. Hence it's worthy to test Henry isotherm in the modelling. Although the above isotherms are mathematically different, the actual difference can be very subtle. The difference between linear (Henry) and Langmuir isotherms can be demonstrated in Fig. 2. While Henry isotherm indicates a linear increment, Langmuir isotherm is distinguished by a plateau region at high concentrations. For surfactant adsorption, however, the isotherm is limited to CMC. If a surfactant has a high CMC, hypothetically greater than c^* in Fig. 2, the two isotherms divert significantly. On contrast, if the CMC is lower than c^*, both isotherms can effectively describe adsorption. Freundlich isotherm, which is an extended form of Henry isotherm with two parameters, is also tested. Frumkin isotherm is an extended form of Langmuir isotherm and thus is not required when Langmuir isotherm works effectively. Similarly, Volmer isotherm was not employed in this study due to its irrelevance to air/water interface [2].

A combination between Eq. (2) and either Eqs. (5), (6) or (7) can be solved for all dynamic concentrations. Consequently, the model was fitted against the dynamic surface tension at multiple concentrations. For Henry isotherm, the dynamic model has only one parameter, K_H. For Langmuir and Freundlich isotherms, two parameters are used for fitting.

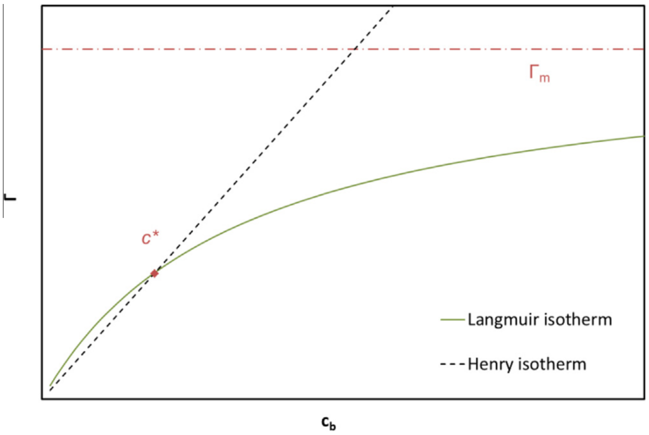

Fig. 2. Langmuir and Henry isotherms.

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