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New methodology to determine the rate-limiting adsorption kinetics mechanism from experimental dynamic surface tension data

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Abstract

We present a new methodology to determine the rate-limiting adsorption kinetics mechanism (diffusion-controlled vs mixed diffusion-barrier controlled), including deducing the kinetics parameters (the diffusion coefficient, D, and the energy-barrier parameter, β), from the experimental short-time dynamic surface tension (DST) data. The new methodology has the following advantages over the existing procedure used to analyze the experimental DST data: (a) it does not require using a model for the equilibrium adsorption isotherm, and (b) it only requires using the experimental short-time DST data measured at two initial surfactant bulk solution concentrations. We apply the new methodology to analyze the experimental short-time DST data of the following alkyl poly(ethylene oxide), C_iE_j, nonionic surfactants: $C_{12}E_4$, $C_{12}E_6$, $C_{12}E_8$, and $C_{10}E_8$ measured using the pendant-bubble apparatus. We find that for $C_{12}E_4$ and $C_{12}E_6$, the effect of the energy barrier on the overall rate of surfactant adsorption can be neglected for surfactant bulk solution concentrations below their respective critical micelle concentrations (CMCs), and therefore, that the rate-limiting adsorption kinetics mechanism for $C_{12}E_4$ and $C_{12}E_6$ is diffusion-controlled at any of their premicellar surfactant bulk solution concentrations. On the other hand, for $C_{12}E_8$ and $C_{10}E_8$, we find that their respective CMC values are large enough to observe a significant effect of the energy barrier on the overall rate of surfactant adsorption. In other words, for $C_{12}E_8$ and $C_{10}E_8$, the rate-limiting adsorption kinetics mechanism shifts from diffusion-controlled to mixed diffusion-barrier controlled as their premicellar surfactant bulk solution concentrations increase. We test the new methodology by predicting the short-time DST profiles at other initial surfactant bulk solution concentrations, and then comparing the predicted DST profiles with those measured experimentally. Very good agreement is obtained for the four C_iE_j nonionic surfactants considered. We also compare the results of implementing the new methodology with those of implementing the existing procedure, and conclude that using a model for the equilibrium adsorption isotherm can lead not only to different values of D and β, but it can also lead to a completely different determination of the rate-limiting adsorption kinetics mechanism. Since the new methodology proposed here does not require using a model for the equilibrium adsorption isotherm, we conclude that it should provide a more reliable determination of the rate-limiting adsorption kinetics mechanism, including the deduced kinetics parameters, D and β.

Keywords: Nonionic surfactants; Adsorption kinetics; Diffusion-controlled; Mixed-controlled; Dynamic surface tension; Alkyl poly(ethylene oxide) nonionic surfactants

1. Introduction

This paper focuses on the adsorption kinetics of *single nonionic surfactants onto a liquid/air surface*. The kinetics of surfactant adsorption is important in applications like film coatings [1,2], spray generation, and the formation of foams and emulsions [3], as well as in phenomena like interfacial turbulence [4], the Marangoni effect [5], thin-film stability [4], surface rheology [4,6], drop impact [7–11], and the spreading of drops on surfaces [12–16]. Comprehensive reviews on the applications and the theory related to the dynamic adsorption of surfactants at surfaces can be found in Refs. [6,17–25].

In order to develop a mechanistic understanding of the various factors that affect the kinetics of nonionic surfactant adsorption, traditionally, the adsorption process has been envisioned to consist of the following three steps [6,17–26]: Step 1—diffusion of the surfactant molecules from the bulk solution to

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the sub-surface,[1] Step 2—adsorption of the surfactant molecules from the sub-surface onto the surface, and Step 3—reorientation of the surfactant molecules at the surface leading to a further reduction of the surface tension. In order to physically understand the effect of Step 2 on the adsorption kinetics, it has been hypothesized that Step 2 involves adsorption across an *energy barrier* [28–35], whose fundamental origin has not been explained to date. Based on this understanding, two different classes of kinetics models have been advanced: (i) Diffusion-controlled adsorption models, which assume that Step 1 controls the overall rate of surfactant adsorption, and (ii) mixed diffusion-barrier controlled adsorption models,[2] which assume that Steps 1 and 2 control the overall rate of surfactant adsorption. The specific form of the kinetics model depends on the equilibrium adsorption isotherm model of the surfactant, since the kinetics model should reduce to the equilibrium adsorption isotherm model at equilibrium conditions. While a diffusion-controlled adsorption model contains *one* kinetics parameter: D, the bulk solution diffusion coefficient of the surfactant molecule, a mixed-controlled adsorption model contains *two* kinetics parameters: D and β, where β is the energy-barrier parameter representing the rate constant for the adsorption of surfactant molecules from the sub-surface onto the surface. As we have recently shown, β is related to the adsorption of a *single* surfactant molecule onto a *clean* surface [36].

The existing procedure used to determine the rate-limiting adsorption kinetics mechanism (diffusion-controlled vs mixed-controlled), as well as to determine the values of the kinetics parameters, D and β, involves the following three steps [35, 37–46]:

Step 1: Choosing a model for the equilibrium adsorption isotherm.

Step 2: Assuming a diffusion-controlled adsorption mechanism, and using the experimental dynamic surface tension (DST) data corresponding to the entire surface tension relaxation profile, measured at a single initial surfactant bulk solution concentration, C_b, to regress for the value of D. This step is then repeated for experimental DST data measured at different C_b values. If the regressed value of D is found to decrease as C_b increases, then this trend is interpreted as indicating the existence of a mixed-controlled adsorption mechanism.

Step 3: If there are indications of the existence of mixed-controlled adsorption, the regressed value of D obtained by analyzing the experimental DST data measured at lower C_b values is considered as the actual diffusion coefficient of the surfactant molecules, and the entire experimental DST data measured at the higher C_b values is used to regress for β.

After implementing this three-step procedure, one can determine: (a) if the adsorption is diffusion-controlled or mixed-controlled, and (b) the values of β (if the adsorption is mixed-controlled) and D. Note that this procedure involves choosing a specific model for the equilibrium adsorption isotherm (Step 1 above). Consequently, *the accuracy of the equilibrium adsorption isotherm model affects the regressed values of the kinetics parameters, D and β* [47,48]. In fact, the regressed values of D and β are found to be quite sensitive to the choice of the equilibrium adsorption isotherm model [47–50]. For example, consider the adsorption kinetics of the nonionic surfactant $C_{12}E_8$ [42]. While three different equilibrium adsorption isotherm models, namely, the Langmuir, the Frumkin, and the Generalized Frumkin adsorption isotherms, all appear to describe the experimental equilibrium adsorption behavior (that is, the equilibrium surface tension vs surfactant bulk solution concentration data) reasonably well, they result in very different values of the regressed kinetics parameters when analyzing the experimental DST behavior. Specifically, the Langmuir model results in a D value of $21 \times 10^{-6}\ \text{cm}^2/\text{s}$, the Frumkin model results in a D value of $11 \times 10^{-6}\ \text{cm}^2/\text{s}$, and the Generalized Frumkin model results in a D value of $8.0 \times 10^{-6}\ \text{cm}^2/\text{s}$. In view of the observed high sensitivity of the regressed values of the kinetics parameters to the chosen equilibrium adsorption isotherm model, Lin et al. [41] and Pan et al. [35] proposed carrying out surface expansion measurements, in addition to performing equilibrium surface tension measurements, to further validate the equilibrium adsorption isotherm model chosen to analyze the experimental DST data. These authors concluded that surface expansion measurements can be useful in testing various equilibrium adsorption isotherm models, and hence, in obtaining more reliable estimates of the kinetics parameters, D and β.

Note that the equilibrium adsorption isotherm models differ in the manner in which they account for the interactions between the adsorbed surfactant molecules [36], and as such, they *should not* affect the value of D, the *bulk solution* diffusion coefficient of a surfactant molecule, and β, which as we have recently shown, is related to the adsorption of a *single* surfactant molecule onto a *clean* surface [36]. Moreover, note that the existing procedure uses the entire experimental DST data measured at all values of C_b to regress for the values of D and β, and therefore, it does not allow for an *independent testing* of its predictive capabilities. Recognizing that a fundamental physical understanding of the energy barrier is still lacking, a reliable determination of the rate-limiting adsorption kinetics mechanism, including extracting reliable values of the kinetics parameters, D and β, for various nonionic surfactant systems, is of great fundamental and practical value.

With the background provided above in mind, in this paper, we develop a new methodology, which does not make use of a model for the equilibrium adsorption isotherm, and can be utilized to determine the rate-limiting adsorption kinetics mechanism and to obtain reliable values of the kinetics parameters, D and β, from experimental DST data. Specifically, the new methodology is based on the short-time analysis of the mixed-controlled model that we presented recently in Ref. [36], an

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[1] The sub-surface is the zone of a few angstroms thickness adjacent to the surface, according to Ward and Tordai [27].

[2] We shall refer hereafter to the mixed diffusion-barrier controlled model as the mixed-controlled model.