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Derivation of a simple equation for close to equilibrium adsorption dynamics of surfactants at air/liquid interface using statistical rate theory

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ABSTRACT

The statistical rate theory was applied for modeling of dynamics of surfactant adsorption at air/liquid interface, when the system is close to equilibrium. By using an approximation in the rate equation of statistical rate theory, a simple equation was derived for close to equilibrium systems. Based on this new equation, it is possible to find the rate constant of surfactant adsorption at air/liquid interface by a linear plot, easily. The applicability of the obtained equation was evaluated by analysis of set of numerically simulated data based on stochastic method and also two different sets of experimental data.

1. Introduction

Dynamic surface tension is an important property in interfacial processes. The rate of surfactant adsorption is important in foaming, wetting, breathing, washability, coating and enhanced oil recovery [1]. Dynamic surface tension has been studied extensively from both experimental and theoretical point of view. The theoretical studies of dynamic surface tension mainly consider the diffusion controlled mechanism [2–6]. Although there are several reports about theoretical studies of dynamic surface tension under adsorption controlled mechanism [5,7] and mixed diffusion and adsorption mechanism [3–5,8]. One of the new theories for adsorption kinetics is statistical rate theory (SRT) [9], which has been used recently for gas/solid [10,11], solid/solution [12,13] and gas/liquid [1,14–16] interfaces. This theory is for the systems where the adsorption is rate controlling step. We have used this theory for analysis of adsorption kinetics at solid/solution interface for single [17] and binary solutes [18] adsorption and also for desorption kinetics [19]. The analytical solution of SRT rate equation led to complex equations, which are not user friendly.

The purpose of the present work is to derive a simple equation for dynamics of surfactant adsorption at air/liquid interface, based on SRT, when the system is close to equilibrium.

2. Theory

For transfer of a molecule from subsurface to the surface and therefore changing the molecular configuration from λ_i to λ_j, the unidirectional transition rate, $J_{\lambda_i \to \lambda_j}$, based on SRT is [1,14]:

$$J_{\lambda_i \to \lambda_j} = k_e \ \exp\left[\frac{S(\lambda_j) - S(\lambda_i)}{k}\right] \tag{1}$$

where k_e is the equilibrium exchange rate and $S(\lambda_i)$ and $S(\lambda_j)$ are entropies of particle distribution λ_i and λ_j. Eq. (1) for the case of adsorption (forward) can be written as [1,14]:

$$J_{\lambda_i \to \lambda_j} = k_e \ \exp\left[\frac{\mu^s(\lambda_i) - \mu^A(\lambda_i)}{kT}\right] \tag{2}$$

where μ^s and μ^A are the chemical potential of surfactant in the subsurface and surface, respectively. For desorption (reverse) we have [1,14]:

$$J_{\lambda_k \to \lambda_j} = k_e \ \exp\left[\frac{\mu^A(\lambda_k) - \mu^s(\lambda_k)}{kT}\right] \tag{3}$$

By combining Eqs. (2) and (3) the net rate of surfactant adsorption will be obtained:

$$J = k_e \left(\exp\left[\frac{\mu^s - \mu^A}{kT}\right] - \exp\left[\frac{\mu^A - \mu^s}{kT}\right] \right) \tag{4}$$

The chemical potentials of surfactant at subsurface and surface are [1,14]:

$$\mu^s = \mu_0^s + kT \ \ln C^s \tag{5}$$

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$$\mu^{A} = \mu_0^{A} + kT\ \ln\left(\frac{\Gamma}{\Gamma_\infty}\right) - \frac{\gamma}{\Gamma_\infty} \qquad (6)$$

where μ_0^{s} and μ_0^{A} are the reference chemical potential of the surfactant at the subsurface and surface respectively. C^{s} is the concentration of surfactant at subsurface, Γ is the surface concentration and Γ_∞ is its maximum value. γ is surface tension of solution. By substitution of Eqs. (5) and (6) into Eq. (4), one arrives [1]:

$$J = \frac{d\Gamma}{dt} = k_a \frac{C^{s}}{\Gamma}\ \exp\left[\frac{-\pi}{kT\Gamma_\infty}\right] - k_d \frac{\Gamma}{C^{s}}\ \exp\left[\frac{\pi}{kT\Gamma_\infty}\right] \qquad (7)$$

where π is surface pressure ($\pi = \gamma_0 - \gamma$), $k_a = k_e \Gamma_\infty \exp(\mu_0^{s} - \mu_0^{A}/kT + \gamma_0/kT\Gamma_\infty)$ is the adsorption rate coefficient and $k_d = k_e/\Gamma_\infty \exp(\mu_0^{A} - \mu_0^{s}/kT - \gamma_0/kT\Gamma_\infty)$ is the desorption rate coefficient. By substitution the following equation of state in Eq. (7)

$$\pi = -kT\Gamma_\infty \ln\left(1 - \frac{\Gamma}{\Gamma_\infty}\right) \qquad (8)$$

One obtains:

$$J = \frac{d\Gamma}{dt} = k_a\left(\frac{C^{s}}{\Gamma}\left(1 - \frac{\Gamma}{\Gamma_\infty}\right) - \frac{1}{K}\frac{\Gamma}{C_s}\left(\frac{1}{1 - \Gamma/\Gamma_\infty}\right)\right) \qquad (9)$$

where K is the adsorption equilibrium constant ($K = k_a/k_d$). This equation is the basic equation for adsorption dynamics at gas/liquid interface based on SRT [1].

3. Derivation of simple equation for close to equilibrium systems

At equilibrium $d\Gamma/dt = 0$, and therefore

$$K^{1/2}C_e = \frac{\Gamma_e}{\left(1 - \Gamma_e/\Gamma_\infty\right)} \qquad (10)$$

or

$$KC_e^2 = \frac{\Gamma_e^2}{\left(1 - \Gamma_e/\Gamma_\infty\right)^2}$$

where C_e is the equilibrium concentration of surfactant in the bulk phase. By substitution of K value from Eq. (10) into Eq. (9) and also considering that for close to equilibrium systems $C^{s} \approx C_e$, one obtains:

$$\frac{d\Gamma}{dt} = k_a\left[\frac{C_e}{\Gamma}\left(1 - \frac{\Gamma}{\Gamma_\infty}\right) - \frac{\left(1 - \frac{\Gamma_e}{\Gamma_\infty}\right)^2 {C_e}^2}{{\Gamma_e}^2}\frac{\Gamma}{C_e}\left(\frac{1}{1 - \frac{\Gamma}{\Gamma_\infty}}\right)\right] \qquad (11)$$

As an approximate we can use $\Gamma \cong \Gamma_e$ in the last term of Eq. (11) for close to equilibrium systems. So

$$\frac{d\Gamma}{dt} = k_a\left[\frac{C_e}{\Gamma}\left(1 - \frac{\Gamma}{\Gamma_\infty}\right) - \frac{C_e}{\Gamma_e}\left(1 - \frac{\Gamma_e}{\Gamma_\infty}\right)\right] \qquad (12)$$

or

$$\frac{d\Gamma}{dt} = \frac{k_a C_e}{\Gamma_e}\left[\frac{\Gamma_e - \Gamma}{\Gamma}\right] \qquad (13)$$

By integration of Eq. (13) for close to equilibrium system at boundary conditions t_1 to t and Γ_1 to Γ

$$\int_{\Gamma_1}^{\Gamma} \frac{\Gamma d\Gamma}{\Gamma_e - \Gamma} = \frac{k_a C_e}{\Gamma_e}\int_{t_1}^{t} dt \qquad (14)$$

$$\ln\left(1 - \frac{\Gamma}{\Gamma_e}\right) + \frac{\Gamma}{\Gamma_e} = \ln\left(1 - \frac{\Gamma_1}{\Gamma_e}\right) + \frac{\Gamma_1}{\Gamma_e} + \frac{k_a C_e}{{\Gamma_e}^2}t_1 - \frac{k_a C_e}{{\Gamma_e}^2}t \qquad (15)$$

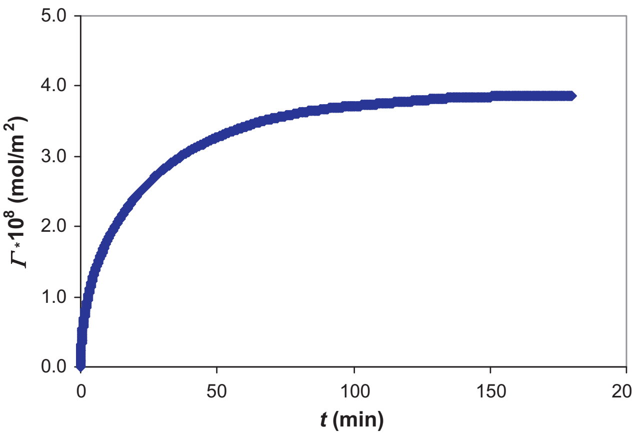

Fig. 1. Generated (t,Γ) data based on SRT (Eq. (9)) using stochastic numerical simulation method with $k_a = 1 \times 10^{-7}$, $k_d = 1 \times 10^{-12}$ and $\Gamma_\infty = 1 \times 10^{-7}$ mol/m^2.

By definition of constants as

$$\beta \equiv \ln\left(1 - \frac{\Gamma_1}{\Gamma_e}\right) + \frac{\Gamma_1}{\Gamma_e} + \frac{k_a C_e}{{\Gamma_e}^2}t_1 \qquad (16)$$

and

$$k \equiv \frac{k_a C_e}{\Gamma_e^2} \qquad (17)$$

Eq. (15) simplifies to:

$$\frac{\Gamma}{\Gamma_e} + \ln\left(1 - \frac{\Gamma}{\Gamma_e}\right) = \beta - kt \qquad (18)$$

This equation shows that the plot of $(\Gamma/\Gamma_e) + \ln(1 - \Gamma/\Gamma_e)$ vs. t is a line with k and β as its slope and intercept, respectively. Therefore, the rate constant of surfactant adsorption onto gas/liquid interface can be easily calculated from the slope of a linear plot. A similar equation was reported for adsorption at solid/solution interface when the system is close to equilibrium [17].

4. Results

Fig. 1 shows the generated data (t,Γ) based on SRT model (Eq. (9)) which were generated by the stochastic numerical simulation method using CKS package. This simulator package is developed by Houle and Hinsberg [20] and was used by us successfully for adsorption kinetic studies [17–19,21]. Fig. 1 shows the variation of surface concentration of surfactant as a function of time for a hypothetical system with $k_a = 1 \times 10^{-7}$, $k_d = 1 \times 10^{-12}$ and $\Gamma_\infty = 1 \times 10^{-7}$ mol/m^2. Fig. 2 shows the applicability of Eq. (18) for this system. The linear plot of Fig. 2 for the close to equilibrium data, confirms Eq. (18).

As an experimental example, Fig. 3 shows the surface concentration of C_8E_4 a non-ionic surfactant as a function of time for 0.1 mmolal bulk concentration at 298.15 K, which was obtained by dynamic surface tension data [8]. Fig. 4 represents the plot of $(\Gamma/\Gamma_e) + \ln(1 - \Gamma/\Gamma_e)$ vs. t for the close to equilibrium data of this system. It is clear that for a real system the plot is also linear and indicates that the Eq. (18) works very well for close to equilibrium systems. Fig. 5 shows the plot of $(\Gamma/\Gamma_e) + \ln(1 - \Gamma/\Gamma_e)$ for the entire experimental data of Fig. 3 (i.e. the data starting from $t = 0$). It is clear that a deviation from the linear plot appear for far from equilibrium data. This indicates that we have to apply Eq. (18) just for close to equilibrium data.

As an another example, the plot of $(\Gamma/\Gamma_e) + \ln(1 - \Gamma/\Gamma_e)$ vs. time for adsorption of $C_{12}E_1$ at air/liquid interface for 10 μmolal bulk concentration at 288.15 K [22] is shown in Fig. 6 for the entire experimental data and in Fig. 7 for the close to equilibrium data.