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On the theory of adsorption kinetics of ionic sufactants at fluid interfaces
4. Deceleration of the adsorption rate due to non-equilibrium distribution of adsorbed ions in the diffuse layer

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Abstract: An approximate analytical solution is obtained for the adsorption kinetics equation derived earlier. On the basis of these relations the importance of the consideration of a non-equilibrium diffuse layer has been shown. To describe the retarded adsorption kinetics the distribution of adsorbed ions in the diffuse layer section of multivalent surfactant ions has been taken into account. The rate of adsorption calculated for a non-ionic surfactant is compared with the adsorption rate for monovalent and bivalent ionic surfactants, respectively.

Key words: Adsorption kinetics – ionic surfactants – non-equilibrium electric double layer

Introduction

The role of the ionic charge of adsorbing molecules and the presence of an electrical double layer (DL) on the kinetics of adsorption was discussed in several papers [1–6]. A physical model was presented in [1] to describe the adsorption kinetics of ionic surfactants. For the first time both the transfer of charged molecules through the electric double layer and the transport of molecules from the bulk to the boundary of the DL was taken into account. In [2] a kinetic equation was obtained to describe the adsorption process of ionic surfactants.

In the present paper we will derive an approximate solution of the equation of adsorption kinetics. It will be proved that the consideration of the deviation of the surfactant ion distribution from equilibrium in the diffuse part of the double layer is of importance for the description of adsorption kinetics of ionic surfactants.

The physical model

The indifferent electrolyte concentration influences the adsorption and thereby the diffuse layer is suppressed or extended depending on the direction of the concentration change. It is important to consider this effect on the adsorption and diffuse layer thickness as being independent. Usually, this is achieved by using an electrolyte mixture consisting of surfactant ions and two inorganic ions, the concentration of which is much higher than that of the surfactant c_s. The surfactant influences the adsorption at the interface and the inorganic electrolyte concentration c_0 controls the diffusion layer thickness. Let us introduce the restriction

$$c_0 \gg c_s \,, \tag{1}$$

which allows to simplify the derivation of the equations and to consider the present case of three ions as a binary electrolyte consisting of ionic surfactant and counterions and neglecting the inorganic co-ions.

Only in the limiting case of a high DL potential, we have:

$$|z_s\, y_s| > 1 \tag{2}$$

(z_s is the surfactant ion valence, $y_s = F\,\Psi_d/RT$, Ψ_d is the Stern potential, F is the Faraday constant,

T is the temperature and R is the gas law constant), and the effect of the DL on adsorption kinetics becomes substantial. If the potential is high enough we obtain

$$\tau_{\text{ads}} \gg \tau_{\text{æ}}, \tag{3}$$

where τ_{ads} characterises the surfactant adsorption time and $\tau_{\text{æ}}$ the time necessary to establish the equilibrium state of the diffuse part of the electric DL. The condition Eq. (3) allows the introduction of the concept of a quasi-equilibrium DL.

To describe the adsorption kinetics of ionic surfactants we need two double-layer models, one for the kinetic state and the other for the equilibrium state of the electric double layer. The equilibrium model used here consists of the following. The surface charge σ is determined by the adsorption of surfactant ions and its time dependence $\sigma(t)$ by the adsorption kinetics process. From Eq. (3), we conclude that at any moment the formation of the diffuse part of the double layer is as fast as the change of the surface charge. That means the diffuse part of the double layer (except the adsorbing ions) is always in a state close to equilibrium, i.e., in a quasi-equilibrium state.

The double-layer model for the kinetic state is derived as follows, considering only the case of an anionic surfactant (for a cationic surfactant all relations can be obtained in an identical way). There are two models to describe the screening of the surface charge σ. The Gouy–Chapman model assumes that the counterions are only distributed in the diffuse layer and compensate σ. In the Stern–Gouy model two layers compensate the surface charge σ: the diffuse layer and the Stern layer. In the following, we will use the picture of the Stern layer developed by Martynov [7].

The kinetics of surfactant adsorption has been shown to be important in the dynamics of the interaction of colloidal particles [8]. The DL model developed in [8] is equivalent to that, which we will use here, but additionally, we take into account specific counterion adsorption.

A strong influence of ion valences on the diffuse layer exists and therefore, a strong effect on adsorption kinetics can be expected, too. The double-layer effect on adsorption kinetics is manifested by a decrease in surfactant concentration in the sublayer, $c_s(x, t)|_{x=0} = c_s(0, t)$, where x is the distance to the interface. This leads to a retardation of the adsorption rate. If the surface charge and the surfactant ions have the same sign the concentration of the surfactant co-ions is decreased near the interface as a result of the double layer action. This decrease in concentration can be rather high under the condition Eq. (2).

In the equilibrium state of the DL the concentration profile of the co-ions can be described by the Boltzmann equation. During the adsorption process this is not applicable. Because of the condition expressed by Eq. (3) the quasi-equilibrium state of the diffuse layer exists only for the non-adsorbing ions. The flux of surfactant ions to the surface is controlled by the adsorption kinetics. Thus, we consider this flux and the deviation of the distribution of surfactant ions from equilibrium state, which is closely connected with this flux. The surfactant ions passing through the diffuse layer are retarded by the electric field of the DL. Assuming a quasi-equilibrium state of the diffuse part of the DL, this electric field can be determined independent of the surfactant fluxes. This idea was applied in [1] to derive the transport equation of surfactants through the diffuse layer. The main result of this approach consists in the following relation:

$$c_s(0,t) = \exp(-|z_s y_s|) \times \left[c_s(\text{æ}^{-1}, t) - \frac{j_s(t)}{D_s} K(y_s) \right], \tag{4}$$

where D_s is the diffusion coefficient of the surfactant ion, $j_s(t) = d\Gamma/dt$ is the flux of adsorbing ions, æ^{-1} is the Debye length, and $K(y_s)$ is the coefficient of electrostatic deceleration of adsorption given by the relation [1, 9]

$$K(y_s) = \int_0^{\text{æ}^{-1}} \exp(|z_s f_0(x)|)\, dx \cong \frac{z^+}{\text{æ}} \frac{\exp(|(z_s - z^+/2)\, y_s|)}{z_s - z^+/2}, \tag{5}$$

where $f_0 = F(\Phi_0(x)/RT$, $\Phi_0(x)$ is the equilibrium potential distribution and z^+ is the counterion valence. For the derivation of Eq. (4) it was only assumed that the potential distribution of $f_0(x)$ is independent of $c_s(x, t)$ and, therefore, of the surfactant flux. At a high concentration of inorganic electrolyte the surfactant ions are only a small part of the DL. Thus, this condition is much better fulfilled now than in the case of binary electrolytes discussed in [1] where the concentration of counterions forming the double layer was of the same order of magnitude as the surfactant ions concentration transported through the double layer.

In this paper we present an improved model with an existing equilibrium between the adsorption layer and the sublayer considering the retardation of the adsorption rate due to the effect of the electric field on the transport of surfactant ions through the DL.

After substituting the concentration $c_s(0,t)$ from Eq. (4) into the Stern–Martynov adsorption isotherm

$$\Gamma(t) = \exp(-W^-)\,\Delta\, c_s(0,t) \tag{6}$$

the equation of adsorption kinetics follows,

$$\Gamma(t) = \Delta \exp[-W^- + z_s y_s(t)] \times\left[c_s(æ^{-1},t) - \frac{d\Gamma}{dt}\frac{K(y_s)}{D_s}\right], \tag{7}$$

where W^- is the adsorption potential of surfactant ion expressed in units of kT, and Δ is the thickness of the adsorption layer.

Adsorption kinetics of ions for the case of their equilibrium distribution in the diffuse layer

We will consider the adsorption kinetics under the assumption that at any time the number of adsorbed ions is described by the Boltzmann equation, i.e., without regard for the ion flow in Eq. (4)

$$c_s(0,t) = \exp(-|z_s y_s|)\, c_s(æ^{-1},t)\,. \tag{8}$$

The substitution of Eq. (8) into Eq. (6) yields

$$\Gamma(t) = \Delta \exp[-W^- + z_s y_s(t)]\, c_s(æ^{-1},t)\,. \tag{9}$$

For this purpose it is convenient to make use of the equation derived by Sutherland [10]

$$\bar{\Gamma}(\Theta) = \left[1 - \exp\left\{\frac{\pi\Theta}{4}\right\} \operatorname{erfc}\left\{\sqrt{\frac{\pi\Theta}{4}}\right\}\right], \tag{10}$$

with $\bar{\Gamma} = \Gamma/\Gamma_{\text{eq}}$ and $\Theta = 4Dtc_s^2/\pi\Gamma_{\text{eq}}^2$. The function erfc($x$) is defined as the complementary error function erfc(x) = 1 − erf(x). It is easy to check that this function monotonically varies between 0 and 1, i.e., it satisfies the initial condition and results in saturation.

The inequality given in [11]

$$\frac{1}{x + \sqrt{x^2+1}} < \exp(x^2) \int\limits_x^\infty \exp(\xi^2)\, d\xi < \frac{1}{x + \sqrt{x^2/2 + 4/\pi}}\,;\ x > 1 \tag{11}$$

allows to approximate Eq. (10) by

$$\bar{\Gamma}(\Theta) = \left[1 - \frac{2}{\sqrt{\pi}} \frac{1}{\sqrt{\pi\Theta/2} + \sqrt{\pi\Theta/4 + 4/\pi}}\right]. \tag{12}$$

On the basis of Eq. (12) the characteristic time of adsorption kinetics can be estimated as

$$\Theta \approx 1, \tag{13}$$

from which we get the relation for the characteristic time of the adsorption kinetics of ionic surfactants when the diffuse layer is assumed to be in equilibrium:

$$T_1 \approx \frac{\Gamma_{\text{eq}}^2}{c_s^2 D}\,. \tag{14}$$

Consideration of a non-equilibrium distribution of adsorbing ions in the diffuse layer

Let us now consider the more exact equation, Eq. (7) (cf. Eq. (27) in [2]), taking into account surfactant ion distribution within the diffuse layer deviating from Boltzmann's distribution

$$\frac{d\bar{\Gamma}}{dt} + \frac{D_s \exp(-z_s y_s)\bar{\Gamma}(t)}{K(y_s)\Delta \exp(-W^-)} = \frac{D_s}{K(y_s)} c_s(æ^{-1},t)\,. \tag{15}$$

Introducing the dimensionless variables

$$\bar{\Gamma} = \Gamma/\Gamma_{\text{eq}} \quad \text{and} \quad \theta = \frac{D_s t c_s}{\Gamma_{\text{eq}} K(y_s^{\text{eq}})}\,, \tag{16}$$

we transform Eq. (15) into the dimensionless form:

$$\frac{d\bar{\Gamma}}{d\theta} + \frac{\exp(-z_s(y_s - y_s^{\text{eq}})\bar{\Gamma}(\theta) K(y_s^{\text{eq}})}{K(y_s)} = \frac{K(y_s^{\text{eq}})}{K(y_s)}\left[1 - \frac{2}{\sqrt{\pi D_s} z_s}\frac{d}{d\theta}\int\limits_0^{\sqrt{\theta}} \bar{\Gamma}(\theta - \tau)\, d\sqrt{\tau}\right]. \tag{17}$$

If the electroneutrality of the double layer is taken into account, y_s can be eliminated from Eq. (17) by using the well-known equation of the Gouy–Chapman theory leading to

$$F z_s \Gamma = F z^+ \frac{4}{æ} \sinh\left(\frac{-z^+ y_s}{2}\right) \cong F z^+ \frac{2}{æ} \exp\left(\frac{-z^+ y_s}{2}\right) \tag{18}$$

from which follows

$$\exp\left[\frac{z^+ (y_s^{\mathrm{eq}} - y_s)}{2}\right] = \Gamma/\Gamma_{\mathrm{eq}} = \bar{\Gamma}\,, \tag{19}$$

and

$$\frac{K(y_s^{\mathrm{eq}})}{K(y_s)} = \exp[-(z_s - z^+/2)(y_s^{\mathrm{eq}} - y_s)] = \bar{\Gamma}^{(1-2z_s/z^+)}\,. \tag{20}$$

From (17) and (20) we obtain

$$\frac{d\bar{\Gamma}}{d\theta} + \bar{\Gamma}^2 \approx \bar{\Gamma}^{(1-2z_s/z^+)} \times \left[1 - \delta \int_0^{\sqrt{\theta}} \frac{d}{d\tau} \bar{\Gamma}(\theta - \tau) d\sqrt{\tau}\right], \tag{21}$$

with

$$\delta = \left[\frac{8}{\pi}\frac{c_0}{c_s} \exp\{(z_s - z^+) y_s^{\mathrm{eq}}\} \frac{(z_s - z^+/2)}{z_s}\right]^{1/2}. \tag{22}$$

To obtain a rough approximation we can restrict the consideration by the condition

$$\delta \ll 1\,. \tag{23}$$

As will be shown below this condition substantially affects the retardation of the electrostatic interaction on the adsorption kinetics. Under the two conditions of Eqs. (18) and (23) the relation Eq. (21) now reads:

$$\frac{d\bar{\Gamma}}{d\theta} + \bar{\Gamma}^2 \approx \bar{\Gamma}^{(1-2z_s/z^+)}\,. \tag{24}$$

Equation (24) suggests an adsorption value at which the contribution of co-ions to the charge of the diffuse layer and to the deceleration of the adsorption process can be neglected. In other words, the adsorption is not equal to zero at the very beginning, but it is much smaller than the equilibrium adsorption value

$$\bar{\Gamma} \ll 1\,. \tag{25}$$

Neglecting the effects of the order of $\bar{\Gamma}$ the following approximate initial condition can be used:

$$\bar{\Gamma}|_{\theta=0} = 0\,. \tag{26}$$

A solution of the problem based on this initial condition will not be exact for the initial period. Nevertheless, its accuracy will increase with increasing θ. The solution of Eq. (24) has the form

$$\theta = \int_0^{\bar{\Gamma}} \frac{\xi^{(2z_s/z^+ - 1)}}{1 - \xi^{(1+2z_s/z^+)}} d\xi\,. \tag{27}$$

Equations (21), (24) and (27) describe the process of adsorption leading to the equilibrium state at infinite time

$$\bar{\Gamma}|_{\theta\to\infty} = 1\,. \tag{28}$$

If we disregard the state close to equilibrium, we obtain

$$\bar{\Gamma}^{(1+2z_s/z^+)} \ll 1\,, \tag{29}$$

and we can simplify the integrand in Eq. (27). Integration now results in

$$\theta \approx \int_0^{\bar{\Gamma}} [\xi^{(2z_s/z^+ - 1)} + \xi^{(4z_s/z^+)}]\, d\xi = \frac{z^+}{2z_s} \bar{\Gamma}^{(2z_s/z^+)} + \frac{z^+}{4z_s + z^+} \bar{\Gamma}^{((4z_s + z^+)/z^+)}\,. \tag{30}$$

Under the condition of Eq. (25), we can omit the second term in (30)

$$\bar{\Gamma}(\theta) = \left[\frac{2z_s}{z^+}\theta\right]^{z^+/2z_s}. \tag{31}$$

These simplifications are equivalent to disregarding the second term on the left-hand side of Eq. (30). This means that the second term in Eqs. (21) and (24) can be omitted under condition (29).

$$\frac{d\Gamma^{(2z_s/z^+)}}{d\theta} + \delta \frac{d}{d\theta} \int_0^{\sqrt{\theta}} \bar{\Gamma}(\theta - \tau) d\sqrt{\tau} \approx 1\,. \tag{32}$$

Equation (32) together with the initial condition (26) can easily be integrated and yields

$$\frac{z^+}{2z_s} \bar{\Gamma}^{(2z_s/z^+)} + \delta \int_0^{\sqrt{\theta}} \bar{\Gamma}(\theta - \tau) d\sqrt{\tau}] \approx \theta\,. \tag{33}$$

The second term on the left-hand side of Eq. (33) is associated with the decrease of surfactant concentration at the outer boundary of the DL. This effect decreases with increasing $\bar{\Gamma}(\theta)$. Thus, the applicability of the adsorption kinetics given by Eq. (31) is restricted both at the initial stage and in the vicinity of equilibrium (Eq. (25)). Nevertheless, the approximation Eq. (31) is a useful solution to the problem of the effect of DL on adsorption kinetics.

In analogy to the discussion of Eq. (12), we will interpret Eq. (30) using a dimensionless time θ of the order of 1 as the characteristic adsorption time. With regard to the definition of θ and $\bar{\Gamma}$ by Eq. (16), we obtain

$$T_2 = \frac{\Delta \exp[-W^- + z_s y_s^{\mathrm{eq}}]\, K(y_s^{\mathrm{eq}})}{D_s} \,. \tag{34}$$

From Eqs. (14), (2) and (34) we get for the time ratio of both models

$$\frac{T_2}{T_1} = \frac{z_s}{2z_s - z^+} \frac{c_s}{c_0} \exp[-(z_s - z^+)\, y_s^{\mathrm{eq}}] \,. \tag{35}$$

The ratio T_2/T_1 characterizes the role of a non-equilibrium DL on the adsorption kinetics of ionic surfactants. If, for example, $y_s^{\mathrm{eq}} \approx 8$–$10$, $z_s = 2$ and $c_s \sim c_0$ the deviation of $c_s(x, t)$ from equilibrium can retard the adsorption kinetics by two orders of magnitude. However, an addition of electrolyte can suppress this effect.

The applicability of Eq. (35) is restricted by the conditions given in Eqs. (1) and (2) which have been used in the approximate theory. The linear adsorption isotherm used means that the degree of filling of the equilibrium adsorption layer should be low, i.e.,

$$\Gamma/\Gamma_\infty = \omega N \Gamma_{\mathrm{eq}} \ll 1 \,, \tag{36}$$

where ω is the area of the adsorbed molecule in cm^2, N is Avogadro's number, Γ_{eq} is the equilibrium adsorption expressed in mol/cm^2, and Γ_∞ is the maximum adsorption expressed in mol/cm^2. Substituting Γ_{eq} into Eq. (36), we obtain:

$$\omega N \Gamma_{\mathrm{eq}} = \omega N \exp[-W^-] c_s \left[\frac{z^+}{z_s} \frac{2}{\text{æ}\Delta} \frac{c_0}{c_s} \times \exp(-W^-) \right]^{(z_s/(z_s + z^+/2))} \ll 1 \,, \tag{37}$$

where ω is estimated under the assumption of isometric adsorbed molecules. The calculation based on Eq. (36), even with regard to the restriction of Eq. (37), shows that T_2 can exceed T_1 by one order of magnitude and more.

Conclusions

The effect of the electrostatic retardation on the adsorption kinetics grows with increasing c_s, $|W^-|$, and z_s, and decreases with increasing c_0, and z^+. That electrostatic retardation is the consequence of the deviation of the distribution of adsorbing ions in the diffuse layer from the Boltzmann distribution. The density of the flow of adsorbing ions decreases according to the present theory, but the equilibrium value of adsorption decreases to the same extent, so that the adsorption time does not change in comparison to the approximation given by Borwankar and Wasan [5, 6].

The most significant restriction of the presented theory is the fact that it is based on a macro-kinetic approach. In this case the discrete nature and finite dimensions of adsorbed ions are ignored. Adsorption is impossible, not only on the portion of the area occupied by the ion adsorbed before, but also in some neighborhood of this area. An ion approaching pre-adsorbed ions will be affected by a strong repulsion at a distance of several diameters of an ion. As the degree of coverage of the surface with adsorbed ions increases transport of ions from the sublayer to the surface will be slowed down. This is not considered within the framework of the macro-kinetic approach and the theory should be developed in this direction.

For a quantitative description of the adsorption process of ionic surfactants at a liquid interface Eq. (21) can be used. Due to its complex structure an analytical solution is not available and numerical algorithms have to be applied. This will be presented in a forthcoming paper together with experimental results of solutions of surfactant having different charge and valency.

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