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Theory of surfactant diffusion in micellar systems with variable aggregation numbers

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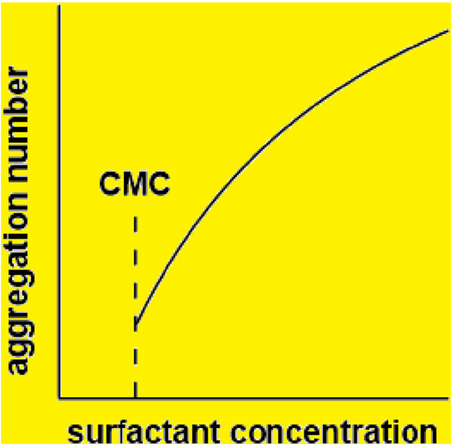
GRAPHICAL ABSTRACT



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ABSTRACT

The theory of diffusion of both nonionic and ionic surfactants in micellar systems is extended to the case with variable aggregation numbers. General relationships for the mobility and diffusion coefficient of surfactants are derived, and their dependence on the aggregation number variability is analyzed. Theoretical reasoning is supplemented by numerical calculations on the example of the sodium dodecyl sulfate micellar solution. It is shown that the effect of the aggregation number variability can be significant even for spherical micelles when investigating the surfactant diffusion in the vicinity of the critical micelle concentration.

1. Introduction

Micelles of colloidal surfactants are typical nanostructures about 4 nm in size and larger. They arise spontaneously in surfactant solutions at attaining a certain concentration (strictly speaking, within a narrow concentration range) called the critical micelle concentration (CMC). In contrast with embryos of a new phase, micelles are not only equilibrium but stable. Among micellization theories, the phase separation approach [1] looks rather crude although suitable for some calculations. It was more successful the quasi-chemical approach [2–6]. It considers an aggregation process like a chemical reaction with the Gibbs equilibrium condition

$$\mu_{\mathrm{M}} = \sum_i n_i \mu_i, \tag{1}$$

where μ is chemical potential, M is the chemical symbol of a micelle, i is

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an ordinal number of species forming the micelle, and n_i is the aggregation number (the number of particles of sort i in a micelle). The standard expression for the chemical potential reads

$$\mu = \mu_s + kT\ln(cf), \tag{2}$$

where μ_s is the standard part of μ, k is the Boltzmann constant, T is temperature, c is concentration (the number of particles per unit volume), and f is the activity coefficient. Putting Eq. (2) for μ_M and μ_i into Eq. (1) yields a general formulation of the mass action law

$$c_M f_M = K_a \prod_i (c_i f_i)^{n_i}, \tag{3}$$

where K_a is a constant of the mass action law in terms of activities, n_i is the aggregation number (the number of particles of sort i in a micelle), the subscript i referring to the monomeric form of a surfactant. Since micellization typically occurs at small concentrations, it is convenient to write the mass action law in the ideal form as

$$c_M = K \prod_i c_i^{n_i}, \tag{4}$$

where K is a constant of the mass action law in terms of concentrations. Expressing the concentrations in the CMC units simplifies Eq. (4) to the form [7]

$$c_M = \prod_i c_i^{n_i}, \tag{5}$$

where the mass-action-law constant disappears. The theory of micellization is based on the joint consideration of the mass action law, Eqs. (3)–(5), and the material balance condition

$$c_{it} = c_i + n_i c_M \tag{6}$$

where c_{it} is the total number of particles of sort i, and only one kind of micelles is supposed for the sake of simplicity.

Considering aggregation numbers to be constants (similarly to stoichiometric coefficients in chemistry), Eqs. (3)–(5) are sufficient for the calculation of c_i and c_M as functions of the total surfactant (or a surfactant mixture) concentration [8,9]. However, thermodynamics requires aggregation numbers to be increasing functions of concentration [6,10,11]. The function kind depends on the micelle structure, which is a consequence of the surfactant molecular structure and is purely individual. Among polymorphous modifications of micelles, spherical micelles are the simplest. After forming a spherical micelle as a closed surfactant monolayer (with no cavity inside), the aggregation number can undergo an only slight increase with the surfactant concentration unless a polymorphous transition occurs. For a long time, the concentration range of existing spherical micelles was considered in theory as suitable for the approximation of constancy of the aggregation number. However, the development of direct methods of measuring aggregation numbers led to the discovery of spherical micelles with variable aggregation numbers [12–16]. The explanation of this phenomenon is simple. Depending on the molecular structure, the micelle formation occurs as a jump for some surfactants and requires a certain concentration range above the CMC for the others. In any case, the concentration range with an almost constant aggregation number is attainable, but it can happen not immediately above the CMC as it was accepted in all theories of micellization. As for non-spherical micelles, the variable character of their aggregation numbers is obvious.

The existing theories of micellization typically contain two kinds of simplification: considering a micellar solution as an ideal mixture of monomers and micelles (replacing Eq. (3) by Eq. (4)) and postulating the constancy of the aggregation number. The movement towards the lifting of these restrictions has already begun [11,17,18]. Among numerous aspects of the theory of micellization, some relations are universal and look alike for micellar systems with constant and variable aggregation numbers. The mass action law is the most popular example. Other relations require separate considerations for constant and variable aggregation numbers.

The present article is devoted to the theory of diffusion in micellar systems. The first variant of the theory was formulated as an equation relating the total surfactant diffusion coefficient to the individual diffusion coefficients of monomers and micelles with given and fixed aggregation numbers [19,20]. It is of note that operating with a diffusion coefficient is a tribute to tradition. The surfactant mobility [21,22] is a more fundamental characteristic of diffusion. So we here will consider mobilities and diffusion coefficients in parallel. We will see that the theory of mobility is formulated irrespective of the constancy or variability of aggregation numbers. By contrast, the relations for diffusion coefficients with variable and constant aggregation numbers are different. The theory will be formulated on the basis of the mass action law, Eq. (3). This implies that diffusion occurs slowly enough to maintain the equilibrium condition expressed in Eq. (1) in the course of diffusion. We also postulate the constancy and uniformity of temperature and pressure to exclude thermo- and barodiffusion. We separately consider the diffusion of nonionic and ionic surfactants. The main goal is to see how diffusion is influenced by such a phenomenon as micellization.

2. The case of a nonionic surfactant

In the case of a single nonionic surfactant in solution, the Gibbs equilibrium condition, Eq. (1), is simplified to the form

$$\mu_M = n\mu_1 = n\mu, \tag{7}$$

where, as above, subscripts M and 1 refer to micelles and monomers, respectively, and symbol μ with no subscript refers to the surfactant as a whole. The equality of μ_1 and μ could be rigorously proved for equilibrium micellar systems [23], and this fact has been taken into account in Eq. (7). For a single nonionic, the mass action law as Eq. (3) can be written in terms of concentration and activity coefficient f

$$c_M f_M = K_a (c_1 f_1)^n. \tag{8}$$

The material balance condition, Eq. (6), takes the form

$$c = c_1 + nc_M, \tag{9}$$

where we use no subscript for the total surfactant concentration c.

Let us turn to equations related to diffusion. The role of mobility u is clear from the equation

$$\mathbf{j} = -uc\nabla\mu, \tag{10}$$

where $\mathbf{j}$ is the surfactant-flux-density vector and $\nabla\mu$ is the surfactant-chemical-potential gradient. Eq. (10) is written for a surfactant as a whole. In more detailed presentation as the sum of the fluxes of micelles and monomers, it yields

$$\mathbf{j} = \mathbf{j}_1 + n\mathbf{j}_M = -u_1 c_1 \nabla\mu_1 - u_M c_M n \nabla\mu_M. \tag{11}$$

Now from Eqs. (7), (10), and (11), we obtain [21]

$$uc = u_1 c_1 + n^2 u_M c_M \tag{12}$$

or, after dividing by c,

$$u = u_1(1-\alpha) + nu_M\alpha, \tag{13}$$

where $\alpha = nc_M/c$ is the micellization degree.

For spherical micelles, the Stokes equation reads

$$u_M = \frac{1}{6\pi\eta r_M}, \quad r_M = \left(\frac{3nv}{4\pi}\right)^{1/3}, \tag{14}$$

where η is the surfactant solution viscosity, r_M is the micelle radius, and v is the surfactant molecule volume. If the aggregation number n is variable, it should grow (together with α) as micellization develops. Eq. (14) then trivially confirms a drop in the micelle mobility. Using Eq. (14) and a similar equation for monomers approximated by spheres of radius r_1, Eq. (13) remarkably yields