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Diffusion in micellar systems: theory and molecular modelling

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Recent development of experimental methods of investigation of diffusion in micellar systems and rethinking of the available material led to an increase in the number of theoretical studies in this field. This review summarizes the achievements in the general theory of micellization based on the law of mass action and in its applications to migration of surfactants in micellar systems. The law of mass action itself is modified to describe aggregative systems not only at low but also at moderate concentrations. New methods for calculating the concentrations of monomers and micelles in nonionic and ionic micellar systems are presented. Methods for estimating the micellar diffusion coefficient and the aggregation number from experimental data on surfactant diffusion are described. The theory of diffusion of electrically neutral micelles in concentrated ionic micellar solutions is developed. Computer simulation is an important tool complementing analytical and experimental methods of investigation of diffusion processes in micellar systems. The review addresses modern methods of molecular modelling of micellar systems, such as the all-atom molecular dynamics, molecular dynamics within coarse-grained models, and Brownian dynamics, which allow one to obtain a most detailed description of the structural and transport properties of micellar solutions. Various versions of cluster analysis and the role of this approach in calculations of surfactant diffusion coefficients in micellar solutions are discussed. The results of calculations of the diffusion coefficients of aggregates with different aggregation numbers, ions and water molecules from the data of all-atom molecular dynamics simulations at different total surfactant concentrations in the presence and in the absence of electrolyte are presented.
The bibliography includes 77 references.

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I. Introduction

Diffusion of matter is of particular importance for any chemical system. Aggregative systems belong to the most complex systems because the same chemical substance in them simultaneously exists in different states. Important examples of aggregative systems are provided by micellar solutions of colloidal surfactants, where a noticeable proportion of the surfactant exists as molecular or ionic aggregates. Surfactant micelles are thermodynamically stable aggregates representing typical nanostructures (a few nanometres and more in size), which emerge spontaneously as the surfactant concentration in a solution increases and reaches the critical micelle concentration (CMC). Unlike

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nuclei of a new phase, micelles are true equilibrium and stable entities having no macroscopic analogues and existing only as small particles with unique structure. Micelles exhibit polymorphism, *i.e.*, they adopt and retain a wide variety of geometric shapes related to the molecular structure of surfactants. This feature is typical of crystals and, seemingly, polymorphism itself is indicative of a solid-like character of micelles, but spectroscopic data suggest that they are in a liquid-like state. The paradox can be solved taking into account the fact that micelles are in fact solid-like particles in the radial direction and liquid-like ones in the other two directions.[1,2]

A huge array of experimental data collected since the discovery of micelles in 1913 still continuously surprises researchers. Let's begin with the fact that micelles in water and in other polar media (so-called 'normal' micelles in contrast to 'reverse' micelles in nonpolar media) are formed in the absence of attraction between surfactant molecules (and even in the presence of repulsive forces acting between surface-active ions). This is related to hydrophobic (generally, solvophobic) effects, namely, water 'forces' surfactant particles to form micelles rather than those particles are brought together through attractive interactions. Yet another amazing feature is the appearance of large micelles at a fixed surfactant concentration above the CMC (micelles consist of a few dozens or even a few hundreds of molecules or ions). Even more surprising is that the 'solubility' of micelles (equilibrium concentration of monomers in a micellar solution) increases with increasing particle size rather than decreases, as is expected from the classical Kelvin equation for small particles. Do micelles really not obey the laws of thermodynamics? At last, contrary to common sense, the addition of an ionic surfactant to its micellar solution causes a decrease rather than increase in the concentration of monomeric surface-active ions of the same surfactant.

The aforesaid holds for equilibrium systems, but even here much has to be understood and relevant theories are in great demand. Modern experimental studies also involve dynamic systems that exhibit some paradoxical effects. For instance, micelles are larger than molecules and of course they move more slowly, but the diffusion coefficient of a surfactant in a micellar system is higher than in a micelle-free solution. The diffusion coefficient of a nonionic surfactant in a micellar solution decreases, whereas that of an ionic surfactant increases with the surfactant concentration. As to the kinetics of micellization and micellar relaxation, where the diffusion coefficients of surfactant monomers and aggregates play a key role, a relevant theory is in the early stage of development, and much work is still to be done. To date, kinetic models for the molecular mechanism of aggregation and partially for the fusion and fission of micelles in solutions of nonionic surfactants have been constructed. The state of the art in this field has been described in a monograph,[2] while recent results are available elsewhere.[3–10]

Since the CMC of most colloidal surfactants are low, micellar systems can be considered as ideal systems in a rather wide concentration range. The equilibrium theory of micellar systems based on the law of mass action was recast on the basis of a new approach to the CMC.[11] Not only a number of paradoxical effects were explained, but also their generalization to multicomponent systems was made. Next, that theory was applied to nonideal systems characterized by rather high CMC.[12] The case of electrically neutral micelles in ionic solutions at moderate concentrations was considered and specific features of surfactant diffusion in such systems were revealed.

Experimental methods of investigation of diffusion in micellar solutions, especially, quasi-elastic dynamic light scattering (DLS) have also been developed in recent decades with application of various types of zetasizers. Taking into account the laser wavelengths, a zetasizer seemingly cannot 'see' molecules or ions in monomeric or weakly associated form and can immediately provide valuable information on micelles. This interpretation of the results obtained by DLS was commonly accepted until a quite recent[13] experimental discovery that DLS, as well as other methods, allows one to determine an average diffusion coefficient of all forms of a surfactant rather than the diffusion coefficient of surfactant micelles. Of course, this leads to the need to revise the interpretation of the whole experimental data array accumulated to date. But how to measure the diffusion coefficient of surfactant micelles? There is a dilemma, *viz.*, if experimental methods fail to select the diffusion coefficient of surfactant micelles from the total diffusion coefficient, theory should help. Recently, there has been an increase in the number of corresponding theoretical studies, so theory and computer simulation not accidentally form the basis for this review. Molecular simulation methods, such as all-atom molecular dynamics, molecular dynamics within coarse-grained models, as well as Brownian dynamics allow one to obtain a comprehensive description of the structural and transport properties of micellar solutions including the properties of individual molecular or ionic aggregates of any size; they belong to the most important tools of nanoscience.[14–16]

The mass action law is thought to be the most reliable basis for developing the theory of micellar systems. This is a very old method familiar to all chemists. However, it has some specific features when applied to micellar systems and has been revisited recently.[11,12] Therefore, it seems reasonable to begin the review with the description of the modern interpretation of the mass action law as applied to micellization.

II. The mass action law in theory of micellization

II.1. Micellization from the standpoint of chemical thermodynamics

Within the framework of thermodynamics, micelles can be interpreted from the phase or chemical standpoint. The macrophase interpretation does not meet stringent requirements;[1,2] however, it can be successfully used as an approximation in calculations.[17–19] By analyzing the micelle size distribution both types of interpretations can be reconciled,[20,21] the chemical interpretation always being rigorous. It implies that the micelle is treated as a new substance M which can dissociate into individual molecules or ions B_{i1} (the subscript i denotes the sort of a molecule or ion, while the subscript '1' specifies monomers), the reaction being reversible

$$M \rightleftharpoons \sum_i n_i B_{i1} \qquad (1)$$

Here, the aggregation numbers n_i (n_i is the number of the type-i particles in the micelle) play the role of stoichiometric coefficients. Considering a micelle as a chemical entity, one can introduce the corresponding chemical potential, μ_M.

Following Gibbs, the equilibrium condition for reaction (1) has the form

$$\mu_{\mathrm{M}} = \sum_i n_i \mu_{i1} \tag{2}$$

Within the formalism of chemical thermodynamics, let us introduce the activities of micelles and monomers (a_{M} and a_{i1}, respectively) and the corresponding activity coefficients $f_{\mathrm{M}} \equiv a_{\mathrm{M}}/c_{\mathrm{M}}$ and $f_{i1} \equiv a_{i1}/c_{i1}$, where c is concentration. A question immediately arises as to how the activity coefficient of monomers is related to the conventional activity coefficients in solution thermodynamics or to the average activity coefficients (for electrolytes)?

Consider a solution of a single colloidal ionic surfactant denoted by the symbol 'B' with an arbitrary number of ions denoted by 'B_i' and same-size micelles, where micellization is complicated by electrolytic dissociation (let the surfactant be a strong electrolyte).[22] The corresponding reaction equation written per unit volume has the form

$$c\mathrm{B} = \sum_i c_{i1}\mathrm{B}_{i1} + c_{\mathrm{M}}\mathrm{M} \tag{3}$$

where c is the total concentration of the surfactant expressed as the number of undissociated molecules per unit volume. The total concentration of the type-i ions is given by cv_i, where v_i is the stoichiometric coefficient. Let the degree of micellization of the type-i ions be

$$\alpha_i = \frac{n_i c_{\mathrm{M}}}{cv_i} \tag{4}$$

$$1 - \alpha_i = \frac{c_{i1}}{cv_i} \tag{4a}$$

Then, we can re-write Eqn (3) per surfactant molecule as follows:

$$\mathrm{B} = \sum_i v_i(1-\alpha_i)\mathrm{B}_{i1} + \frac{v_j \alpha_j}{n_j}\mathrm{M} \tag{5}$$

where j is an arbitrary number from the set allowed for the subscript i (the entire coefficient at M is invariant with respect to j).

Now, following Gibbs, the equilibrium condition for reaction (5) is given by

$$\mu = \sum_i v_i(1-\alpha_i)\mu_{i1} + \frac{v_j \alpha_j}{n_j}\mu_{\mathrm{M}} \tag{6}$$

The aggregative equilibrium condition (2) is simultaneously valid. Substituting expression (2) into Eqn (6) gives

$$\mu = \sum_i v_i(1-\alpha_i)\mu_{i1} + \frac{v_j \alpha_j}{n_j}\sum_i n_i\mu_{i1} = \sum_i v_i\mu_{i1} \tag{7}$$

Here, in each multiplication event, the invariant in the second term is denoted by the subscript with which it is multiplied.

In accordance with the equilibrium condition for the reaction of electrolytic dissociation, the quantity in the right-hand side of Eqn (7) is the chemical potential of an electrically neutral monomeric surfactant molecule in solution. The quantity in the left-hand side of Eqn (7) is the chemical potential of the surfactant itself. It follows that the chemical potential of an aggregative system is determined by those of monomers. In addition, expression (7) shows that the equilibrium condition for electrolytic dissociation is not affected by micellization in terms of the chemical potential. However, would we like to refine the expression for the chemical potential by introducing the activity coefficient, this should be done in different manner in the absence and in the presence of micelles.

Actually, we may even have no information on micelles and use only the nominal concentration of the type-i ions, cv_i, which becomes real only for a strong electrolyte in the absence of micellization. Then, as applied to the type-i ions, the conventional expression for the chemical potential can be written in the form

$$\mu_i = \mu_{i\mathrm{s}} + kT\ln(cv_i f_i) \tag{8}$$

where $\mu_{i\mathrm{s}}$ is the standard component of the chemical potential, k is the Boltzmann constant, T is absolute temperature of the solution and f_i is the activity coefficient of the type-i ions. In the presence of micelles, one uses the real concentration of the type-i monomeric ions, $c_i = cv_i(1-\alpha_i)$ and has

$$\mu_i = \mu_{i\mathrm{s}} + kT\ln[cv_i(1-\alpha_i)f_{i1})] \tag{9}$$

instead of expression (8).

Having compared Eqns (8) and (9) and chosen the standard components identically, one gets

$$f_i = (1-\alpha_i)f_{i1} \equiv f_{i\mathrm{a}}f_{i1} \tag{10}$$

where $f_{i\mathrm{a}} \equiv 1 - \alpha_i$.

The identity (10) shows that the activity coefficient of an ion is determined by two factors. One of them is expressed through the degree of micellization (generally, aggregation) and can be referred to as the aggregative activity coefficient (it has the same form for nonelectrolytes as well). The other factor is the conventional activity coefficient of a monomer with allowance for all interactions.

By successively substituting expressions (8) and (9) into (7) and equating the results to each other one gets

$$\sum_i v_i \ln f_i = \sum_i v_i \ln[(1-\alpha_i)f_{i1}] \tag{11}$$

Having divided Eqn (11) by $v \equiv \sum_i v_i$ and passed to the average activity coefficients using a scheme typical of electrolytes

$$f_{\pm} \equiv \prod_i f_i^{v_i/v} \tag{11a}$$

one obtains

$$f_{\pm} = f_{\pm}\prod_i (1-\alpha_i)^{v_i/v} \tag{12}$$

The second factor in expression (12) can be treated as the average aggregative activity coefficient, f_{a}, of the electrolyte

$$f_{\mathrm{a}} \equiv \prod_i (1-\alpha_i)^{v_i/v} \tag{13}$$

Eventually, rearrangement of the factors in Eqn (12) leads to

$$f_{\pm} = f_{\mathrm{a}} f_{\pm 1} \tag{14}$$

The condition (14) is also valid for nonionic surfactants, but the average activity coefficient should be replaced by the conventional activity coefficient.

Two practically important conclusions from the aforesaid are as follows. First, theory should differentiate between the activity coefficients $f_{\pm}$ and $f_{\pm 1}$. In an ideal aggregative system, only the latter turns into unity, while the former retains the aggregative component. Second, $f_{\pm}$ can be determined experimentally, and in order to pass to $f_{\pm 1}$, the aggregative component given by expression (13) should be eliminated from $f_{\pm}$. These recommendations are for those engaged in with calculations.

II.2. Formulations of the mass action law

Passage from the chemical potentials to activities in the aggregative equilibrium condition (2) causes the mass action law to take the form

$$a_{\mathrm{M}} = K_{\mathrm{a}} \prod_i a_{i1}^{n_i} \tag{15}$$

where K_{a} is the constant of the mass action law written in terms of activities and a_{i1} are the activities of monomers. In expression (1), the aggregation numbers n_i play the role of stoichiometric coefficients with the difference that they can vary. Moreover, thermodynamics requires that the aggregation number be an increasing function of concentration.[1,2] However, if the maximum of the particle size distribution is so sharp that only preset-size micelles exist (this situation is typical of spherical micelles), the aggregation number changes with concentration more slowly than all other parameters.[11] Then, the assumption of constant aggregation numbers (quasi-chemical approximation) is quite admissible within a concentration interval spanning at least ten CMC units above the CMC.

Since for many surfactants the CMC is low, one can take $f_i = 1$ in the concentration range near the CMC. Then, expression (15) is simplified:

$$c_{\mathrm{M}} = K \prod_i c_{i1}^{n_i} \tag{16}$$

The mass action law is most often written in the form of Eqn (16). Popularity of this expression is due not only and not so much to the fact that it is simpler than relation (15). The case in point is that the theory of micellization is based on a combination of the mass action law and the material balance condition

$$c_i = c_{i1} + n_i c_{\mathrm{M}} \tag{17}$$

(c_i is the total concentration of the type-i surfactant). Expression (17) includes the same variables as those appearing in formula (16). Substitution of Eqn (16) into (17) gives

$$c_i = c_{i1} + n_i K \prod_i (c_{i1})^{n_i} \tag{17a}$$

In particular, for the type of particles characterized by the highest surface activity (let this type be denoted by '1') one has

$$c_1 = c_{11} + n_1 K \prod_i (c_{i1})^{n_i} \tag{17b}$$

or, in terms of the degree of micellization $\alpha_1 = (c_1 - c_{11})/c_1$,

$$c_1 \alpha_1 = n_1 K \prod_i c_i^{n_i} (1 - \alpha_i)^{n_i} \tag{18}$$

The proportions of different-type particles in the initial mixture of surfactants can be specified by the ratio $c_i = b_i c_1$, where $b_i (i = 1, 2, \ldots)$ are certain constants. Then, Eqn (18) takes the form

$$\frac{\alpha_1}{\prod_i b_i^{n_i} (1 - \beta_i \alpha_1)^{n_i}} = n_1 K c_1^{n-1} \tag{19}$$

where $n \equiv \sum_i n_i$ is the total aggregation number, $\alpha_i = \beta_i \alpha_1$ and $\beta_i \equiv n_i / n_1 \, b_i \, (b_1 = \beta_1 = 1)$.

Now we will consider the constant of the mass action law. It appears in the equilibrium reaction (1); however, it is clear that expression (1) is a general form of representation of a multistep process because accidental coupling of a large number of monomers to form a micelle seems to be improbable. Figuratively speaking, many a little makes a mickle, and the formation of a micelle requires many elementary coupling acts, each of them being characterized by its own constant of the mass action law. We have to relate these constants to K in Eqn (19) and then look around. For single-component micelles, the problem was solved a few decades ago,[23,24] but for multicomponent micelles this was done quite recently.[11] In the text below we will follow the pathway described in Ref. 11. Let us analyze how the micellization process is developed. The formation of a micelle begins with the coupling of two monomers with the highest surface activity: $\mathrm{B}_1 + \mathrm{B}_1 = \mathrm{B}_2$. The aggregative equilibrium condition for this act is $\mu_2 = 2\mu_1$, which leads to the mass action law with the constant K_2:

$$c_2 = K_2 c_{11}^2 \tag{20}$$

where $K_2 \equiv \exp(2\mu_{1\mathrm{s}} - \mu_{2\mathrm{s}})$.

The next step is the attachment of a type-i particle to the aggregate B_2 ($\mathrm{B}_2 + \mathrm{B}_i = \mathrm{B}_{2i}$) at

$$c_{2i} = K_{2i} c_2 c_{i1} \tag{21}$$

where $K_{2i} \equiv \exp(\mu_{2\mathrm{s}} + \mu_{i\mathrm{s}} - \mu_{2i\mathrm{s}})$.

An alternative treatment of the formation of B_{2i} as one-step process ($\mathrm{B}_1 + \mathrm{B}_1 + \mathrm{B}_i = \mathrm{B}_{2i}$) leads to

$$c_{2i} = K c_{11}^2 c_{i1} \tag{22}$$

where $K \equiv \exp(2\mu_{1\mathrm{s}} + \mu_{i\mathrm{s}} - \mu_{2i\mathrm{s}})$.

A comparison of expressions (20)–(22) gives $K = K_2 K_{2i}$. This corresponds to the known rule that the total equilibrium constant equals the product of the elementary constants. Arguing by analogy, one arrives at the following result. If the aggregation number of the type-1 particles in the micelle is n_1, there are a total of $n_1 - 1$ events of attachment a monomer to an aggregate and, therefore, $n_1 - 1$ elementary equilibrium constants K_{1k} ($k = 2, 3, \ldots, n_1$). Then, the contribution of the type-1 particles to the micellar constant K is

$$\prod_{k=2}^{n_1} K_{1k}$$

For all other types of particles, the number of the elementary constants K_{ik} is equal to the corresponding aggregation numbers and their total contribution is given by

$$\prod_{k=1}^{n_i} K_{ik}$$

Eventually, one gets

$$K = \prod_{k=2}^{n_1} K_{1k} \prod_{i>1} \prod_{k=1}^{n_i} K_{ik} \equiv \bar{K}^{n-1} \tag{23}$$

where $\bar{K}$ is the geometric mean of all elementary constants (recall that n is the sum of all aggregation numbers).

Substituting (23) into Eqn (19) gives

$$\frac{\alpha_1}{(1-\alpha_1)^{n_1} \prod\limits_{i>1} (b_i - \alpha_1 n_i/n_1)^{n_i}} = n_1 (\bar{K} c_1)^{n-1} \tag{24}$$

In this expression the product $\bar{K}c_1$ is raised to a very high power $n-1$, which means that the result becomes negligible at $\bar{K}c_1 < 1$ and giant at $\bar{K}c_1 > 1$. In practice, going from the former fo the latter case occurs with increasing the total concentration of the type-1 particles, which provides an explanation for abrupt micellization. Expression (24) allows the CMC ($c_{1\mathrm{m}}$) to be defined as

$$\bar{K} c_{1\mathrm{m}} = 1 \tag{25}$$

$$c_{1\mathrm{m}} = \bar{K}^{-1} \tag{25a}$$

This CMC definition makes it possible to write the constant of the mass action law in the form

$$K = c_{1\mathrm{m}}^{1-n}. \tag{26}$$

Now it can be experimentally measured with ease. Finally, substitution of formula (26) into Eqn (16) gives one more expression for the mass action law:

$$\tilde{c}_{\mathrm{M}} = \prod_i \tilde{c}_{i1}^{\,n_i} \tag{27}$$

where a tilde means that the concentration is measured in the CMC units. The equality (27) is the simplest form of the mass action law.

The aforesaid concerned an ideal mixture of monomers and micelles, where the mass action law had the form of Eqn (16). Similar reasoning can also be done for a more complicated case described by relation (15) (the meaning of the activity coefficients was clarified in the preceding Section). Now we will present some results.[12] Having expressed the CMC through the total concentration c of the mixture of particles and the total concentration of each type of particles, c_i, through the mole fraction x_i, one gets

$$c_i = c x_i \tag{28}$$

Then, Eqn (19) is transformed to

$$\frac{\alpha_1}{\prod\limits_i (1-\beta_i \alpha_1)^{n_i}} = n_1 K_{\mathrm{a}} c^{\,n-1} x_1^{\,n_1-1} \prod_{i>1} x_i^{n_i} \frac{1}{f_{\mathrm{M}}} \prod_i f_{i1}^{n_i} \tag{29}$$

Using the algorithm employed to derive formula (23) with replacement of concentration by activity and K by K_{a}, one has

$$K_{\mathrm{a}} = \prod_{k=2}^{n_1} K_{1k} \prod_{i>1} \prod_{k=1}^{n_i} K_{ik} \equiv \bar{K}_{\mathrm{a}}^{n-1} \tag{30}$$

Let us denote

$$\bar{x}^{\,n-1} \equiv x_1^{\,n_1-1} \prod_{i>1} x_i^{n_i} \tag{31}$$

and

$$\bar{f}^{\,n-1} \equiv \frac{1}{f_{\mathrm{M}}} \prod_i f_{i1}^{n_i} \tag{31a}$$

Substituting (30), (31) and (31a) into Eqn (29), one gets

$$\frac{\alpha_1}{\prod\limits_i (1-\beta_i \alpha_1)^{n_i}} = n_1 (\bar{K}_{\mathrm{a}} \bar{x} c \bar{f}\,)^{n-1} \tag{32}$$

This makes it possible to define the CMC (c_{m}, the subscript m shows that the quantity corresponds to the CMC)

$$\bar{K}_{\mathrm{a}} \bar{x} c_{\mathrm{m}} \bar{f}_{\mathrm{m}} = 1 \tag{32a}$$

$$c_{\mathrm{m}} = (\bar{K}_{\mathrm{a}} \bar{x} \bar{f}_{\mathrm{m}})^{-1} \tag{32b}$$

and to obtain the expression for the constant of the mass action law

$$K_{\mathrm{a}} = c_{\mathrm{m}}^{1-n} \bar{x}^{1-n} \bar{f}_{\mathrm{m}}^{\,1-n} = c_{\mathrm{m}}^{1-n} \bar{x}^{1-n} f_{\mathrm{Mm}} \prod_i f_{i1\mathrm{m}}^{\,-n_i} \tag{32c}$$

Substitution of (32c) into Eqn (15) gives a dimensionless form of the mass action law for a nonideal system

$$\tilde{c}_{\mathrm{M}} \tilde{f}_{\mathrm{M}} = \bar{x}^{1-n} \prod_i (\tilde{c}_{i1} \tilde{f}_{i1})^{n_i} \tag{33}$$

Here, a tilde denotes that the concentrations are given in the CMC units and the activity coefficients are given in the units related to the CMC ($\tilde{c}_{\mathrm{M}} \equiv c_{\mathrm{M}}/c_{\mathrm{m}}$, $\tilde{f}_{\mathrm{M}} \equiv f_{\mathrm{M}}/f_{\mathrm{Mm}}$, $\tilde{c}_{i1} \equiv c_{i1}/c_{\mathrm{m}}$, $\tilde{f}_{i1} \equiv f_{i1}/f_{i1\mathrm{m}}$).

The relations examined above describe arbitrary mixtures of surfactant molecules and/or ions in a chosen solvent. These can be mixtures of nonionic or ionic surfactants, as well as mixtures of both types of surfactants. To clarify how these relations operate, we will consider solutions of a single nonionic[25] or ionic[26] surfactant as the simplest examples.

II.3. The case of a single nonionic surfactant

This case corresponds to solvated (if solvation occurs) molecules of a single nonionic surfactant. Since the CMC of nonionic surfactants are 1 to 2 orders of magnitude lower than those of ionic surfactants (*e.g.*, 10^{-5} mol litre^{-1}), we will undoubtedly use expression (27). In our case, the subscript i is equal to 1 and can be omitted. The second subscript, '1', specifies monomers and should be retained. Keeping in mind that all concentrations are given in the

CMC units and omitting a tilde, one can write the mass action law (27) in the simplest form

$$c_M = c_1^n \tag{34}$$

From Eqns (19) and (26) one gets

$$c = \left[\frac{\alpha}{(1-\alpha)^n n}\right]^{1/(n-1)} \tag{35}$$

This expression specifies the total surfactant concentration as explicit function of the degree of micellization and aggregation number. From the mass action law it follows that the degree of micellization differs from zero at any total concentration including concentrations below the CMC. The α and n values increase with concentration, but the aggregation number is the most slowly changing parameter of the theory [11] and can to a good approximation be considered constant in a concentration range from one to two orders of magnitude above the CMC (in the CMC units). The plot of the function $c(\alpha)$ at $n = 100$ is shown in Fig. 1. Since the curve emerges from the origin, it is S-shaped and has a point of inflection; however, the α values at $c < 1$ are so small that the plot in this region coincides with the ordinate axis on the length scale chosen.

The theory of micellization based on the mass action law treats relations (34) and (35) in combination with the material balance condition for the surfactant

$$c = c_1 + nc_M = c_1 + nc_1^n \tag{36}$$

As can be seen, the concentration of monomers becomes equal to the CMC ($c_1 = 1$) at a surfactant concentration $c = n + 1$, which is much higher than the CMC. From condition (36) it also follows that at $c_1 = 1$, one should have $c_M = 1$, *i.e.*, the concentration dependences of monomers, $c_1(c)$, and micelles, $c_M(c)$, intersect at this point. To plot these dependences, we will use formula (35) and represent c_1 and c_M as explicit functions of α

$$c_1 = \left[\frac{\alpha}{(1-\alpha)n}\right]^{1/(n-1)} \tag{37}$$

$$c_M = \left[\frac{\alpha}{(1-\alpha)n}\right]^{n/(n-1)} \tag{38}$$

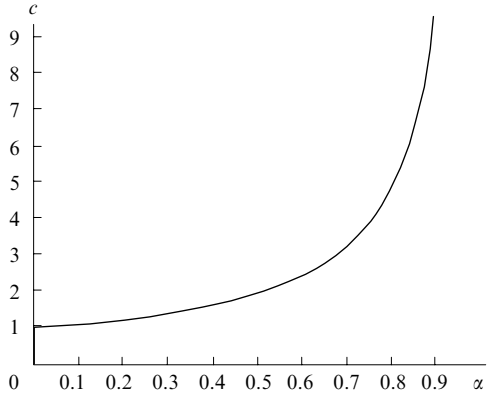


Figure 1. Total surfactant concentration (in CMC units) as function of the degree of micellization according to expression (35) at $n = 100$.[25]

Expressions (35) and (37) parametrically define (through α) the dependence of c_1 on c, while expressions (35) and (38) parametrically define the dependence of c_M on c at a given n. These dependences at $0 < \alpha < 0.9$ and $n = 100$ are shown in Fig. 2.

Simple shape of the $c_1(c)$ and $c_M(c)$ plots is in sharp contrast to the complexity of the analytical representation of these dependences by formulas (35), (37) and (38). Clearly, simple analytical approximations can also be used. For instance, the $c_1(c)$ dependence can be approximated by two straight lines passing below and above the CMC [25]

$$c_1 = c \quad (c < 1) \tag{39}$$

$$c_1 = \frac{n - \sqrt{n/2}}{n-1} + \frac{\sqrt{n/2} - 1}{n(n-1)}(c-1) \quad (1 < c < n+1) \tag{39a}$$

Now consider the function $c_M(c)$. By definition, one has $c_M = (c - c_1)/n$; substitution of expression (39) leads to

$$c_M = \frac{\sqrt{n/2} - 1}{n(n-1)} + \left[1 + \frac{\sqrt{n/2} - 1}{n(n-1)}\right]\frac{c-1}{n} \approx \tag{40}$$

$$\approx \frac{\sqrt{n/2} - 1}{n(n-1)} + \frac{c-1}{n} \quad (1 < c < n+1)$$

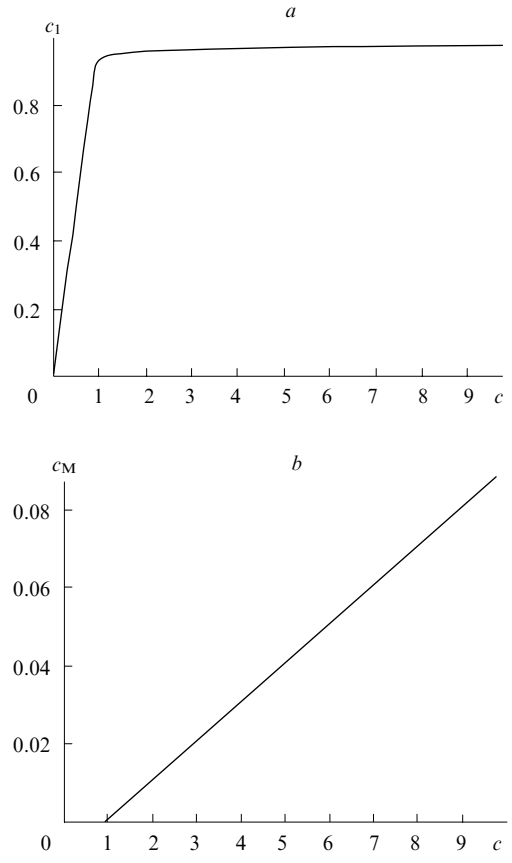


Figure 2. Concentration of monomers (*a*) and micelles (*b*) plotted *vs.* total surfactant concentration at degrees of micellization (α) in the range $0 < \alpha < 0.9$ (concentrations are given in the CMC units).[25]

Formulas (39), (39a) and (40) for the monomer and micelle concentrations above the CMC refine the commonly used approximation $c_1 \approx 1$, $c_M \approx (c-1)/n$. This makes it possible to carry out more accurate calculations, in particular, within the framework of the diffusion theory (see below).

II.4. The case of a single ionic surfactant

Of course, the expressions for the mass action law given above are also applicable to ionic surfactants (here, ions act as particles). However, in the case of electrolytes, it is commonly accepted to use the notion of the total electrolyte concentration, so the formalism based on the concentration of the most surface-active particles or on the total concentration of all particles (see above) is in some way inconvenient. Therefore, we will intentionally modify the mass action law to apply it to ionic surfactants. Consider the case of a single ionic surfactant with an arbitrary number of ions. For the sake of simplicity, let c be the total concentration of the surfactant, cv_i be the total concentration of the type-i ions (v_i is the stoichiometric coefficient) and c_i be the monomeric concentration of the type-i ions. Then, the mass action law (15) takes the form

$$c_M f_M = K_a \prod_i (c_i f_i)^{n_i} \tag{41}$$

The difference with the derivation of relation (33) consists in that here the total concentration of ions is expressed through v_i instead of x_i [see Eqn (29)]. This is not a simple replacement of notations because the mole fractions and the stoichiometric coefficients characterize different properties. However, the reasoning logic remains the same and the final result [12] is quite similar to formula (33)

$$\tilde{c}_M \tilde{f}_M = \prod_i (\tilde{c}_i \tilde{f}_i)^{n_i} \prod_i v_i^{-n_i} \tag{42}$$

where tilde denotes that the concentrations are given in the CMC units (c_m) and each activity coefficient is given in the units related to the CMC. The mass action law (42) can be written in a more compact form by introducing the quantity $\tilde{c}'_i \equiv c_i/c_m v_i = c_i/c_{im}$,

$$\tilde{c}_M \tilde{f}_M = \prod_i (\tilde{c}'_i \tilde{f}_i)^{n_i} \tag{43}$$

Now each monomer concentration (not the micelle concentration!) is measured in its own units.

Often, transition to nonideal behaviour is due to an increase in the surfactant concentration in the micellar system. In the case of ionic surfactants this is accompanied by unavoidable increase in the degree of counterion binding,[1,2] which can lead to the formation of electrically neutral micelles. The feasibility of this situation was demonstrated [27] taking sodium hexanesulfonate as an example. This compound has a short hydrocarbon chain and forms micelles in aqueous solution at a rather high concentration ($\sim$0.56 mol litre^{-1}), which causes a complete counterion binding. In this case, the activity coefficient of micelles loses the electrostatic component and becomes less significant. As to the activity coefficients of monomeric ions, we develop a theory for a concentration range near the CMC (otherwise, the aggregation number cannot be considered constant). At low CMC, the concentration interval of interest spans a range of one to two orders of magnitude with respect to the CMC, but at high CMC, it can be as narrow as a fraction of the CMC. If the relative change of the activity coefficients in this concentration interval is not too large, the approximation $\prod_i \tilde{f}_i \approx 1$ may appear to be convenient and the mass action law (43) will take its quasi-ideal form

$$\tilde{c}_M = \prod_i (\tilde{c}'_i)^{n_i} \tag{44}$$

If the neutral micelle has the same ionic composition as the initial surfactant, one has

$$\frac{n_i}{n_k} = \frac{v_i}{v_k} \tag{45}$$

$$\frac{n_i}{v_i} = n^* \quad (i, k = 1, 2, \ldots) \tag{45a}$$

where n^* is the aggregation number in terms of neutral molecules. Like in the case of relations (35), (37) and (38), one gets

$$\tilde{c} = \left[\frac{\alpha}{(1-\alpha)^n n^*}\right]^{1/(n-1)} \tag{46}$$

$$\tilde{c}'_i = \left[\frac{\alpha}{(1-\alpha) n^*}\right]^{1/(n-1)} \tag{47}$$

$$\tilde{c}_M = \left[\frac{\alpha}{(1-\alpha) n^*}\right]^{n/(n-1)} \tag{48}$$

These formulas parametrically define the functions $\tilde{c}'_i(\tilde{c})$ and $\tilde{c}_M(\tilde{c})$ whose plots [12] at $n^* = 50$ and $n = 100$ are in qualitative agreement with the plots shown in Fig. 2. The corresponding intersection point specified by the subscript s can be found by equating expressions (47) and (48) to each other

$$\alpha_s = \frac{n^*}{n^*+1} \tag{49}$$

$$\tilde{c}_s = n^* + 1 \tag{49a}$$

$$(\tilde{c}'_i)_s = (\tilde{c}_M)_s = 1 \tag{49b}$$

The functions $\tilde{c}'_i(\tilde{c})$ and $\tilde{c}_M(\tilde{c})$ are of importance for calculations, but their definition in implicit form is inconvenient. They can be specified explicitly using the following approximations [12]

$$\tilde{c}'_i = \frac{n - \sqrt{n/2}}{n-1} + \frac{\sqrt{n/2}-1}{n^*(n-1)}(\tilde{c}-1) \quad (1 < \tilde{c} < n^*+1) \tag{50}$$

$$\tilde{c}_M = \frac{\sqrt{n/2}-1}{n^*(n-1)} + \left[1 + \frac{\sqrt{n/2}-1}{n^*(n-1)}\right]\frac{\tilde{c}-1}{n^*} \approx \frac{\tilde{c}-1}{n^*} \tag{51}$$

$$(1 < \tilde{c} < n^*+1)$$

The case of electrically neutral micelles is very similar to that of nonionic surfactant micelles. Therefore, it is not surprising that formulas (50) and (51) are analogous to expressions (39a) and (40), respectively.

Consider a general case of a solution of an ionic surfactant where all dissolved particles bear electric charges. The results for an ideal mixture of monomers and micelles in a 1 – 1-electrolyte are as follows.[26] There are two types of ions (type-1 ion is the surface-active ion and type-2 ion is the counterion; $n_1 \equiv n$, $n_2 = n\beta$, $\alpha_1 \equiv \alpha$, $\alpha_2 = \alpha\beta$; β is the degree of counterion binding) and three types of charged particles characterized by the concentrations c_1, c_2 and c_M (all concentrations are given in the CMC units and a tilde is omitted). A combination of the mass action law written in the form

$$c_M = c_1^n c_2^{n\beta} \tag{52}$$

and the material balance condition leads to

$$c = \left[\frac{\alpha}{n(1-\alpha)^n(1-\alpha\beta)^{n\beta}}\right]^{1/[n(1+\beta)-1]} \tag{52a}$$

As in the case of nonionic surfactant, the problem will be solved within the framework of the quasi-chemical approximation assuming that n and β are constants. Then, expression (52a) unambiguously defines the surfactant concentration as a function of the degree of micellization.

If the function $c(\alpha)$ is known, expressions for other concentrations can be found

$$c_1 = \left[\frac{\alpha(1-\alpha)^{n\beta-1}}{n(1-\alpha\beta)^{n\beta}}\right]^{1/[n(1+\beta)-1]} \tag{53}$$

$$c_2 = \left[\frac{\alpha(1-\alpha\beta)^{n-1}}{n(1-\alpha)^n}\right]^{1/[n(1+\beta)-1]} \tag{54}$$

$$c_M = \left[\frac{\alpha^{n(1+\beta)}}{n^{n(1+\beta)}(1-\alpha)^n(1-\alpha\beta)^{n\beta}}\right]^{1/[n(1+\beta)-1]} \tag{55}$$

They implicitly (through the parameter α) specify the dependence of all other concentrations on the surfactant concentration. At preset n and β (*e.g.*, $n = 100$ and $\beta = 0.8$),[26] these functions can be calculated with ease on a computer. The $c(\alpha)$ and $c_M(c)$ plots are qualitatively similar to those shown in Figs 1 and 2; however, the dependences $c_1(c)$ and $c_2(c)$ should be considered separately in more detail. The plots for the interval $0 < \alpha < 0.95$ are presented in Fig. 3. In the vicinity of the CMC, the concentration of the surface-active ion passes through a maximum and them decreases with increasing surfactant concentration (this is a well-known phenomenon; for a detailed recent treatment, see Ref. 11). Contrary to this, the counterion concentration is a steadily increasing function of the degree of micellization and the total surfactant concentration.

Among the calculated parameters, the degree of counterion binding β is least reliable. Indeed, its theoretical definition is ambiguous, while practical determination depends on the measuring technique;[1,2] besides, suggests itself to be a fitting parameter in calculations. Therefore, the influence of the β values on the course of the most complicated concentration dependence $c_1(c)$ was studied separately.[26] The results are shown in Fig. 4. The smaller

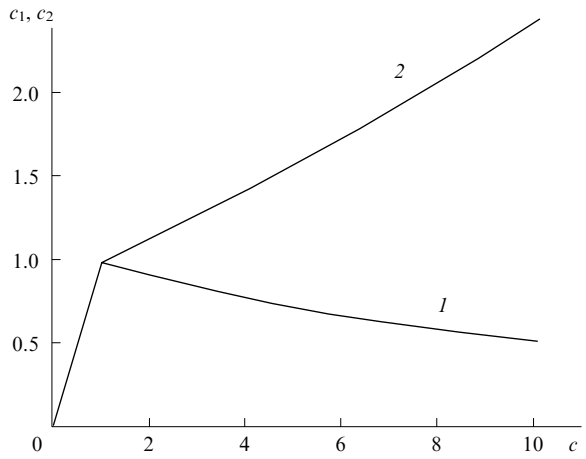


Figure 3. Concentrations of monomeric surface-active ions (*1*) and counterions (*2*) plotted *vs.* total surfactant concentration at degrees of micellization in the range $0 < \alpha < 0.95$ for $n = 100$ and $\beta = 0.8$ (concentrations are given in the CMC units).[26]

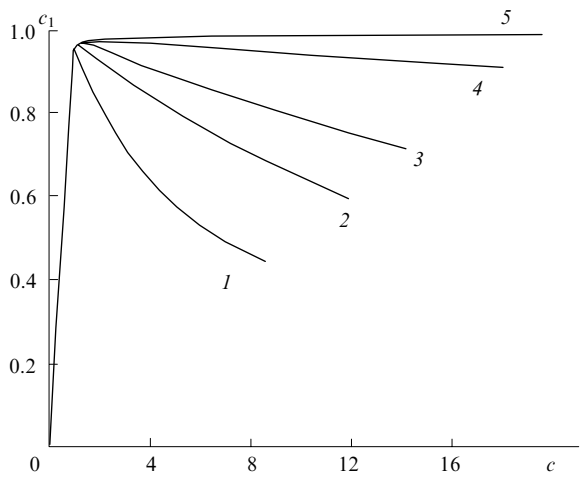


Figure 4. Concentration isotherms of surface-active ion at different degrees of counterion binding:[26]
$\beta = 0.6$ (*1*), 0.9 (*2*), 0.95 (*3*), 0.99 (*4*), and 1 (*5*); concentrations are given in the CMC units.

the β value the sharper the c_1 maximum; also, the closer the β value to unity the higher the similarity between the $c_1(c)$ plots in the case under study and in the case of nonionic surfactant (see Fig. 2); at $\beta = 1$, the maximum disappears.

Since the function $c_M(c)$ monotonically increases while the function $c_1(c)$ monotonically decreases upon passing through the maximum, their plots intersect. The right-hand sides of expressions (53) and (55) are equal to each other at the intersection point; this immediately gives

$$\alpha_s = \frac{n}{n+1} \tag{56}$$

Parameters of the intersection point are determined by substituting expression (56) into Eqns (52) – (55). Thus, the use of the mass action law allows one to calculate all concentration dependences for the ideal ionic micellar system.

Summing up, the approximations used to represent the functions $c_1(c)$, $c_2(c)$ and $c_M(c)$ in explicit form (probably, with some loss of accuracy) [26] are as follows:

$$c_1 = 1 - k_1(c-1) \tag{57}$$

$$c_2 = 1 + k_2(c-1) \tag{57a}$$

$$c_M = k_M(c-1) \tag{57b}$$

where k_1, k_2 and k_M are positive coefficients; it is assumed that $c_1 = c_2 \approx 1$ and $c_M \approx 0$ at $c = 1$. Of course, these formulas are valid only at $1 \leqslant c \leqslant c_s$. The coefficients can be calculated from the expressions

$$k_1 \equiv \frac{1-c_{1s}}{c_s-1} = \frac{[n(1-\beta)+1]^{n\beta/[n(1+\beta)-1]}-1}{n+1-[n(1-\beta)+1]^{n\beta/[n(1+\beta)-1]}} \tag{58}$$

$$k_2 \equiv \frac{c_{2s}-1}{c_s-1} = \frac{n(1-\beta)+1-[n(1-\beta)+1]^{n\beta/[n(1+\beta)-1]}}{n+1-[n(1-\beta)+1]^{n\beta/[n(1+\beta)-1]}} \tag{58a}$$

$$k_M \equiv \frac{c_{Ms}}{c_s-1} = \frac{1}{n+1-[n(1-\beta)+1]^{n\beta/[n(1+\beta)-1]}} \tag{58b}$$

They look somewhat cumbersome; however the coefficients are to be calculated only once, after that all the necessary dependences can be computed further in explicit form using expressions (57) – (57b). For instance, at $n = 100$ and $\beta = 0.8$ one has $k_1 \approx 0.0298$, $k_2 \approx 0.176$ and $k_M \approx 0.010$. Undoubtedly, this simple trick will be useful for calculations.

III. Micellar mobility and the micelle diffusion coefficient

III.1. Surfactant mobility in micellar systems

Since it was established that diffusion is driven by the chemical potential gradient rather than the concentration gradient, Fick's laws discovered in the mid-19th century and the diffusion coefficient appearing in the corresponding expressions are no longer of paramount importance. However, the diffusion coefficient has become the research practice so deep that is still used in both theory and experiments. This also holds for the studies of diffusion in micellar systems. Among the publications reported before 2009 (see a review [13]), two theoretical [28, 29] and a number of experimental studiess [30 – 34] may be highlighted. Despite prevalence of terminology based on diffusion coefficient, the most fundamental characteristic of diffusion is in fact the mobility of particles. Therefore, we begin the presentation of the material in this Section in terms of mobility,[35] of course, having at hand the formulas for the transition to the diffusion coefficient.

Generally, the mobility is defined as the limiting velocity of a particle in a given medium under the action of a unit force. In other words, if the force **f** is applied to a particle and the particle is characterized by the stationary velocity **v**, the particle mobility u (the vectors **f** and **v** are collinear) is given by

$$u \equiv \frac{|\mathbf{v}|}{|\mathbf{f}|} \tag{59}$$

The most famous example is provided by the motion of a hard sphere of radius r in a medium with the viscosity η under the action of the force **f** specified by the Stokes formula

$$\mathbf{f} = 6\pi\eta r\,\mathbf{v} \tag{60}$$

Substituting the right-hand side of Eqn (60) into (59) gives the expression for the particle mobility

$$u = \frac{1}{6\pi\eta r} \tag{61}$$

In the case of diffusion, the role of the force **f** is played by the gradient of the chemical (electrochemical) potential μ taken with the opposite sign, so formula (59) takes the form

$$u_i \equiv \frac{|\mathbf{v}_i|}{|-\nabla\mu_i,|} \tag{62}$$

where the subscript i denotes the type of particles. Since we aim at establishing specific features of micellization, the problem should be simplified to the greatest extent. Therefore, we fix the temperature and pressure and restrict ourselves to the case of a low surfactant concentration. The complexity of a micellar system is that diffusion always simultaneously involves different types of particles. However, at low concentrations, they can be treated independently. This simplifies the diffusion equations. In particular, by multiplying both sides of expression (62) by the concentration c_i one gets

$$\mathbf{v}_i c_i = \mathbf{j}_i = -u_i c_i \nabla\mu_i \tag{63}$$

where $\mathbf{j}_i$ is the flux density of the type-i particles. The Fick first law duplicates the equation of motion (63) in the form

$$\mathbf{j}_i = -D_i \nabla c_i \tag{64}$$

where D_i is the diffusion coefficient. The equality of the right-hand sides in Eqns (63) and (64) establishes a relation between the diffusion coefficient and the mobility of the type-i particles

$$D_i = u_i \frac{\partial\mu_i}{\partial \ln c_i} \tag{65}$$

However, not all conditions are specified at the moment. Let the chemical potential gradients be small (in this case, the mobility can be considered constant) and the diffusion rate be sufficiently low for the mass action law to hold at each point of the system. Our aim is to relate the mobility of a surfactant in a micellar system to detailed characteristics of constituting particles and to assess the influence of micellization on the surfactant mobility.

We begin with the simplest case of a single nonionic surfactant. Irrespective of the transformations of the substance in the course of transfer, Eqn (63) can be written as

$$\mathbf{j} = -uc\nabla\mu \tag{66}$$

where c is the total concentration of the surfactant. The micellar solution in hand can be treated in more detail. Assuming that only one type of micelles M and only one

type of monomeric particles (subscript 1) are present in the solution, from Eqn (63) one gets

$$\mathbf{j}_1 = -u_1 c_1 \nabla \mu_1 \tag{67}$$

$$\mathbf{j}_M = -u_M c_M \nabla \mu_M. \tag{67a}$$

By the aggregative equilibrium condition (2) one has

$$\nabla \mu_M = n \nabla \mu_1 = n \nabla \mu \tag{68}$$

where n is the aggregation number (equivalence of μ_1 and μ was proved in Section II.1). As can be seen, there are two collinear vectors, $\mathbf{j}_1$ and $\mathbf{j}_M$. To relate the total mobility u in Eqn (66) to the mobilities u_1 and u_M in expressions (67) and (67a), respectively, one can write the total flow of matter

$$\mathbf{j} = \mathbf{j}_1 + n\mathbf{j}_M \tag{69}$$

and substitute Eqns (66) – (68), which leads to

$$uc = u_1 c_1 + n^2 u_M c_M. \tag{70}$$

Having divided by c, one gets

$$u = u_1(1 - \alpha) + n u_M \alpha \tag{71}$$

where $\alpha = n c_M / c$ is the degree of micellization of the surfactant given by formula (4).

From the equality (61), for spherical micelles one has

$$u_M = \frac{1}{6\pi\eta r_M} \tag{72}$$

where $r_M = (3n\upsilon/4\pi)^{1/3}$ is the micelle radius (υ is the volume of a surfactant molecule). Equation (72) shows that the larger the aggregation number of a micelle the lower the mobility of the micelle. This trivial result immediately follows from the Stokes formula. If a monomeric surfactant molecule is approximated by a sphere, the Stokes formula gives

$$u_1 = \frac{1}{6\pi\eta r_1} \tag{73}$$

where $r_1 = (3\upsilon/4\pi)^{1/3}$. Substituting expressions (72) and (73) into relation (71) leads to

$$u = \frac{1 + (n^{2/3} - 1)\alpha}{6\pi\eta r_1} \tag{74}$$

This is a remarkable and non-trivial result. Although the mobility of micelles is lower than that of monomers, the development of micellization (an increase in the degree of micellization α) is accompanied by an increase rather than decrease in the average surfactant mobility u. The case in point is that the micelle moves more slowly but simultaneously transfers so many molecules that on going to the micellar transfer mechanism the molecular flux density increases as if the mobility of surfactant molecules under the molecular mechanism increased. This increase is particularly pronounced in the vicinity of the CMC, where the derivative of α with respect to c is maximum.

To write expression (70) using the conventional diffusion coefficient D, it is sufficient to use formula (65). For an ideal behaviour of monomers and micelles one has

$$D = \frac{c_1 D_1 + n^2 c_M D_M}{kT} \frac{\mathrm{d}\mu}{\mathrm{d}c} \tag{75}$$

and only the derivative $\mathrm{d}\mu/\mathrm{d}c$ should be calculated. Of course, the ideal solution approximation is inapplicable to the dissolved surfactant because of molecular aggregation [see relation (10)]. But we can replace μ by μ_1 and apply the formula of an ideal behaviour

$$\frac{\mathrm{d}\mu_1}{\mathrm{d}c_1} = \frac{kT}{c_1} \tag{75a}$$

to the latter. Then, Eqn (75) is transformed to

$$D = \frac{c_1 D_1 + n^2 c_M D_M}{c_1} \frac{\mathrm{d}c_1}{\mathrm{d}c} \tag{76}$$

From the material balance condition (17) (in this case, $c = c_1 + n c_M$) and the mass action law (16) (in this case, $c_M = K c_1^n$) one gets

$$c_1 \frac{\mathrm{d}c}{\mathrm{d}c_1} = c_1 + n^2 c_M \tag{77}$$

Eventually, substitution of $\mathrm{d}c/\mathrm{d}c_1$ from Eqn (77) into expression (76) gives [28, 35]

$$D = \frac{c_1 D_1 + n^2 c_M D_M}{c_1 + n^2 c_M} \tag{78}$$

Formula (78) is an analogue of relationship (70) in terms of diffusion coefficient. Also, there exists an analogue of formula (74) (see Ref. 35)

$$D = \frac{kT}{6\pi\eta r_1} \frac{1 + (n^{2/3} - 1)\alpha}{1 + (n - 1)\alpha} \tag{79}$$

In the right-hand side of this equation the numerator and denominator include the increasing functions α, but the denominator increases more rapidly and therefore the diffusion coefficient decreases with increasing degree of micellization. Thus, our consideration of a dilute micellar solution of a single nonionic surfactant suggests that the surfactant mobility increases while the diffusion coefficient decreases in the initial stage of the development of micellization.

Now consider a micellar solution of a single ionic surfactant. For the sake of simplicity, we assume that the surfactant molecule dissociates into two types of ions with the stoichiometric coefficients ν_1 and ν_2. In the simplest case of monomodal micelle size distribution, three types of dissolved particles are present in the system. These are surface-active ions (subscript 1), counterions (subscript 2) and micelles (subscript M) with the aggregation numbers n_1 and n_2, respectively. Similarly to Section II.4, we introduce simplified notations, namely, c is the total concentration of the surfactant, $c\nu_i$ is the total concentration of the type-i ions and c_i is the monomeric concentration of the type-i ions. Formally, we deal with one dissolved substance (electrolyte) and can therefore again write the equation of

motion (66) relating the chemical potential μ to the electrolyte molecule. Taking into account three types of dissolved particles, there are three equations

$$\mathbf{j}_{l1} = -u_1 c_1 \nabla\mu_1 \tag{80}$$

$$\mathbf{j}_{21} = -u_2 c_2 \nabla\mu_2 \tag{80a}$$

$$\mathbf{j}_{M} = -u_M c_M \nabla\mu_M \tag{80b}$$

Let us find how the average electrolyte mobility u is related to the particle mobilities appearing in these equations.

The aggregative equilibrium condition has the form

$$\mu_M = n_1\mu_1 + n_2\mu_2 \tag{81}$$

This allows one to convert Eqns (80)–(80b) using $\nabla\mu_1$ and $\nabla\mu_2$ only. Let us introduce the total flux for each type of ions

$$\mathbf{j}_i = \mathbf{j}_{i1} + n_i \mathbf{j}_M \quad (i = 1, 2). \tag{82}$$

Using the equality (81), one can write

$$\mathbf{j}_1 = -(u_1 c_1 + u_M c_M n_1)\nabla\mu_1 \tag{82a}$$

$$\mathbf{j}_2 = -(u_2 c_2 + u_M c_M n_2)\nabla\mu_2 \tag{82b}$$

Since the diffusion flux of an electrolyte is electrically neutral,[36] the total flux densities of the surface-active ion and counterion should meet the condition

$$\frac{\mathbf{j}_1}{\nu_1} = \frac{\mathbf{j}_2}{\nu_2} (= \mathbf{j}) \tag{83}$$

Each of these ratios is obviously equal to the molecular flux density $\mathbf{j}$ of the electrolyte. Thus, the fluxes $\mathbf{j}_1$ and $\mathbf{j}_2$ are collinear and formulas (82a), (82b), (83) allow one to find a relation between $\nabla\mu_1$ and $\nabla\mu_2$

$$\frac{|\nabla\mu_2|}{|\nabla\mu_1|} = \frac{\nu_2(u_1 c_1 + n_1^2 u_M c_M) - \nu_1 n_1 n_2 u_M c_M}{\nu_1(u_2 c_2 + n_2^2 u_M c_M) - \nu_2 n_1 n_2 u_M c_M} \tag{84}$$

This expression makes it possible to represent the total flux of any type of ions using the gradient of only one chemical potential ($\nabla\mu_1$ or $\nabla\mu_2$). For instance, one has

$$\mathbf{j}_1 = -\nu_1 \frac{u_1 c_1 u_2 c_2 + n_1^2 u_2 c_2 u_M c_M + n_2^2 u_1 c_1 u_M c_M}{\nu_1(u_2 c_2 + n_2^2 u_M c_M) - \nu_2 n_1 n_2 u_M c_M} \nabla\mu_1 \tag{85}$$

Having divided both sides of formula (85) by ν_1, the flux density of the ionic surfactant is also a function of one gradient $\nabla\mu_1$

$$\mathbf{j} = \frac{\mathbf{j}_1}{\nu_1} = -\frac{u_1 c_1 u_2 c_2 + n_1^2 u_2 c_2 u_M c_M + n_2^2 u_1 c_1 u_M c_M}{\nu_1(u_2 c_2 + n_2^2 u_M c_M) - \nu_2 n_1 n_2 u_M c_M} \nabla\mu_1 \tag{86}$$

Now we return to Eqn (66) as applied to the ionic surfactant. In the theory of electrolytes one has [36]

$$\mu = \nu_1\mu_1 + \nu_2\mu_2 \tag{87}$$

From Eqns (84) and (87) one gets

$$\nabla\mu = \frac{\nu_1^2 u_2 c_2 + \nu_2^2 u_1 c_1 + (\nu_1 n_2 - \nu_2 n_1)^2 u_M c_M}{\nu_1(u_2 c_2 + n_2^2 u_M c_M) - \nu_2 n_1 n_2 u_M c_M} \nabla\mu_1 \tag{88}$$

Having substituted expression (88) into Eqn (66) and compared the result obtained with formula (86), the desired relation is as follows:

$$uc = \frac{u_1 c_1 u_2 c_2 + n_1^2 u_2 c_2 u_M c_M + n_2^2 u_1 c_1 u_M c_M}{\nu_1^2 u_{21} c_2 + \nu_2^2 u_{11} c_1 + (\nu_1 n_2 - \nu_2 n_1)^2 u_M c_M} \tag{89}$$

The difference $\nu_1 n_2 - \nu_2 n_1$ in the denominator characterizes the deviation of the micelle from electrical neutrality. Division of the numerator and denominator in the right-hand side of equality (89) by c followed by division of both sides of the equality (89) by c leads to the formula for the mobility of the ionic surfactant

$$\begin{aligned} u = \big[&u_1 u_2(1-\alpha_1)(1-\alpha_2) + u_1 u_M \alpha_2(1-\alpha_1)n_2 + \\ &+ u_2 u_M \alpha_1(1-\alpha_2)n_1\big]\big[u_1(1-\alpha_1)\nu_2 + u_2(1-\alpha_2)\nu_1 + \\ &+ u_M \alpha_1 n_1 \nu_2 (1-\beta)^2\big]^{-1} \end{aligned} \tag{90}$$

where α_i is the degree of micellization of the type-i ion (i = 1, 2) and β is the degree of counterion binding. For the 1–1 electrolyte ($\nu_1 = \nu_2 = 1$), formula (90) can be simplified using notations $\alpha_1 \equiv \alpha$ and $\alpha_2 = \alpha\beta$

$$\begin{aligned} u = \big[&u_1 u_2(1-\alpha)(1-\alpha\beta) + u_1 u_M \alpha\beta(1-\alpha)n_2 + \\ &+ u_2 u_M \alpha(1-\alpha\beta)n_1\big] big[u_1(1-\alpha) + u_2(1-\alpha\beta) + \\ &+ u_M \alpha(1-\beta)^2 n_1\big]^{-1} \end{aligned} \tag{91}$$

To compare the particle mobilities, we will use the Stokes formula. From Eqn (61) one has

$$u_2 = u_1 \frac{r_1}{r_2} \equiv u_1\kappa \tag{92}$$

$$u_M = u_1 \frac{r_1}{r_M} = u_1 \left(\frac{\upsilon_1}{\upsilon_M}\right)^{1/3} = \frac{u_1}{n_1^{1/3}} \left(1 + \frac{\beta}{\kappa^3}\right)^{-1/3} \tag{92a}$$

where κ is the ratio of the effective radius of the surface-active ion to the radius of the counterion; here we use the additivity of volumes in the micelle

$$\upsilon_M = n_1\upsilon_1 + n_2\upsilon_2 = n_1\upsilon_1\left(1 + \frac{\beta\upsilon_2}{\upsilon_1}\right) \tag{92b}$$

It is typical of ionic surfactants that the surface-active ion is much larger than the counterion and $\kappa^3 \gg 1$. Since $\beta < 1$, u_M from expression (92a) can be estimated as $u_M \approx u_1 n_1^{-1/3}$. Substitution of this estimate and formula (92) into Eqn (91) leads to

$$u \approx u_1 \frac{\kappa(1-\alpha)(1-\alpha\beta) + \big[(1-\alpha)\beta + \kappa(1-\alpha\beta)\big]n_1^{2/3}\alpha}{1 + \kappa + \big[n_1^{2/3}(1-\beta)^2 - 1 - \kappa\beta\big]\alpha} \tag{93}$$

In the initial stage of micellization the terms with α^2 can be neglected and formula (93) takes the form

$$u \approx u_1 \frac{\kappa + \big[(\kappa+\beta)n_1^{2/3} - \kappa(1+\beta)\big]\alpha}{1 + \kappa + \big[n_1^{2/3}(1-\beta)^2 - 1 - \kappa\beta\big]\alpha} \tag{94}$$

The numerator in the right-hand side includes an increasing function of α. Different variants are possible for the denominator; however, the coefficient at α in the numerator is in any case much larger than in the denominator. Therefore, expression (94) leads to unambiguous conclusion that mobility of an ionic surfactant increases as the micellization process is developed. The reason seems to be the same as in the case of nonionic surfactant, namely, the phenomenon is due to the transport properties of micelles.

Now consider the diffusion coefficients. From Eqns (67) and (67a) for the entire electrolyte and for each type of particles one has

$$D = u\frac{\partial\mu}{\partial \ln c} \tag{95}$$

$$D_1 = u_1\frac{\partial\mu_1}{\partial \ln c_1} \tag{95a}$$

$$D_2 = u_2\frac{\partial\mu_2}{\partial \ln c_2} \tag{95b}$$

$$D_\mathrm{M} = u_\mathrm{M}\frac{\partial\mu_\mathrm{M}}{\partial \ln c_\mathrm{M}} \tag{95c}$$

Taken altogether with the mass action law and the material balance conditions, formulas (95)–(95c) give the expression for the diffusion coefficient of the ionic surfactant [28, 35]

$$D = \frac{c_1c_2D_1D_2 + c_1c_\mathrm{M}n_2^2D_1D_\mathrm{M} + c_2c_\mathrm{M}n_1^2D_2D_\mathrm{M}}{c_1v_2^2D_1 + c_2v_1^2D_2 + c_\mathrm{M}(n_1v_2 - n_2v_1)^2D_\mathrm{M}} \times \tag{96}$$

$$\times \frac{c_1v_2^2 + c_2v_1^2 + c_\mathrm{M}(n_1v_2 - n_2v_1)^2}{c_1c_2 + c_1c_\mathrm{M}n_2^2 + c_2c_\mathrm{M}n_1^2}$$

This is an analogue of expression (78) for the nonionic surfactant and the key relation for the diffusion coefficient of ionic surfactants. Note that both formulas include only the concentration ratios; therefore, can be expressed in any units including the CMC units. In the case of a 1–1 electrolyte ($v_1 = v_2 = 1$), Eqn (96) takes the form

$$D = \frac{c_1c_2D_1D_2 + c_1c_\mathrm{M}n_2^2D_1D_\mathrm{M} + c_2c_\mathrm{M}n_1^2D_2D_\mathrm{M}}{c_1D_1 + c_2D_2 + c_\mathrm{M}(n_1 - n_2)^2D_\mathrm{M}} \times \tag{97}$$

$$\times \frac{c_1 + c_2 + c_\mathrm{M}(n_1 - n_2)^2}{c_1c_2 + c_1c_\mathrm{M}n_2^2 + c_2c_\mathrm{M}n_1^2}$$

A thorough analysis of relation (97) is available in the literature.[29, 33] Here we will analyze a more general expression (96). As shown in Section II.4, c_2 and c_M are the increasing functions of the total concentration of the surfactant c, but the monomeric concentration of the surface-active ion, c_1, passes through a maximum near the CMC. This complicates our analysis. However, the ratios c_2/c_1 and c_M/c_1 are monotonically increasing functions. Therefore, it is reasonable to re-write formula (96) in the form

$$\frac{D}{D_1} = \frac{c_2 + c_\mathrm{M}n_2^2D_\mathrm{M}/D_2 + (c_2/c_1)c_\mathrm{M}n_1^2D_\mathrm{M}/D_1}{c_2 + c_\mathrm{M}n_2^2 + (c_2/c_1)c_\mathrm{M}n_1^2} \times \tag{98}$$

$$\times \frac{v_2^2 + (c_2/c_1)v_1^2 + (c_\mathrm{M}/c_1)(n_1v_2 - n_2v_1)^2}{v_2^2D_1/D_2 + (c_2/c_1)v_1^2 + (c_\mathrm{M}/c_1)(n_1v_2 - n_2v_1)^2D_\mathrm{M}/D_2}$$

Now all terms of both factors are increasing functions. The numerator and denominator of the first factor include the same concentration terms, but in the numerator they are supplemented with the coefficients D_M/D_1 and D_M/D_2, both being smaller than unity because $D_\mathrm{M} < D_1$ and $D_\mathrm{M} < D_2$. This means that the numerator of the first factor increases more slowly than the denominator and therefore the first factor is a decreasing function of the surfactant concentration. Similar reasoning for the second factor leads to an opposite conclusion, namely, this factor is an increasing function of the surfactant concentration. Thus, generally, expression (98) is the product of a decreasing function and an increasing function; this is a typical situation for the appearance of an extremum. In the aforesaid, the detailed diffusion coefficients D_1, D_2 and D_M were assumed to be constant; therefore, the case in point was a range of relatively low concentrations above the CMC_1. For the 1–1 surfactants, this region corresponds to a minimum of the total diffusion coefficient,[29] so we can say this is a general trend. Thus, unlike the case for the nonionic surfactant, the diffusion coefficient of an ionic surfactant increases rather than decreases with increasing the total surfactant concentration above the CMC. This was confirmed experimenrtally.

On going to concentrated micellar systems the role of viscosity increases, and all the detailed diffusion coefficients begin to decrease. However, according to the Stokes law, viscosity influences all diffusion coefficients identically, so all their ratios and the entire right-hand side of formula (98) remain unchanged. Of course, this also holds for the entire left-hand side of formula (98); however, since D_1 now decreases with concentration, the total diffusion coefficient D should also decrease under the action of viscosity. Therefore, the diffusion coefficient of the surfactant should again pass through an extremum (in this case, a maximum); this was repeatedly verified in experiments.

All the aforesaid suggests that the theory becomes more complicated even for a surfactant with two types of ions. The expression for the diffusion coefficient is especially cumbersome and it should be noted that the corresponding expression written in terms of mobility is much simpler. Thus, the mobility, which is a more fundamental parameter than the diffusion coefficient, makes the theory simpler and more practical.

III.2. Diffusion of a nonionic surfactant

Now we will dwell on practical applications of formula (78). Since concentration can be expressed in any units, we will use the CMC units to ensure correspondence with the expressions derived in Section II.3. Recall that D_1 and D_M are the monomer and micelle diffusion coefficients, respectively. They can be determined with ease in the experiments with pre-micellar and micellar solutions, respectively. Both coefficients would be considered constant concentrations if it was not for viscosity, which changes with the surfactant concentration and immediately influences the diffusion coefficient [see Egn (79)]. If different-type particles have the same or similar geometric shape, all diffusion coeffi-

cients are identically affected by the viscosity. The effect of viscosity can be eliminated by going to the ratio of diffusion coefficients. In any case, by re-writing expression (78) in the form

$$\frac{D}{D_1} = \frac{c_1 + n^2 c_M D_M / D_1}{c_1 + n^2 c_M} \tag{99}$$

and assuming a constant value of the D_M/D_1 ratio, we diminish the role of the viscosity and make the calculations of the micelle diffusion coefficient more reliable. Let us look how these calculations are performed.

In accordance with approximations (39) – (40), the relative contributions of the addends in the denominator of Egn (99) are characterized by the ratio (parameter κ had a different meaning in the preceding Section)[25]

$$\kappa \equiv \frac{c_1}{n^2 c_M} = \frac{n^2 - n\sqrt{n/2} + (\sqrt{n/2} - 1)(c-1)}{n^2(\sqrt{n/2} - 1) + n^2(n-1)(c-1)} \tag{100}$$

For the CMC ($c = 1$), expression (100) gives

$$\kappa = \frac{1 - \sqrt{n/2}\, n^{-1}}{\sqrt{n/2} - 1} \ll 1 \tag{101}$$

Above the CMC, κ further decreases as the surfactant concentration increases. Consequently, having only slightly increased the CMC, we have the right to drop the first term in the denominator of expression (99) and to write the following:

$$\frac{D}{D_1} \approx \frac{D_M}{D_1} + \kappa \tag{102}$$

where κ is given by expression (100) that can also be simplified. Similarly to formula (39a), numerator of the variable term remains small compared to the constant term in a wide concentration range ($1 < c < n + 1$). If we restrict our consideration to a concentration interval of at most ten CMC units wide, the variable term will be negligible and we thus can drop it. As to the denominator of expression (100), one deals with the opposite situation, *viz*., the variable term increases with concentration so rapidly that becomes much larger than the constant term even at $c = 2$ (by a factor of 16.3 at $n = 100$). At $c > 2$, the constant term can be neglected with certainty, and one gets the following approximation for κ:

$$\kappa \approx \frac{n - \sqrt{n/2}}{n(n-1)(c-1)} \quad (2 < c < 11) \tag{103}$$

The boundaries of the concentration range are specified approximately in order to provide a reasonable 'distance' from the CMC to maintain a correct situation in the denominator and to meet the ideality conditions for the entire micellar system. By introducing a coefficient

$$k \equiv \frac{n - \sqrt{n/2}}{n(n-1)} \tag{104}$$

one can re-write relationship (102) in the form[25]

$$\frac{D}{D_1} \approx \frac{D_M}{D_1} + \frac{k}{c-1} \tag{105}$$

According to expression (105), the diffusion coefficient of the surfactant is an increasing linear function of the ratio $1/(c-1)$ in the concentration range chosen (*i.e*., D_1 decreases with increasing concentration). Therefore, the relative diffusion coefficient of micelles, D_M/D_1, can be determined as the Y-intercept when the linear dependence is extrapolated to zero ($1/(c-1) \to 0$). A similar method was used to determine the diffusion coefficient of Triton X-100 micelles [Triton X-100 is polyethylene glycol *p*-(1,1,3,3-tetramethylbutyl)phenyl ether].[37] However, an analogue[37] of the coefficient k (which also included the constant of the mass action law) was 'a thing in itself' and there was a feeling that no valuable information could be extracted from that parameter. Contrary to this, in formula (105) the coefficient k is unambiguously related to the aggregation number [see expression (104)], which opens the opportunity to determine the aggregation number of micelles from the concentration dependence of the diffusion coefficient of the surfactant.

This is traditionally achieved by going from the diffusion coefficient to the aggregation number *via* the hydrodynamic radius of micelle. However, one should know the geometric shape of micelle and hydration numbers (in order to determine the true volume which is divided by the volume of one surfactant molecule to give the aggregation number). Since the mass action law is independent of the micelle shape and intrinsically includes hydration (although the hydration number can be unknown), formula (105) can be used ignoring those restrictions.

However, practical application of expression (105) to determine the aggregation number faces some difficulties. At $10 < n < 100$, the coefficient k decreases from 0.086 to 0.0094. Thus, at realistic n values, the parameter k is so small that reliable experimental determination of its value requires that the diffusion coefficient be measured with very high accuracy. The diffusion coefficients of nonionic surfactants (*e.g*., Triton X-100[37] and sulfobetaines[13]) were determined with lower accuracy, but it's not only that. When discussing formula (78), mention was made that the monomer diffusion coefficient, D_1, can be determined with ease in the experiments with pre-micellar solutions, but if the solution viscosity changes with concentration, D_1 also changes with concentration. Therefore, the D_1 value in expression (105) is actually the total surfactant diffusion coefficient, D, in the entire solution rather than the pre-micellar solution. We thus have to determine that actual D value. As an alternative, one can use D_1 as a constant of the pre-micellar solution with the viscosity η_0 if each D value is recalculated, thus going from the actual viscosity η to the viscosity η_0. It is implied that measurements of the surfactant diffusion coefficient in solution are necessarily accompanied by the solution viscosity measurements.

It is just this approach that was used in the studies of aqueous solution of pentaethylene glycol monohexyl ether (C_6E_5), namely, a correction was made for each measured value of the diffusion coefficient by multiplying it by η/η_0.[27] Six experimental points measured at concentrations above the CMC were linearly approximated at $k \approx 0.0180$ and $D_M/D \approx 0.374$ (see Fig. 5). At this k value, Egn (104) has the solution $n = 51.1$, which is in good agreement with the value $n = 54$ used in the calculations to fit the experimental data.[27]

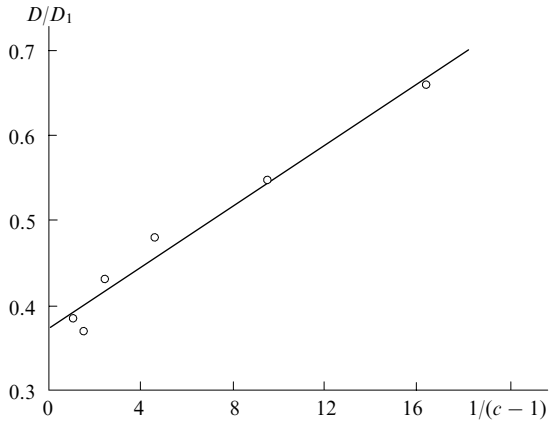


Figure 5. Determination of the micelle diffusion coefficient and aggregation number from the concentration dependence of the surfactant diffusion coefficient.[25]

III.3. Diffusion of ionic surfactant with electrically neutral micelles

In Section II.4 we considered a micellar solution of an ionic surfactant with electrically neutral micelles. Let us analyze how surfactant diffusion occurs in this system and whether the micelle diffusion coefficient can be determined. For the sake of simplicity the surfactant will be treated as 1 – 1 electrolyte. We begin with Egn (97) for an ideal system. Assuming electrically neutral micelles ($c_1 = c_2$, $n_1 = n_2 = n^*$), Egn (97) is simplified (concentrations are given in the CMC units)

$$D = \frac{c_1 D_1 D_2 + n^{*2} c_M D_M (D + D_2)}{D_1 + D_2} \frac{2}{c_1 + 2n^{*2} c_M} \tag{106}$$

Further simplification is also possible. For the same reasons as in the case of Egn (99), the concentration c_1 is negligible as compared to the second addend in the denominator of the second factor in formula (106) and can be dropped. Then, one gets

$$D = D_M + \frac{D^* c_1}{n^{*2} c_M} \tag{107}$$

$$D^* \equiv \frac{D_1 D_2}{D_1 + D_2} \tag{107a}$$

Substitution of relationships (50) and (51) into expressions (107), (107a) completely specifies the concentration dependence of the surfactant diffusion coefficient. In the simplest approximation one has

$$c_1 \approx \frac{n - \sqrt{n/2}}{n - 1} \tag{108}$$

$$c_M \approx \frac{c - 1}{n^*} \tag{108a}$$

and expressions (107) and (107a) can be written as [12]

$$D = D_M + \frac{D^* N}{c - 1} \tag{109}$$

$$N \equiv \frac{2n^* - \sqrt{n^*}}{n^*(2n^* - 1)} \tag{109a}$$

where we use the condition $n = 2n^*$. Formula (109) specifies a linear dependence of D on $1/(c - 1)$ and its extrapolation to zero gives the diffusion coefficient of surfactant micelles D_M, while the aggregation number can be determined from the slope.

This procedure was used in the studies of a sodium hexanesulfonate solution with electrically neutral micelles.[12, 27] Consider Fig. 6. The initial experimental data (open circles) show an almost linear dependence *1*, as predicted by Egn (109). This is somewhat surprising since the data were not corrected for viscosity and the system is nonideal (see Section II.4) and generally should not be described by expression (109). Indeed, applying the viscosity correction causes the same experimental points to fall on curve *2* (except the dilution region on the right) rather than a straight line. Now the only reason is the deviation from ideality and it seems that Fig. 6 clearly demonstrates how the nonideality influences the diffusion coefficient. According to Egn (65), the general expression for the diffusion coefficient of an ionic surfactant can be written as follows:

$$D = u\left[\left(\frac{\partial \mu}{\partial \ln c}\right)_{id} + \nu k T \frac{\partial \ln f_\pm}{\partial \ln c}\right] \tag{110}$$

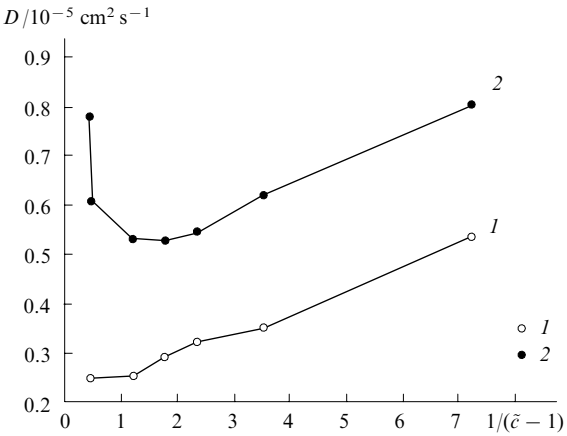


Figure 6. Data [27] on the diffusion coefficient of sodium hexanesulfonate without (*1*) and with (*2*) inclusion of a viscosity correction.[12]

where the first term describes the ideal component while the second addend includes the total number of ions per molecule (ν) and the average activity coefficient of the electrolyte $f_\pm$ (see Section II.1). A typical dependence of $\ln f_\pm$ on $\ln c$ is presented in Fig. 7.[12, 33] As the concentration increases, the contribution of nonideality to D becomes positive and abruptly increases. Just the same is observed in curve *2* in Fig. 6.

The shape of curve *1* in Fig. 6 can be treated as a result of mutual compensation of the nonideality and viscosity corrections. Indeed, the former is always positive, while the latter is always negative, so they unavoidably cancel each other. This creates an illusion of ideality; therefore the phenomenon can be called quasi-ideal behaviour of the micellar system. Let us test whether the methods developed for ideal systems can be used in this case. Statistical

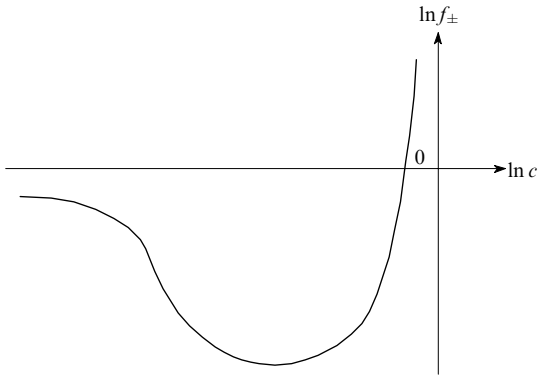


Figure 7. Typical dependence of $\ln f_\pm$ on $\ln c$.[12]

processing of experimental data for curve *1* gives a linear equation

$$D \times 10^{-5} \approx 0.221 + \frac{0.0424}{c - 1} \qquad (111)$$

Having compared expressions (109) and (111), one gets $D_M \approx 0.221 \times 10^{-5}$ and $D^*N \approx 0.0424 \times 10^{-5}$ cm^2 s^{-1}. An estimate using experimental data[27] is $D^* \approx 0.3964 \times 10^{-5}$ cm^2 s^{-1}, which leads to $N \approx 0.107$. Then, from Egn (109a) one gets $n^* = 8.2$, which is close to an actual value of 10.[27] Taking into account the fact that the D_M value is close to 0.215 (this value was determined by fitting),[27] one can conclude that our calculations is like that for an ideal system. Generally, success will depend on the degree of mutual cancellation of the nonideality and viscosity effects. This can be judged by how well the experimental points fall on the straight line.

IV. Molecular modelling of diffusion within coarse-grained models, Brownian dynamics and all-atom dynamics

IV.1. Computational studies of diffusion in micellar solutions: the choice of the model and method

Molecular modelling helps to improve and test theoretical models and to follow the behaviour of micellar systems on the molecular level, while experimental methods in some cases do not allow this to be done. Besides, in contrast to theory operating with low concentrations, molecular modelling makes it possible to study concentrated systems. Thus, methods of molecular modelling complement the theory and link modern theoretical and experimental approaches to the description of diffusion in micellar systems.

Molecular modelling was successfully used to study micellar solutions of ionic and nonionic surfactants (see reviews [14 – 16]). Some attention was also paid to calculations of the diffusion coefficients of particles present in micellar solutions, namely, counterions,[38 – 41] surfactant monomers,[39, 42, 43] solvent molecules[40, 41, 44 – 46] and aggregates.[39 – 41, 47 – 51]

At a specified total concentration of a surfactant, a real micellar solution contains aggregates with different aggregation numbers. In the case of spherical micelles, the relative dispersion of the aggregation numbers is usually assumed to be small; however, it was reported that the root-mean-square deviation can be as large as 15% to 30% of the average aggregation number.[2, 52] These aggregates are hard to distinguish in the laboratory experiments even using modern equipment and methods. This holds for, *e.g.*, DLS and NMR studies. As a consequence, the properties of a micellar solution determined by these methods are in fact a result of averaging over aggregates with different aggregation numbers. Nevertheless, properties of individual micelles can be investigated by methods of molecular modelling with different degree of detail for intermolecular and ionic interactions in surfactant solutions (see below). Among the most widely used numerical approaches for investigation of the transport and structural properties of individual molecular or ionic aggregates with arbitrary aggregation numbers, there are molecular dynamics within coarse-grained models, Brownian dynamics and all-atom molecular dynamics.

IV.2. Molecular dynamics simulations within coarse-grained models

A model of a chemical substance, either all-atom or coarse-grained, used in molecular modelling is a simplified representation of a real physicochemical system. The all-atom models explicitly include, within the simulation box, all atoms of the substance in question. Coarse-grained models have a simpler structure compared to the all-atom models. Considering coarse-grained models of surfactant solutions, one can deal with a simplified structure of the solvent, solute, or both of them. Of course, this is accompanied by simplification of the model energy interactions in the system under study. Taken altogether, these features make calculations using coarse-grained models much faster than calculations with the all-atom models.

In a multiscale modelling[49] of a micellar system, stochastic description of micellization kinetics was related to the mechanism of changes in the aggregation numbers of micelles, which was studied by molecular dynamics simulation. Molecular dynamics of fast processes in a micellar solution with spherical nonionic micelles was studied using a coarse-grained model for the surfactant and solvent. It was assumed that a key role in micelle formation is played by the molecular process of monomer addition/removal. The kinetic coefficients for the monomer addition/removal from micelles were determined from Brownian dynamics simulations and then used to describe the micellization kinetics. This made it possible to construct a model for the formation and disintegration of nonionic micelles on different time scales. The diffusion coefficients of nonionic micellar aggregates were also determined from molecular dynamics simulations and it was concluded that the Stokes – Einstein equation correctly describes diffusion of the systems in question.[49]

The united-atom model is widely used in molecular modelling including studies of micellar solutions. It treats the CH_2 and CH_3 units of chain molecules as unified interaction sites. The solvent is often described using the all-atom approach. Such a combination seems to be a reasonable alternative to all-atom simulation of the entire solution. At the same time, when modelling the transport properties of surfactant aggregates, it is advisable to make sure that they have a correct size because the absence of explicit hydrogen atoms in the hydrocarbon tail of surfactant monomers can immediately influence the size and, therefore, the diffusion coefficient of the aggregate. The united-atom model for surfactant molecules was used in combination with the all-atom model for water in a molec-

ular dynamics study [48] devoted to determination of the diffusion coefficients of dodecylphosphocholine aggregates with different aggregation numbers.

IV.3. Brownian dynamics

Molecular modelling using the Brownian and Langevin (or stochastic) dynamics methods is based on numerical solution of the differential equations of motion with random forces. Here, the solvent is included implicitly, *i.e.*, the simulation box contains no molecules or coarse-grained particles simulating the solvent. The effect of solvent on the solute particles is specified by augmenting the classical equations of motion with additional terms that describe the viscous friction force proportional to the particle velocity and a random force simulating collisions of solvent molecules with solute particles. Brownian dynamics is a simplified version of Langevin dynamics in the high-friction limit. To make Brownian and Langevin dynamics simulations more realistic, one can use effective potentials of interatomic (or intermolecular) van der Waals and Coulomb interactions, obtained from the results of, *e.g.*, all-atom simulations.[53] The advantage of the Brownian and Langevin dynamics methods consists in high performance compared to molecular dynamics simulations using the all-atom models and within the coarse-grained models with explicitly specified solvent, because the largest number of degrees of freedom fall on the solvent in a dilute solution. Theoretical foundations of the Langevin and Brownian dynamics methods are available in a monograph.[54]

The diffusion coefficients of micelles, surface-active ions and counterions in a solution of dodecyltrimethylammonium bromide were determined [39] using Brownian dynamics simulation with a micellar solution model including charged spheres and a solvent specified implicitly (through the dielectric constant). The diffusion coefficients of micelles in aqueous tetradecyltrimethylammonium bromide solution containing sodium bromide additive were determined both experimentally (by NMR spectroscopy and DLS) and theoretically from Brownian dynamics simulations.[47]

IV.4. All-atom molecular dynamics

Among the existing classical models, the all-atom representation of a micellar solution is most expensive from the standpoint of computational cost. However, it provides a more accurate description of the properties of a system under study compared to coarse-grained models, first of all, in considering transport phenomena. The case in point is that time passes faster in the coarse-grained models compared to real molecular processes, and the extent of acceleration is hard to determine. All-atom models give more realistic dynamics of the systems in hand.

Classical molecular dynamics simulations with all-atom models are carried out using partial atomic charges and the Lennard-Jones (LJ) potentials taken from one or another force field; these parameters are fixed throughout the simulation. Models for chain molecules include the characteristic bond lengths, bond angles and some other parameters. Then, the dynamics of a system chosen is simulated by numerically solving the classical equations of motion. Corresponding computational procedures have been described in detail in monographs.[54, 55]

An example of application of the coarse-grained and all-atom models in studies of micellar systems is provided by a molecular dynamics simulation [43] of aqueous solutions of sodium dodecyl sulfate (SDS) and pentaethylene glycol monododecyl ether ($C_{12}E_5$) carried out to determine the mean escape time of monomers from micelles based on the Smoluchowski theory. Preliminary calculations were performed to determine the potential of mean force acting on the monomer moving away from the micelle centre of mass and the diffusion coefficient of individual monomer in water. The dependence of the potential of mean force on the distance from the aggregate centre of mass was established using the umbrella sampling method within the framework of the all-atom and coarse-grained models. The mean escape time of monomers for the $C_{12}E_5$ nonionic micelle appeared to be more than ten times longer than for the SDS ionic micelle.

Now we will consider specific features of all-atom dynamics simulations of diffusion in micellar solutions of ionic surfactants in more detail taking published data [40, 41, 51, 56] as examples. Those studies were devoted to modelling of (i) self-aggregation of surface-active ions in aqueous SDS solutions (model for the SDS molecule is shown in Fig. 8) including solutions with 1 : 1 electrolyte [41] and 2 : 1 electrolyte [56] additives; (ii) transport properties of ionic aggregates, ions and water molecules, and (iii) structural properties of ionic micellar solutions.

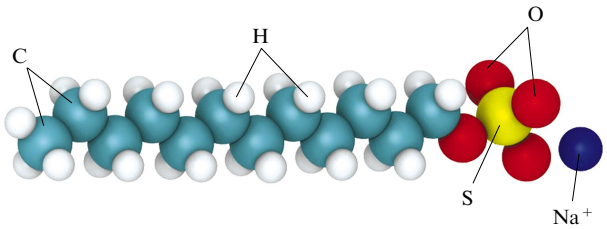


Figure 8. All-atom model for SDS molecule.

The molecular dynamics trajectories, *i.e.*, the dependences of the atomic coordinates and velocities on time, were obtained [40, 41, 51, 56] using the MDynaMix software package [57] and the classical force field CHARMM36.[58] The properties of interest were determined from the molecular dynamics trajectories using certain utilities incorporated into the MDynaMix package and original programmes. The water model was CHARMM TIP3P, or TIPS3P.[59 – 61] This is a modification of the TIP3P model [62] (unlike TIP3P, the TIPS3P model includes a nonzero LJ potential for hydrogen atoms). The simulation was carried out in the *NPT* statistical ensemble using a cubic simulation box with periodic boundary conditions. The temperature and pressure were controlled using the Nosé thermostat with the temperature $T = 298$ K and the Nosé – Hoover barostate [63] with a target pressure of 1 atm. A double-time-step algorithm [64] with short and long steps of 0.2 and 2 fs, respectively, was used instead of imposing restrictions on the interatomic bond lengths. Electrostatic interactions were treated using Ewald summation.[55, 65] The cutoff radius of the LJ interactions calculated in each short step was 5 Å. The LJ potentials calculated in each long step and the Ewald sum component calculated in the real space were cut off at $R_{cut} = 12$ Å. In addition to the cutoff radius R_{cut} for the real space, the accuracy of calculations of the Ewald sum is affected by two more parameters, namely, the cutoff radius in the Fourier space and the so-called convergence parameter. In the MDynaMix software package, these parameters are specified using two special constants, *A*

and B. The accuracy of calculations of the Ewald sum component in the real space is determined by the value of the complementary error function erfc(A). The constant B specifies the cutoff radius of the Ewald sum component calculated in the Fourier space. The accuracy of calculations of this component is given by $\exp(-B)$. Studies [40, 41, 51, 56] were carried out using the default values $A = 2.8$ and $B = 9$ specified in the MDynaMix package.

V. Cluster analysis for the determination of aggregate diffusion coefficients

V.1. Identification of aggregates

Molecular modelling studies of the transport and structural properties of aggregates first of all require identification of constituent monomers, *i.e.*, a cluster analysis of the simulation box.[40, 56, 66, 67] A typical snapshot of a solution in a simulation, box is shown in Fig. 9. In the course of simulation, a number of aggregates with variable aggregation numbers may appear in the box. Therefore, a reliable algorithm for automated identification of monomers constituting aggregates is necessary for the determination of the aggregate diffusion coefficients from analysis of the molecular dynamics trajectories.[56] In the case of ionic surfactants, one should first of all establish a criterion for membership of two surface-active ions to the same aggregate. Having done this, the number of aggregates in the simulation box and the corresponding aggregation numbers can be determined recursively. For instance, let three surface-active ions (A, B and C) be located in the simulation box. First, the membership criterion is used to determine whether the A and B ions belong to the same aggregate. Assume that the criterion is met and the surface-active ions A and B belong to the same aggregate. In this case, the third ion, C, also belongs to the same aggregate provided that the criterion is met for at least one pair of ions (A and C or B and C). This algorithm can be easily generalized to an arbitrary number of surface-active ions in the simulation box.

In an aqueous SDS solution the surface-active ions aggregate through the hydrophobic effect, and certain segments of hydrocarbon 'tails' of different surface-active ions become in close proximity to one another (see Fig. 9). It was proposed [56] to consider two surface-active ions as belonging to the same aggregate if the minimum distance between any carbon atoms of different surface-active ions is shorter than some preset distance R_{min} that is chosen empirically. If only one aggregate is visually observed in a system for long, a minimum value, R_{min}, at which all surface-active ions in the system belong to the same aggregate should be selected. For instance, the same value $R_{min} = 5.521$ Å was chosen [56] for all systems containing 16 SDS molecules and different numbers of water molecules (3200, 4800, 6400). Then, the R_{min} value obtained can be used for automated analysis of more complex situations where the system contains a number of aggregates (see the snapshot for the SDS solution with three aggregates in Fig. 10).

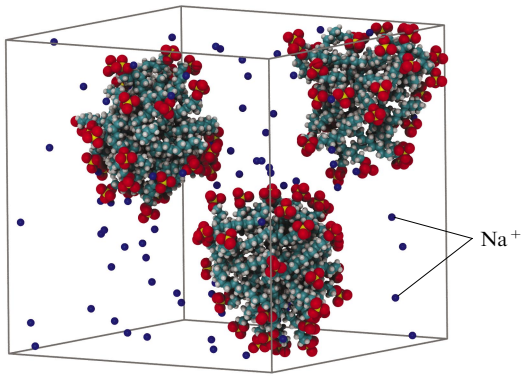


Figure 10. A snapshot of a system containing 96 SDS molecules, 9600 water molecules (three ionic aggregates).[51]
Water molecules are not shown.

After the formation and subsequent identification of an aggregate one can calculate the translational diffusion coefficient for the aggregate centre of mass using the Einstein equation for the diffusion coefficient of a particle

$$D = \lim_{t \to \infty} \frac{\langle \Delta r(t)^2 \rangle}{6t} \qquad (112)$$

where $\langle \Delta r(t)^2 \rangle$ is the mean square displacement of the particle over a period of time t. Expression (112) is applicable if $\langle \Delta r(t)^2 \rangle$ is a linear function of time in a certain

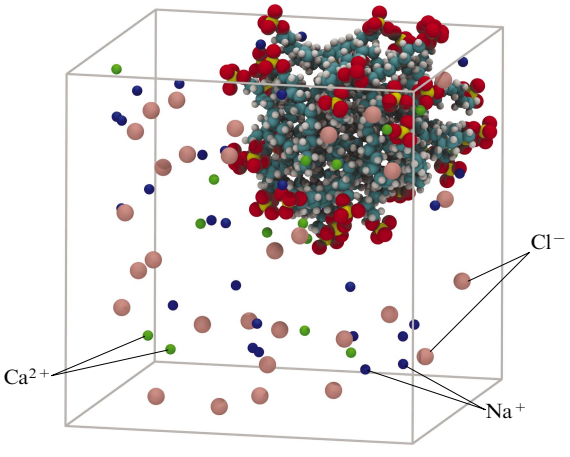


Figure 9. A snapshot of a system containing 32 SDS molecules, 16 $CaCl_2$ molecules and 3200 water molecules (data taken from Ref. 56).
Water molecules are not shown.

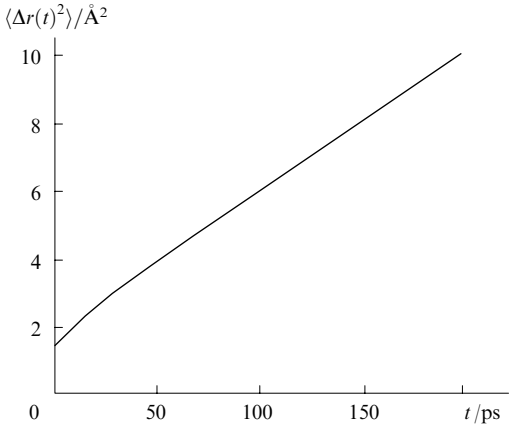


Figure 11. Time dependence of the mean square displacement of the aggregate with the aggregation number $n = 16$ for the system containing 16 SDS molecules and 1600 water molecules.[41]

range of t values. An example of the dependence $\langle \Delta r(t)^2 \rangle$ on time for ionic SDS aggregate is presented in Fig. 11. To reduce the error in calculations of the diffusion coefficient D, the square displacement $\Delta r(t)^2$ is averaged over a large number of conditionally independent time intervals of specified duration (200 ps for the plot in Fig. 11) that were selected from the overall molecular dynamics trajectory. The translational diffusion coefficients of water molecules and counterions in an ionic micellar solution can be determined analogously.[41] When calculating the diffusion coefficients of counterions and water molecules, the averaging is performed not only over time, but also over the ensemble of particles. That is why the diffusion coefficients of counterions and especially water molecules are determined much more accurately than those of aggregates.

V.2. The degree of counterion binding to aggregates with different aggregation numbers

The degree of counterion binding to a micelle is an important characteristic of the thermodynamic and transport properties of micellar solutions of ionic surfactants. As mentioned above (see Section II.4), this parameter is the least reliably determined both in theory and in the experiment. The degree of counterion binding is a quantitative measure of the ability of an ionic aggregate to hold counterions in close proximity. Clearly, it should depend on the aggregation number of surface-active ions in a micelle. An all-atom molecular dynamics simulation[38] showed that the diffusion coefficient of a counterion located in the first hydration shell of an ionic micelle and bound to it is smaller that of the same ion in the bulk phase. This is an example of the effect of counterion binding to aggregates on the transport properties of micellar solutions. The theory of the effect of the binding coefficient on the average diffusion coefficient and surfactant mobility in solutions at different total concentrations of surfactant was considered above (see Sections II.4 and III.1).

There are various approaches to evaluation of the degree of counterion binding by methods of molecular modelling. One of them is to study the radial distribution function of counterions relative to the centre of an ionic aggregate and the corresponding potential of mean force.[51, 56]

The radial distribution functions $g(r)$ of Na^+ counterions and water hydrogen and oxygen atoms relative to the aggregate centre of mass are shown in Fig. 12. They were obtained for two systems containing 16 and 64 SDS molecules (100 water molecules per SDS molecule). One aggregate with the aggregation number $n = 16$ and 64 is formed in each system. As can be seen, the radial distribution functions of counterions in both systems have maxima outside the aggregates (characteristic radii R_s of aggregates are shown by vertical dashed lines). This suggests that aggregates bind counterions located at distances of a few Ångström outside the aggregate surface. The counterion binding to aggregates mainly occurs through Coulomb interactions, and the higher $g(r)$ peak of counterions (*i.e.*, higher counterion – aggregate binding energy) for the aggregate with the aggregation number equal to 64 is due to the larger (in absolute value) charge of the aggregate. The rapid decrease in the $g(r)$ function of counterions at $r < R_s$ is probably caused by repulsion of counterions approaching the aggregate centre of mass from the aggregate due to the effect of the excluded volume. It was concluded[41] that nonzero values of the function $g(r)$ at $r < R_s$ are due to changes in the aggregate shape in the course of simulation rather than penetration of counterions inside the aggregate. As the aggregate extends along one (or two) axes, counterions and water molecules can approach its centre to shorter distances than in the case of nearly spherical aggregate.

The behaviour of the radial distribution functions of the hydrogen and oxygen atoms relative to the aggregate centre of mass (see Fig. 12) suggests that water molecules approach the aggregate centre to a shorter distance compared to counterions (this is particularly noticeable for the smaller aggregate in Fig. 12 *a*). Probably, this is due to the

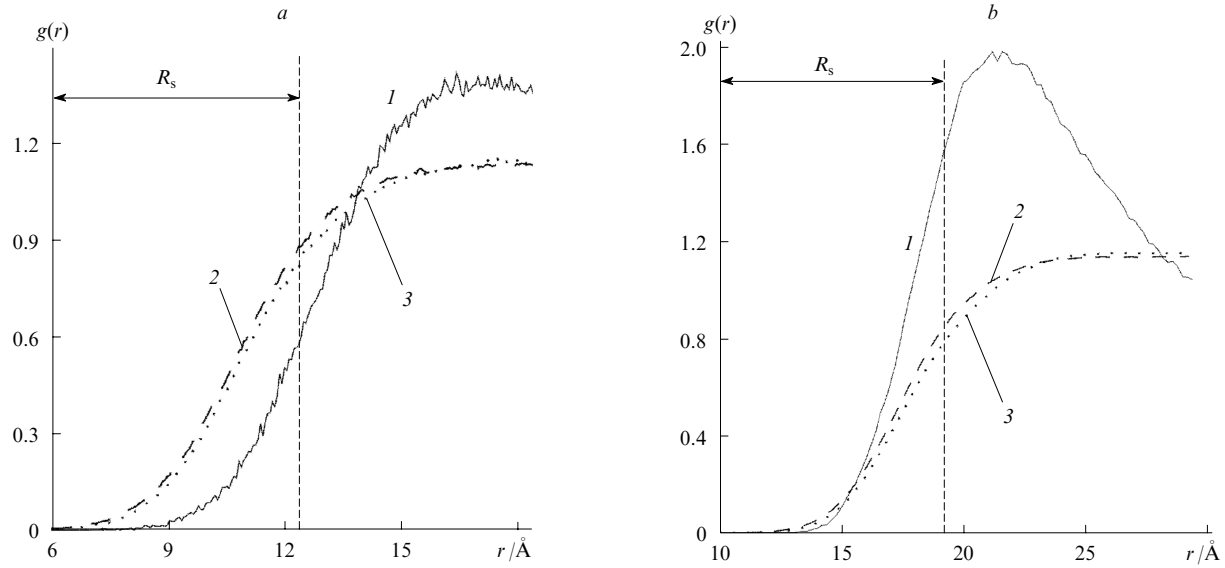


Figure 12. Radial distribution functions $g(r)$ of Na^+ counterions (*1*) and water hydrogen (*2*) and oxygen atoms (*3*) relative to the aggregate centre of mass for the systems containing different numbers of water molecules and SDS.
The system contains 16 SDS molecules and 1600 H_2O molecules, $n = 16$ (*a*)[41] and the system contains 64 SDS molecules and 6400 H_2O molecules, $n = 64$; data taken from Ref. 51 (*b*).

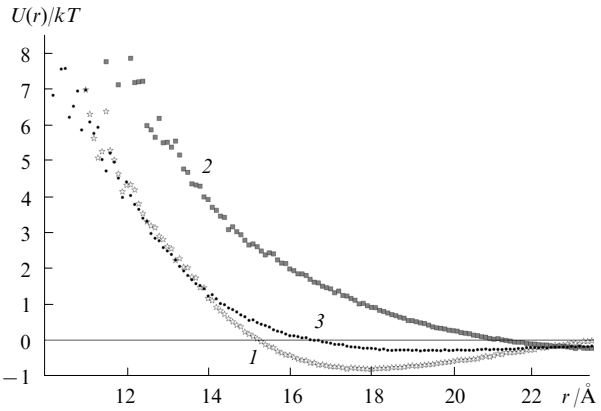


Figure 13. Dimensionless potentials of mean force, $U(r)/kT$, applied to Ca^{2+} (*1*), Cl^- (*2*) and Na^+ ions (*3*) as functions of the distance r from the aggregate centre of mass for the system containing 32 SDS molecules, 3200 H_2O molecules and 16 $CaCl_2$ molecules.[56]

fact that the hydrated sodium ions are larger than water molecules. The $g(r)$ plots of water oxygen and hydrogen atoms have no local maxima near the aggregate surface; thus, one can conclude that the aggregate surface is only partially wetted with water.[56]

Figure 13 presents the dimensionless potentials of mean force $U(r)/kT$

$$\frac{U(r)}{kT} = -\ln g(r) \tag{113}$$

plotted using the radial distribution functions for a system containing 32 SDS molecules, 3200 H_2O molecules and 16 $CaCl_2$ molecules.[56] As can be seen, chloride ions are repelled from the aggregate (the derivative of the potential with respect to r retains its sign in the whole range of r values, *i.e.*, the direction of the force does not change), whereas the sodium and calcium ions are repulsed from the aggregate due to the effect of the excluded volume at short distances, being attracted to the aggregate due to Coulomb interactions when at longer distances. The depth of the potential well in the curve for the calcium – aggregate interaction is of the order of kT, *i.e.*, the doubly charged calcium ion becomes tightly bound to the aggregate in contrast to the singly charged sodium counterion (potential well is too shallow).

VI. Diffusion coefficients of surfactants in solutions from the results of all-atom molecular dynamics simulation

VI.1. Dependence of the aggregate effective size and diffusion coefficient on the aggregation number and simulation box size

Undoubtedly, it is of interest to study the equilibrium properties of micellar systems containing a large number of surfactant molecules using the results of all-atom molecular dynamics simulations. At corresponding surfactant concentrations, such systems may contain free surface-active monomers, short-lived pre-micellar aggregates with a variety of aggregation numbers (dimers, trimers, *etc.*) and relatively stable micelles. All-atom molecular dynamics simulations of the systems in question is computationally expensive and time-consuming. However, even small micellar systems with one, two or three aggregates, which are quasi-stable in sufficiently small simulation boxes, can be used to study the transport properties of these aggregates.[40, 41, 51]

Calculations of aggregate diffusion coefficients go hand in hand with the determination of aggregate size. The characteristic radius of spherical SDS aggregates was determined by two methods.[40, 41, 51, 56] One of them was as follows. Having determined the coordinates of the aggregate centre of mass, the characteristic radius R_s can be estimated from the expression [68]

$$R_s = \sqrt{5/3}\, R_g \tag{114}$$

where R_g is the average radius of gyration of the aggregate. Although formula (114) relates R_S to the radius of gyration of a hard sphere with constant density, it can also be used to estimate the radius of a spherical aggregate assembled from surface-active ions. The second method for the determination of the SDS aggregate radius involves calculations of the radial distribution function $g(r)$ of sulfur atoms relative to the aggregate centre of mass. Sulfur atoms are incorporated into the hydrophilic head group of SDS molecule, being located on the aggregate surface when in water. Position of the maximum of the $g(r)$ function on the r axis gives an estimate of the characteristic radius of a spherical aggregate. Figure 14 demonstrates that the coordinate of the maximum of the radial distribution function of sulfur atoms is close to the aggregate radius R_s obtained from expression (114). These methods for the determination of R_s for spherical aggregates with different aggregation numbers give consistent results.[40, 41, 51, 56]

The diffusion coefficients of (i) SDS aggregates with different aggregation numbers and (ii) water molecules and counterions were determined from all-atom molecular dynamics simulations of aqueous SDS solution.[40] The results obtained for the SDS aggregates were found to be

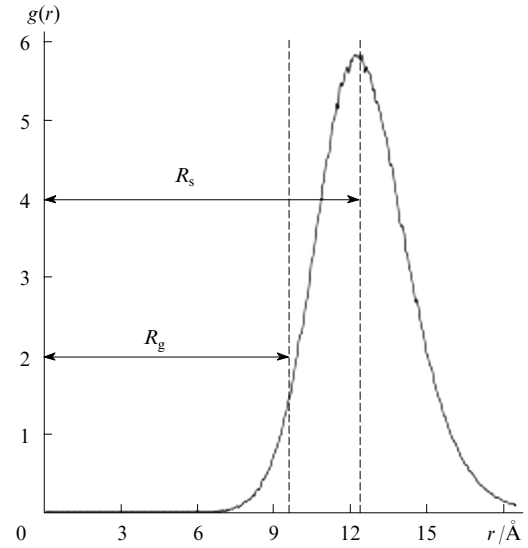


Figure 14. Radial distribution function $g(r)$ of sulfur atoms relative to the aggregate centre of mass (aggregation number $n = 16$) for the system containing 16 SDS molecules and 1600 water molecules (data taken from Ref. 41).

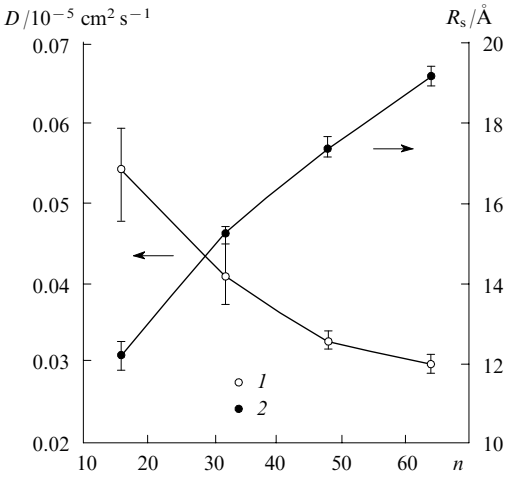


Figure 15. Diffusion coefficients (*1*) and radii (*2*) of aggregates with the aggregation numbers $n = 16$, 32, 48, 64 at constant total surfactant concentration (data taken from Ref. 51).

of the same order of magnitude as those found from DLS experiments at high surfactant concentrations.[13]

Figure 15 presents the diffusion coefficients, D, of spherical aggregates and their characteristic radii R_s determined [51] using expressions (112) and (114) for the aggregation numbers $n = 16$, 32, 48, and 64 in aqueous SDS solution. These results were obtained at rather high, constant total concentration of SDS in solution. As should be expected, an increase in the aggregation number causes a monotonic increase in R_s and a monotonic decrease in D.

The dependence of the diffusion coefficient D of an SDS aggregate with the aggregation number $n = 16$ on the simulation box size (in other words, on the total surfactant concentration in solution) was studied.[51] The results obtained are presented in Fig. 16 as the plot of the diffusion coefficient D *vs.* average reciprocal length $1/\langle l \rangle$ of a cubic simulation box side. The dependence $D(1/\langle l \rangle)$ is nearly linear in the concentration range studied and the diffusion coefficient of the aggregate increases with increasing simulation box size. A similar behaviour of the diffusion coefficient was earlier observed for other molecular systems.[69 – 73]

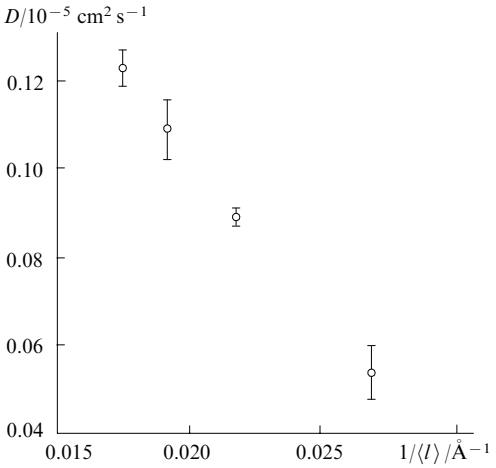


Figure 16. Diffusion coefficient of the aggregate with the aggregation number $n = 16$ plotted *vs.* average reciprocal length $1/\langle l \rangle$ of simulation box side (data taken from Ref. 51).

VI.2. Diffusion coefficients of co-ions and counterions

Diffusion coefficients of sodium and chloride ions, water molecules and aggregates in aqueous SDS solution (both in salt-free system and in solution with added sodium chloride) were determined from the results of an all-atom molecular dynamics simulation.[41] In particular, a number of systems were studied, each containing 16 surface-active ions assembled into an ionic aggregate with the aggregation number $n = 16$, 16 sodium ions, 1600 water molecules and different numbers of sodium chloride molecules (N_{NaCl}) represented by corresponding numbers of Na^+ and Cl^- ion pairs. The diffusion coefficients of sodium ions, chloride ions and water molecules are plotted *vs.* number of sodium chloride molecules added to the simulation box (*i.e.*, concentration of the added salt) in Fig. 17.

It was reported [41] that the diffusion coefficients of sodium ions (D_{Na^+}), chloride ions (D_{Cl^-}) and water molecules (D_{H_2O}) presented in Fig. 17 decrease with increasing salt concentration in solution. For the salt-free SDS solution, one had $D_{Na^+} = (1.33 \pm 0.01) \times 10^{-5}$ and $D_{H_2O} = (2.65 \pm 0.01) \times 10^{-5}$ cm^2 s^{-1}. The diffusion coefficients for the solution with the highest salt concentration (48 NaCl molecules added to the SDS solution) were as follows: $D_{Na^+} = (1.03 \pm 0.01) \times 10^{-5}$ and $D_{H_2O} = (2.26 \pm 0.02) \times 10^{-5}$ cm^2 s^{-1}. The co-ion diffusion coefficient, D_{Cl^-}, decreases from $(1.55 \pm 0.03) \times 10^{-5}$ for the system with eight NaCl molecules added to $1.16 \pm 0.02) \times 10^{-5}$ cm^2 s^{-1} for the system containing 48 NaCl molecules.

The characteristic size of sodium ion used in molecular simulation using the CHARMM36 force field is smaller than that of chloride ion. Figure 17 shows that the diffusion coefficients of sodium ions are lower than those of chloride ions throughout the entire concentration range of the added salt. The same was also observed both experimentally [74] and in a molecular dynamics simulation [75] for the diffusion coefficients of sodium and chloride ions in a surfactant-free aqueous NaCl solution. A possible reason is that water

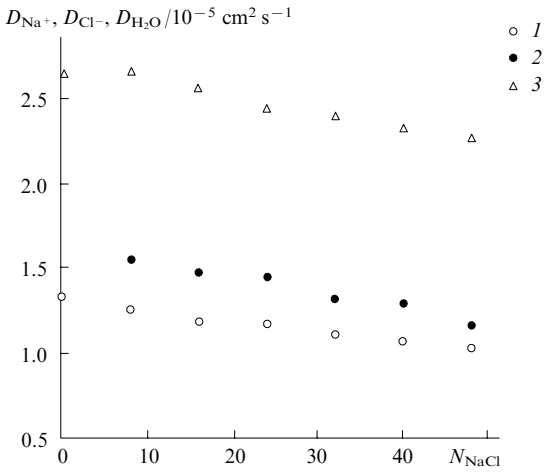


Figure 17. Diffusion coefficients of sodium ions (*1*), chloride ions (*2*) and water molecules (*3*) in aqueous SDS solution plotted *vs.* number of sodium chloride molecules added to the system containing 16 SDS molecules and 1600 water molecules (data taken from Ref. 41).

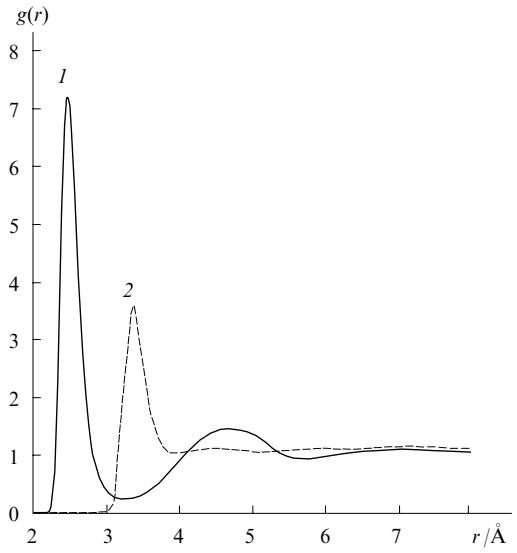


Figure 18. Radial distribution functions of water oxygen atoms relative to the sodium ions (*1*) and chloride ions (*2*) for the system containing 32 SDS molecules, 32 NaCl molecules and 3200 water molecules.[41]

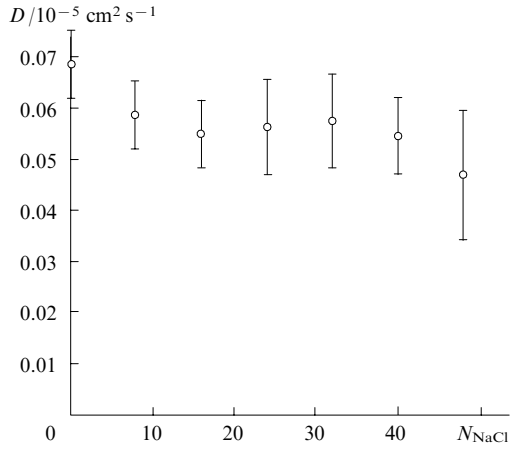


Figure 19. Diffusion coefficient of the aggregate (aggregation number $n = 16$) plotted *vs.* number of NaCl molecules added to the system containing 16 SDS molecules and 1600 water molecules.[41]

has different structure in the vicinity of sodium and chloride ions.

The effective size of hydrated sodium and chloride ions was estimated using the radial distribution functions of water oxygen atoms relative to the sodium and chloride ions in aqueous SDS solution calculated[41] for a system containing 32 SDS molecules, 32 NaCl molecules and 3200 water molecules (see Fig. 18). The distribution of oxygen atoms relative to sodium ions is bimodal with two clearly seen peaks at $r_1 \approx 2.476$ and $r_2 \approx 4.7$ Å, whereas their distribution relative to chloride ions is monomodal with a peak at $r \approx 3.372$ Å. It follows that sodium ion has two hydration shells, while chloride ion has only one hydration shell. This provides an explanation for slower diffusion of Na^+ ions compared to Cl^- ions in both aqueous NaCl solution and in aqueous SDS solution containing NaCl.

VI.3. Dependence of diffusion coefficient of ionic aggregates on the concentration of the added salt

Experiments revealed a dependence of the micelle diffusion coefficient on the concentration of salt added to the micellar solution.[76, 77] An all-atom molecular dynamics simulation[41] of the dependence of the diffusion coefficient of a small SDS aggregate with the aggregation number $n = 16$ on the concentration of NaCl added showed that an increase in the number of NaCl molecules in the system causes the diffusion coefficient of the aggregate to become lower than in the salt-free solution (Fig. 19). Taking into account the results presented in Figs 17 and 19, mention may be made that an increase in the concentration of the added salt in the SDS solution led to a decrease in the diffusion coefficients of sodium and chloride ions, water molecules and aggregate, although the aggregation number remained unchanged and the aggregate radius R_s determined from expression (114) was almost independent of the salt concentration throughout the concentration range studied. The observed decrease in the diffusion coefficient of SDS aggregate with increasing salt concentration in the solution can be due to both increasing viscosity of the micellar solution and to increasing number of counterions bound to the aggregate and, therefore, to increasing effective size of the aggregate.

VII. Conclusion

Of course, this review is not comprehensive by content. The theory of diffusion given above is based on the equilibrium ratios of the mass action law, which means that only slow processes (at rather small gradients of the chemical potentials) were considered. A more complete theory of diffusion in micellar systems under nonequilibrium conditions was also developed[28] in terms of diffusion coefficients. However, that theory cannot be considered simple since even its relations for the equilibrium conditions look like expression (96). Yet another limitation of the available theory is the quasi-chemical approximation, *i.e.*, the aggregation number is considered constant. This implies a spherical shape of micelles and operation in the concentration range near the CMC. Other types of micelles are intensively explored in practice, and the theory here obviously lags behind. Also, it seems not improbable that theory can be improved within the framework of the law of mass action because this fundamental thermodynamic relation is not limited to constant aggregation numbers. One can say there is favourable forecast for the development of theory.

A synonym of the term 'molecular modelling', namely, *mathematical experiment*, emphasizes that this area of knowledge is simultaneously related to theory and experiment. Molecular modelling is based on mathematical equations, principles of statistical mechanics and theoretical models for chemical substances. Its aim is not only to demonstrate good agreement with experimental results, but also to explain them and, ideally, to obtain valuable information on the system in hand, which is inaccessible to the existing experimental methods. The authors hope that their review concerned with investigations of micellar solutions by methods of molecular modelling will be of interest for both theoreticians and experimentalists and will help to obtain a more complete and accurate description of diffusion in these systems.

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