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Thermodynamics of ionic micelles

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ABSTRACT. The present state of the thermodynamics of ionic micellar systems is examined and the principal characteristics of these systems are discussed: the charge and activity coefficients of the micelles, the concentration of the monomers and the degree of binding of the counterions, and the dependence of the critical micelle formation concentration on the length of the hydrocarbon chain of the surfactant and on the added electrolytes. The thermodynamics of the micellar cell and the methods for the calculation of the electrostatic contribution to its energy are described.

The bibliography includes 107 references.

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I. Introduction

The formation of surfactant micelles is one of the most interesting phenomena in the physical chemistry of solutions. It is characteristic of colloidal surfactants in the molecules of which hydrophilic (polar, including ionogenic) and lipophilic (hydrophobic) groups (hydrocarbon or fluorocarbon chains usually play the function of such groups) are well balanced. The micelles are molecular or ionic aggregates whose size is about 3–100 nm and which arise after the attainment of the critical concentration for micelle formation (CCM). Micelles are formed over a fairly narrow concentration range. It appeared natural to explain the results of the first observations[1–5] by the fact that micelles are formed under the influence of the attractive forces between surfactant molecules. However, this is true only of micelles in non-polar media. The true cause of micelle formation in aqueous solutions is the hydrophobic effect—the tendency of water to liquidate internal cavities and to expel hydrophobic bodies (especially hydrocarbon groups), which is due to the intermolecular interactions and the structure of water. Treatment of micelle formation as the water aggregation process[6] was the first step in the elucidation of the hydrophobic effect, numerous manifestations of which (the formation of adsorption layers, membranes, vesicles, etc.) play an important role in the self-organisation processes in molecular systems. Micelles may be formed only above a temperature characteristic of its surfactant, called the Krafft point (crystallisation takes place below this temperature). In the equilibrium micellar solution, there is a stable distribution of micelles with respect to size, shape, and composition with an extremely sharp maximum, which is a feature in terms of which micellar systems resemble monodisperse systems.

The first advances in the theory of micelle formation[3–6] were associated with the application of the Law of Mass Action. In this approach (it can be called quasi-chemical), the surfactant aggregation process is regarded as a reversible chemical reaction of the type

$$\sum_i n_i A_i \rightleftarrows M, \qquad (1)$$

where n is the aggregation number, i.e. the number of molecules or ions of the given kind involved in the formation of a single micelle, A and i are the symbol and number of the micelle component, and M is the symbol for the micelle. The lifetime of the surfactant molecule in the micelle can be of the order of 10^{-7} s[7,8] and the half-life of the micelle is between 10^{-3} and 1 s,[9–11] so that reaction (1) should be assigned to the class of fast reactions. The aggregation numbers n_i, which play the role of stoichiometric coefficients in Eqn. (1), are not strictly speaking constant (they increase with increasing surfactant concentration), but in the region of the CCM their variation can be neglected. The observed sharp transition to micelle formation can then be readily accounted for on the basis of the Law of Mass Action by the large aggregation number (several tens and more).

Micelle formation resembles not only a chemical reaction but also a process involving the segregation of a new phase. If this is the pure surfactant phase, then the addition of the latter to the system should not alter its state. In order to justify the phase treatment of micelles, the phase rule and the apparent identity of the Krafft point and the triple point have been resorted to,[12,13] but these arguments proved to be erroneous†.[14–17] Furthermore, direct measurements of the surface tension of a micellar solution and of the activity coefficients of the surfactants[18,19] established that the parameters of state vary steadily with concentration, as in the usual solution, even above the CCM. However, the functions of state of molecular (ionic) and micellar solutions are different and the transition through the CCM can therefore be interpreted as a second order phase transition.[20] The concept of the macroscopic phase is inapplicable to an individual micelle, but it can be regarded as a kind of microphase and, using the concept of the thermodynamics of curved surfaces,[21] a definite pressure and surface tension can be attributed to it. It is significant that this microphase has no macroscopic analogue, because a micellar solution can exist under experimental conditions

† The phase rule cannot be extended automatically to disperse systems and the difference between the Krafft point and the triple point became evident after a more detailed investigation of phase diagrams.

in equilibrium with the solid or liquid crystals surfactant phases and micelles are evidently not nuclei of these phases.

In quasi-chemical and phase approaches, there is a tendency to describe the micelle as a molecule or as a phase respectively. However, the micelle occupies an intermediate position between them. Whereas in the thermodynamic description of the molecule as a component of the solution attention is concentrated usually on the external energy while in the description of the phase the internal energy is exclusively concentrated upon; for the micelle both are equally important. The quasi-chemical approach is useful when its external degrees of freedom are examined and many important properties of the micellar solution can be described on the hypothesis that the micelle is an unmodified entity. On the other hand, in the analysis of the internal state of the micelle (in the language of the quasi-chemical approach, this can mean, in particular, the calculation of the Law of Mass Action constant), the phase approach is entirely appropriate because the micelle is regarded as a microphase. The combination of both approaches makes it possible to describe rationally the thermodynamics of the micellar solution[22] and below we shall follow this recipe.

Micelles are of very considerable practical interest. It is sufficient to recall their wide-scale employment in micellar catalysis, emulsion polymerisation, and other fields of the solubilisation phenomenon, i.e. the dissolution by the micellar solution of substances which are sparingly soluble in an aqueous medium in the absence of micelles. Extensive experimental data on micelles (data for the CCM, the aggregation numbers, the diffusion coefficient, the size, charge, geometrical shape, and degree of dissociation of micelles, etc.) have been published in a series of reviews.[13,23-33] There are more data about ionic micelles with which the study of micelle formation began. The critical concentration for micelle formation from ionic surfactants is 1–2 orders of magnitude higher than for non-ionic surfactants and the number of parameters characterising micelles is greater than for molecular substances (the electrical parameters are added). The interpretation of the experimental results, which depend greatly also on the purity of the surfactant, is also correspondingly more complex. On the one hand, the theory of ionic micelles is based on the general theory of micelle formation in aqueous solutions, including the analysis of the hydrophobic effect, and, on the other, its task is to estimate the contribution of electrostatic interactions to the micelle formation process. This task, which has been recognised at least since 1956,[34] has been considered in a series of studies.[13,35-55] In its development, the theory of ionic micelles was based on the advances in the general theory of solutions of charged colloidal particles[56] and the theory of electrolyte solutions in relation to reacting mixtures[57-62] and polyelectrolytes.[63-69] Considerable progress in the thermodynamic theory of ionic micellar systems was attained in the 1980's. This can be explained by at least two causes: the rapid improvement of the computer techniques and the introduction of new experimental research methods. Wide-scale prospects have arisen, for example, from the direct measurement of the electrical potential of the surface of the micelle, essential for thermodynamic calculations, by the fluoroescent probe method[70] (previously only its charge was determined).

This review considers mainly ionic micelles—more precisely their specific properties which distinguish ionic surfactant micelles from all others. On the other hand, certain results are applicable also to the micelles of non-dissociating surfactants, in particular to zwitter-ionic surfactant micelles (lecithin, betaines, etc.), in the molecules of which the opposite charges of the dipole are separated by a considerable distance (for example, by several CH_2 groups).

II. The micellar system as an electrolyte solution

1. The aggregation number and charge of the micelle. Degree of binding of counterions

The quasi-chemical approach presupposes that the micellar system is single-phase, i.e. is a solution, and that any ionic micelle is no more than a large multicharged ion. Its size is determined by the size and aggregation number of the surface-active ion (or ions) and its charge is determined by the aggregation number and degree of binding of counterions. In a specific concentration range above the CCM (usually within the limits of variation of the concentration by 1–2 orders of magnitude) micelles are spherical in shape. The volume of the hydrocarbon core of the micelle is calculated as the volume of a sphere whose radius is equal to the length of the extended largest hydrocarbon group in the surfactant molecule and the aggregation number is found by dividing this volume by the overall volume of the groups of the surfactant molecule forming part of the core (if necessary, account is taken of the additional packing conditions[26,71-75]). Under the usual conditions, the maximum length (l_{max}, m) and volume (V, m^3) of the linear aliphatic group is determined from the formulae[26]

$$l_{max} = (1.5 + 1.265n_C)\cdot 10^{-10},$$
$$V = (27.4 + 26.9n_C)\cdot 10^{-30}. \quad (2)$$

where n_C is the number of carbon atoms in the group. Accordingly, when the surfactant molecule contains only one such group, the aggregation number n is defined as follows:

$$n = 4\pi l_{max}^3/3V = 4\pi(1.5 + 1.265n_C)^3/(27.4 + 26.9n_C). \quad (3)$$

It is seen from Eqn. (3) that n is an increasing function of n_C. For $n_C = 12$, we obtain $l_{max} = 1.67$ nm, $V = 0.350$ nm^3, and $n = 55.5$ from Eqns. (2) and (3). We may note that the theoretical value of the aggregation number cannot be regarded as either minimal or maximal. If the hydrocarbon chain is not fully uncoiled, then the aggregation number may be less. If a proportion of the chains are not wholly incorporated in the core and continue to remain in contact with water (this possibility is indicated by data for the permeation of water into the interior of micelles[76-83]), then the aggregation number can be actually greater. For the most thoroughly investigated ionic surfactant—sodium dodecyl sulphate (SDS)—n = 60–70 and above has been obtained in many experiments, but, in the assessment of the experimental results, the question of the possible admixtures increasing the aggregation number always arises. An unusually low aggregation number (n = 27) of thoroughly purified SDS has been reported.[84]

For a specified aggregation number, the charge of the micelle is determined by the degree of binding of counterions. The very concept of binding has many meanings.[41] It can be understood as the recombination of ions (binding via chemical forces) or as simple electrostatic attraction, which depends on distance. Even if the degree of dissociation of the micelle is known and the radial statistical distribution of the counterions has been found, one cannot state what proportion of such counterions can be regarded as bound. It is assumed arbitrarily, for example, that the counterions in the first coordination sphere can be regarded as bound.[39] The ambiguity of the concept of binding is manifested also in the interpretation of experimental data, which creates a considerable scatter in the degrees of dissociation of counterions (from 0.46 to 0.86 for SDS[85]). Since this concept originates from the idea of the micelle as a kinetic entity, it is logical to make an attempt to base the concept of the degree of binding on kinetic considerations. Although this approach

does not in fact permit the determination of the exact value of the degree of binding, it does create the possibility of discovering its dependence on the parameters of state.

The critical concentrations for the micelle formations for the majority of ionic surfactants are so low that, in the absence of micelle formation, the average energy of the Coulombic interaction of a pair of ions (u_{ik}), given by

$$u_{ik} = z_i z_k e^2/(4\pi\varepsilon_0\varepsilon\bar{r}) \tag{4}$$

[$z_i e$ and $z_k e$ are the charges of ions of the ith and kth kinds respectively, u is the elementary charge, $\bar{r}$ the average interionic distance, ε_0 the electrical constant (permittivity) and ε the dielectric constant], is less than the average energy of thermal motion. Thus, for an aqueous SDS solution at 25 °C, we have CCM = c_m = 8.1 M, $\bar{r} = (2c_m)^{-1/3} \simeq 46.8 \times 10^{-16}$ m, and, when ε = 80, we have the ratio $u_{ik}/kT \simeq 0.15$ (k is the Boltzmann constant and T the absolute temperature). Under these conditions, the binding of oppositely charged ions is impossible. In the presence of micelles, the situation changes. Suppose that the aggregation number is n, whence the energy of the interaction of the primary core of the micelle with an individual ion is greater by the factor n than the value calculated using Eqn. (4) and, whereas this energy is an order of magnitude smaller than kT for n = 1, when n = 100 it is already an order of magnitude greater than kT. Such a micellar core will bind the counterions. In the general case, the degree of binding is

$$\beta = -\sum_k n_k z_k \Big/ \sum_i n_i z_i > 0,$$

where n_i and n_k are the aggregation numbers of the surface-active ions and counterions respectively (the minus sign is due to the different signs of z_i and z_k). The charge on the micelle is given by the expression

$$q_M = e\left(\sum_i n_i z_i + \sum_k n_k z_k\right) = e(1-\beta)\sum_i n_i z_i, \tag{5}$$

and a sufficient condition for the absence of binding of counterions by the micelle is

$$e^2(1-\beta)|z_k|\sum_i n_i|z_i|/(4\pi\varepsilon_0\varepsilon\bar{r}kT) \lesssim 1, \tag{6}$$

where $z_k e$ is the greatest of the charges on the counterions (ions with a large charge interact more strongly with the core of the micelle and are the first to be bound).

Eqn. (6) must hold for a certain parameter $\beta < 1$, which indicates the presence of a charge on the ionic micelle. Thus, for SDS, condition (6) holds in the vicinity of the CCM for $\beta \geqslant 0.87$, which means that the real value of β is less than 0.87. If it is assumed that a certain constant value of b on the left-hand side of Eqn. (6) corresponds to the equilibrium degree of binding, then the expression

$$\beta = 1 - 4\pi b\varepsilon_0\varepsilon\bar{r}kT \Big/ \left(e^2|z_k|\sum_i n_i|z_i|\right) \tag{7}$$

makes it possible to determine β as the parameter of state, namely as a function of temperature, concentration, aggregation numbers, and ionic charges. The temperature dependence of β is expressed both explicitly and in terms of the slowly varying functions $\bar{r}(T)$ and $\varepsilon(T)$. As can be seen from Eqn. (7), β diminishes with increase in temperature but in the accessible temperature range this variation is fairly slight.

The concentration dependence of β is manifested mainly in terms of the quantity $\bar{r}$ (and at high concentrations also in terms of ε).

In the presence of micelles, we have

$$\bar{r} = \left(\sum_i c_{i1} + c_M\right)^{-1/3}, \tag{8}$$

where $\sum_i c_{i1}$ is the overall volume concentration of the monomeric ions of both signs and c_M is the concentration of micelles. Above the CCM, both these quantities depend only slightly on the overall surfactant concentration: c_{i1} varies slightly, because the substance is consumed mainly in the formation of micelles and c_M varies slightly because of the large aggregation number. This leads to a very weak dependence of β on the overall surfactant concentration. Thus at concentrations above the CCM for a uni-univalent electrolyte, where the aggregation number of the surface-active ion is n, the doubling of the concentration of the species requires an increase in the overall surfactant concentration by the factor $2n$, i.e. by 2–3 orders of magnitude; under these conditions, r diminishes only by 20% and β even less.

As can be seen from Eqn. (7), the degree of binding is greater the higher the valence of the counterion and the higher the primary charge on the micelle (in particular the larger the micelle). The size of the micelle, its aggregation number, and its primary charge increase, as we have seen, with increase in the length of the hydrocarbon chain in the homologous series of surfactants. However, this entails a decrease in the CCM and an increase in $\bar{r}$, so that the numerator and denominator in Eqn. (7) change in the same direction. Experiment shows[86] that the degree of binding β is independent of the length of the hydrocarbon chain in the range accessible to study. Measurements of the activity and self-diffusion coefficients as well as NMR data[41] confirm the qualitative relations which follow from Eqn. (7): for spherical micelles, β is almost independent of temperature and surfactant concentration and also of the concentration of an extraneous electrolyte, but it does increase on passing to cylindrical micelles, which is always accompanied by an increase in their size.[86] The approximate constancy of β and aggregation numbers makes the micelle resemble a chemical compound and gives rise to the possibility of a quasi-chemical approach to the description of micelle formation.

2. The chemical potential and the activity coefficient of micelles

Statistical mechanics yields the following expression for the chemical potential of the molecules or ions of the solute:

$$\mu_i = \mu_i^0 + w_i + kT\ln a_i\lambda_i^3 \equiv g_i^0 + kT\ln a_i\lambda_i^3, \tag{9}$$

where μ^0 is the contribution of internal degrees of freedom, w the work of introducing one molecule (ion) through a vacuum into the solvent, $a \equiv cf$ the activity (c is the concentration and f the activity coefficient), λ the average de Broglie wavelength for a single molecule (ion), g^0 the partial Gibbs free energy for a molecule (ion) in the solvent with the centre of gravity at rest, and the subscript i characterises the kind of species. The work of introducing a species w depends on the charge q of the species:[87]

$$w(q) = w(0) + q\varphi - qP_0/\varepsilon_0 - (q^2/8\pi\varepsilon_0 r)\cdot(1 - 1/\varepsilon + \varkappa/r). \tag{10}$$

where $w(0)$ is the work of introducing the species in the absence of charge, φ the electrical potential of the bulk phase, P_0 the excess polarisation of the solvent at a neutral species (the constant part of polarisation which is independent of the charge), $\varkappa q/8\pi r^2$ the induced part of polarisation, and r the radius of the species. Since not one ion but a neutral combination of ions (a molecule) is in fact introduced into the solvent, the second term on the right-hand side of

Eqn. (10) is insignificant. The remaining part $w(q)$, called the chemical work of solvation of the ion, depends appreciably on the nature of the latter.

By analogy with Eqn. (9), we shall formulate an expression for the chemical potential of the micelle:

$$\mu_M = G_M^0 + kT \ln a_M \lambda_M^3, \quad (11)$$

where G_M^0 is the Gibbs free energy of the micelle with its centre of gravity at rest in the specified solvent, $a_M \equiv c_M f_M$ the activity of the micelle (c_M is the volume concentration of micelles and f_M the micellar activity coefficient), and λ_M the average de Broglie wave length of an individual micelle:

$$\lambda_M \equiv h (2\pi m_M kT)^{-1/2}, \quad (12)$$

where $m_M \equiv \sum_i n_i m_i$ is the mass of the micelle and m_i the mass of an individual ion (molecule).

The formulation of the chemical potential μ in terms of its standard value μ_s, corresponding to a selected concentration c_s, is very widely used in physical chemistry. For solutions of colloidal surfactants, c_s = 1 M is generally adopted and the following expression is used:

$$\mu = \mu_s^* + kT \ln c' f,$$

where

$$\mu_s^* \equiv \mu_s - kT \ln f_s = g^0 + kT \ln c_s \lambda^3, \quad (13)$$

where c' is a dimensionless quantity numerically equal to the molarity and μ_s^* the chemical potential in the hypothetical ideal unimolar solution. In the treatment of the activity coefficient f, it is necessary to distinguish two cases where the micelles ar segregated and not segregated as an individual component. If the surfactant is a strong electrolyte dissociating via the reaction

$$A = \sum_i \nu_i A_i, \quad (14)$$

where ν_i are stoichiometric coefficients, then its average activity coefficient $f_\pm$ is usually defined by the identity

$$\ln f_\pm \equiv \sum_i (\nu_i/\nu) \ln f_i \quad (15)$$

(the terms f_i are the activity coefficients of the individual ions and $\nu = \sum_i \nu_i$ is the total number of ions formed on dissociation of one surfactant molecule). When the micelle is differentiated as a single ion, the same surfactant dissociation reaction assumes the form

$$A = \sum_i \nu_i (1 - \alpha_i) A_i + (\nu_j \alpha_j / n_j) M, \quad (16)$$

where $\alpha_i = n_i c_M / \nu_i c$ is the degree of micellar aggregation of the ith ion (c_M is the concentration of micelles and c the overall concentration of the surfactant) and the subscript j can be assigned to any ion. By analogy with Eqn. (15), one can write for the mean activity coefficient

$$\ln f_\pm^* \equiv \sum_i (\nu_i/\nu^*)(1 - \alpha_i) \ln f_i + (\nu_j \alpha_j / \nu^* n_j) \ln f_M,$$
$$\nu^* \equiv \nu - \sum_i \nu_i \alpha_i + \nu_j \alpha_j / n_j. \quad (17)$$

The number of ions ν^* formed on dissociation of one molecule is now less than ν and the activity coefficients in Eqn. (17) have a different significance than in Eqn. (15). On the other hand, if the activity coefficients of the individual ions f_i defined by Eqns. (15) and (17) are set equal to one another, then Eqn. (15) yields the mean activity coefficient of the surfactant in the monomeric form. In fact, the micellar solution can be formally regarded as a solution of two electrolytes where the molecules of the first are identical with those of the surfactant and yield on dissociation ν monomeric ions, while those of the second are neutral micelles which split off counterions on dissociation. The mean activity coefficient of the first electrolyte is in fact the quantity $f_\pm$ defined by Eqn. (15) when the real activity coefficients f_i of the individual ions are substituted in it. However, this is not the quantity determined experimentally in accordance with the stoichiometry of Eqn. (14): according to Eqn. (17), the coefficients f_i refer to the real concentrations of the ions $c\nu_i(1-\alpha_i)$, while the experimental values usually refer to the stoichiometric concentrations $c\nu_i$. This increases each ionic coefficient by the factor $1-\alpha_i$ and, if the additional contribution of the micelles themselves is affected [in the region of existence of spherical micelles, the coefficient $\nu_j\alpha_j/n_j$ in Eqns. (16) and (17) is very small], the experimental mean activity coefficient of the surfactant in the micellar solution $f_\pm^e$ satisfies the condition

$$f_\pm^e = \prod_i [(1 - \alpha_i) f_i]^{\nu_i/\nu} \quad (18)$$

For a 1-1 electrolyte, Eqn. (18) can be written in the form[52]

$$f_\pm^e = [(1 - \alpha)(1 - \alpha\beta) f_1 f_2]^{1/2}, \quad (19)$$

where $\alpha \equiv \alpha_1$, $\beta \equiv \alpha_2/\alpha$ is the counterion binding coefficient, the subscript 1 corresponds to the surface-active ion, and 2 corresponds to the counterion.

It has been shown[52,53] that the Guggenheim–Pitzer method,[57,66,88] usually used for concentrated solutions of simple electrolytes, is applicable to the description of the activity coefficients in a micellar system. The expressions for the activity coefficients of ions and micelles of a 1 : 1 electrolyte assume the form

$$\ln f_1 = \ln f_{1D} + B_{1\gamma}(1 - \alpha\beta) c,$$
$$\ln f_2 = \ln f_{2D} + B_{1\gamma}(1 - \alpha) c + B_{n\gamma}\alpha c/n,$$
$$\ln f_M = n^2\delta^2 (1 - \beta)^2 \ln f_{MD} + B_{n\gamma}(1 - \alpha\beta) c, \quad (20)$$

where the terms B_{ik} are the parameters of specific ionic interactions (the surfactant concentration c is expressed on the molal scale) and f_{iD} is the Debye component of the activity coefficient specified by standard expressions of the theory of electrolyte solutions:

$$\ln f_{iD} = -A_\gamma I^{1/2}/(1 + b_i I^{1/2}), \quad (21)$$

$$I \equiv [2 - \alpha - \alpha\beta + n\delta^2 (1 - \beta)^2 \alpha] c/2, \quad (22)$$

where I is the ionic strength, A_γ and b_i are constants (it is often assumed that $b_1 = b_2 = b_M = 1$) and δ is the so called micelle charge shielding factor— is actually an adjustable parameter for the description of micelles within the framework of the Debye–Hückel theory (the values $\beta = 0.77$ and $\delta = 0.52$ were used by Burchfield and Woolley[52]). It follows from Eqn. (22) that, with a specified overall surfactant concentration, the ionic strength of the solution increases with increase in the content of micelles if $n > (1 + \beta)/\delta^2(1 - \beta)^2$, whilst otherwise it decreases. Comparison of the quantities obtained on substituting the parameters defined by formula (20) in Eqn. (19) with the experimental values of the mean activity coefficients both above and below the CCM[19,85,89] (it is also possible to compare the osmotic coefficients[52]) permits the determination of the coefficients $B_{1\gamma}$ and $B_{n\gamma}$ (in particular,

$B_{1\gamma} = B_{n\gamma} = 0$ has been found for SDS[52]) and hence one can calculate various thermodynamic characteristics of micelle formation.[52-55]

3. The micellar equilibrium. Expression for the law of mass action constant

The equilibrium condition

$$\sum_i n_i\mu_i = \mu_M. \qquad (23)$$

corresponds to the chemical reaction (1). It can be shown (see, for example, Kuni and Rusanov[90]) that condition (23) is strictly applicable only to the aggregation equilibrium. The entire difference consists in the fact that, at chemical equilibrium, the quantities n_i are strictly constant (they are stoichiometric coefficients), whilst at aggregation equilibrium they are generally speaking variable, since the average aggregation numbers depend on the parameters of state. On the other hand, if one uses not the average numbers but the distribution of the micelles with respect to size, then for each size one can assume that the numbers n_i are constant (determining the type of molecular or ionic aggregate) and one can consider the micellar equilibrium similarly to a multistep chemical equilibrium with participation of many intermediates (see the relevant reviews[91,92]). Condition (23) then makes it possible to find the equilibrium distribution of micelles with respect to size.[22] Within the framework of the monodisperse approach, the numbers n_i are variable but their dependence on the surfactant concentration is weak, so that over a limited concentration range, for example, in the region of existence of spherical micelles, the numbers can be regarded as approximately constant.

Substitution of Eqns. (9) and (11) in Eqn. (23) leads to the relation

$$a_M \Big/ \prod_i a_{i1}^{n_i} = \left(\prod_i \lambda_i^{3n_i}/\lambda_M^3\right) \exp\left[\left(\sum_i n_i g_i^0 - G_M^0\right)\Big/kT\right] \equiv K_a. \qquad (24)$$

For a specified temperature, pressure, solvent composition, and aggregation numbers, the right-hand side of Eqn. (24) is constant. the equation expresses the Law of Mass Action for the micelle formation process in terms of activities. If one goes over to the traditional formulation of the Law of Mass Action with a constant K_c, which is strictly speaking not constant and depends on the concentration, then Eqn. (24) becomes

$$c_M \Big/ \prod_i c_{i1}^{n_i} = K_a \prod_i f_{i1}^{n_i}/f_M \equiv K_c. \qquad (25)$$

The presence of the second subscript 1 in Eqn. (24) and (25) emphasises the fact that the activities, concentrations, and activity coefficients refer to monomeric ions and molecules in solution.

In Eqns. (24) and (25), the constants K_a and K_c are dimensional. In order to go over to dimensionless constants, we introduce, as in Eqn. (13), a standard concentration c_s, divide both sides of Eqn. (25) by $c_s/\prod_i c_s^{n_i}$, and put c_s = 1 M. Eqn. (25) then retains its form subject to the condition that all the concentrations are expressed on molar scale (in reality these are dimensionless quantities numerically equal to the molarities) and the constant K_a, which is now dimensionless, is defined by the expression

$$K_a \equiv \left(\prod_i c_s^{n_i}\lambda_i^{3n_i}/c_s\lambda_M^3\right) \exp\left[\left(\sum_i n_i g_i^0 - G_M^0\right)\Big/kT\right]. \qquad (26)$$

Since the quantities λ refer not to a mole but to an individual species, on substitution of the standard concentration c_s = 1 M in Eqn. (26), it must be expressed in terms of the number of species per unit volume (the Avogadro number in 1 dm^3). According to Eqn. (25), the quantities K_a and K_c differ from one another by a multiplier which includes the activity coefficients. Having determined this multiplier as described in the previous subsection, for example, with the aid of Eqns. (20), and knowing the value of K_c (usually determined from the CCM), it is possible to find the constant K_a.

Expressing the concentration of ions and micelles in terms of the overall surfactant concentration c taking into account the degrees of aggregation α_i and the stoichiometric coefficients ν_i (the subscript 1 is assigned to the surface-active ion), we obtain from Eqn. (25)

$$\ln K_c = \ln(\alpha_1\nu_1/n_1) + (1-n)\ln c - \sum_i n_i \ln \nu_i - \sum_i n_i \ln(1-\alpha_i) \qquad (27)$$

Since the overall aggregation number $n \equiv \sum_i n_i$ is large, the first term on the right-hand side of Eqn. (27) is small compared with the second. Near the CCM, where the degree of aggregation is several per cent, the last term is also small and both these terms may be neglected. The third term automatically becomes zero if the surfactant molecule gives rise to one ion of each kind on dissociation.

The first successes of the micelle formation theory[3-6] were associated with the application of the Law of Mass Action in its traditional form [Eqn. (25)] on the assumption that K_c = const. The activity coefficients are neglected also in modern theory (see, for example, Mijnlieff[93]). This is to some extent justified by the fact that, firstly, when one is dealing with small concentrations, the activity coefficients are close to unity and, secondly, the interaction of the dissolved species with one another, leading to the activity coefficients differing from unity, is in the case of micelle formation a preliminary and not a decisive factor (micelle formation is caused by the hydrophobic effect).

The quantity $-kT \ln K_\alpha$ yields the standard Gibbs free energy of micelle formation per micelle and the quantity

$$\Delta G_a = -(RT/n_1)\ln K_a \qquad (28)$$

is calculated per gram-ion of the surface-active ion with an aggregation number n_1. When K_a is replaced by K_c, the standard Gibbs free energy of micelle formation is defined as follows:

$$\Delta G_c = -(RT/n_1)\ln K_c \simeq (RTn/n_1)\ln c_m + RT\sum_i (n_i/n_1)\ln \nu_i, \qquad (29)$$

where c_m is the CCM. For 1–1 electrolytes, we have

$$\Delta G_c \simeq RT(1+\beta)\ln c_m. \qquad (30)$$

This is perhaps the most familiar relation of the thermodynamics of micelle formation. Some workers express the CCM in terms of the mole fraction x_m in the calculation of ΔG_c, but, since at low concentrations $x_m \simeq c_m/c_0$ (c_0 is the solvent concentration), in practice this means a change in ΔG_c by the constant quantity $RT(1+\beta)\ln c_0$. The different physical significance of the Gibbs free energy in Eqns. (28) and (29) must be emphasised. Whereas ΔG_a is the isothermal-isobaric work of formation of micelles from one mole of the surfactant in a unimolar ideal solution, ΔG_c is the same work subject to the condition that the unimolar solution is not ideal but is characterised by activity coefficients which correspond to the CCM in the real solution. It is seen from Eqn. (25) that, in contrast to K_a, K_c depends on the concentration and ΔG_c is therefore strictly speaking not a standard quantity.

The use of the stoichiometrically mean activity

$$a_{\pm}^{e} = \sum_{i} a_{i1}^{\nu_i/\nu} = f_{\pm}^{e} c \qquad (31)$$

in Eqn. (24) leads to the expression

$$\ln K_a \cong -(n_1\nu/\nu_1)\ln a_{\pm} + \sum_{i\geqslant 2}(n_1\nu_i/\nu_1 - n_i)\ln a_{i1} \qquad (32)$$

(the term $\ln a_M$ is neglected), whose substitution in Eqn. (28) affords

$$\Delta G_a/RT \cong (\nu/\nu_1)\ln a_{\pm} + \sum_{i\geqslant 2}(n_i/n_1 - \nu_i/\nu_1)\ln a_{i1}. \qquad (33)$$

The concept of the critical activity for micelle formation $a_{\pm m}^{\nu}$, corresponding to the CCM, was used by Nakagaki and Handa[94] and the following formula was proposed for the calculation of ΔG_a:

$$\Delta G_a/RT \simeq (\nu/\nu_1)\ln a_{\pm}, \qquad (34)$$

However, as can be seen from Eqns. (33) and (34), it is fairly approximate.

The coefficients of $\ln a_{i1}$ in Eqn. (33) (for a 1–1 electrolyte, these are the β–1 coefficients) must be zero for an electrically neutral micelle. An approximate electroneutrality is attained either at the concentration several orders of magnitude higher than the CCM (but it is then not permissible to neglect the term $\ln a_M$) or in the presence of an excess of an extraneous electrolyte. Nevertheless, it has been shown[94] that the use of Eqn. (34) yields somewhat better results than those obtained from Eqn. (29).

4. Dependence of the critical concentration for micelle formation on the length of the hydrocarbon chain of the surfactant molecule

We shall characterise the length of the hydrocarbon chain by the number of carbon atoms n_c. Since micelle formation is caused by the hydrophobic effect, the derivative $\partial\Delta G_a/\partial n_c$ (the hydrophobic effect per chain unit) must be approximately constant for a sufficiently long chain and the same for different surfactants. Near the CCM, a similar rule should hold also for the derivative $\partial\Delta G_c/\partial n_c$ and, according to Eqn. (29), also for the derivative $\partial \ln c_m/\partial n_c$, and the absolute value of the latter for surfactants which do not generate ions ($n = n_1$) should be greater by the factor n/n_1 (by the factor $1 + \beta$, i.e. 1.5–2, for a 1–1 electrolyte) than for ionic surfactants. In fact, experiment shows that the slopes of the $\lg c_m$–n_c curves for non-ionic and zwitter-ionic surfactants are almost the same and close to –0.5 (the slope is –0.517 for alkyl hexaethylene glycol ethers and –0.49 for n-alkylbetaines[94]). Although the $\lg c_m$–n_c relations do remain linear for ionic surfactants, their slope is appreciably smaller: it amounts to –0.29 for alkyltrimethylammonium bromides, –0.30 for sodium alkyl sulphates, –0.28 for sodium alkanecarboxylates,[95] and –0.25 for sodium alkyl phosphates[94] (the smaller slope, in absolute magnitude, for sodium alkyl phosphates is evidently associated with the higher value of β induced by the presence of the doubly charged ion). There exist analogous data also for other homologous series of ionic surfactants.[96]

Since the activity coefficients of non-ionic and zwitter-ionic surfactants at the CCM are virtually unity, the above slope (about –0.5) is characteristic also of the linear relation between $\lg a_m$ and n_c, where a_m is the critical activity for micelle formation. An analogous approach to ionic surfactants with $a_m \equiv a_{\pm m}^{\nu}$[94] made it possible to establish the following values of the derivatives $\partial \lg a_{\pm m}^{\nu}/\partial n_c$ for the above four homologous series: –0.54, –0.58, –0.52, and –0.50 respectively. The closeness of these values to –0.5, which is characteristic of other types of surfactants, confirms that the nature of the micelle formation is the same.

5. The influence of added electrolytes on the CCM

To make the treatment concrete, we shall consider cases where the extraneous electrolyte and the surfactant have a common ion which is a counterion for the micelle. In the presence of an excess of counterions, the micelle is almost electrically neutral, the second term on the right-hand sides of Eqns. (32) and (33) disappears, and condition (34) holds to a high degree of approximation. From Eqn. (32), we have

$$\ln a_{\pm}^{\nu} \simeq -(\nu_1/n_1)\ln K_a \equiv \text{const}. \qquad (35)$$

Suppose that the surfactant yields on dissociation only two kinds of ions ($i = 1, 2$, the subscript 1 corresponding to the surface-active ion and 2 to the counterion). On passing from the mean activities to the concentrations of the monomeric ions c_{11} and c_{21} in Eqn. (35), we obtain

$$\nu_1 \ln c_{11} + \nu_2 \ln c_{21} + \nu \ln f_{\pm} \cong -(\nu_1/n_1)\ln K_a. \qquad (36)$$

We apply this condition to the CCM. Substitution of $c_{11} \simeq c_m\nu_1$ and $c_{21} \simeq c_m\nu_2 + c'\nu_2'$ (the quantities referring to the extraneous electrolyte are designated by a prime) leads to the expression

$$\ln c_m + (\nu/\nu_1)\ln f_{\pm} \simeq -(\nu_2/\nu_1)\ln(c_m\nu_2 + c'\nu_2') - (1/\nu_1)\ln K_a - \ln\nu_1. \qquad (37)$$

Eqn. (37) indicates the dependence of the CCM for an ionic surfactant on the concentration of the extraneous electrolyte in the presence of a common ion. The left-hand side of Eqn. (37) is a linear function of $\ln(c_m\nu_2 + c'\nu_2')$, the slope of the straight line being determined by the coefficient $-\nu_2/\nu_1$. When Eqn. (37) was tested experimentally, the slopes of the linear relation proved to be –0.9 for SDS and potassium dodecanoate and –1.8 for sodium dodecyl phosphate[94] against the theoretical values of –1 and –2. Although a discrepancy, associated with some inaccuracy of Eqn. (37) itself, does exist, the ratio of the quantities obtained is as expected: in the presence of a doubly charged surface-active ion (dodecyl phosphate), the slope is twice as steep. We may note that, if no account is taken of the activity coefficient (as is usually in fact done), the dependence of $\ln c_m$ on $\ln(c_m\nu_2 + c'\nu_2')$, whilst remaining linear, ceases to correspond to the expected relation associated with the difference between the ionic charges. Thus the slope becomes –0.67 for SDS, –0.6 for potassium dodecanoate, and –0.9 for sodium dodecyl phosphate.[94]

6. Concentration of monomeric ions

The results of kinetic studies,[10] of direct measurements of activities by an e.m.f. method,[19] and of the determination of the self-diffusion coefficients[86,97] show that above the CCM the activity and concentration of the monomeric surface-active ions diminished after the addition of the surfactant to the solution. This finding, which appears at first sight to be improbable, is in reality thermodynamically legitimate and its prediction dates back to as early as 1935.[5] This theory has been formulated[41] within the framework of the electrostatic model, but, for the understanding of the essential feature of the problem, the general considerations associated with the Law of Mass Action are sufficient. As already mentioned in the Introduction, above the CCM the chemical potential and hence the mean activity of surfactants increase only slightly with increasing content of the surfactant in solution. This is consistent with the requirement for the thermodynamic stability of the solution but says nothing about the behaviour of the activities of

individual ions. We shall turn initially to the electroneutrality condition for a micellar solution:

$$c_M z_M = -\sum_i c_{i1} z_i, \tag{38}$$

where z_i is the charge of the monomeric ions and $z_M \equiv \sum_i n_i z_i$ is the charge of the micelle (the number of elementary charges). The overall charge of the micelles appears on the left-hand side of Eqn. (38), while the charge of the rest of the solution (we shall speak of the 'charge of the solution') is on the right-hand side. Surface-active ions predominate in the micelles and counterions predominate in the solution, so that the charges of the micelles and the solution have the opposite signs. However, condition (38) does not express this trivial fact alone. Since the number of micelles increases after the addition of the surfactant, there is a corresponding increase (in absolute magnitude) also in the charge of the solution and this means that the concentration of the monomeric counterions in the solution increases faster than the concentration of the monomeric surface-active ions. In order that the mean activity of the surfactant should increase with increase in its content, it is essential that the activity of at least one of the ions should increase and this ion is evidently the counterion.

In order to discover something about the surface-active ions, we turn to the Law of Mass Action in the form of Eqn. (24). Having first formulated the electroneutrality condition [Eqn. (38)] in terms of the activities, i.e.

$$a_M z_M / f_M = -\sum_i a_{i1} z_i / f_i, \tag{39}$$

and having eliminated a_M from Eqns. (24) and (39), we obtain

$$f_M \sum_i a_{i1} z_i / f_i = -z_M K_a \prod_i a_{i1}^{n_i} \tag{40}$$

or

$$\sum_i c_{i1} z_i = -z_M K_c \prod_i c_{i1}^{n_i}. \tag{41}$$

The activities of the monomeric ions a_{i1} appear on both sides of Eqn. (40), but, whereas the left-hand side depends only slightly on these quantities, on the right-hand side, where there are power functions with large power exponents, such dependence is very marked. Clearly Eqn. (40) cannot hold if all the activities vary in the same direction, i.e. if they all increase with increase in the overall surfactant concentration. A compensation effect on the right-hand side of Eqn. (40) is necessary—some of the activities must increase whilst others must decrease and, since we know that the activity of the counterions increases, then the activity of the surface-active ions must in fact decrease. Analogous reasoning is possible also in terms of Eqn. (41) for the concentration of the monomeric ions, assuming that the quantity K_c is a weak function of concentrations (with activity coefficients close to unity). Thus the conclusion that the concentrations and activities of the monomeric surface-active ions decrease above the CCM can be regarded as thermodynamically justified.

The foregoing can be illustrated by the simplest specific example. Assuming to a very rough approximation that

$$K_c = (n_1 + n_2) \ln c_m = \text{const},$$

and adopting $c_m = 8.3 \times 10^{-3}$, $n_1 = 65$, and $n_2 = 39$ (for $\beta = 0.6$[86]) for SDS, we obtain from Eqn. (41) the equation

$$\ln (c_2 - c_1) = 520.74 + 65 \ln c_1 + 39 \ln c_2, \tag{42}$$

from which it is possible to calculate the concentrations of the monomeric dodecyl sulphate ion (c_1), the monomeric sodium ion (c_2), and the micelles (c_M) as a function of the overall surfactant concentrations $c = c_1 + \nu_1 c_M = c_2 + \nu_2 c_M$. It is seen from Table 1 that the functions $c_2(c)$ and $c_M(c)$ increase monotonically over the entire concentration range, whereas the function $c_1(c)$ has a maximum near the CCM.

Table 1. The concentrations (10^{-3} M) of monomeric ions and micelles in aqueous sodium dodecyl sulphate solution calculated from Eqn. (42).

c	c_1	c_2	c_M
6.01	5.98	5.99	$3.85 \cdot 10^{-4}$
6.33	6.09	6.19	$3.85 \cdot 10^{-3}$
6.82	6.40	6.56	$6.46 \cdot 10^{-3}$
8.4	5.91	6.91	$3.85 \cdot 10^{-2}$
17.7	4.85	10	0.20
248	1.27	10^2	3.80

III. Thermodynamics of the micellar cell

The Gibbs free energy of the micelle G_M^0 with the centre of gravity at rest plays an important role in Eqns. (24) and (26) for the Law of Mass Action constant. We shall now proceed to its analysis. The quantity G_M^0 includes the work of introducing the micelle into the solution to which the energy changes not only in the micelle itself but also in the surrounding solution contribute. We shall therefore define the concept of the micellar cell as the combination of the micelle and its environment. In principle, the entire micellar solution, containing, apart from the differentiated micelle at rest, also other (moving) micelles, can be included in the micellar cell. The micellar cell is electrically neutral and represents an autonomous thermodynamic system which can be regarded as a two-phase system. The hydrocarbon (fluorocarbon) core of the micelle is usually regarded as the internal phase (α) while the solution surrounding the micelle is treated as the external phase (β), an interfacial tension σ being attributed to the interface between them containing the electrical double layer (EDL). The interfacial tension satisfies, as usual, the Laplace equation

$$p^\alpha - p^\beta = \sigma (c_1 + c_2), \tag{43}$$

where p is the pressure and c_1 and c_2 are the principal curvatures of the selected interface. We may note that in general the applicability of the macroscopic condition (43) to small objects such as micelles is not open to doubt only for spherical micelles (the mechanics of spherical micelles have been described in detail[98]). For micelles of more complex shape, there is a possibility of the appearance of anisotropy in the interfacial tension and of effects which are non-linear in terms of curvature. In the most general case, the Laplace equation can be replaced by the equation

$$p^\alpha - p^\beta = \sigma_1 c_1 + \sigma_2 c_2 + C_1 c_1^2 + C_2 c_2^2, \tag{44}$$

where σ_1 and σ_2 are the interfacial tensions along the principal

directions and C_1 and C_2 are certain coefficients. If the micelles are spherical ($\sigma_1 = \sigma_2$, $c_1 = c_2$, and $C_1 = C_2$), it is possible to eliminate the quadratic terms by selecting a special position on the interface, which Gibbs called the tension surface. The case of a cylindrical ($c_2 = 0$) micelle with spheroidal ends (in the mechanics of a cylindrical micelle, the interfacial tension is usually assumed to be isotropic)[99] is also favourable in this respect. However, in the very widely used ellipsoidal micelle model, the neglect of the quadratic terms in Eqn. (44) is hardly permissible.

1. Fundamental equations for the Gibbs free energy

For computational purposes, it is essential that the micelle at rest considered should be characterised by the same aggregation number as the moving micelles in the solution. However, the existence of the micelle in the state at rest cannot fail to affect its chemical potential and hence the fixation of the micelle displaces it from equilibrium with the solution. In studying the thermodynamics of a micellar cell, one should therefore make provision for the case where the micelle proper is not in diffusional equilibrium with the solution [the thermal and mechanical equilibria, defined by Eqn. (44), can be regarded as attained] and in essence plays the role of only a source of an external field in relation to its environment. In this case, the components of the micelle are formally segregated in a special group although they do consist of the same species as the solution. When account is taken of this factor, the joint formulation of the First and Second Laws of Thermodynamics leads to the following fundamental equations for the Gibbs free energy G of the micellar cell:

$$dG = -SdT + Vdp^{\beta} + \sum_i \mu_i dN_i + \sum_i \mu_i^0 dn_i, \tag{45}$$

$$G = -(p^{\alpha} - p^{\beta})V_M + \sigma A + \sum_i \mu_i N_i + \sum_i \mu_i^0 n_i, \tag{46}$$

where S is the entropy, T the temperature, and V the volume of the micellar cell, μ_i and μ_i^0 are the chemical potentials respectively in solution and in the micelle with the centre of gravity at rest, N_i is the number of species of the ith kind in the solution, n_i their aggregation number, A the area of the micelle interface, and V_M the volume which the interface encloses.

If the micelle is spherical, then condition (43) converts Eqn. (46) into the form

$$G = \sigma A/3 + \sum_i \mu_i N_i + \sum_i \mu_i^0 n_i. \tag{47}$$

Yet another equation (of the Gibbs–Duhem type) follows from a comparison of Eqn.s (47) and (45):[22]

$$d(\sigma A/3) = -SdT + Vdp^{\beta} - \sum_i N_i d\mu_i - \sum_i n_i d\mu_i^0. \tag{48}$$

Eqns. (45)–(48) refer to the micellar cell. We define the Gibbs free energy of the micelle proper by the equations

$$G_M^0 = G - \sum_i \mu_i N_i = \sigma A/3 + \sum_i \mu_i^0 n_i, \tag{49}$$

$$dG_M^0 = -SdT + Vdp^{\beta} - \sum_i N_i d\mu_i + \sum_i \mu_i^0 dn_i. \tag{50}$$

On subtracting the Gibbs–Duhem equation (51) for the solution (phase β)

$$0 = -S^{\beta}dT + V^{\beta}dp^{\beta} - \sum_i N_i^{\beta} d\mu_i \tag{51}$$

from Eqns. (50) and (48), we obtain the fundamental equations in terms of excess quantities:

$$dG_M^0 = -\bar{S}_M^0 dT + V_M dp^{\beta} - \sum_i \bar{N}_i d\mu_i + \sum_i \mu_i^0 dn_i, \tag{52}$$

$$d(\sigma A/3) = -\bar{S}_M^0 dT + V_M dp^{\beta} - \sum_i \bar{N}_i d\mu_i - \sum_i n_i d\mu_i^0, \tag{53}$$

where $\bar{S}_M^0 \equiv S - S^{\beta} = S_M^0 + \bar{S}$ includes the entropy of the micelle S_M^0 and the excess entropy $\bar{S}$ contributed by the solution and $\bar{N}_i$ is the excess number of species of the ith kind at the surface of the micelle. By analogy with $\bar{S}_M^0$, it is possible to introduce a quantity G_M^0 intermediate between G[Eqn. (47)] and G_M^0 [Eqn. (49)]:

$$\bar{G}_M^0 = G_M^0 + \bar{G} = \sigma A/3 + \sum_i \mu_i \bar{N}_i + \sum_i \mu_i^0 n_i \tag{54}$$

and to formulate the fundamental equation

$$d\bar{G}_M^0 = -\bar{S}_M^0 dT + V_M dp^{\beta} + \sum_i \mu_i d\bar{N}_i + \sum_i \mu_i^0 dn_i. \tag{55}$$

The excess quantities $\bar{G}$, $\bar{S}$, and $\bar{N}_i$ are associated with the fact that the structure of the solution changes near the micelle. Statistical mechanics yields the following useful relations for the quantity $\bar{N}_i$:

$$(\bar{N}_i + \delta_{iM})/kT = \partial \ln c_M/\partial \mu_i = \partial c_i/c_M \partial \mu_M, \tag{56}$$

where c is the concentration and δ_{iM} the Kronecker symbol (the case $i = M$ corresponds to the distribution of mobile micelles in the field of th micelle at rest).

The fundamental equations for the internal energy ($U = G + TS - p^{\beta}V$), the [Helmholtz] free energy ($F = G - p^{\beta}V$), the enthalpy ($H = G + TS$), and the grand thermodynamic potential

$$\left(\Omega = G - p^{\beta}V - \sum_i \mu_i N_i\right)$$

of the micellar cell, can be readily obtained from the above equations for the Gibbs free energy.

2. Thermodynamics of the charging of the micellar cell

A characteristic feature of the ionic micellar cell is the presence of the ionic EDL and of a Coulombic contribution to the Gibbs free energy. There exist different methods for estimating the contribution. The commonest is the artificial procedure, proposed by Debye, involving the imaginary charging of the ion (for a more detailed description, see Deryagin[56]). If for a specified number of ions the charges of the latter $e\xi_i$ can be varied smoothly (from zero to ez_i), new variables ξ_i appear in eqns. (45), (48), (50), (52), (53) and (55) together with the additional term (on the right-hand side)

$$e\sum_i (N_i + n_i)\varphi_i d\xi_i, \tag{57}$$

where φ_i is the average electrical potential generated by all the ions in the system with the exception of one ion of the ith kind. In an inhomogeneous system, like the micellar cell, we have

$$\varphi_i = (N_i + n_i)^{-1} \int\int\int \varphi_i(\mathbf{r})\, c_i(\mathbf{r})\, d\mathbf{r}, \tag{58}$$

where $\varphi_i(\mathbf{r})$ is the average force potential generated by all the ions except one ion of the ith kind at the point $\mathbf{r}$ in space and $c_i(\mathbf{r})$ is the local concentration of ions of the ith kind; the integration is carried out over the entire volume of the system.

A similar additional term [formula (57)] appears in the fundamental equations for the energy, the [Helmholtz] free energy, the

enthalpy, and the grand thermodynamic potential. The work of charging the micellar cell is found by integrating Eqns. (45), (52), and others for fixed characteristic variables:

$$(\Delta G^{el})_{T,p^{\beta},N_i,n_i} = (\Delta G^{el}_{M})_{T,p^{\beta},\mu_i,n_i} =$$
$$= (\Delta U^{el})_{S,V,N_i,n_i} = (\Delta F^{el})_{T,V,N_i,n_i} =$$
$$= (\Delta H^{el})_{S,p^{\beta},N_i,n_i} = (\Delta \Omega^{el})_{T,V,\mu_i,n_i} =$$
$$= e\sum_i (N_i + n_i)\int_0^{z_i} \varphi_i d\xi_i. \qquad (59)$$

Here the symbol Δ denotes the change in the corresponding thermodynamic function and the superscript *el* shows that the change is due to the appearance of electrical charges. A chain of equations (59) naturally does not imply that the electrical contributions to different thermodynamic functions are always the same: they are the same under different external conditions and therefore differ under the same conditions. Thus under isothermal conditions we have

$$\Delta U = \Delta F + T\Delta S \qquad (60)$$

and, whereas ΔF is specified by Eqn. (59), ΔU now has a different value. Here it is appropriate to point out a common error in the use of Eqn. (60) for the calculation of the electrostatic contribution to the [Helmholtz] free energy: it is assumed that the Coulombic energy (apparently the very term provokes an error) is always ΔU and ΔF is found by substituting ΔU in Eqn. (60). Nevertheless, the Coulombic energy [the right-hand side of Eqn. (59)] is equal to the energy change ΔU only for an isentropic charging process, while Eqn. (60) is isothermal and one cannot substitute in it ΔU defined by Eqn. (59). When Eqn. (60) is used correctly, the Coulombic energy is set equal not to ΔU but to ΔF and substitution of ΔF, defined by Eqn. (59), makes it possible to calculate by this formula the unknown value of ΔU for the isothermal charging process (naturally provided that ΔS is known).

An analogous comment can also be made concerning the Gibbs–Helmholtz equation:

$$\Delta U = d(\Delta F/T)/d(1/T), \qquad (61)$$

which follows from Eqn. (60), provided that account is taken of the thermodynamic relation

$$\Delta S = -\partial \Delta F/\partial T. \qquad (62)$$

Integration of Eqn. (61) yields

$$\Delta F = T\int_0^{1/T} \Delta U d(1/T). \qquad (63)$$

The use of Eqn. (63) for the calculation of the electrostatic contribution to the [Helmholtz] free energy (see, for example, the study of Jönsson and Wennerström[42]) would be significant if the isothermal contribution to the energy were known [as in the initial formula (60), ΔU in Eqns. (61) and (63) refers to an isothermal process], but Eqn. (59) does not allow the determination of these contributions. Thus it must be recognised that Eqns. (60) and (63) are relatively unsuitable for the calculation of the electrostatic [Helmholtz] free energy ΔF^{el} (for condensed phases, $\Delta F^{el} \simeq \Delta G^{el}$). Furthermore, there is no need for them, since the quantities ΔF^{el} and ΔG^{el} can be determined directly from Eqn. (59).

Eqns. (59) yield the total change in the thermodynamic functions during the charging process with allowance for all possible concomitant phenomana (solvent polarisation, changes in the steric structure of the system, etc.). If the distribution in space of all the charged species, and not only the micelle ions (we recall that a micelle is in a state of rest), had been kept unchanged during such a process, then, by virtue of the linear relation between φ_i and ξ_i, the right-hand side of Eqn. (59) would have been determined by the elementary electrostatic relation

$$e\sum_i (N_i + n_i)\int_0^{z_i} \varphi_i d\xi_i = (e/2)\sum_i (N_i + n_i)\varphi_i z_i =$$
$$= (1/2)\iiint \sum_i \varphi_i(\mathbf{r})\rho_i(\mathbf{r})\,d\mathbf{r}, \qquad (64)$$

in which Eqn. (58) and the quantity $\rho_i(\mathbf{r}) = ez_i c_i(\mathbf{r})$—the local charge density generated by ions of the ith kind—are used. In fact, however, the positions of the ions change during the charging process and the linear relation between φ_i and ξ_i is lost. There are also other difficulties which preclude the calculation of the right-hand side of Eqn. (59) in a general form. A number of artificial procedures and approximations, to which we shall now turn, make it possible to obtain simpler expressions for the electrostatic component of the thermodynamic functions (to make the treatment concrete, we shall consider the Gibbs free energy).

3. A two-stage charging process

We imagine that the charging process is divided into two stages. We assume that initially, before charging, an amount of work ΔG_0 was performed under isothermal-isobaric conditions to achieve a reversible rearrangement of the system to the situation which corresponds to the final state of equilibrium in the presence of charges on the species. In the second stage, the charging of the species takes place for their specified distribution in space. The work of the second stage is defined by Eqn. (64) and one can then write

$$\Delta G^{el} = \Delta G_0 + (1/2)\iiint \sum_i \varphi_i(\mathbf{r})\rho_i(\mathbf{r})\,d\mathbf{r} \qquad (65)$$

(here and henceforth the subscripts to ΔG^{el} will be omitted).

For a spherical micelle, the use of Eqn. (47) and the change to spherical coordinates permit the formulation

$$\Delta G^{el} = \Delta(\sigma A/3)^{el} + \sum_i N_i \Delta\mu_i^{el} + \sum_i n_i (\Delta\mu_i^{0})^{el} \qquad (66)$$

or, when account is taken of Eqn. (65),

$$\Delta G^{el} = \Delta(\sigma A/3)_0 + \sum_i N_i(\Delta\mu_i)_0 + \sum_i n_i(\Delta\mu_i^{0})_0 +$$
$$+ 2\pi\int_0^R \sum_i \varphi_i(r)\rho_i(r)\,r^2 dr, \qquad (67)$$

where R is the radius of the micellar cell in its "charged" state (for $r = R$, there exists a virtually homogeneous phase β). The quantity

$$(\Delta\mu_i)_0 = (4\pi/N_i)\int_0^R \Delta\mu_i(r)\,c_i(r)\,r^2 dr \qquad (68)$$

has the significance of the average change in the chemical potential of the species of the ith kind, since in the first stage the rearrangement links the system to a non-equilibrium state (for this reason, $\Delta G_0 > 0$), while the chemical potential has different values at different points.

According to Eqn. (13),

$$\Delta\mu_i(r) = kT\ln[c_i(r)/c_{i0}(r)] + kT\Delta\ln f_{i0}(r), \qquad (69)$$

where the subscript 0 indicates the absence of charge. Whereas the concentration components of $\Delta\mu_i(\mathbf{r})$ and $\Delta\mu_i^{el}$ at the specified point

in space are the same, the force components are significantly different. Unspecified dispersion forces, whose overall balance is relatively insensitive to the position of the species in solution, contribute to the quantities $\Delta \ln f_{i0}(r)$ and $\Delta(\sigma A/3)_0$, while the main force contribution to the quantities $\Delta\mu_i^{el}$ and $\Delta(\sigma A/3)^{el}$ comes from the strong Coulombic interactions (one can easily imagine that $\Delta\mu_i^{el} > 0$ and $\Delta(\sigma A/3)^{el} < 0$). The approximation

$$|kT\,\Delta \ln f_{i0}(r)| \ll \Delta\mu_i^{el},\ |\Delta(\sigma A/3)_0| \ll |\Delta(\sigma A/3)^{el}|, \tag{70}$$

is suggested, and, when it is valid, Eqn. (67) reduces to the form

$$\Delta G^{el} \cong 4\pi kT \sum_i \int_0^R c_i(r) \ln [c_i(r)/c_{i0}(r)]\, r^2 dr + 2\pi \int_0^R \sum_i \varphi_i(r)\rho_i(r)\, r^2 dr. \tag{71}$$

4. The average field approximation

In order to evaluate the integral in Eqn. (71), one must know the functions $\varphi_i(r)$ and $\rho_i(r)$, the determination of which constitutes an extremely complex electrostatic problem. Even for homogeneous solution, it cannot be regarded as solved. In the modern versions of the Debye–Hückel theory, the quantity φ_i is calculated for low concentrations as the potential generated by the ionic atmosphere around the specified ion with the centre of gravity at rest. Account is thereby taken approximately of the two-particle correlations of the ions in the solution. However, the system which we shall be examining is much more complex. At the centre of the micellar cell, we have the micelle with the centre of gravity at rest, which generates a field in which the ions of the micellar cell, forming the ionic atmosphere of the micelle, move. If one imagines that one of these ions has been stopped and the potential generated by the ionic cloud is sought, then in essence this implies allowance for three-particle correlations with participation of the micelle. Here a reasonable approximation involves the neglect of the correlations of the ions in the strong field of the micelle, i.e. the neglect of the perturbation of the ionic atmosphere of the micelle arising as a result of the arrest of one of the ions. In terms of this approximation, the potential $\varphi_i(r)$ is replaced by the average potential $\varphi(r)$ generated by all the ions of the micellar cell without exception. The potential $\varphi(r)$ "no longer senses" the individual components of the system and in the summation with respect to i is taken outside the summation sign.

In terms of the approximation indicated, Eqn. (59) for ΔG^{el} assumes the form

$$\Delta G^{el} \approx 4\pi e \sum_i \int_0^{z_i} d\xi_i \int_0^R \varphi(r)\, c_i(r)\, r^2 dr = = 4\pi \int_0^1 (d\lambda/\lambda) \int_0^R \varphi(r,\lambda)\,\rho(r,\lambda)\, r^2 dr, \tag{72}$$

where $\lambda \equiv \xi_i/z_i$ is the Debye parameter of the "switching on" of the charge ($0 \leqslant l \leqslant 1$) and $\rho(r,\lambda) \equiv \sum \xi_i c_i(r,\lambda)$ is the variable charge density. The formulation of Eqn. (71) is simplified correspondingly:

$$\Delta G^{el} \cong 4\pi kT \sum_i \int_0^R c_i(r) \ln [c_i(r)/c_{i0}(r)]\, r^2 dr + 2\pi \int_0^R \varphi(r)\rho(r)\, r^2 dr, \tag{73}$$

where $c_i(r)$, $\varphi(r)$, and $\rho(r)$ correspond to $\lambda = 1$. As can be seen from Eqn. (73), by virtue of the electroneutrality of the micellar cell, the potential $\varphi(r)$ is determined to within an arbitrary constant—it is usually reckoned from the value of φ^β in the bulk phase β. We may note that the transition to the average potential immediately converts ΔG^{el} into an excess quantity, since in the bulk phase the integrand expression now becomes zero. For this reason, one can put $R = \infty$ in Eqns. (72) and (73).

5. The switching on of the hydrophobic interaction

Eqns. (72) and (73) have been derived by the method involving the imaginary charging of ions in the presence of a complete micelle. Since micelles exist by virtue of the hydrophobic effect, one may say that we have "switched on" the charge for a constant hydrophobic interaction. Conversely, we shall now try to achieve the imaginary "switching on" of the hydrophobic interaction for a constant ionic charge so that the ions gradually pass from the solution to the micelle. Although the charges of the ions themselves remain unchanged in this process, the charge on the micelle gradually increases and the same work which we calculated by the ion charging method is expended on the formation of the EDL.

If the assembly of the micelle from the ions of the solution proceeds with a constant overall number of ions, then, according to Eqn. (45),

$$(dG)_{T,p^\beta,N_i+n_i} = \sum_i (\mu_i^0 - \mu_i)\, dn_i, \tag{74}$$

and if it takes place for constant chemical potentials of the solution, then, according to Eqn. (50),

$$(dG_M^0)_{T,p^\beta,\mu_i} = \sum_i \mu_i^0 dn_i. \tag{75}$$

In terms of the average field potential, where the electrical component of the electrochemical potential is represented approximately by the term $ez_i\varphi$, the electrostatic contributions on the right-hand sides of Eqns. (74) and (75) are the same, since the bulk phase β, to which μ_i refers, does not participate in these contributions by virtue of its electroneutrality. Assuming now that

$$\sum_i (\mu_i^0 - \mu_i)^{el} dn_i \simeq \sum_i (\mu_i^0)^{el} dn_i \simeq \approx e \sum_i z_i \varphi_M dn_i = \varphi_M dq_M, \tag{76}$$

where φ_M and q_M are respectively the average potential and the charge of the micelle, we obtain, after integrating Eqns. (74) and (75),

$$(\Delta G^{el})_{T,p^\beta,N_i+n_i} = (\Delta G_M^{el})_{T,p^\beta,\mu_i} = = (\Delta U^{el})_{S,V,N_i+n_i} = (\Delta F^{el})_{T,V,N_i+n_i} = = (\Delta H^{el})_{S,p^\beta,N_i+n_i} = (\Delta\Omega^{el})_{T,V,\mu_i} \cong \int_0^{q_M} \varphi_M dq_M. \tag{77}$$

An expression of this type for the [Helmholtz] free energy of a charged colloidal particle was proposed previously by Deryagin.[56,100] If the micelle has a single-layer charge and φ_M is identical with the potential φ_l of the surface of a micelle with a radius l, then the right-hand side of Eqn. (77) can be transformed into[56]

$$\int_0^{q_M} \varphi_1 dq_M = (1/2) \int_l^\infty \varepsilon (rd\varphi/dr)^2 dr - 4\pi \int_0^\rho d\rho \int_l^\infty \varphi(r)\, r^2 dr. \tag{78}$$

In the general case of a complex charge structure of the micelle, we have

$$\varphi_M = (1/q_M) \int_l^{l+\delta} \varphi(r)\,\rho(r)\, r^2 dr, \tag{79}$$

where δ is the thickness of the charged layer. For a two-layer charge on spheres with radii l and $l + \delta$, one can write for the

average potential of the micelle

$$\varphi_M = (\varphi_1 q_1 + \varphi_2 q_2)/(q_1 + q_2), \quad (80)$$

where the subscripts 1 and 2 refer to the coordinates l and $l + \delta$ respectively.

IV. Model calculations of the electrostatic contribution to the Gibbs free energy of the micellar cell

Eqns. (72), (73), and (77) provide three ways of calculating the electrostatic contribution to the Gibbs free energy of the micellar cell, but, in order to be able to use them, one must know the functions $\varphi(r)$ and $\rho(r)$. The relation between them is given by the Poisson equation, which assumes the following form for a spherically symmetrical system:

$$(\varepsilon_0/r^2)\, d\,(r^2 \varepsilon d\varphi/dr)/dr = -\rho = -e \sum_i z_i c_i, \quad (81)$$

where $\varepsilon = \varepsilon(r)$ is the dielectric constant and ε_0 the electrical constant (permittivity). However, the functions $\varphi(r)$ and $\rho(r)$ themselves are not then determined. In order to find them, one must have at least one other relation or one must specify the functions $c_i = c_i(r)$ and hence $\rho(r)$ in an explicit form. This is done in model approaches to the consideration of which we shall now proceed.

1. Static models

In static models, the distribution of ions in space is assumed to be specified and constant. In this case Eqns. (72) and (73) become identical:

$$\Delta G^{el} \simeq 2\pi \int_0^R \varphi(r)\, \rho(r)\, r^2 dr, \quad (82)$$

and, bearing in mind the proportionality between the charge and potential characteristic of static models, Eqn. (77) can be written in the form

$$\Delta G^{el} \cong \varphi_M q_M/2, \quad (83)$$

which is equivalent to Eqn. (82).

As an example, we shall consider the spherical condenser model. If the charges are distributed in the form of two oppositely charged thin concentric layers with radii l and $l + \delta$, it follows from Eqns. (82) and (83) that

$$\Delta G^{el} \cong (q_1^2/8\pi\varepsilon_0\varepsilon)\,[1/l - 1/(l+\delta)], \quad (84)$$

where q_1 is the charge of the primary plate. For ionic micelles, Eqn. (84) is naturally too rough, but it can constitute a satisfactory approximation for non-ionic micelles with a dipolar EDL. Then $q_1 = \sum_i n_i D_i/\delta_i$, where D_i and δ_i are the dipole moment and the distance between the centres of the opposite charges of the dipole of the ith kind respectively. The spherical condenser model is satisfactorily applicable to zwitter-ionic surfactants. The opposite charges in their molecules are separated from one other and a distinct spherical condenser is created in the micelles with an energy close to that of ionic micelles.

The determination of the effective dielectric constant in the dipolar ELD constitutes an interesting problem. Water molecules naturally cannot become wedged between the charges of the same dipole but they can enter the EDL—can be located between the dipoles. Their presence influences the capacitance of the dipolar condenser, so that the dielectric constant ε retains its significance. The attempt to estimate this quantity by the spectral probe method, i.e. by introducing into the micelles small amounts of added substances (for example, dodecypyridinium iodide), whose spectra are sensitive to the polarity of the medium, led to the following values of ε:- $\varepsilon = 46$ for octyl β-D-glucoside $C_8H_{17}OCHC_5H_{10}O_5$, $\varepsilon = 36$ for the dodecyl ether of tricosaethylene glycol $C_{12}H_{25}.(OCH_2CH_2)_{23}OH$, and $\varepsilon = 37$ for *N*-dodecylbetaine $C_{12}H_{25}N^+.(CH_3)_2CH_2COO^-$.[82]

When applied to an ionic micelle, Eqn. (84) corresponds to the model with total binding of the counterions ($\beta = 1$). We obtain $\Delta G^{el}/nkT \simeq 2.2$ for SDS with $n = 56$, $T = 293$ K, $\varepsilon = 80$, $l = 1.97$ nm, and $\delta = 0.55$ nm (diameter of the hydrated sodium ion). The opposite case is represented by the model in which there is no binding of the counterions ($\beta = 0$). With the aid of this simplest and most approximate for the models, which, however, is used for calculations (see, for example, Eriksson et al.[101]) we obtain $\Delta G^{el}/nkT \simeq 10.2$ for SDS having assumed that $\delta = \infty$ in Eqn. (84). Since the real distribution of ions in the EDL is intermediate between these cases, the first and second models yield electrostatic contributions to the Gibbs free energy which are respectively too low and too high. More accurate values are obtained using the Boltzmann distribution.

2. The linearised Poisson–Boltzmann equation

As an additional equation relating φ and c_i, which enter into the Poisson equation (81), the Boltzmann formula is normally employed, i.e.

$$c_i(r) = c_i^{\beta} \exp[-ez_i\varphi(r)/kT], \quad (85)$$

which follows from the equilibrium condition $\mu_i(r) = \text{const.}$ [see Eqn. (9)] for

$$w_i + kT \ln f_i \cong ez_i\varphi.$$

In static mechanics, the Boltzmann formula can be rigorously justified only for low concentrations when the average energy of the Coulombic interaction of the species is much smaller than kT and only the first term of the series expansion of the exponential function on the right-hand side of Eqn. (85) need be retained:

$$c_i(r) = c_i^{\beta}[1 - ez_i\varphi(r)/kT]. \quad (86)$$

Substitution of Eqn. (86) in Eqn. (81) yields the linearised Poisson–Boltzmann equation

$$(\varepsilon_0/r^2)\, d\,(r^2 \varepsilon d\varphi/dr)/dr = \varphi e^2 \sum_i c_i^{\beta} z_i^2/kT, \quad (87)$$

from the solution of which for a specified function $\varepsilon(r)$ it is possible to find the distribution of the potential φ in the micellar cell. It is usually assumed that $\varepsilon = \text{const.}$ and Eqn. (87) is written in the form

$$(1/r^2)\, d\,(r^2 d\varphi/dr)/dr = \varphi\left[e^2 \sum_i c_i^{\beta} z_i^2/\varepsilon_0 \varepsilon kT\right] \equiv \varphi/\delta_D^2, \quad (88)$$

where δ_D is the Debye radius. The solution of Eqn. (88) for the micellar cell represents a trivial repetition of the Debye–Hückel theory. The final result depends on the part of the counterions and the part of the space of the micellar cell to which the Boltzmann formula is applied. We shall consider three cases.

Case 1. The Boltzmann formula is applied to the entire space with the exception of the primary core of the micelle with the charge q_1 localised on a sphere with a radius l. Then, according to the Debye–Hückel theory, we have

$$\varphi(r) = \varphi_1 \equiv \varphi(l) = q_1\delta_D/4\pi\varepsilon_0\varepsilon l(l+\delta_D), \quad (89)$$

for $r \leqslant l$ and

$$\varphi(r) = [q_1\delta_D/4\pi\varepsilon_0\varepsilon(l+\delta_D)\,r]\exp[-(r-l)/\delta_D], \quad (90)$$

for $r \geqslant l$;

$$\rho(r) = -\varepsilon_0\varepsilon\varphi(r)/\delta_D^2. \quad (91)$$

The charge q_1 is generated either by the surface-active ions of the micelle alone or jointly by the latter with the bound counterions. the latter situation is apparently a characteristic of spherical micelles in which the packing of the functional groups is least dense compared with micelles of other shapes and leaves room for the permeation of counterions.[102]

It is simplest to use Eqn. (77) for the calculation of ΔG^{el} with $q_M = q_1$ and $\varphi_M = \varphi_1$, for which it is necessary to know only φ_1 determined from Eqn. (89). Since according to Eqn. (89) φ_1 and q_1 are proportional to each other, we obtain

$$\Delta G^{el} \cong \int_0^{q_1} \varphi_1 dq_1 = \varphi_1 q_1/2 = (q_1^2/8\pi\varepsilon_0\varepsilon)\,[1/l - 1/(l+\delta_D)]. \quad (92)$$

From Eqn. (72), the same result can be arrived at by a much longer procedure.[103] The analogy between Eqns. (92) and (84) shows that, in the model described by the linearised Poisson–Boltzmann equation, the diffuse part of the EDL can be effectively reduced to the dense outer plate of a spherical condenser. For SDS ($n = 56$, $l = 1.97$ nm, $\delta_D = 3.33$ nm at the CCM, $T = 293$ K), we obtain $\Delta G^{el}/nkT \simeq 509/\varepsilon$ on the assumption that the counterions are not involved in the generation of the charge ($q_1 = -en$), which yields $\Delta G^{el}/nkT \simeq 6.36$ for $\varepsilon = 80$. On the other hand, if all the bound counterions also contribute to q_1 [$q_1 = -en(1-\beta)$], we have $\Delta G^{el}/nkT \simeq 1$ (evidently this is the smallest value for the given model) for $\beta = 0.6$[86] and $\varepsilon = 80$.

Case 2. The Boltzmann formula is applied starting with a distance $l + \delta_1$ from the centre of the micellar cell, although the primary charge is again on a sphere with a radius l. The parameter δ_1 has the significance of the distance of closest approach of free counterions (the bound counterions can be located on a sphere with a radius l). Evidently Eqn. (90) remains in force but l is replaced by $l + \delta_1$. The electrostatic contribution to the Gibbs free energy is correspondingly given by the expression[45]

$$\Delta G^{el} \simeq (q_1^2/8\pi\varepsilon_0\varepsilon)\,[1/l - 1/(l+\delta_1+\delta_D)], \quad (93)$$

which differs trivially from Eqn. (92) by the shift of the outer plate of the condenser by a distance δ_1.

Case 3. The Boltzmann formula is again applied starting with the distance $l + \delta_1$ but under conditions where the bound counterions can also be located in the second layer of charges. In the two-layer model, $q_M = q_1 + q_2$ and φ_M is specified by Eqn. (80). The surface potential of the micelle (this is now φ_2) is specified by the right-hand side of Eqn. (89) with l replaced by $l + \delta_1$ and q_1 replaced by q_M. We obtain accordingly

$$\varphi_M = q_1^2\delta_1/4\pi\varepsilon_0\varepsilon_1 q_M l(l+\delta_1) + q_M\delta_D/4\pi\varepsilon_0\varepsilon(l+\delta_1)(l+\delta_1+\delta_D), \quad (94)$$

where ε_1 is the effective dielectric constant in the $l \leqslant r \leqslant l + \delta_1$ layer. Hence

$$\Delta G^{el} \simeq \frac{\varphi_M q_M}{2} = \frac{q_1^2}{8\pi\varepsilon_0\varepsilon_1}\left(\frac{1}{l} - \frac{1}{l+\delta_1}\right) + \frac{q_M^2}{8\pi\varepsilon_0\varepsilon}\left(\frac{1}{l+\delta_1} - \frac{1}{l+\delta_1+\delta_D}\right). \quad (95)$$

In this case ΔG^{el} is interpreted as the electrical energy of two condensers with the charges $\pm q_1$ and $\pm q_M$ on their plates. Formulae for more complex micellar structures can be obtained analogously.

3. The non-linearised Poisson–Boltzmann equation

Substitution of Eqn. (85) in Eqn. (81) yields the non-linearised Poisson–Boltzmann equation

$$(\varepsilon_0/r^2)\,d(r^2\varepsilon d\varphi/dr)/dr = -e\sum_i z_i c_i^\beta \exp[-ez_i\varphi/kT]. \quad (96)$$

Sufficiently accurate solutions of this equation can be achieved by numerical methods (the details of the calculations can be found in a number of communications[35,41,67,68,104]), but if one is interested not in the detailed description of the EDL of the micellar cell but only in its energy relations (which in fact control the micelle formation process), then, with the aid of the non-linearised Poisson–Boltzmann equation (96) with ε = const., it is possible to transform Eqn. (73) into a form which does not require the knowledge of the entire function $\varphi(r)$. Since the Boltzmann formula is inapplicable to the central part of the micellar cell, we shall divide the integration region in Eqn. (73) into two parts: from zero to $l + \delta_1$ and from $l + \delta_1$ to R. The contribution to the first integral by the region $r < l + \delta_1$ will be neglected, since the change in concentration in it can be associated solely with the volume charging effect, which we shall assume to be small. The rest of the first integral in eqn. (73) will be formulated using Eqn. (85) as follows (assuming that $R = \infty$):

$$kT\int_{l+\delta_1}^{\infty}\sum_i c_i(r)\ln[c_i(r)/c_i^\beta]\,r^2dr = -\int_{l+\delta_1}^{\infty}\varphi(r)\rho(r)\,r^2dr, \quad (97)$$

after which Eqn. (73) assumes the form

$$\Delta G^{el} \cong 2\pi\int_0^{l+\delta_1}\varphi(r)\rho(r)\,r^2dr - 2\pi\int_{l+\delta_1}^{\infty}\varphi(r)\rho(r)\,r^2dr. \quad (98)$$

The first term will be estimated, in conformity with Eqn. (79), as $\varphi_M q_M/2$, which can be calculated by the following procedure.[41] We multiply both sides of Eqn. (96) by $r^3 d\varphi/dr$ and write their integrals in the form

$$\frac{\varepsilon_0}{2}\int_{r=l+\delta_1}^{r=\infty}\frac{1}{\varepsilon r}\,d\left(\varepsilon r^2\frac{d\varphi}{dr}\right)^2 = kT\sum_i c_i^\beta\int_{r=l+\delta_1}^{r=\infty} r^3 d[\exp(-ez_i\varphi/kT)]. \quad (99)$$

Integration by parts, taking into account the boundary condition $d\varphi/dr = -q_M/4\pi\varepsilon_0\varepsilon_1(l+\delta_1)^2$ with $r = l + \delta_1$ and $\varphi = 0$, $d\varphi/dr = 0$, $r^2 d\varphi/dr = 0$, and $r^3\varphi = 0$ for $r = \infty$ yields

$$-q_M^2/8\pi\varepsilon_0\varepsilon_1(l+\delta_1) + 2\pi\varepsilon_0\int_{r=l+\delta_1}^{r=\infty}(rd\varphi/dr)^2\,d(\varepsilon r) =$$

$$= -3kT\sum_i\{V_M[c_i(l+\delta_1) - c_i^\beta] + \overline{N}_i\}, \quad (100)$$

where $V_M \equiv (4\pi/3)(l+\delta_1)^3$ and $\overline{N}_i$ is the excess (relative to the bulk phase β) number of ions of the ith kind in the diffuse plate of the

EDL:

$$\bar{N}_i = 4\pi \int_{l+\delta_1}^{\infty} (c_i - c_i^{\beta}) r^2 dr. \quad (101)$$

The relation between the second integral in Eqn. (98) and the integral in Eqn. (100) is found by integration by parts using the Poisson equation (81):

$$2\pi \int_{l+\delta_1}^{\infty} \varphi\rho r^2 dr = -\varphi(l+\delta_1) q_M/2 + 2\pi\varepsilon_0 \int_{l+\delta_1}^{\infty} \varepsilon (rd\varphi/dr)^2 dr. \quad (102)$$

If it is assumed that, when $r > l + \delta_1$, the dielectric constant assumes a constant value, then the integrals in Eqn. (100) and on the right-hand side of Eqn. (102) become identical. On substituting Eqns. (100) and (102) in Eqn. (98), we then obtain

$$\Delta G^{el} \cong \varphi_M q_M/2 + \varphi(l+\delta_1) q_M/2 - q_M^2/8\pi\varepsilon_0\varepsilon_1 (l+\delta_1) + 3kT \sum_i \{V_M [c_i (l+\delta_1) - c_i^{\beta}] + \bar{N}_i\}. \quad (103)$$

In the special case where the micelle has a single-layer charge [$\delta_1 = 0$, $q_M = q_1$, and $\varphi_M = \varphi(l) \equiv \varphi_1$], we have

$$\Delta G^{el} \cong \varphi_1 q_1 - q_1^2/8\pi\varepsilon_0\varepsilon_1 l + 3kT \sum_i \{V_M [c_i(l) - c_i^{\beta}] + \bar{N}_i\}. \quad (104)$$

As an example, we shall consider the calculation of ΔG^{el} by Eqn. (104) for SDS at 20 °C. The numerical solution of Eqn. (96) for $\varepsilon = 79.7$, $n = 56$, $q_1 = 8.9 \times 10^{-18}$ C, and $l = 1.97$ nm yields $ez_1\varphi(l) \simeq 6.5\ kT$.[41] From the electroneutrality condition, we obtain $\bar{N}_2 \simeq 56$ and from the Boltzmann formula we have $c_2(l) - c_2^{\beta} \simeq 5.51$ M for $c_2 = 8.3 \times 10^{-3}$ M (CCM). From Eqn. (104), we then find $\Delta G^{el}/nkT \simeq 5.0$. Using the same initial data, we obtained above 6.36 by Eqn. (92), so that the linearised Poisson–Boltzmann equation yields a result which is too high.

4. A modified non-linearised Poisson–Boltzmann equation

If the dielectric constant in the Poisson–Boltzmann equation is assumed to be a function not of the spatial coordinates but of the electric field, then the very form of the equation changes. Such an equation is referred to as modified.[38,39] Apart from dielectric saturation, the intrinsic volume of the counterions is taken into account in it.

The dependence of the dielectric constant of a polar liquid on the electric field strength E is described by the expression[105]

$$\varepsilon(E) = n_0^2 + [4\pi cD(n_0^2+2)/3.3E] L(0.55(n_0^2+2)DE/kT), \quad (105)$$

where n_0 is the refractive index of the liquid (for long waves), c the number of its molecules per unit volume, D their dipole moment, and $L(x) \equiv \coth x - 1/x$ the Langevin function. For water, the effect of dielectric saturation begins to be manifested as $E = 10^8$ V m^{-1} is approached. At the surface of a micelle, $E = q_M/4\pi\varepsilon_0\varepsilon(l+\delta_1)^2$. If the counterions do not enter into the primary charge sphere, then $q_M = ezn$ and, taking into account Eqn. (2), we have

$$E = ezl_{max}^3/3\varepsilon_0\varepsilon(l+\delta_1)^2 v.$$

For members of a homologous series (excluding the initial members), $l_{max} \simeq l + \delta_1$ and $l_{max}/v \simeq$ const., so that all the micelles of the homologous series are characterised by approximately the same value of E. Its estimation for the specific case of SDS yields $E = 2.6 \times 10^8$ V m^{-1} for $n = 56$ and $\varepsilon = 80$, which means that in reality $\varepsilon < 80$: at the surface of the alkyl sulphate micelle dielectric saturation takes place. The substitution of $E = -\partial\varphi/\partial r \equiv -\varphi$ converts Eqn. (105) into

$$\varepsilon = n_0^2 - aL(-b\varphi')/\varphi', \quad (106)$$

where a and b are coefficients in Eqn. (105). The substitution of Eqn. (106) in Eqn. (81) yields in its turn a modified Poisson equation.

The presence of a strong electric field increases greatly the concentration of counterions at the surface of the micelle. Their intrinsic volume, which is not taken into account in the usual Boltzmann formula, becomes significant under these conditions. A refined Boltzmann formula has been proposed:[38]

$$c_j = c_{j_0} \exp(-z_j e\varphi/kT)/\{1 + (1/N) \times \times \sum_i' c_{0i} [\exp(-z_i e\varphi/kT) - 1]\}, \quad (107)$$

where N is the maximum possible occupation number by hydrated ions and the prime denotes summation with respect to ions having the same sign as that of the ion j (in this model only like ions are treated as hard spheres, while unlike ions are allowed to penetrate one another). The quantity N is assumed to be the same for all the ions; the ion with the maximum charge should be treated with greater precision [from Eqn. (107), it is also seen that N must be referred to unit volume].

Substitution of Eqns. (106) and (107) in Eqn. (96) leads to a modified non-linearised Poisson–Boltzmann equation. Its numerical solution for divalent counterions at a concentration of 1×10^{-3} M[38] shows that the influence of the intrinsic dimensions of the ions on their distribution near the surface of the micelle (in a layer 0.8 nm thick) begins to have an effect at a potential of the primary core of the micelle $\varphi_1 > 100$ mV and increases sharply with increase in the potential. For $\varphi_1 < 100$ mV, the use of the usual (unmodified) non-linearised Poisson–Boltzmann equation does not introduce an error. According to the data of Frahm et al.,[39] the values of φ_1 for sodium alkyl sulphate micelles at 35 °C are $\varphi_1 = -87$ mV for $n_c = 10$, $\varphi_1 = -120$ mV for $n_c = 12$, $\varphi_1 = 155$ mV for $n_c = 14$, and $\varphi_1 = -195$ mV for $n_c = 16$. For SDS at 25 °C in the region of the CCM, $\varphi_1 \simeq -130$ mV, but, since in this case the counterions are singly charged, one may hope that the application of the usual Poisson–Boltzmann equation still does not entail a large error.

If φ_1 has been determined experimentally (for example, by the fluoroescent probe method[39,70]), then the modified non-linearised Poisson–Boltzmann equation makes it possible to calculate the primary charge on the micelle and also the distributions $\varphi(r)$ and $c_i(r)$. Information about the primary charge is especially valuable, since, for a specified aggregation number, this makes it possible to find the number of counterions which have entered the primary plate of the EDL. According to Frahm et al.,[39] the primary charge on the SDS micelle for $n = 55$ and $l = 1.8$ nm is 26.8 ± 1.9 elementary charges, i.e. only half of the charge of the 55 surface-active ions. On the other hand, if it is assumed, as was done above, that $l = 1.97$ nm, then, for the potential $\varphi_1 = 130$ mV, the charge on the micelle is about 32 elementary charges, so that even in the primary plate of the EDL the degree of binding of the counterions reaches 42%. If apart from this one takes into account the additional shielding of the charge by the counterions in a shell 0.5 nm thick adjoining the core, then the degree of binding reaches $\beta = 0.55$ (Frahm et al.[39] obtained $\beta = 0.65$ for $l = 1.8$ nm). Accordingly, one can put forward the following picture of the distribution of the 55 counterions around the core of micelle: 23 enter into the primary layer of the EDL, 7 into the shell adjoining the core, and 25 into the

diffuse part of the EDL. In this case we are dealing with a two-layer charge on the micelle and the quantity ΔG^{el} can be calculated from Eqn. (103). However, the result of the calculation is sensitive to the postulated value of ε_1. The maximum value of $\Delta G^{el}/nkT \simeq 5.5$ is obtained for $\varepsilon_1 = 80$. On the other hand, if, for example, $\varepsilon_1 = 40$, then $\Delta G^{el}/nkT \simeq 4.2$.

The Poisson–Boltzmann equation has been modified[46] with the aid of the semiempirical relation[106]

$$\varepsilon(E) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)/(1 + BE^2), \qquad (108)$$

where the subscripts correspond to $E = 0$ and $E = \infty$ ($E_\infty = 6$) and B is a constant. Apart from the revised description of the EDL, Beunen and Ruckenstein[46] formulated the problem of the more accurate calculation of the work of formation of the primary plate of the EDL of the micelle. It is usually assumed that, when the ions are bound to one another, their contribution to the electrostatic energy vanishes. This would be the case if oppositely charged ions did indeed penetrate one another. In fact, they form dipoles, which interact with the surface-active ions of the micelle. The extent of such ion–dipole interaction can be estimated, for example, within the framework of the lattice model (taking into account the interaction of neighbours).[46] The values $\beta = 0.65$ for spherical micelles and $\beta = 0.88$ for cylindrical micelles were obtained by this method for SDS with $l = 2.03$ nm.

V. Conclusion

In terms of the average field approximation, the electrostatic contributions to the Gibbs free energy of the micellar cell and to the standard Gibbs free energy of micelle formation are the same, so that, by estimating ΔG^{el}, we thereby determine also the electrostatic contribution to the Law of Mass Action constant. If one takes into account the fact that the hydrophobic effect amounts to about $-1.5\ kT$ per CH_2 group, then the contribution by $\Delta G^{el}/nkT$ of the order of 4–5 must be recognised as relatively small. It is significant that $\Delta G^{el} > 0$ (while the main contribution by the hydrophobic effect is negative) and, as can be seen from Eqn. (30), this increases CCM (for $\Delta G^{el}/nkT = 4.6$, the critical concentration for micelle formation is 100 times greater than in the absence of the electrostatic contribution). It is necessary to note that the influence of ions on the micelle formation process can be mediated by the hydrophobic effect itself, because the dissolved ions influence the structure of water.[51,81] The marked dependence of the size of the dodecyl sulphate micelles on the nature of the counterion[51] provides an interesting illustration of this finding, although a theory of this phenomenon has not yet been developed.

In estimating the electrostatic contribution to the Gibbs free energy, we considered spherical micelles for which this contribution is a maximum. Analogous calculations can be performed also for cylindrical micelles, but in this case the electrostatic effects are smaller because of the denser packing of the surface-active ions and the greater degree of binding of the counterions. As regards the phenomenon of the polymorphic transformation of the micelles itself (from spherical to cylindrical and from cylindrical to lamellar), we confined ourselves only to a general comment in this review. Some workers (see, for example, Refs. 71 and 75) treat the phenomenon in terms of a purely geometrical aspect taking into account only the shape of the molecules and their packing. In reality, such processes are controlled by energy relations. A rigorous study of polymorphic transformations of micelles, like that of the polymorphic transformations of small crystals, is based on the generalised Gibbs–Curie principle[107] using [as in Eqns. (47) and (49)] the concept of surface tension. For the latter, as for many other thermodynamic quantities, it is also possible to differentiate and calculate in one way or another the electrostatic contribution characteristic of ionic micelles (see, for example, Rusanov[22]). However, a detailed examination of these questions is outside the framework of this review.

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