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PHYSICAL CHEMISTRY OF SOLUTIONS

Point Excesses in the Theory of Ordinary and Micellar Solutions

A. I. Rusanov, F. M. Kuni, and A. K. Shchekin

St. Petersburg State University (Petrodvorets Branch), Petrodvorets, 198504 Russia
e-mail: rusanov@AR1047.spb.edu

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Abstract—Point excesses of substances and thermodynamic properties and the role they play in the solvation and binding of counterions in solutions of electrolytes, including micellar systems, are analyzed. A complete system of fundamental thermodynamic equations for point excesses is formulated. Statistical mechanics equations that relate point excesses of substances to the electrochemical potentials and concentrations of components are derived. For ionic micellar systems, a relation between point excesses and charges and concentrations of ions and micelles is obtained. The results are substantiated by direct calculations of point excesses with the use of the Debye–Hückel method.

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INTRODUCTION

It is not a revelation that methods of the theory of surface phenomena or their analogues prove useful for consideration of solutions. A field of molecular forces appears at the boundary between two phases. This field causes changes in the density, composition, and structure of substances in the surface layer. As suggested by Gibbs, such changes are characterized by excess (with respect to the bulk phase far from the surface) values. An example is adsorption as material excess per unit surface area. However, in the bulk of a solution, similar molecular forces act, and any solution particle (molecule, ion, or colloid particle) can be a source of external field with respect to other solution particles.

Such phenomena, characteristic of solutions, as association and solvation are quite similar to adsorption. We, however, then deal with point rather than surface (or even linear also considered in the theory of surface phenomena) excesses, because substance concentration occurs in all directions from the field source. An example of such an analysis was given in [1] for the work of ion solvation in the Born model. It was shown that the chemical work of solvation (bearing no relation to interphase electric potential and the work of ion transfer through an interphase boundary and only related to solution rearrangement close to an ion) is given by point excess $\overline{\Omega}$ of the grand thermodynamic potential.

The binding of counterions by charged solution particles is also akin to adsorption. Special attention was given in the literature to micelles of ionic surface active substances [2–4]. Starting with fundamental work [2], a key problem was that of relating point excesses of a substance to the thermodynamic characteristics of bulk (homogeneous) solution. For this purpose, the statistical thermodynamics equations

$$\frac{\partial c_{\mathrm{M}}}{\partial \mu_{\mathrm{M}}^{\mathrm{E}}} = \frac{c_{\mathrm{M}}[1 + \overline{N}_{\mathrm{M(M)}}]}{kT}, \tag{1}$$

$$\frac{\partial c_i}{\partial \mu_{\mathrm{M}}^{\mathrm{E}}} = \frac{c_{\mathrm{M}}\overline{N}_{i(\mathrm{M})}}{kT} \tag{2}$$

were used. Here, c_{M} and $\mu_{\mathrm{M}}^{\mathrm{E}}$ are the concentration and electrochemical potential of micelles in the bulk phase, c_i is the concentration of ions of kind i, $\overline{N}_{\mathrm{M(M)}}$ and $\overline{N}_{i(\mathrm{M})}$ are the point excesses of micelles and ions of kind i on one micelle, k is the Boltzmann constant, and T is the absolute temperature of the solution. Equation (1) is unquestionable (for nonionic systems, a similar equation was obtained in [5]). Equation (2) and the results that follow from it, however, need be corrected in our view. In this work, we address the problem of the relation between point excesses and the equilibrium thermodynamic properties of solutions.

THE THERMODYNAMICS OF POINT EXCESSES

First, let us formulate several general propositions valid for solutions of any nature. We consider an infinite homogeneous medium comprising uncharged particles. At a fixed position, any of them becomes a source of an external field for the whole medium, and it makes no difference whether this particle is a constituent of the medium or is introduced from outside. Let a system consisting of a substance be inside a sphere with radius R whose center coincides with the position of the fixed particle. The R value is selected to be much larger than the effective radius of point field action, and all the

local properties of the medium in the region of the boundary of the system remain the same as before the field was switched on. As far as the whole medium is concerned, as mentioned above, it is infinite and extends outside the limits of the system under consideration. The field causes system structuring, and it changes its energy U to U_k, where the index k indicates the kind of the particle and shows that the changed energy value depends on the kind of the particle as a source of the field. For a spherically symmetrical system, the fundamental equations for U_k are the same as in the theory of curved surface layers [6],

$$\delta U_k = T\delta S_k - p_{\mathrm{N}}(R)4\pi R^2\delta R + \sum_i \mu_i \delta N_{i(k)}, \quad (3)$$

$$U_k = TS_k - 4\pi\int_0^R p_{\mathrm{T}} r^2 dr + \sum_i \mu_i N_{i(k)}, \quad (4)$$

$$S_k\delta T - 4\pi\delta\int_0^R p_{\mathrm{T}} r^2 dr + p_{\mathrm{N}}(R)4\pi R^2\delta R + \sum_i N_{i(k)}\delta\mu_i = 0, \quad (5)$$

where S_k is the entropy of the system; T is the temperature; p_{N} ($\equiv p_{rr}$) and p_{T} ($\equiv p_{\theta\theta} = p_{\varphi\varphi}$) are the local values of the normal and tangential components of the pressure tensor in the spherical system of coordinates r, θ, φ with the origin at the source of the field; and μ_i and $N_{i(k)}$ are the chemical potential and the number of particles of the ith kind. The source of the field acts on medium particles, and these forces cause changes in the local density of medium components (i = 1, 2, …) close to the source and, therefore, the total number of component particles $N_{i(k)}$ inside the volume $4\pi R^3/3$. The $N_{i(k)}$ number also depends on the kind of the particle (k) creating the field (which is why this value has two indices).

Equation (5) for intensive values is a generalization of the Gibbs–Duhem equation for the system under consideration; it is independent of the selection of the thermodynamic potential. Conversely, when we pass to the Helmholtz energy F_k and the grand canonical potential Ω_k, Eqs. (3) and (4) take the form

$$\delta F_k = -S_k\delta T - p_{\mathrm{N}}(R)4\pi R^2\delta R + \sum_i \mu_i \delta N_{i(k)}, \quad (6)$$

$$F_k = -4\pi\int_0^R p_{\mathrm{T}} r^2 dr + \sum_i \mu_i N_{i(k)}, \quad (7)$$

$$\delta\Omega_k = -S_k\delta T - p_{\mathrm{N}}(R)4\pi R^2\delta R - \sum_i N_{i(k)}\delta\mu_i, \quad (8)$$

$$\Omega_k = -4\pi\int_0^R p_{\mathrm{T}} r^2 dr. \quad (9)$$

Note that the local pressure tensor value is strictly defined in statistical mechanics for any inhomogeneous system. For this reason, integral equations (4), (7), and (9) do not contain the quasi-chemical approximation and are exact equations of equilibrium thermodynamics.

Let us turn to the derivation of fundamental equations for point excesses. It is sufficient to subtract from (3)–(9) the same equations written for a homogeneous system (in the absence of a field) at the same equilibrium T and μ_i values and, naturally, at the same given R value. It should be taken into account that, at $r = R$, the properties of the medium in the perturbed and unperturbed states are equal, and the corresponding terms are eliminated by subtraction. As concerns the tangential pressure p_{T}, the usual isotropic pressure p corresponds to it in a homogeneous medium. Excess values will be marked by bars. The point excess energy $\bar{U}_k \equiv U_k - U$ is obtained in the form

$$\delta\bar{U}_k = T\delta\bar{S}_k + \sum_i \mu_i \delta\bar{N}_{i(k)}, \quad (10)$$

$$\bar{U}_k = T\bar{S}_k - 4\pi\int_0^R (p_{\mathrm{T}} - p) r^2 dr + \sum_i \mu_i \bar{N}_{i(k)}, \quad (11)$$

where $\bar{S}_k \equiv S_k - S$ is the point excess entropy and $\bar{N}_{i(k)} \equiv N_{i(k)} - N_i$ is the point excess of the number of particles of kind i on a particle of kind k. This value can also be written as

$$\bar{N}_{i(k)} \equiv 4\pi\int_0^R [c_{i(k)} - c_i] r^2 dr, \quad (12)$$

where $c_{i(k)} = c_{i(k)}(r)$ is the local concentration of particles of kind i in the field of a particle of kind k and c_i is the concentration of particles of kind i in a homogeneous medium in the absence of a field.

An analogue of Gibbs–Duhem equation (5) for point excess values is

$$\bar{S}_k\delta T - 4\pi\delta\int_0^R (p_{\mathrm{T}} - p) r^2 dr + \sum_i \bar{N}_{i(k)}\delta\mu_i. \quad (13)$$

The point excess Helmholtz energy $\bar{F}_k \equiv F_k - F$ takes the form

$$\delta\bar{F}_k = -\bar{S}_k\delta T + \sum_i \mu_i \delta\bar{N}_{i(k)}, \quad (14)$$

$$\bar{F}_k = -4\pi\int_0^R (p_T - p)r^2 dr + \sum_i \mu_i \bar{N}_{i(k)}, \quad (15)$$

and the point excess grand thermodynamic potential $\bar{\Omega}_k \equiv \Omega_k - \Omega$ is given by

$$\delta\bar{\Omega}_k = -\bar{S}_k \delta T - \sum_i \bar{N}_{i(k)} \delta\mu_i, \quad (16)$$

$$\bar{\Omega}_k = -4\pi\int_0^R (p_T - p)r^2 dr. \quad (17)$$

Considering (17), Eqs. (13) and (16) coincide. This means that fundamental equation (16) for point excess grand thermodynamic potential $\bar{\Omega}_k$ simultaneously plays the role of the Gibbs–Duhem equation and is the most important equation in the theory of solutions. As mentioned, the $\bar{\Omega}_k$ value itself is the chemical work of solvation, or, in other words, the work of transfer of a particle of kind k from a fixed position in the vacuum into a fixed position in the medium under consideration. It is shown in statistical thermodynamics [7, 8] that this work is written through the total activity coefficient γ_k, which can in turn be represented as the product of zero γ_k^0 (when the particle is introduced into a pure solvent) and concentration f_k activity coefficients of the solute,

$$\bar{\Omega}_k = kT\ln\gamma_k = kT\ln\gamma_k^0 + kT\ln f_k. \quad (18)$$

Equation (18) shows that the $\bar{\Omega}_k$ value plays a central role in the theory of solutions.

Let us turn to ionic systems. For thermodynamic equations, this reduces to the formal replacement of the chemical potentials of ions μ_i by the electrochemical potentials

$$\mu_i^E = \mu_i + ez_i\varphi, \quad (19)$$

where e is the elementary positive charge, z_i is the charge number of ions of kind i, and φ is the electric potential at the point of ion location. For equilibrium homogeneous solutions of electrolytes, φ is understood as an internal phase potential (the Galvani potential). Therefore, $ez_i\varphi$ is the work of transfer of a charged particle from infinity in the vacuum into the system under consideration provided its structure (including homogeneous charge distribution) does not change. Note that this is the work of the first stage of the introduction of a charged particle. The work of the second stage, when point excesses are formed, contributes to μ_i on the right-hand side of (19), more exactly, to the activity coefficient (similarly to (18)), which now includes contributions not only of solvation but also of interionic interactions.

Note that, if the source of the field is one of the ions of the system (at its fixed position in space), the specified work $ez_i\varphi$ is not done. This is the difference between the introduction of an ion from outside and bringing one of the system ions to a "stop." There is one more difference, namely, whereas bringing an ion to a stop does not disturb the condition of system electrical neutrality, the introduction of an ion from outside seemingly violates this condition. However, in reality, this difference comes to naught. Indeed, if a point charge is introduced into the electrically neutral system under consideration, it polarizes the medium. The nearest polarization charge balances the charge introduced, and the far polarization charge goes beyond the boundary of the medium (to infinity), in any event, outside the boundary of the system with radius R. This leads us to conclude that, irrespective of the method for creating a point electric field, the system under consideration should be considered electrically neutral taking into account the charge of the source of the field. For a system in the absence of a field and in the presence of a field created by an ion of kind k, the electrical neutrality condition is written as

$$\sum_i z_i N_i = 0, \quad (20)$$

$$z_k + \sum_i z_i N_{i(k)} = 0, \quad (21)$$

where the summation is formally over all the components (the terms corresponding to uncharged particles automatically disappear because their charge numbers are zero).The subtraction of (20) from (21) gives the electroneutrality condition in terms of point excesses,

$$z_k + \sum_i z_i \bar{N}_{i(k)} = 0. \quad (22)$$

The conclusion can be drawn that all the fundamental equations obtained in this section are also applicable to systems of charged particles if chemical potentials present in them are replaced with electrochemical potentials. It is well known that the division of the latter into two terms, as in (19), is fundamentally conventional (although fruitful in practice). The true thermodynamic variables are undivided electrochemical potentials. Recall that, for a charged particle, (16) takes the form

$$\delta\bar{\Omega}_k^E = -\bar{S}_k \delta T - \sum_i \bar{N}_{i(k)} \delta\mu_i^E, \quad (23)$$

where $\bar{\Omega}_k^E$ is the work of the introduction of a charged particle from the vacuum into a fixed solution point.

The chemical work of the solvation and binding of counterions $\overline{\Omega}_k$ is obtained as

$$\overline{\Omega}_k = \overline{\Omega}_k^{\mathrm{E}} - ez_k\varphi. \tag{24}$$

After this, activity coefficients are introduced as shown in (18).

In this section, we restricted ourselves to consideration of thermodynamic potentials determined for a given volume. Of course, this does not exhaust thermodynamics, but any other thermodynamic potentials are trivially related to them and to each other, and the corresponding equations can easily be obtained. The system of fundamental equations for point excess values can therefore be considered constructed.

STATISTICAL THERMODYNAMICS EQUATIONS AND THE RELATION OF POINT EXCESSES TO THE EQUILIBRIUM CHARACTERISTICS OF SOLUTIONS

These problems require the use of statistical mechanics equations. Note that all of them will be related to homogeneous media, or, in other words, to the bulk phase of a solution of an electrolyte. It is another matter that these equations will include point excesses of substances. The strong point of statistical mechanics is exactly the ability to relate point excesses to the equilibrium characteristics of solutions. One of the most important results of statistical thermodynamics is a detailed equation for the chemical potential. Borrowing it from [8, Eqs. (47.6), (47.7), and denotations (22.29)], let us write the electrochemical potential of particles of the kth kind (now treated as usual solution ions rather than separate external field sources) in the form

$$\begin{aligned}\mu_k^{\mathrm{E}} &= \overline{\Omega}_k^{\mathrm{E}} + kT\ln c_k + kT\ln\Lambda_k^3 \\ &= \overline{\Omega}_k + kT\ln c_k + kT\ln\Lambda_k^3 + ez_k\varphi.\end{aligned} \tag{25}$$

Here, c_k is the concentration (number per unit volume) of particles of the kth kind in a homogeneous solution. The Λ_k^{-3} value, which depends on temperature and the mass of particles, is the kinetic part of the partition function for the translational motion of a particle of kind k, and $kT\ln\Lambda_k^3$ is its contribution to the Helmholtz energy. The passage from the first to second form of Eq. (25) (we shall need it below) corresponds to Eq. (24) and electrical neutrality condition (22).

Let us differentiate (25) on the assumption of constant temperature and mass of particles of the kth kind. Taking into account fundamental equation (23) (where variation symbols should be replaced with differentials), we obtain

$$d\mu_k^{\mathrm{E}} = -\sum_i \overline{N}_{i(k)} d\mu_i^{\mathrm{E}} + kTd\ln c_k. \tag{26}$$

It then follows that

$$\left(\frac{\partial \ln c_k}{\partial \mu_i^{\mathrm{E}}}\right)_{T,\,\mu_{j\neq i}^{\mathrm{E}}} = \frac{\overline{N}_{i(k)} + \delta_{ik}}{kT}, \tag{27}$$

where δ_{ik} is the Kronecker symbol and the partial derivative with respect to the electrochemical potential μ_i^{E} is taken at constant values of the other electrochemical potentials μ_j^{E} $(j \neq i)$. Equation (27) is similar to Eq. (6) in [5] for particles with dissipative interactions (also see in [8, Eq. (47.4)]). Drawing an analogy between point excesses and adsorption, the component whose concentration is differentiated in (27) plays the role of a sorbent, and the component with respect to whose electrochemical potential the differentiation is performed plays the role of a sorbate component. Relating the index i to an ion, we can, in particular, state that the $\overline{N}_{i(k)}$ number characterizes the binding of counterions if the index k relates to another ion with the opposite sign and the solvation of the ion if the index k relates to a neutral solvent component.

At $k = i$, (27) becomes

$$\left(\frac{\partial \ln c_i}{\partial \mu_i^{\mathrm{E}}}\right)_{T,\,\mu_{j\neq i}^{\mathrm{E}}} = \frac{\overline{N}_{i(i)} + 1}{kT}. \tag{28}$$

We can then draw an analogy with self-adsorption. If the index i relates to a neutral solvent component, the point excess $\overline{N}_{i(i)}$ can have any sign if there are several such components. Although a determining role is then played by attraction forces between particles, the appearance of negative solvation can be caused by competition with other solvation shell components. If the index i in (28) relates to an ion, we always have $\overline{N}_{i(i)} < 0$ because of the mutual repulsion of like ions. At the same time, note that the left-hand side of (28) is always positive by virtue of thermodynamic stability conditions. It follows that the condition $\overline{N}_{i(i)} > -1$ should always be satisfied; for ions, $|\overline{N}_{i(i)}| < 1$. We show below that this condition is indeed fulfilled.

Let us apply (27) to micellar solutions, where micelles (index M) coexist with monomeric ions and solvent molecules. In (27), the indices i and k can take on arbitrary values, including M, which leads to the equations

$$\left(\frac{\partial \ln c_{\mathrm{M}}}{\partial \mu_i^{\mathrm{E}}}\right)_{T,\,\mu_{j\neq i}^{\mathrm{E}}} = \frac{\overline{N}_{i(\mathrm{M})} + \delta_{i\mathrm{M}}}{kT}, \tag{29}$$

$$\left(\frac{\partial \ln c_i}{\partial \mu_{\mathrm{M}}^{\mathrm{E}}}\right)_{T,\,\mu_{j\neq i}^{\mathrm{E}}} = \frac{\bar{N}_{\mathrm{M}(i)} + \delta_{i\mathrm{M}}}{kT}, \tag{30}$$

$$\left(\frac{\partial \ln c_{\mathrm{M}}}{\partial \mu_{\mathrm{M}}^{\mathrm{E}}}\right)_{T,\,\mu_{j\neq \mathrm{M}}^{\mathrm{E}}} = \frac{\bar{N}_{\mathrm{M}(\mathrm{M})} + 1}{kT}. \tag{31}$$

If the index i relates to the solvent (or the system is not ionic), Eqs. (29)–(31) characterize solvation effects in micelles. If the index i relates to an ion, the $\bar{N}_{i(\mathrm{M})}$ point excess, in particular, characterizes the binding of counterions by micelles when the charge of the ion is opposite to that of micelles, and $\bar{N}_{\mathrm{M}(i)}$, the binding of micelles by monomeric ions. Clearly, $\bar{N}_{\mathrm{M}(\mathrm{M})}$ gives the exact excess of the number of micelles on one of them. Eq. (31) coincides with (1), but (29) and (30) are inconsistent with (2) ([2, Eq. (12)]).

For micelles, equation (25) for the electrochemical potential can be rewritten as

$$\begin{aligned}\mu_{\mathrm{M}}^{\mathrm{E}} &= \bar{\Omega}_{\mathrm{M}}^{\mathrm{E}} + kT\ln c_{\mathrm{M}} + kT\ln\Lambda_{\mathrm{M}}^{3} \\ &= \bar{\Omega}_{\mathrm{M}} + kT\ln c_{\mathrm{M}} + kT\ln\Lambda_{\mathrm{M}}^{3} + ez_{\mathrm{M}}\varphi,\end{aligned} \tag{32}$$

where z_{M} is the electric charge of a micelle (for a nonionic micelle, $z_{\mathrm{M}} = 0$). The work

$$\bar{\Omega}_{\mathrm{M}}^{\mathrm{E}} = \bar{\Omega}_{\mathrm{M}} + ez_{\mathrm{M}}\varphi \tag{33}$$

is spent to introduce a separate micelle from the vacuum into some solution (also containing other micelles) point with the phase electric potential φ. The $kT\ln\Lambda_{\mathrm{M}}^{3}$ value has the meaning of the kinetic contribution of translational motion into the Helmholtz energy of a micelle, and the $W_{\mathrm{M}} \equiv \bar{\Omega}_{\mathrm{M}}^{\mathrm{E}} + kT\ln\Lambda_{\mathrm{M}}^{3}$ value can also therefore be understood as the work of the introduction of one micelle, but including the thermal motion of the micelle introduced in solution. Using (32), we then obtain work W_{M} in the form

$$W_{\mathrm{M}} = \mu_{\mathrm{M}}^{\mathrm{E}} - kT\ln c_{\mathrm{M}}. \tag{34}$$

Let us differentiate (34) with respect to μ_i^{E} at constant temperature and other electrochemical potentials. Taking into account that $(\partial\mu_{\mathrm{M}}^{\mathrm{E}}/\partial\mu_i^{\mathrm{E}})_T = \delta_{iM}$ and Eq. (29), we obtain

$$\left(\frac{\partial W_{\mathrm{M}}}{\partial \mu_i^{\mathrm{E}}}\right)_{T,\,\mu_{j\neq i}^{\mathrm{E}}} = -\bar{N}_{i(\mathrm{M})}. \tag{35}$$

Although Eq. (35) plays a key role in the theory of the coefficients of binding of counterions by an ionic micelle [2–4], it has not been consistently substantiated earlier.

THE TREATMENT OF AN IONIC MICELLAR SOLUTION WITH COATED MICELLES IN THE APPROXIMATION OF IDEALITY

Let us consider an ionic micellar system in more detail. We have to repeat the calculations performed in [2]; the main idea of that work was the independent derivation of Eq. (27) taking into account electric contributions only from the conditions of solution electrical neutrality and ideality. Note that, in this section, we do not turn to dilute solutions and consider solutions of the same concentration as previously. We simply pass to another method of description, another model, and another formalism. This will be done as follows. A multiple-charge micelle formed by surface active ions of one sign is called "naked" in the literature. Just this micelle with charge z_{M} creates a strong field around it and point excesses $N_{i(\mathrm{M})}$ of other particles described in the preceding sections. Suppose that the excesses of counterions partially become bound (when the mean electric interaction energy becomes higher than kT) in a strong micelle field, and excess values become aggregation numbers n_i. The charge number of the micelle then decreases to

$$z_{\mathrm{M}^*} = z_{\mathrm{M}} + \sum_i n_i z_i. \tag{36}$$

Clearly, $n_i < \bar{N}_{i(\mathrm{M})}$, because otherwise we would have $z_{\mathrm{M}^*} = 0$ according to (22). It can nevertheless be expected that $z_{\mathrm{M}^*} \ll z_{\mathrm{M}}$. Such micelles are called coated; they will be denoted by M*.

The approaches used in this and previous sections are different because, in this section, we deal with coated micelles. As far as strict equations of the preceding section are concerned, they are equally applicable to naked and coated micelles. Equations (29)–(31) take the form

$$\left(\frac{\partial \ln c_{\mathrm{M}^*}}{\partial \mu_i^{\mathrm{E}}}\right)_{T,\,\mu_{j\neq i}^{\mathrm{E}}} = \frac{\bar{N}_{i(\mathrm{M}^*)} + \delta_{i\mathrm{M}^*}}{kT}, \tag{37}$$

$$\left(\frac{\partial \ln c_i}{\partial \mu_{\mathrm{M}^*}^{\mathrm{E}}}\right)_{T,\,\mu_{j\neq i}^{\mathrm{E}}} = \frac{\bar{N}_{\mathrm{M}^*(i)} + \delta_{i\mathrm{M}^*}}{kT}, \tag{38}$$

$$\left(\frac{\partial \ln c_{\mathrm{M}^*}}{\partial \mu_{\mathrm{M}^*}^{\mathrm{E}}}\right)_{T,\,\mu_{j\neq \mathrm{M}^*}^{\mathrm{E}}} = \frac{\bar{N}_{\mathrm{M}^*(\mathrm{M}^*)} + 1}{kT}, \tag{39}$$

where excesses with bars relate to coated micelles and are therefore much smaller in magnitude than for naked micelles. These point excesses relate to particles weakly bound by the electric field. For counterions, the difference of excesses for naked and coated micelles at equal electrochemical potentials is just their aggregation number,

$$n_k = \bar{N}_{k(\mathrm{M})} - \bar{N}_{k(\mathrm{M}^*)} \tag{40}$$

(this concept is absent in the formalism of naked micelles).

According to the main postulate of the approach used in this section, the charge of coated micelles and initial concentrations of free ions decrease to the extent that their interaction with each other is insignificant. In other words, coated micelles and monomeric ions form an almost ideal mixture at aggregation equilibrium. As a first approximation, we can ignore interactions between dissolved particles in this mixture and approximately assume that the concentration activity coefficient f_k is one, while the zero activity coefficient is some function of temperature. We then obtain $d\overline{\Omega}_k = 0$ from (18) at the given temperature. According to (25), the electrochemical potential μ_j^{E} for arbitrary j is

$$d\mu_j^{\mathrm{E}} = kTd\ln c_j + ez_j d\varphi \tag{41}$$

(it must be borne in mind that, at $j = \mathrm{M}^*$, z_j and μ_j^{E} are replaced with z_{M^*} and $\mu_{\mathrm{M}^*}^{\mathrm{E}}$). In essence, Eq. (41) ignores $kTd\ln f_j$ compared with $kTd\ln c_j$.

For the present (up to Eq. (54)), let the index i characterize the kind of particles the electrochemical potential of which varies as φ changes when other chemical potential stay fixed. We then have

$$d\mu_i^{\mathrm{E}} \neq 0, \tag{42}$$

$$d\mu_k^{\mathrm{E}} = 0 \quad (k \neq i). \tag{43}$$

It follows from (41) and (43) that

$$dc_k = -\frac{ez_k c_k}{kT} d\varphi \quad (k \neq i). \tag{44}$$

The solution electroneutrality condition remains valid as potential φ is varied. That is, the condition

$$dc_i = -\frac{1}{z_i} \sum_{k(k \neq i)} z_k dc_k \tag{45}$$

or (taking into account (44))

$$dc_i = \frac{e}{kTz_i}\left(\sum_{k(k \neq i)} z_k^2 c_k\right) d\varphi \tag{46}$$

is met. It follows from (41) and (46) that

$$\begin{aligned} d\mu_i^{\mathrm{E}} &= \frac{e}{z_i c_i}\left(\sum_{k(k \neq i)} z_k^2 c_k\right) d\varphi + ez_i d\varphi \\ &= \frac{e}{z_i c_i}\left(\sum_k z_k^2 c_k\right) d\varphi. \end{aligned} \tag{47}$$

The ionic strength of solution,

$$I \equiv \frac{1}{2}\sum_k z_k^2 c_k \tag{48}$$

can be introduced to represent (47) in the form

$$d\mu_i^{\mathrm{E}} = \frac{2eI}{z_i c_i} d\varphi. \tag{49}$$

Substituting (49) into (44) yields

$$dc_k = -\frac{z_k z_i c_k c_i}{2IkT} d\mu_i^{\mathrm{E}} \quad (k \neq i). \tag{50}$$

It follows from (46) and (49) and definition (48) that

$$dc_i = \frac{c_i}{kT}\left(1 - \frac{z_i^2 c_i}{2I}\right) d\mu_i^{\mathrm{E}}. \tag{51}$$

Equations (50) and (51) yield

$$\left(\frac{\partial \ln c_k}{\partial \mu_i^{\mathrm{E}}}\right)_{T, \mu_{j \neq i}^{\mathrm{E}}} = -\frac{z_k z_i c_i}{2IkT} \quad (k \neq i), \tag{52}$$

$$\left(\frac{\partial \ln c_i}{\partial \mu_i^{\mathrm{E}}}\right)_{T, \mu_{j \neq i}^{\mathrm{E}}} = \frac{1}{kT}\left(1 - \frac{z_i^2 c_i}{2I}\right). \tag{53}$$

These equations describe the mutual influence of particles of different kinds caused by phase potential variations φ in (41). Clearly, (52) and (53) can be combined to obtain

$$\left(\frac{\partial \ln c_k}{\partial \mu_i^{\mathrm{E}}}\right)_{T, \mu_{j \neq i}^{\mathrm{E}}} = \frac{1}{kT}\left(\delta_{ik} - \frac{z_k z_i c_i}{2I}\right). \tag{54}$$

This equation is valid not only at $k \neq i$ but also at $k = i$ (unrelated to the constraint imposed in (43)), also when k or i relates to coated micelles. This is the equation that we sought. It is correct under taking into account the electric contributions and the solution ideality.

Let us compare (27) and (54). The derivatives on their left-hand sides are taken under equal conditions. We can therefore equate the right-hand sides of these equations. This gives

$$\overline{N}_{i(k)} = -\frac{z_k z_i c_i}{2I}. \tag{55}$$

According to (55), as expected, the sign of the $\overline{N}_{i(k)}$ point excess is opposite to the sign of the $z_k z_i$ product, and the point excess of the ith ion disappears at infinite dilution (as $c_i \longrightarrow 0$) in the presence of background electrolyte.

Applying (55) to coated micelles (the i and k indices can then be M*), we obtain

$$\overline{N}_{i(\mathrm{M}^*)} = -\frac{z_{\mathrm{M}^*} z_i c_i}{2I}, \tag{56}$$

$$\overline{N}_{M^*(i)} = -\frac{z_i z_{M^*} c_{M^*}}{2I}, \quad (57)$$

$$\overline{N}_{M^*(M^*)} = -\frac{(z_{M^*})^2 c_{M^*}}{2I}. \quad (58)$$

These equations determine the point excesses of coated micelles in terms of the charges and concentrations of ions and coated micelles. Equation (58) coincides with Eq. (11) from [2] except that, in the latter, I_f in the denominator stands for twice ionic strength (48).

After the multiplication of both sides of (55) by z_i and the summation over i, it is easy to see using definition (48) that (55) satisfies electrical neutrality condition (22). Ionic strength definition (48) also allows us to state that the $\overline{N}_{i(i)}$ point excess is always smaller than one in magnitude, that is, the requirement that follows from (28) is fulfilled.

DIRECT CALCULATIONS OF POINT EXCESSES BY THE DEBYE–HÜCKEL METHOD

We will show how point excesses $\overline{N}_{i(k)}$ can be found by the Debye–Hückel method if only electric contributions to $\overline{N}_{i(k)}$ are taken into account. Clearly, with micellar solutions, we must restrict our consideration to coated micelles whose charges are not very large. As far as naked micelles are concerned, their high charges prevent us from applying the Debye–Hückel theory to them in the region of concentrations of interest for practice. Suppose that a charged particle of kind k is introduced from outside into some point inside a homogeneous medium that satisfies the electrical neutrality condition

$$\sum_i z_i c_i = 0 \quad (59)$$

and contains charged particles of various kinds in a nonconducting solvent.

Let us introduce a spherical system of coordinates with the origin at the center of the particle introduced and radial variable r. We assume that system particles can approach the particle introduced by distances no less than r_0, which is the radius of repulsive core caused by short-range forces (this radius does not appear in the final results). The introduced particle of kind k creates a spherically symmetrical cloud of all charged system particles around it. The concentrations $c_{i(k)}$ in the cloud are functions of the distance r from the center of the cloud. As $r \geq r_0$, the exact excess (12) definition can be written as

$$\overline{N}_{i(k)} \equiv 4\pi \int_{r_0}^{\infty} [c_{i(k)} - c_i] r^2 dr. \quad (60)$$

The electric potential created by the cloud and the charge introduced ez_k will be denoted by Φ. This potential also depends on r and also on k (for brevity, this dependence is omitted).

The solution is considered dilute to the extent that the mean Coulomb interaction energy of two particles is much smaller than their mean kinetic energy. Using the Boltzmann distribution for the concentrations $c_{i(k)}$ in the cloud and linearizing the distribution, we obtain

$$c_{i(k)} = c_i \exp\left(-\frac{ez_i}{kT}\Phi\right) = c_i - \frac{e\Phi}{kT} z_i c_i, \quad (r \geq r_0), \quad (61)$$

where it is taken into account that $\Phi \longrightarrow 0$ and $c_{i(k)} \longrightarrow c_i$ as $r \longrightarrow \infty$. Using (59) and (61), we obtain the charge density ρ in the cloud in the form

$$\rho \equiv e\sum_i z_i c_{i(k)} = -\frac{e^2\Phi}{kT}\sum_i z_i^2 c_i, \quad (r \geq r_0). \quad (62)$$

Substituting (62) for charge density ρ in the Poisson equation, we obtain the linearized Poisson–Boltzmann equation for the cloud,

$$\frac{1}{r}\frac{d^2}{dr^2}(r\Phi) = \kappa^2\Phi, \quad (r \geq r_0), \quad (63)$$

where κ is the inverse Debye length defined as

$$\kappa^2 \equiv \frac{4\pi e^2}{\varepsilon kT}\sum_i z_i^2 c_i \quad (64)$$

(here, ε is the permittivity, also absent from the final result). A physically admissible solution to (63) is

$$\Phi = \frac{A}{r}e^{-\kappa r} \quad (r \geq r_0), \quad (65)$$

where A is the constant of integration. According to (65), the normal component of induction on the surface $r = r_0$ is $\varepsilon A/r_0^2$ (it is taken into account that, for dilute solutions, $\kappa r_0 \ll 1$ holds with much safety). At $r \leq r_0$, the induction is fully determined by the charge introduced into the solution, and the normal induction component is ez_k/r_0^2 on the $r = r_0$ surface. The A constant in (65) can be found from the continuity of the normal induction component. This gives

$$\Phi = \frac{ez_k}{\varepsilon r}e^{-\kappa r} \quad (r \geq r_0) \quad (66)$$

in agreement with the Debye–Hückel theory. Equation (66) substantiates the limiting behavior $\Phi \longrightarrow 0$ as $r \longrightarrow \infty$ used in (61).

Let us find the charge of the cloud q_k. We have

$$q_k \equiv 4\pi \int_{r_0}^{\infty} \rho r^2 dr. \quad (67)$$

Using (62), (64), and (66), (67) and the condition $\kappa r_0 \ll 1$ for integral calculations, we obtain $q_k = -ez_k$, as expected. Indeed, according to (66), the induction flux through a spherical surface with an infinite radius r is zero. For the total charge inside this surface, which is the sum of the charge q_k of the cloud and the charge ez_k of the particle introduced, we then have $q_k + ez_k = 0$, which gives $q_k = -ez_k$. As the particle introduced is not a constituent of the system but only creates an external electric field (and repulsive core field) in it, it cannot violate electrical neutrality of the whole system. For this reason, in addition to the charge q_k, the charge $-q_k$ is also formed in an electrically neutral medium. This charge is, however, smeared over such a large volume at infinite medium dimensions that the condition $\sum_i ez_i c_{i(k)} = 0$ is in reality fulfilled at some distance from the particle introduced. This was already mentioned in the first section.

Using (61) and (62), we can write

$$c_{i(k)} - c_i = \left[z_i c_i \Big/ \left(e \sum_i z_i^2 c_i \right) \right] \rho \quad (68)$$

(this equation does not contain the potential Φ). Let us integrate both sides of (68) over the region $r \geq r_0$. On the left-hand side of the resulting equality, we take into account (60), and, on the right-hand side, (67) and the equality $q_k = -ez_k$. This gives

$$\overline{N}_{i(k)} = -\frac{z_k z_i c_i}{\sum_i z_i^2 c_i}. \quad (69)$$

Equation (69) with definition (48) substantiates (55). The above reasoning clarifies the conditions of the applicability of (55). Equation (69) only includes electrical contributions because, in dilute solutions, short-range contributions are small compared with long-range electrical contributions.

Suppose that any of the charged particles of the initial medium, for instance, a particle of kind k, is the center of the formation of the screening cloud of other charged medium particles around it. This is just what occurs in the Debye–Hückel theory. Clearly, all equations (59)–(69) will as previously be valid. However, because the particle in the center of the cloud is now a medium constituent, the sum of its charge ez_k and cloud charge q_k (67) gives the charge of the whole medium. The equality $q_k + ez_k = 0$ then corresponds to electroneutrality condition. The $\overline{N}_{i(k)}$ value in (60) and (69) is now the excess of the number of particles of kind i in the screening cloud around any of the charged particles of kind k in the medium.

Equation (69) can be applied not only to ordinary but also to micellar solutions provided micelles are coated, because linearization (61) is possible for such solutions. A comparison of (69) and (55) (bearing in mind definition (48)) shows that, for monomeric ions of a given concentration, they coincide. When applied to coated micelles, (69) takes the form of (56)–(58). It follows that the Debye–Hückel theory substantiates the results obtained in the preceding section.

Note in conclusion that, although we concentrated on calculations of exact excesses of the numbers of particles of various kinds present in the system, the results of the first section and Eq. (55) allow us to obtain equations for point excess entropy and other thermodynamic values.

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