SOME PROBLEMS IN THE THEORY OF POLYELECTROLYTES AT SMALL DEGREES OF IONIZATION

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When polymeric molecules dissociate in a solution of a normal electrolyte, macroions are formed with the charge $Q = \alpha z$ where z is the degree of polymerization and α the degree of ionization of the macromolecules. In theoretical studies aiming at calculating the distribution of the potential at the surface of the macroions it was supposed, first, that at $\alpha \leqslant 0.1$ the macroions have a nearly spherical shape and, second, it was assumed that the charge of the macroion is distributed uniformly along the surface with a certain average density [1-3]. The first supposition is quite reasonable, since the charges formed on the separate chains of the macromolecule at small α on the average are at mutual distances surpassing the diameter of the screening double layer formed around each of them. This statement is correct in the broad range of foreign electrolyte concentrations at which Debye-Huckel's theory of solutions is applicable. Meanwhile the interactions between the charges of the macroion are very small, because they are screened by the electrolyte, but the interaction between the charges of the macromolecular coil and the surrounding electrolyte becomes of importance. As regards the assumption that the charge of the macroions is distributed uniformly over the surface, we must say that it does not correspond to reality and may lead to considerable errors because, actually, the charges are at a great mutual distance. Just as was done in the studies mentioned above, in the present paper we do not take into account the mutual interaction between the macroions, because their concentration in the solution is small.

In the present investigation the unevenness of the charge distribution along the surface of the macroion is taken into account. In our conception the macromolecules have the form of densely packed coils of spherical shape bearing charges in their surface region. We are interested in the start of the dissociation of the macromolecules, which, in the first instance, takes place in the regions directly adjoining the electrolyte. The number of charges inside the coils is negligibly small when the swelling of the macromolecules is low. The size of the polymeric coil or macroion is much greater than the average sizes of the microions of a normal electrolyte. Therefore, in a high degree of accuracy it may be taken that the polymer-electrolyte boundary surface is plane. The polymeric molecule (the left half-space) constitutes a dielectric with the dielectric constant ε_1 and the electrolyte solution (right half-space) constitutes one with the dielectric constant ε_2. We will derive the potential distribution at the boundary surface between the two media. The point charges fixed at the polymer surface are assumed to be distributed in the form of a network with an average distance between adjacent charges $d > 2\,\varkappa$ where $1/\varkappa$ is of the order of the radius of the screening ion shell which borders on a given charge from the side of the electrolyte. In this approximation the effect of adjacent charges on the potential distribution near a given charge q will be negligible. Strictly speaking, the charge q has a certain extension, but in the calculations we assume that it is a point charge and has its location not on the boundary surface but at a certain depth h inside the polymer. The latter assumptions are introduced to facilitate the calculations. In the final formulas we will let h tend to zero and we will get a result valid for a point charge on the surface. The origin of the coordinate will be chosen on the boundary surface of the media in the point where the charge q is located. The inside of the solution is chosen as the positive direction of the z-axis. The boundary surface constitutes the xy plane (see Fig. 1).

The potential distribution in region I is given by Poisson's equation

$$\Delta\Psi = -\frac{4\pi}{\varepsilon_1} q\,\delta(x)\,\delta(y)\,\delta(z+h), \tag{1}$$

and that in region II by the equation

$$\Delta\psi = -\frac{4\pi}{\varepsilon_2}\sum_{i=1}^{s} e\, n_i z_i\, e^{-z_i e\varphi/T}, \tag{2}$$

T is the temperature expressed in energy units.

The number $\underline{s}$ of ion species in the solution is one more than that in the same electrolyte without dissolved polymer. This extra ion species is formed as a result of the dissociation of the macromolecules. In our considerations the value of $z_i e\varphi/T \ll 1$, just as is assumed in the theory of Debije-Huckel, since the charge $\underline{q}$ is small. At the same time it is assumed that the surrounding electrolyte has such a concentration that Debije-Huckel's theory remains valid. We linearize equation (2) by expanding the exponential functions into a power series of $z_i e\varphi/T$ and taking only the first two terms of the expansion. The constant term appearing at the right hand side of the linearized equation (2) may be neglected in a high degree of accuracy, since at the very small degrees of ionization $\alpha \leq 0.1$ the number of additional ions formed by dissociation of macromolecules is very small when compared with the number of microions of the electrolyte. Then equation (2) gets the form

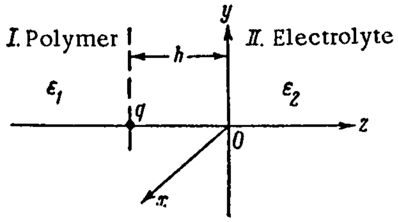

Fig. 1.

$$\Delta\varphi - \varkappa^2\varphi = 0, \tag{3}$$

where

$$\varkappa^2 = \frac{4\pi e^2}{\varepsilon_2 T}\sum_{i=1}^{s} n_i z_i^2 . \tag{4}$$

In this way our problem has been reduced to that of solving the equations (1) and (3), which are valid in the regions $-\infty < z \leqslant 0$ and $0 \leqslant z < \infty$, respectively, for the boundary conditions

$$\Psi\,|_{z=0} = \varphi\,|_{z=0},\quad \varepsilon_1 \frac{\partial\Psi}{\partial z}\bigg|_{z=0} = \varepsilon_2\frac{\partial\varphi}{\partial z}\bigg|_{z=0},\quad \varphi\,|_{z=\infty} = \Psi\,|_{z=-\infty} = 0. \tag{5}$$

Of the greatest interest is the solution of equation (3), which gives the potential distribution in the electric double layer adjoining the boundary surface from the side of the electrolyte in the limiting case $h \to 0$ [4].

$$\varphi(\rho, z) = 2q\int_{\varkappa}^{\infty} J_0\left(\sqrt{\lambda^2-\varkappa^2}\,\rho\right)\frac{e^{-\lambda z}\lambda\, d\lambda}{\varepsilon_1\sqrt{\lambda^2-\varkappa^2}+\varepsilon_2\lambda}, \tag{6}$$

where J_0 is Bessel's function of order zero $\rho = \sqrt{x^2+y^2}$.

The drawback of the solution given lies in the fact that it represented in the form of an integral the exact value of which cannot be obtained, but for several physically important cases it may be calculated with a good degree of accuracy [4]. Near the boundary surface of the media at $z \ll 1/\varkappa$ one may obtain from (6) in a satisfactory degree of accuracy the equation:

$$\varphi(\rho,z) \approx \frac{2q}{\varepsilon_1+\varepsilon_2}\,\frac{e^{-\varkappa\sqrt{\rho^2+z^2}}}{\sqrt{\rho^2+z^2}}. \tag{7}$$

The approximate result turns out to be spherically symmetric. It differs from Debije's solution by the fact that in the denominator there occurs a certain "average" dielectric constant

$$\bar{\varepsilon} = \frac{\varepsilon_1+\varepsilon_2}{2}.$$

By using equation (7) for the potential one may easily determine the electrostatic free energy of the system and the activity coefficients of the electrolyte ions. By the usual calculation method we get the following equation for the electrostatic free energy per unit volume of the system [4, 5]:

$$\Phi = -\frac{-\sum_i n_i z_i^2 |e|^2}{3\varepsilon_2}\varkappa - \frac{n_p \nu q^2 \varkappa}{2\bar{\varepsilon}}, \tag{8}$$

where n_p is the number of macroions per unit volume, ν the number of charges on a macromolecule. The first term at the right hand side of (8) represents the electric free energy per unit volume of the normal electrolyte containing no macroions, as is calculated in Debije-Huckel's approximation. The second term gives the extra energy originating from the presence of νn_p charges fixed to macroions. In order to determine the activity coefficients of a given ion species k we use the standard relation

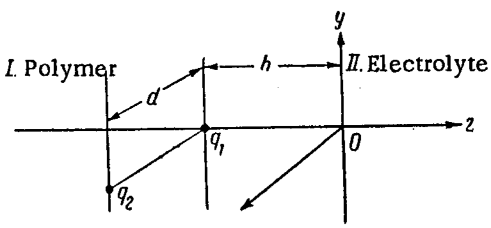

Fig. 2.

$$\ln \gamma_k = \frac{1}{T}\frac{\partial \Phi}{\partial n_k}, \tag{9}$$

which upon substituting Φ from (8) and taking into account the dependence of $\varkappa$ on n_k (4) gives the formula

$$\ln \gamma_k = -\frac{z_k^2 |e|^2 \varkappa}{2\varepsilon_2 T} - \frac{n_p \nu q^2 \varkappa z_k^2}{4\bar{\varepsilon} T \sum_{i=1}^{s} n_i z_i^2}. \tag{10}$$

The formula obtained was compared with the experiment in a paper of the authors [4]. If the distance between the charges on the surface of the macroions $d \leq 2/\varkappa$, then the arising forces of repulsion will change the shape of the said ions [6]. It is not difficult to estimate these forces. For this it is necessary to take into account the interaction between adjoining charges on the surface, when one determines the free energy of the system. We will consider two charges q_1 and q_2 with mutual distance d on the surface (see Fig. 2).

The potential distribution in region I is described by the equation

$$\Delta \Psi = -\frac{4\pi}{\varepsilon_1}[q_1 \delta(x)\delta(y)\delta(z+h) + q_2 \delta(x-d)\delta(y)\delta(z+h)]. \tag{11}$$

In region II the potential $\varphi(x, y, z)$ satisfies equation (2). Equation (11) is linear. Its solution consists of the superposition of the two solutions corresponding to the first and the second term of the right hand side of (11). When $q_1 = q_2 = q$, then these solutions differ only by the fact that in the second term $x-d$, instead of x, occurs. We write down the relation, as is obtained for this φ in the accuracy with which φ was calculated from (7), for $h = 0$:

$$\varphi(x, y, z) = \frac{2q}{\varepsilon_1+\varepsilon_2}\left(\frac{e^{-\varkappa\sqrt{\rho^2+z^2}}}{\sqrt{\rho^2+z^2}} + \frac{e^{-\varkappa\sqrt{\rho'^2+z^2}}}{\sqrt{\rho'^2+z^2}}\right), \tag{12}$$

where $\rho' = \sqrt{(x-d)^2 + y^2 + z^2}$.

The repulsion force between the ionic shells surrounding the charges is easily determined by means of the well-known formula

$$p = -\frac{\partial}{\partial d}(\Phi_d - \Phi_\infty), \tag{13}$$

where Φ_d is the electric free energy of the system consisting of the two charges together with the ionic shells, when the distance between the former is equal to d; Φ_∞ corresponds to $d = \infty$ and does not depend on d. Therefore,

$$p = \frac{\partial \Phi_d}{\partial d}. \tag{14}$$

The value of Φ_d consists of the two parts: a) the free energy change of the system, when the surface charges are varied from zero their final value; b) the free energy of the initial solution, when the charge on the macromolecules is zero. The second part does not depend on d, therefore [4]

$$p = -\frac{\partial}{\partial d}\left(2\int_0^q \Psi_0\, dq\right), \tag{15}$$

where Ψ_0 is the value of the potential at the point where the given charge is located, when the latter's own potential is not taken into account:

$$\Psi_0 = \Psi_\alpha + \frac{2q}{\varepsilon_1 + \varepsilon_2}\frac{e^{-\varkappa d}}{d}. \tag{16}$$

The potential Ψ_α does not depend on d, since this potential originates from the ionic atmosphere of the charge considered. Upon substituting (16) into (15) and rearranging we get

$$p = \frac{2q^2}{\varepsilon_1 + \varepsilon_2}(1 + \varkappa d)\frac{e^{-\varkappa d}}{d}. \tag{17}$$

Already at $\varkappa d \sim 1$ the magnitude of p differs little from the repulsion force between two point charges in the absence of an electrolyte. This points out that at a raised degree of ionization of the macromolecule the repulsion forces between the chains, as originate from the electrostatic interaction, may play an important role in determining the chain configuration.

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