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Abstract

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SOME QUESTIONS IN THE THEORY OF POLYELECTROLYTES AT LOW DEGREES OF IONIZATION

Upon dissociation of polymer molecules in a solution of an ordinary electrolyte, macroions with charge $Q = \alpha z$ are formed, where z is the degree of polymerization and α is the degree of ionization of the macromolecules. In theoretical works devoted to calculating the distribution of the potential near the surface of macroions, it was assumed, first, that for $\alpha \lesssim 0.1$ the macroions have a shape close to spherical, and, second, it was assumed that the charge of the macroion is uniformly distributed over the surface with some mean density ($^{1-3}$). The first assumption is quite satisfactory, since the charges formed on individual units of the macromolecule at small α are, on average, separated from one another by distances exceeding the diameter of the screening double layer formed around them. This assertion is valid over a wide range of concentrations of the external electrolyte for which the Debye-Hückel theory of solutions is applicable. In this case the interaction between the charges of the macroion is very small owing to their screening by the electrolyte; the interaction between the charges of the macromolecular coil and the surrounding electrolyte becomes essential. As for the assumption of uniformity of the surface charge of macroions, it does not correspond to reality and may lead to considerable errors because of the large distance between charges. Both in the works mentioned above and in the present work, the interaction between different macroions is not taken into account because of their low concentration in the solution.

In the present work the discreteness of the charge distribution on the surface of the macroion is taken into account. In our treatment the macromolecules have the form of densely packed coils of spherical shape, carrying charges in their surface part. We are interested in the onset of dissociation of the macromolecules, occurring primarily in regions immediately adjacent to the electrolyte. The number of charges inside the coil is negligibly small for weak swelling of the macromolecule. The size of the polymer coil, or macroion, is considerably larger than the mean sizes of the microions of the ordinary electrolyte. Therefore, with a high degree of accuracy one may regard the polymer-electrolyte interface as planar. The polymer molecule (the left half-space) is a dielectric with dielectric constant ε_1, while the electrolyte solution (the right half-space) has dielectric constant ε_2. Let us find the distribution of the potential near the interface. The discrete charge fixed on the polymer surface is assumed to be distributed in the form of a lattice with mean distance between neighboring charges $d > 2/\varkappa$, where $1/\varkappa$ is of the order of the radius of the screening ionic cloud adjacent from the electrolyte side to the given charge. In this approximation the influence of neighboring charges on the distribution of the potential near a given charge q will be negligible. The charge q is, strictly speaking, extended; however, in the calculations we shall assume that it is pointlike and is located not at the interface, but at some depth h inside the polymer. The latter assumptions are introduced for convenience of calculation. In the final formulas h will be set equal to zero.

to zero, and we obtain the result for the case of a surface point charge. The origin of coordinates is chosen on the interface, at the point where the charge q is located. The positive direction of the z axis is chosen into the solution. The xy plane is the interface (see Fig. 1).

The distribution of the potential in region I is described by Poisson' s equation

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

in region II—by the equation

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

where T is the temperature in energy units.

The number of ion species s in the solution is greater by one than in the same electrolyte without polymer dissolved in it. This additional species of ions is formed as a result of the dissociation of macromolecules. In our treatment the quantity $z_i e\varphi/T \ll 1$, as in the Debye-Hückel theory, because of the small magnitude of the charge q. At the same time, the concentration of the surrounding electrolyte solution is assumed to be such that the validity of the Debye-Hückel theory is not violated. We linearize equation (2), expanding the exponential in a series in powers of $z_i e\varphi/T$, retaining the first two terms of the expansion. The constant arising on the right-hand side of the linearized equation (2) may, to a high degree of accuracy, be neglected, since at very small degrees $\alpha \ll 0.1$ the number of additional ions formed upon dissociation of the macromolecules is very small in comparison with the number of microions of the electrolyte. Then equation (2) takes the form

Fig. 1

Fig. 1

Figure 1: Fig. 1

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

where

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

Thus, the problem has been reduced to determining the solutions of equations (1) and (3), specified respectively in the regions $-\infty < z \leq 0$ and $0 \leq z < \infty$, under the boundary conditions

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

Of greatest interest is the solution of equation (3), which gives the distribution of the potential in the double electric layer adjacent to the interface on the electrolyte side as $h \to 0$ (^{4}),

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

where J_0 is the Bessel function, $\rho = \sqrt{x^2 + y^2}$.

The inconvenience of this solution is that it is represented in the form of an integral, whose exact value cannot be obtained; however, for a number of physically important cases it can be computed with a good degree of accuracy (^{4}). Near the interface, for $z \ll 1/\varkappa$, one may

obtain, with a satisfactory degree of accuracy, the expression from (6):

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

The approximate result turned out to be spherically symmetric. It differs from the Debye solution for a point charge by the presence in the denominator of a certain "mean" dielectric constant

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

Fig. 2

Figure 2: Fig. 2

With the aid of the expression for the potential (7), one can easily determine the electrostatic free energy of the system and the activity coefficients of the electrolyte ions. By the usual method of calculation we obtain the following expression for the free electrostatic energy per unit volume of the system ([4,5]):

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

where n_p is the number of macroions per unit volume, ν is the number of charges on a macromolecule. The first term on the right in (8) is the electrical free energy per unit volume of an ordinary electrolyte containing no macroions, calculated in the Debye–Hückel approximation. The second term gives the addition due to the presence of νn_p charges fixed on the macroions. To determine the activity coefficients of ions of a given type k, we use the standard relation

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

which, after substituting Φ from (8) and taking into account the dependence of χ on n_k from (4), gives

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

The formula obtained was compared with experiment in the authors' work ([4]). If the distance between charges on the surface of the macroions $d \ll 2/\chi$, then the repulsive forces that arise must alter their shape ([6]). It is not difficult to estimate these forces. For this it is necessary to determine the free energy of the system taking into account the interaction between neighboring charges on the surface. Consider two charges q_1 and q_2 at the surface, the distance between which is d (see Fig. 2).

Fig. 2

The distribution of the potential in region I is described by the equation

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

In region II the potential $\varphi(x, y, z)$ satisfies equation (2). Equation (11) is linear. Its solution is a superposition of two solutions corresponding to the first and second terms on the right-hand side of (11). If $q_1 = q_2 = q$, then these solutions differ only in that in the second $x - d$ stands in place of x. Let us write the resulting φ with the accuracy with which φ was calculated

from (7), for $h = 0$:

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

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

The force of interaction between the ionic clouds surrounding the charges is readily determined by the well-known rule

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

where Φ_d is the electrical free energy of the system of two charges and the adjacent ionic clouds when the distance between them 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 quantity Φ_d consists of two parts: (a) the change in the free energy of the system when the surface charges change from zero to their final value; (b) the free energy of the initial electrolyte solution at zero charge on the macromolecule. 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 the function Ψ_0 is the value of the potential at the point where the given charge is located, excluding its own potential:

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

The potential Ψ_α does not depend on d, since it is the potential due to the ionic atmosphere of the given charge. Substituting (16) into (15) and carrying out the transformations, we obtain

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

Already at $\varkappa d \sim 1$ the quantity p differs little from the force of interaction between two point charges in the absence of an electrolyte. This indicates that, as the degree of ionization of the macromolecule increases, the repulsive forces between units caused by electrostatic interaction may play a substantial role in determining the configuration of monomer units.

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