POTENTIAL DISTRIBUTION AT THE SURFACE OF A STRONGLY IONIZED POLYMER MACROMOLECULE IN A SOLUTION OF AN ELECTROLYTE

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Translated from Doklady Akademii Nauk SSSR, Vol. 142, No. 2,
pp. 399-402, January, 1962
Original article submitted October 14, 1961

It is known from experimental data that at high degrees of ionization polymer molecules in solution begin to unwind under the influence of the electrostatic repulsion of the charges of like sign attached to them [1]. Even at $\alpha \approx 0.6$-0.8, the macroions of the polymer are completely unwound, and take on the form of cylindrical rods having the length zb, where z is the degree of polymerization or the number of monomer units, and b is the hydrodynamic length of the monomer unit.

In [2], a measurement was made of the potential distribution at the surface of the cylindrical macromolecules, surrounded by a cloud of counterions, in a solution, containing no ordinary electrolyte.

The present paper considers a similar problem, but only in the presence of a non-polymer electrolyte. In this case, the external electrolyte shields the electrostatic repulsion forces between the macroions, provided that the concentration of the latter is small. At large concentrations of the non-polymer electrolyte, a cylindrical macromolecule can wind back up again because of the shielding of the charges located on neighboring monomer units. However, at large values of $\alpha \approx 0.6$-0.8, and at concentrations of a non-polymer electrolyte of the type of NaCl or KCl, reaching 0.1 mole/liter, and 0.1-0.5 monomole/liter for the polymer, the radius of the shielding double layer can be greater than the mean distance between charges. This distance, for $\alpha \sim 0.6$-0.8, is of the order of the length of one monomer unit, $b = 5.1 \cdot 10^{-8}$ cm, while the radius of the shielding double layer, at the concentrations mentioned above, is of the order of 10^{-7} cm.

Let us consider a cylindrical polymer macromolecule of length $h = zb$, and radius a, with $h \gg a$. Then the problem will, to a high degree of accuracy, have cylindrical symmetry. The cylinder will contain on its whole surface ν charges with a mean density $\sigma = -\nu e/2\pi ah$, where $e = 4.8 \cdot 10^{-10}$ CGS units. The system as a whole, containing the macroion, the counter-ions, and the electrolyte, is electrically neutral.

The potential distribution in the region surrounding the cylinder satisfies the Poisson-Boltzmann equation

$$\Delta\Psi = -\frac{4\pi}{D}\rho. \tag{1}$$

For the case of mono-monovalent electrolyte with monovalent counter-ions

$$\rho = n_1 e_1 e^{-e_1\Psi/kT} + n_2 e_2 e^{-e_2\Psi/kT}, \tag{2}$$

where n_1 is the total number of counter-ions and electrolyte ions of the same sign as the counter-ions, and n_2 is the number of ions having a charge with a sign the same as the sign of the charge on the surface of the macroion, per unit volume at $\Psi = 0$. Obviously, $e_1 = -e_2$. The space surrounding the macroion we shall divide into two r regions. In the region $a \leq r < R$, the potential is assumed so large that $|e\Psi/kT| \gg 1$. In the second region, $R < r < \infty$, the potential satisfies the opposite condition $|e\Psi/kT| \ll 1$.

In finding the potential at $a \leq r < R$, (2) may be simplified by neglecting the second term on the right-hand side since it is small compared with the first term. This means that, near the macroion, ions of the opposite sign, i.e., ions of the first sort, predominate. Then in this region Eq. (1) takes

$$\Delta\Psi_1 = -\frac{4\pi}{D} n_1 e_1 \exp\left(-\frac{e_1\Psi_1}{kT}\right). \tag{3}$$

The exact solution of this equation is well known for the case of cylindrical symmetry. In our case, this solution must be fitted with the solution for small potentials at the boundary of the regions at $r = R = R_0 + a$. However, the resulting transcendental equations, containing the integration constants and the unknown quantity R_0, are extremely akward, and do not lend themselves to satisfactory solution. To simplify the calculations we can make use of the fact that the width of the region in which $| e\Psi_1 / kT | \gg 1$, is small compared with the radius of the cylinder a. Then Eq. (6) may be solved under the assumption that the surface of the macromolecule is plane, thus

$$\frac{d^2\Psi_1}{dx^2} = -\frac{4\pi}{D} n_1 e_1 \exp\left(-\frac{e_1\Psi_1}{kT}\right). \tag{4}$$

The solution has the form

$$\Psi_1 = \frac{kT}{e_1} \ln\left[\frac{\varkappa_1^2}{2\beta^2}\sinh^2(\beta x - \delta)\right]. \tag{5}$$

The coordinate x is calculated from the surface of the macromolecule, and at the boundary between the two regions $x = R - a = R_0$, and

$$\varkappa_1^2 = \frac{4\pi n_1 e_1^2}{DkT}. \tag{6}$$

In the region where $| e\Psi_2/kT | \ll 1$, Eq. (2) may be linearized. Then, with an accuracy to terms of second order in $e\Psi_2/kT$, we have

$$\Delta\Psi_2 = -\frac{4\pi}{D} e_1 (n_1 - n_2) + \varkappa_2^2\Psi_2, \tag{7}$$

where

$$\varkappa_2^2 = \frac{4\pi e^2 (n_1 - n_2)}{DkT}. \tag{8}$$

The solution of the resulting inhomogeneous equation (7), bounded at $r \to \infty$, has the form

$$\Psi_2 = \frac{4\pi e_1 (n_1 - n_2)}{DkT} + CK_0(\varkappa_2 r), \tag{9}$$

where

$$K_0(\varkappa_2 r) = \int_0^\infty \exp(-\varkappa_2 r \cosh\eta)\, d\eta.$$

To determine the constants C, β, and δ, we may use the following relationships.

The condition for electrical neutrality of the system consisting of the macromolecule and the surrounding electrolyte

$$ve = 2\pi ah \int_0^{R_0} \rho_1\, dx + 2\pi h \int_{R=R_0+a}^{\infty} \rho_2 r\, dr. \tag{I}$$

The continuity of the potential and the field gradient at the boundary between the solutions at $x = R_0$ and $r = R_0 + a$:

$$\Psi_1|_{x=R_0} = \Psi_2|_{r=R_0+a}; \tag{II}$$

$$\left.\frac{d\Psi_1}{dx}\right|_{x=R_0} = \left.\frac{d\Psi_2}{dr}\right|_{r=R_0+a}. \tag{III}$$

At the boundary between the solutions the following relationships [3] must be satisfied with a sufficient degree of accuracy

$$\frac{e\Psi_1}{kT} = -1. \tag{IV}$$

After substituting in Eqs. (I)-(IV) the explicit form of ρ_1 and ρ_2 expressed in terms of Ψ_1 and Ψ_2

$$\rho_1 = n_1 e_1 \exp\left(-\frac{e_1\Psi_1}{kT}\right),$$

$$\rho_2 = e_1(n_1 - n_2) - \frac{D}{4\pi}\varkappa_2^2\Psi_2$$

followed by substituting the explicit forms of Ψ_1 and Ψ_2 given in Eqs. (5) and (9), we obtain a system of four transcendental equations. This system is very awkward. It may be simplified by making a reasonable estimate of the value of R_0. The value of R_0 depends on the concentrations of polymer and electrolyte, R_0 decreasing with increase in the concentrations, remaining less than $1/\varkappa_1$ but of the same order of magnitude. On the other hand, $1/\varkappa_1 \sim 1/\varkappa_2$. For an extended cylindrical macromolecule, the radius a, as found experimentally, has the value $5 \cdot 10^{-8} \leq a \leq 10^{-7}$ cm.

	$\varkappa_2^2 \cdot 10^{-14}$, cm^{-2}	$\varkappa^2 \cdot 10^{-14}$, cm^{-2}	$R_0 \cdot 10^8$ cm	$\left\|\frac{e\Delta\Psi}{kT}\right\|_{exp}$	$\left\|\frac{e\Delta\Psi}{kT}\right\|_{theo}$
$C_p = 0.1$ monomole/liter $C_{el} = 0.1$ mole/liter	1.45	1.03	≈5.7	≈2.7	≈3.3
$C_p = 0.05$ monomole/liter $C_{el} = 0.04$ mole/liter	0.62	0.42	≈9	≈4.2	≈5.6
$C_p = 0.02$ monomole/liter $C_{el} = 0.01$ mole/liter	0.188	0.136	≈9.8	≈6	≈8.8

Over a wide range of concentrations of polymer and electrolyte from $C_p = 0.1$ monomole/liter, and $C_{el} = 0.1$ mole/liter to $C_p = 0.01$ monomole/liter and $C_{el} = 0.01$ mole/liter, the value of $1/\varkappa_2$ changes very little, remaining equal, in order of magnitude, to 10^{-7}cm. Therefore, in the present case, the values of a and R_0 are close to one another. We can make use of this fact, and, in the system of equations (I)-(IV), we can replace the values of R_0 with a in those places where a substantial simplification results. We retain R_0 in the functions coth $(\beta R_0 - \delta)$ and sinh $(\beta R_0 - \delta)$, and then, in calculating it, we verify whether or not it is justifiable to make the substitution $R_0 \approx a$ (see the table). As a result we obtain the following expressions for the constants [3]:

$$C = -\frac{2kT}{e_1}\left(\frac{n_1}{n_1 + n_2}\right)\frac{1}{K_0(2\varkappa_2 a)}; \tag{10}$$

$$\beta^2 = \varkappa_2^2\left(\frac{n_1}{n_1 + n_2}\right)^2 f^2(2\varkappa_2 a) - \frac{\varkappa_1^2 \cdot 2{,}71}{2}; \tag{11}$$

$$\coth\delta = -\frac{\nu c^2}{kTDha\beta} - \left(\frac{n_1}{n_1 + n_2}\right)\frac{\varkappa_2 f(2\varkappa_2 a)}{\beta}; \tag{12}$$

$$R_0 = \frac{\delta}{\beta} + \frac{1}{\beta}\operatorname{arc\,coth}\sqrt{\frac{1{,}35\varkappa_1^2}{\beta^2} + 1}, \tag{13}$$

where $f(2\varkappa_2 a) = K_1(2\varkappa_2 a)/K_2(2\varkappa_2 a)$ is a slowly varying function of its argument at $\varkappa_2 a \sim 1$. Therefore the substitution $R_0 \approx a$ has an insignificant effect on the function.

The potential difference between the surface of the macromolecule and the volume of the solution is:

$$\Delta\Psi = \frac{kT}{e_1}\left\{\ln\left[\frac{\varkappa_1^2}{2\beta^2}\sinh^2\delta\right] - \frac{n_1 - n_2}{n_1 + n_2}\right\} \tag{14}$$

or, in dimensionless form:

$$\frac{e_1\Delta\Psi}{kT} = \ln\left[\frac{\varkappa_1^2}{2\beta^2}\sinh^2\delta\right] - \frac{\alpha C_p}{\alpha C_p + 2C_{el}}, \tag{15}$$

where the following substitutions have been made: $n_1 = (\alpha C_p + C_{el})N/10^3$, and $n_2 = C_{el}N/10^3$. Here N is Avogadro's number and α is the degree of ionization.

The solution of the problem will be more accurate if $R_0 \ll a$, i.e., in the case of large cylindrical colloidal particles, since the approximation of a plane surface holds right up to the place where the potentials are joined together. For the case $R_0 \approx a$, the difference between the plane and the cylindrical case in the region $a \leq r \leq R_0 + a$ will be appreciable at $r \sim (R_0 + a)$. But in view of the fact that the potential in both cases is described by rather complicated logarithmic functions, this difference has an insignificant effect on the total potential difference between the volume of the solution and the surface of the macromolecule.

We have given a comparison of formula (15) with the experimental data at $\alpha = 0.8$ [4] (see the table) for a solution of polymethacrylic acid in the presence of NaCl. The values $a = b = 5 \cdot 10^{-8}$ are taken from the experimental data for a broad class of polymers. As may easily be seen, at small values of C_p and C_{el}, the disagreement with the experimental data becomes appreciable because of the increasing diffuseness of the double layer, where $1/\varkappa_2$ becomes appreciably larger than a, and the condition $R_0 \sim a$ holds only in order of magnitude.

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