Corresponding Member of the Academy of Sciences of the USSR V. G. LEVICH and Yu. I. YALAMOV

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Abstract

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Corresponding Member of the Academy of Sciences of the USSR V. G. LEVICH and Yu. I. YALAMOV

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

It is known from experimental data that, at high degrees of ionization of polymer molecules in solution, they begin to uncoil under the action of the electrostatic repulsion of like charges fixed on them (1). Already at $\alpha \approx 0.6$—0.8, polymer macroions uncoil completely and assume the form of cylindrical rods of length zb, where z is the degree of polymerization or the number of monomer units, and b is the hydrodynamic length of a monomer unit.

In papers (2), the distribution of the potential at the surface of cylindrical macromolecules surrounded by clouds of counterions was determined in a solution containing no ordinary electrolyte.

In the present work an analogous problem is considered, but in the presence of a low-molecular-weight electrolyte. In this case the external electrolyte screens the electrostatic repulsion forces between macroions, provided that the concentration of the latter is small. At high concentrations of low-molecular-weight electrolyte, a reverse coiling of the cylindrical macromolecule may occur owing to screening of the charges located on neighboring monomer units. However, at large $\alpha \approx 0.6$—0.8 and at concentrations of low-molecular-weight electrolyte of the NaCl and KCl type reaching 0.1 mole/liter, and polymer 0.1—0.5 monomole/liter, the radius of the screening double layer may prove to be greater than the mean distance between charges. This distance at $\alpha \sim 0.6$—0.8 is of the order of the length of one monomer unit $b = 5.1 \cdot 10^{-8}$ cm, whereas the radius of the screening double layer at the concentrations indicated 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 contains on its entire surface ν charges with average density $\sigma = -\nu e/2\pi a h$, where $e = 4.8 \cdot 10^{-10}$ CGSE. The entire system as a whole, containing the macroion, counterions, and electrolyte, is electroneutral.

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

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

For the case of a univalent-univalent electrolyte with univalent counterions,

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

where n_1 is the sum of the number of counterions and electrolyte ions of the same sign as the counterions, and n_2 is the number of ions whose charge sign coincides with the sign of the surface charge of the macroion, per unit volume at $\Psi = 0$. Obviously, $e_1 = -e_2$. We divide the region surrounding the macroion into two parts with respect to r. In the region $a \ll r < R$ the potential is assumed to be so large that $|e\Psi/kT| \gg 1$. In the second region $R < r < \infty$ the potential satisfies the opposite condition $|e\Psi/kT| \ll 1$.

When finding the potential for $a \ll r < R$, one can simplify (2) by discarding the second term on the right-hand side because it is small compared with the first. This means that near the macroion, ions of the opposite sign predominate, i.e., ions of the first kind. Equation (1) will then take the following form in this region:

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

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

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

Its solution has the form

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

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

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

In the region where $|e\Psi_2/kT| \ll 1$, equation (2) can be linearized. Then, accurate 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 obtained inhomogeneous equation (7), bounded as $r \to \infty$, has the form

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

where

$$K_0(\varkappa_2 r) = \int_0^\infty \exp(-\varkappa_2 r \operatorname{ch}\eta)\, d\eta.$$

To determine the constants C, β, and δ, the following relations may be used.

The condition of electroneutrality of the system consisting of the macromolecule and the surrounding electrolyte:

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

The continuity of the potential and of the field strength at the junction of the solutions, for $x = R_0$ or $r = R_0 + a$:

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

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

At the junction, with a sufficient degree of accuracy, relation (3) must be satisfied:

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

After substituting into relations (I)–(IV) the explicit form of ρ_1 and ρ_2 in terms of Ψ_1 and Ψ_2,

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

$$\rho_2 = e_1(n_1 - n_2) - \frac{D}{4\pi}\chi_2^2\Psi_2,$$

with subsequent substitution, in place of Ψ_1 and Ψ_2, of their explicit expressions (5) and (9), we obtain a system of 4 transcendental equations. This system is very cumbersome. It can be simplified by a reasonable estimate of the magnitude of R_0. The value of R_0 depends on the concentrations of polymer and electrolyte; as the concentrations increase, R_0 decreases, remaining smaller than $1/\chi_1$, but in order of magnitude they are close to one another. On the other hand, $1/\chi_1 \sim 1/\chi_2$. In the case of an extended cylindrical macromolecule, its radius a, as established experimentally, has values $5 \cdot 10^{-8} \leq a \leq 10^{-7}$ cm.

Over a wide range of polymer and electrolyte concentrations, from $C_p = 0.1$ monomol/l, $C_{\text{el}} = 0.1$ mol/l to $C_p = 0.01$ monomol/l; $C_{\text{el}} = 0.01$ mol/l, the value $1/\chi_2$ changes only weakly, remaining of the order of 10^{-7} cm. Therefore, in the present case the quantities a and R_0 are close to one another. We may use this fact and replace, in the system of relations (I)–(IV), the quantity R_0 by a in those places where this leads to a substantial simplification. In the functions $\operatorname{cth}(\beta R_0 - \delta)$ and $\operatorname{sh}(\beta R_0 - \delta)$ we shall retain R_0, and then, calculating it, verify the validity of the replacement $R_0 \approx a$ (see Table 1). As a result we obtain the following expressions for the constants (3):

$$C = -\frac{2kT}{e_1}\left(\frac{n_1}{n_1 + n_2}\right)\frac{1}{K_0(2\chi_2 a)}; \tag{10}$$

$$\beta^2 = \chi_2^2\left(\frac{n_1}{n_1 + n_2}\right)^2 f^2(2\chi_2 a) - \frac{\chi_1^2 \cdot 2.71}{2}; \tag{11}$$

$$\operatorname{cth}\delta = -\frac{\gamma e^2}{kTDha\beta} - \left(\frac{n_1}{n_1 + n_2}\right)\frac{\chi_2 f(2\chi_2 a)}{\beta}; \tag{12}$$

$$R_0 = \frac{\delta}{\beta} + \frac{1}{\beta}\operatorname{arc\,cth}\sqrt{\frac{1.35\chi_1^2}{\beta^2} + 1}, \tag{13}$$

where $f(2\chi_2 a) = K_1(2\chi_2 a)/K_2(2\chi_2 a)$ is a slowly varying function of its argument for $\chi_2 a \sim 1$. Therefore the replacement $R_0 \approx a$ has little effect on this function.

The potential difference between the surface of the macromolecule and the bulk of the solution is

$$\Delta\Psi = \frac{kT}{e_1}\left\{\ln\left[\frac{\chi_1^2}{2\beta^2}\,\mathrm{sh}^2\,\delta\right] - \frac{n_1 - n_2}{n_1 + n_2}\right\} \tag{14}$$

or, in dimensionless form,

$$\frac{e_1\Delta\Psi}{kT} = \ln\left[\frac{\chi_1^2}{2\beta^2}\,\mathrm{sh}^2\,\delta\right] - \frac{\alpha C_p}{\alpha C_p + 2C_{\mathrm{el}}}, \tag{15}$$

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

The solution of the problem will be more accurate in the case $R_0 \ll a$, i.e., in the case of large cylindrical colloidal particles, since the approximation of a plane surface remains valid up to the point where the potentials are matched. In the case $R_0 \simeq a$, the difference between the plane and cylindrical cases in the region $a \ll r \ll R_0 + a$ will be appreciable for $r \sim (R_0 + a)$. But since in both cases the potential is described by rather similar logarithmic functions, this discrepancy will have only a slight effect on the total potential difference between the bulk of the solution and the surface of the macromolecule.

Table 1

	$\chi_2^2 \cdot 10^{-14}$, cm^{-2}	$\chi_1^2 \cdot 10^{-14}$, cm^{-2}	$R_0 \cdot 10^8$, cm	$\left\lvert\frac{e\Delta\Psi}{kT}\right\rvert_{\mathrm{exp}}$	$\left\lvert\frac{e\Delta\Psi}{kT}\right\rvert_{\mathrm{theor}}$
$C_p = 0.1$ monomol/l$C_{\mathrm{el}} = 0.1$ mol/l	1.45	1.03	≈ 5.7	≈ 2.7	≈ 3.3
$C_p = 0.05$ monomol/l$C_{\mathrm{el}} = 0.04$ mol/l	0.62	0.42	≈ 9	≈ 4.2	≈ 5.6

	$\chi_2^2 \cdot 10^{-14}$, cm^{-2}	$\chi_1^2 \cdot 10^{-14}$, cm^{-2}	$R_0 \cdot 10^8$, cm	$\left\lvert \frac{e\Delta\Psi}{kT} \right\rvert_{\text{exp}}$	$\left\lvert \frac{e\Delta\Psi}{kT} \right\rvert_{\text{theor}}$
$C_p = 0.02$ monomol/l$C_{\text{el}} = 0.01$ mol/l	0.188	0.136	≈ 9.8	≈ 6	≈ 8.8

We compared formula (15) with experimental data for $\alpha = 0.8$ (4) (see Table 1) for a solution of polymethacrylic acid in the presence of NaCl. The values $a = b = 5 \cdot 10^{-8}$ were taken from experimental data for a broad class of polymers. As is readily seen, at small C_p and C_{el} the discrepancy with the experimental data becomes appreciable because of the increase in the diffuseness of the double layer, for which $1/\chi_2$ becomes noticeably larger than a, and the condition $R_0 \sim a$ is valid only to order of magnitude.

Institute of Electrochemistry
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.