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**SHORT-RANGE INTERACTION IN A POLYELECTROLYTE
SOLUTION CONTAINING A MIXTURE OF MONO- AND DIVALENT
COUNTERIONS**

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ABSTRACT

The osmotic coefficient and the excess free energy have been calculated for a polyelectrolyte solution with mixtures of mono and divalent counterions. The results have been obtained by applying the cylindrical cell model in the Poisson-Boltzmann approximation. The short-range interaction between polyion and counterions, described by a square-well potential, has also been taken into account. The results of osmotic coefficient are presented as functions of the equivalent fraction of monovalent counterions for different values of ionic radii, depth of the potential well, and concentration.

INTRODUCTION

The cylindrical cell model which considers the electrostatic interactions among ions has usually been applied for the interpretation of thermodynamic properties of polyelectrolyte solutions with a fair success. Several times it appears, however, that the

discrepancy between experimental results and theoretical calculations is rather large [1,2,3] and consequently, it has stimulated some attempts [4,5,6] in order to improve the calculations by introducing the non-Coulombic, short-range interaction into the model.

In the present study we are interested in a polyelectrolyte solution containing a mixture of mono and divalent counterions. The first theoretical approach to this problem has been published long ago [7] followed by an experimental verification [8,9,10]. The same system has also been treated by applying the line charge model [11]. In both cases the electrostatic interaction has only been taken into account. In this contribution the influence of short-range interactions between polyion and counterions, represented by a square-well potential, on the osmotic coefficient and excess free energy will be presented.

THE MODEL AND THE POTENTIAL

The polyelectrolyte solution is represented as an ensemble of cylindrical cells with radius R and length h ($h \gg R$). In the axis of each cell is fixed a cylindrical polyion of radius a and length $h = vb$, where b is the length of the monomer unit. The charge of the polyion is $-v e_0$, supposed to be spread uniformly over its surface. In the free volume of the cell is a mixture of mono and z -valent counterions with the total charge equal in number but opposite in sign to the charge of the polyion. By denoting the radius of monovalent counterions with r_1 and z -valent with r_2 , it follows for the distances of closest approach $a_1 = a + r_1$ and $a_2 = a + r_2$. The short-range interactions of the non-Coulombic type are represented by a square-well potential V_{nc} for monovalent counterion:

$$\begin{aligned} V_{nc} &= \infty, & 0 \leq r < a_1 \\ V_{nc} &= -E_1, & a_1 \leq r \leq b_1 \\ V_{nc} &= 0, & b_1 < r \leq R \end{aligned} \quad (1)$$

and for z-valent counterions:

$$\begin{aligned} V_{nc} &= \infty, & 0 \leq r < a_2 \\ V_{nc} &= -E_2, & a_2 \leq r \leq b_2 \\ V_{nc} &= 0, & b_2 < r \leq R \end{aligned} \quad (2)$$

where r is the cylindrical coordinate and E_1 and E_2 are positive quantities. By supposing the additivity of Coulombic and non-Coulombic potential and by denoting

$$\eta_1 = e^{E_1/kT} \quad \text{and} \quad \eta_2 = e^{E_2/kT} \quad (3)$$

the Poisson-Boltzmann equation for this system reads

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi}{dr} \right) = - \frac{e_0}{\epsilon_0 \epsilon} \left[n_1^0 \exp\left(-\frac{e_0 \psi}{kT}\right) \eta_1 + z n_z^0 \exp\left(-\frac{z e_0 \psi}{kT}\right) \eta_2 \right] \quad (4)$$

with the boundary conditions

$$\left(\frac{d\psi}{dr} \right)_a = \frac{v e_0}{2\pi \epsilon_0 \epsilon a h}, \quad \left(\frac{d\psi}{dr} \right)_R = 0. \quad (5)$$

The values of the parameters η_1 and η_2 are given in equations (1) and (2). In equations above ψ is the electrostatic potential, k the Boltzmann constant, T the absolute temperature, e_0 the elementary charge, ϵ_0 the vacuum and $\epsilon \epsilon_0$ the solvent permittivity, n_1^0 and n_z^0 the number density of mono and z-valent counterions at $\psi = 0$.

To simplify the notation the dimensionless quantities are introduced

$$\left. \begin{aligned} y &= -\frac{e_0 \psi}{kT}, & t &= \ln \frac{r}{a}, & \gamma &= \ln \frac{R}{a} \\ t_1 &= \ln \frac{a_1}{a}, & t_{11} &= \ln \frac{b_1}{a}, & t_2 &= \ln \frac{a_2}{a}, & t_{22} &= \ln \frac{b_2}{a} \\ \lambda &= \frac{v e_0^2}{4\pi \epsilon_0 \epsilon k T h} \end{aligned} \right\} \quad (6)$$

The parameter λ is proportional to the linear charge density of the polyion which is the basic property of each polyelectrolyte. Furthermore, we introduce the equivalent fractions N_1^0 and N_z^0 in the place where $\psi = 0$ and their average values \bar{N}_1 and \bar{N}_z

$$\left. \begin{aligned} N_1^0 &= \frac{n_1^0}{n_1^0 + z n_z^0}, & N_z^0 &= \frac{z n_z^0}{n_1^0 + z n_z^0}, & \bar{N}_1 &= \frac{\bar{n}_1}{\bar{n}_1 + z \bar{n}_z}, & \bar{N}_z &= \frac{z \bar{n}_z}{\bar{n}_1 + z \bar{n}_z} \end{aligned} \right\} \quad (7)$$

and the ratio $\xi = \frac{\bar{n}_1 + z \bar{n}_z}{n_1^0 + z n_z^0}$.

The Poisson-Boltzmann equation and the boundary conditions now read

$$\begin{aligned} \frac{d^2 y}{dt^2} &= \frac{4\lambda}{(e^{2\gamma} - 1)\xi} e^{2t} \left[\eta_1 N_1^0 e^y + \eta_2 N_z^0 e^{zy} \right] \\ \left(\frac{dy}{dt} \right)_0 &= -2\lambda, \quad \left(\frac{dy}{dt} \right)_\gamma = 0 \end{aligned} \quad (8)$$

The average values \bar{N}_1 and \bar{N}_z may be obtained from

$$\bar{N}_1 = \frac{2 N_1^0}{\xi(e^{2\gamma} - 1)} \int_0^\gamma \eta_1 e^{y+2t} dt, \quad \bar{N}_z = \frac{2 N_z^0}{\xi(e^{2\gamma} - 1)} \int_0^\gamma \eta_2 e^{zy+2t} dt \quad (9)$$

Within the integration interval, $0 \leq t \leq \gamma$, each of the parameters η_1 and η_2 assumes three different values as indicated in equations (1) and (2). Let us repeat this condition in the new notation

$$\eta_1 = \begin{cases} 0, & 0 \leq t < t_1 \\ \eta_1, & t_1 \leq t \leq t_{11} \\ 1, & t_{11} < t \leq \gamma \end{cases} \quad \eta_2 = \begin{cases} 0, & 0 \leq t < t_2 \\ \eta_1, & t_2 \leq t \leq t_{22} \\ 1, & t_{22} < t \leq \gamma \end{cases} \quad (10)$$

Because equation (8) cannot be solved analytically we applied the Runge-Kutta method of the third order for numerical computation. The values of N_1^0 and N_Z^0 were chosen arbitrarily and the parameter ξ was found by an appropriate iteration procedure.

THE FREE ENERGY AND THE OSMOTIC COEFFICIENT

The excess free energy A_{ex} of a polyelectrolyte has three contributions

$$A_{ex} = U_{nc} + U_c - TS_{cf} \quad (11)$$

where U_{nc} is the non-Coulombic contribution, U_c the Coulombic contribution and S_{cf} is the configurational entropy [12]. U_{nc} was calculated from

$$U_{nc} = -E_1 \int_{a_1}^{b_1} n_1^0 e^y \eta_1 dV - E_2 \int_{a_2}^{b_2} n_Z^0 e^{zy} \eta_2 dV \quad (12)$$

The final expression is

$$U_{nc} = -2 \nu k T V_m \left\{ \eta_1 \ln \eta_1 n_1^0 \int_{t_1}^{t_{11}} e^{y+2t} dt + \eta_2 \ln \eta_2 n_Z^0 \int_{t_2}^{t_{22}} e^{zy+2t} dt \right\} \quad (13)$$

where $V_m = \pi a^2 b$ is the volume of the monomer unit. The Coulombic contribution U_c was calculated in two different ways, according to equations (14) and (15), giving different but equivalent expressions

$$U_c = \frac{1}{2} \int_V \rho \psi dV + \frac{1}{2} \int_S \sigma \psi(a) dS \quad (14)$$

$$U_c = \frac{\epsilon_0 \epsilon}{2} \int_V (\text{grad } \psi)^2 dV \quad (15)$$

where ρ is the local volume charge density and σ is the charge density on the surface of the polyion. The configurational entropy S_{cf} due to nonuniform distribution of counterions within the cell was calculated from

$$S_{cf} = -k \sum_{i=1}^z \int \left(n_i \ln n_i - \bar{n}_i \ln \bar{n}_i \right) dV \quad (16)$$

where n_i is the local concentration of mono and z -valent counterions and \bar{n}_i its average value.

From equation (14) it follows

$$U_c = \frac{1}{2} \nu k T y(0) - \nu k T V_m \left\{ \int_0^\gamma \eta_1 n_1^0 e^{y+2t} dt + \int_0^\gamma \eta_2 n_z^0 e^{zy+2t} dt \right\} \quad (17)$$

and from equation (15)

$$U_c = \frac{\nu k T}{4\lambda} \int_0^\gamma \left(\frac{dy}{dt} \right)^2 dt . \quad (18)$$

In both integrals of equation (17) the condition (10) has to be taken into account. The expression for S_{cf} is too long and for that reason it is not reproduced here.

The calculation of A_{ex} is a very long procedure and it will not be presented here. Therefore, we give only the final expression of the excess free energy per monomer unit by introducing equation (14) into equation (11)

$$\left(\frac{A_{ex}}{\nu k T} \right) = \frac{1}{2} y(0) + \bar{N}_1 \ln \frac{N_1^0}{\xi N_1} + \frac{\bar{N}_z}{z} \ln \frac{N_z^0}{\xi N_z} + \quad (19)$$

$$V_m \eta_1 n_1^0 \int_0^\gamma e^{y+2t} dt + V_m \eta_2 n_z^0 \int_0^\gamma e^{zy+2t} z y dt$$

and equation (15) into equation (11)

$$\left(\frac{A_{\text{ex}}}{v k T}\right)_2 = \frac{1}{4\lambda} \int_0^\gamma \left(\frac{dy}{dt}\right)^2 dt + \bar{N}_1 \ln \frac{N_1^0}{\xi N_1} + \frac{\bar{N}_z}{z} \ln \frac{N_z^0}{\xi N_z} + 2V_m \eta_1 n_1^0 \int_0^\gamma e^{y+2t} y dt + 2V_m \eta_2 n_z^0 \int_0^\gamma e^{zy+2t} z y dt \quad (20)$$

In equations (19) and (20) the fraction $(e^{2\gamma} - e^{2t_1}) / (e^{2\gamma} - e^{2t_2})$ was approximated by 1 which simplifies the writing and does not make an appreciable error. By multiplying equation (19) by 2 and subtracting equation (20) from it, we obtain the simple expression

$$\frac{A_{\text{ex}}}{v k T} = y(0) - \frac{1}{4\lambda} \int_0^\gamma \left(\frac{dy}{dt}\right)^2 dt + \bar{N}_1 \ln \frac{N_1^0}{\xi N_1} + \frac{\bar{N}_z}{z} \ln \frac{N_z^0}{\xi N_z} \quad , \quad (21)$$

very suitable for numerical evaluation.

The osmotic coefficient can be obtained from the partial derivative of A_{ex} with respect to volume [13]. The most convenient expression [12], adapted for this case is

$$\Phi = \frac{n_1^0 + n_z^0}{\bar{n}_1 + \bar{n}_z} \quad (22)$$

which reads in our notation
$$\Phi = \frac{z N_1^0 + N_z^0}{\xi (z \bar{N}_1 + \bar{N}_z)} \quad (23)$$

RESULTS AND DISCUSSION

All equations in the previous section were developed for the general case of mono and z-valent counterions. The numerical calculations have been made, however, for mixtures of mono and divalent counterions which are more frequently encountered in biological and industrial systems. For all calculations the following values of the

parameters characterizing the polyion were applied: $a = 0.8$ nm, $b = 0.252$ nm, and $\lambda = 2.84$. For counterions the following values of ionic radii were taken: $r_1 = 0.33$ nm (e. g. Cs^+) which gives $a_1 = 1.13$ nm, and $r_2 = 0.46$ nm (e. g. Be^{2+}) [14] which gives $a_2 = 1.26$ nm. In Figure 3 we have for comparison $a_1 = 0.8$ nm; 1.0 nm; 1.13 nm and $a_2 = 0.8$ nm; 1.1 nm; 1.26 nm. The relation between the concentration parameter γ and concentration c_m in moles of monomer units per liter is

$$\gamma = \ln \frac{R}{a} = -\frac{1}{2} \ln(10^3 N_A V_m) - \frac{1}{2} \ln c_m, \quad (24)$$

where N_A is the Avogadro number. Thus, we have $\gamma = 1.5$ ($c_m = 0.163$ mol/l), $\gamma = 2$ ($c_m = 0.06$ mol/l), $\gamma = 3$ ($c_m = 0.00812$ mol/l), and $\gamma = 4$ ($c_m = 0.0011$ mol/l). For almost all calculations the value $\gamma = 2$ was applied. The range of the short-range interaction, $b_1 = 1.4$ nm and $b_2 = 1.6$ nm, was the same in all cases.

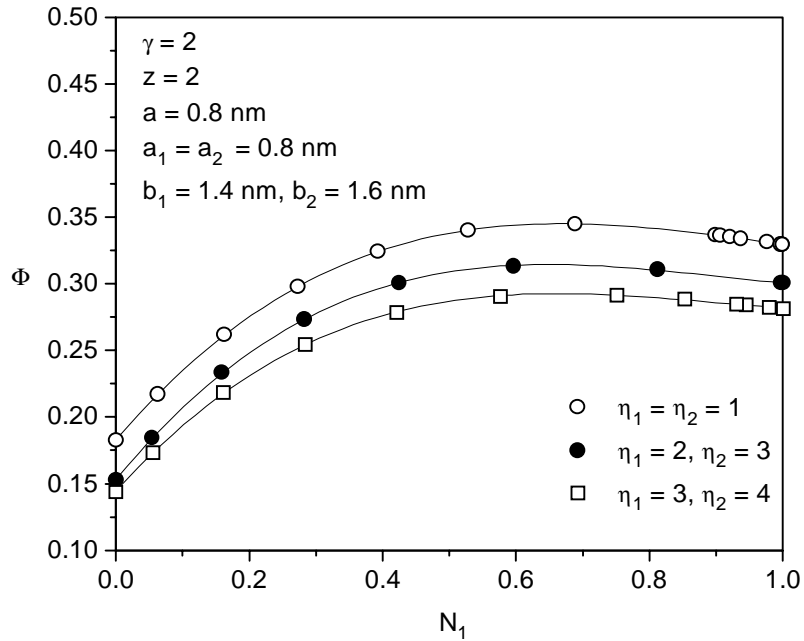


FIGURE 1. The influence of the short-range interaction on the osmotic coefficient. Counterions are point charges.

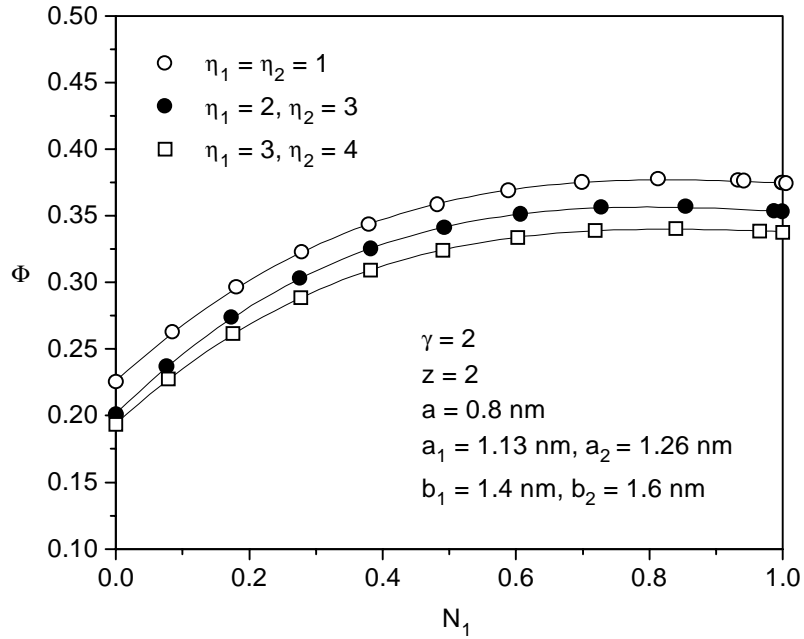


FIGURE 2. The influence of the short-range interaction on the osmotic coefficient. Radii of counterions are $r_1 = 0.33$ nm and $r_2 = 0.46$ nm.

The greater part of the figures presented in this article is devoted to the osmotic coefficient because, it can be obtained directly from the experiment, and gives an approximate information about the distribution of counterions inside the cell. The concentration of counterions at the border of the cell is decisive for the value of the osmotic coefficient, as shown in equation (22). A low value of Φ signifies that counterions are gathering around the polyanion and, as a result, a decrease of concentration is produced at the border of the cell. A comparison of Figures 1 and 2 reveals that a lower depth of the potential well (higher values of η_1 and η_2) gives rise to a stronger attraction of counterions to the polyanion, irrespective of the ionic size and the value of \bar{N}_1 . Furthermore, larger counterions are less attracted by the polyanion causing a higher value of Φ , as seen in Figure 3. The dependence of the osmotic coefficient on concentration is presented in Figure 4 and 5 for two different cases. For lower concentrations (higher values of the parameter γ) the well expressed maxima appear what has been confirmed by the experiments [8].

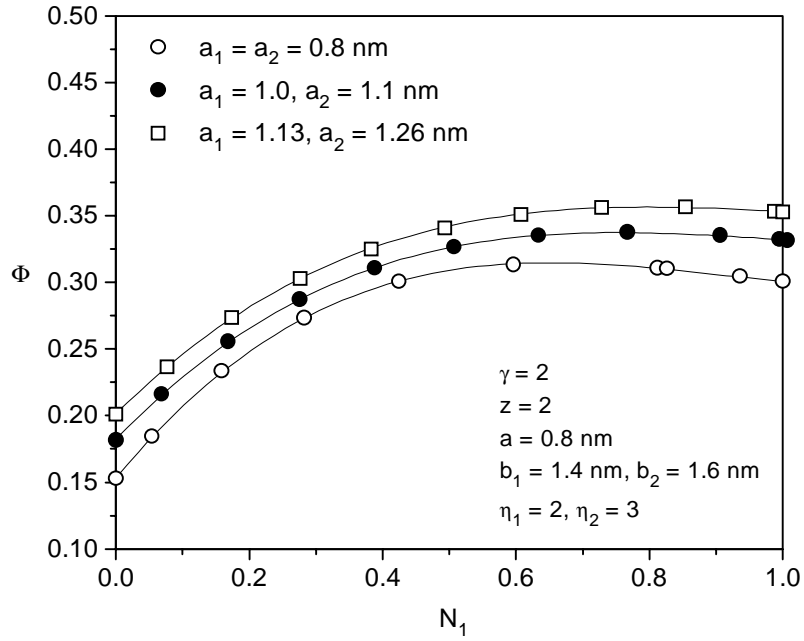


FIGURE 3. The influence of radii of counterions on the osmotic coefficient.

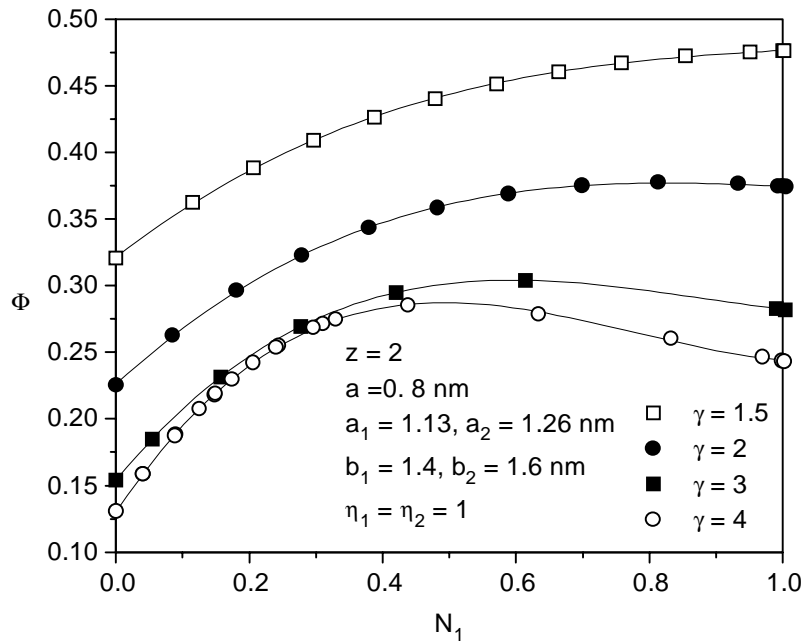


FIGURE 4. Dependence of the osmotic coefficient on concentration in the absence of the short-range interaction.

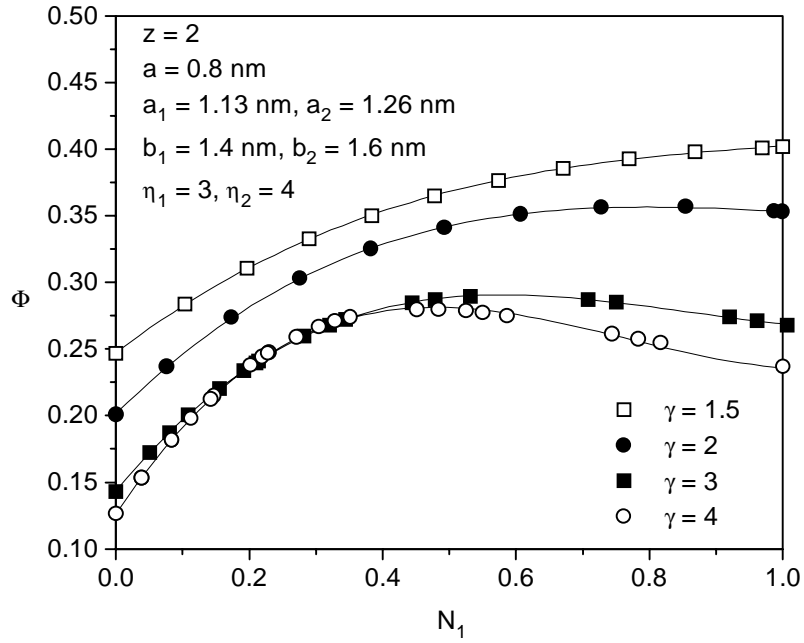


FIGURE 5. Dependence of the osmotic coefficient on concentration in the presence of the short-range interaction.

In Figures 6 and 7 the excess free energy is plotted against \bar{N}_1 for different values of γ and of the parameters η_1 and η_2 . In this case, a simple interpretation which would be analogous to that applied with osmotic coefficient is not possible.

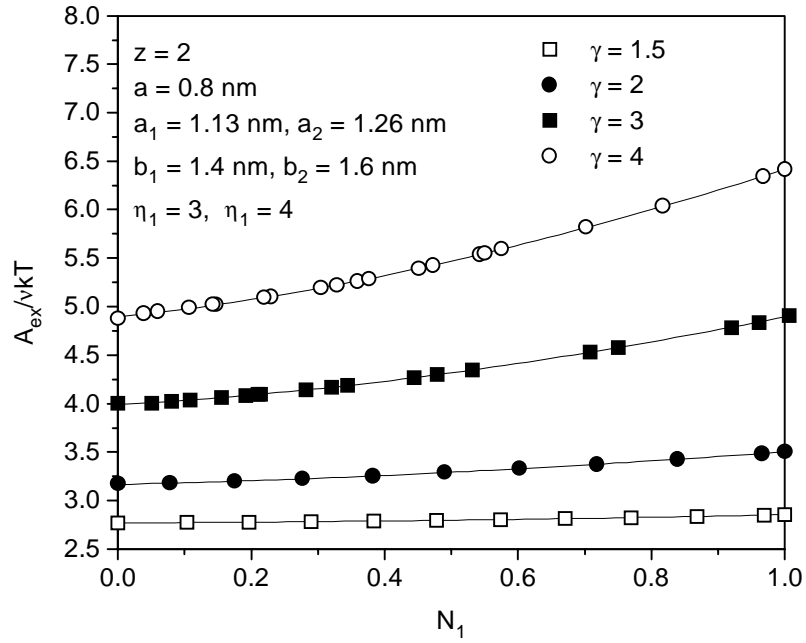


FIGURE 6. Dependence of A_{ex} / ikT on concentration.

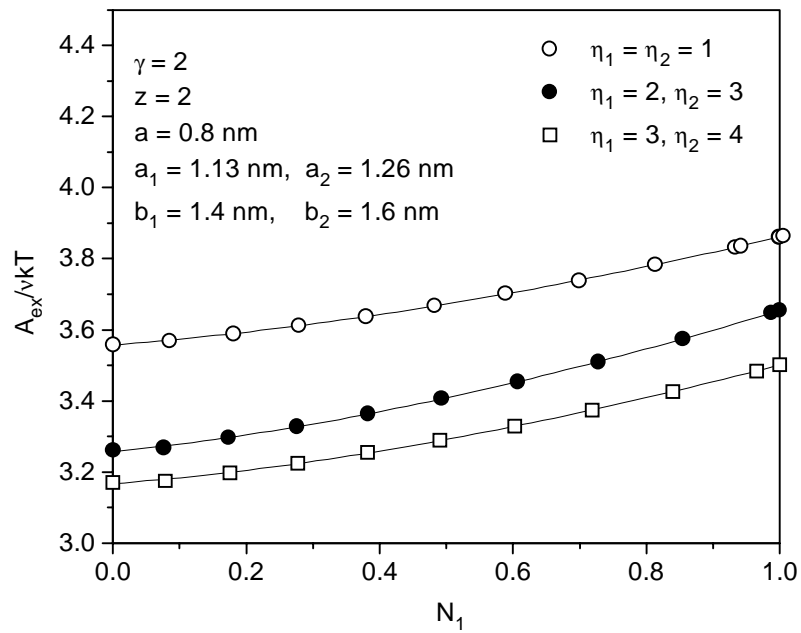


FIGURE 7. The influence of short-range interaction on A_{ex} / ikT .

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POVZETEK

Za raztopino polielektrolita z mešanico eno- in dvovalentnih protioionov smo na osnovi celičnega modela s cilindrično simetrijo in z uporabo Poisson-Boltzmannove enačbe izračunali osmozni koeficient in presežno prosto energijo. Pri računu smo upoštevali tudi kratkosežne interakcije med polioionom in protioioni, opisane s pravokotnim potencialom. Vrednosti osmoznega koeficienta smo podali kot funkcijo ekvivalentnega ulomka enovalentnih protioionov za različne vrednosti ionskih radijev, globine potencialne jame in koncentracije.