

Water-Soluble Highly Charged Fullerene Derivatives as Spherical Electrolytes.

Electrostatic Contributions to Thermodynamic Functions of Systems Containing Mixtures of Counterions Differing in Charge and Size[†]

Jože Škerjanc

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5,
1000 Ljubljana, Slovenia

Received 08-05-2006

[†] Dedicated to the memory of Prof. Dr. Davorin Dolar

Abstract

The Poisson-Boltzmann equation has been solved to obtain the electrostatic potential for the spherical cell model of a fullerene molecule at which charged functional groups are attached. The fullerene macroion is surrounded by mixtures of small counterions differing in size and charge. The electrostatic internal and free energies, degree of binding of counterions, osmotic coefficient, and distribution of counterions around the charged fullerene shell are calculated. These properties are presented as functions of radii, charges and mole fractions of counterions.

Key words: Poisson-Boltzmann equation, spherical cell model, thermodynamic functions, polyelectrolyte solutions, fullerene electrolytes, fullerenehexamalononic acid

1. Introduction

The influence of size and charge of small ions (counterions) on thermodynamic properties of solutions containing charged macromolecules (polyions) of opposite charge is well known.^{1,2} Quite a few papers have been devoted also to studies of polyelectrolyte solutions containing mixtures of counterions. It has been observed theoretically as well as experimentally that polyelectrolyte solutions with mixtures of counterions display interesting dependence of equilibrium properties on the mole fraction of a counterion species. For example, the osmotic coefficient of solutions of polystyrenesulfonates with mixtures of monovalent and divalent³ or trivalent⁴ counterions show distinct maxima when plotted against mole fraction. On the other hand, corresponding curves for the apparent molar enthalpies^{4,5} and volumes^{4,6} for the same systems have a sigmoidal shape. This striking behavior has been also interpreted theoretically in the light of the cylindrical cell model.³⁻⁷

Recently, we have reported⁸⁻¹³ on the first physicochemical studies of aqueous solutions of fullerene electrolytes, new type electrolytes that fill up the gap between simple electrolytes and polyelectrolytes. T_h symmetric derivative of fullerene C_{60} , at which

six malonic acid molecules have been attached, T_h - $C_{60}(C(COOH)_2)_6$, has been isolated and characterized by some fundamental data and properties. It has been found that fullerenehexamalononic acid, $C_{60}(COOH)_{12}$, has properties of a diprotic acid. The first carboxylic group of the malonic acid functional group behaves as an almost strong acid, whereas the second group is a weak acid. Its sodium salt, $C_{60}(COONa)_{12}$, has the properties of a highly charged strong electrolyte. For experimentalists as well as theoreticians working in the field of electrolyte solutions, such an electrolyte might be attractive at least for two reasons. One of them is that this solute is a good example of a highly asymmetric electrolyte due to the high charge number of the bulky ion. Another one is the charming spherical symmetry of the fullerene macroion that justifies the use of the spherical model for theoretical interpretation of this system.

The solution of the Poisson-Boltzmann equation in spherical geometry has been recently discussed¹⁴⁻¹⁷ for solutions of colloidal particles containing only counterions, or counterions and coions. The electrostatic potential and ion concentration profiles around or within a charged sphere have been presented, in some cases also the electrophoretic mobility of a spherical particle in these media.

In this article we shall extend our previous calculations on solutions of fullerene electrolytes containing one kind of counterions¹⁰ to solutions with mixtures of counterions which differ in charge and size. We shall apply the Poisson-Boltzmann equation and the spherical cell model to calculate some fundamental thermodynamic properties: the electrostatic internal and free energies, degree of binding, osmotic coefficient, and the distribution functions of counterions around the fullerene macroion. These properties will be presented as functions of the counterion radii and charge, as well as their mole fraction in the mixture.

2. Electrostatic Potential

As stated above, the general equations derived here refer to a spherical cell model of a fullerene electrolyte solution containing mixtures of counterions. The approximations and assumptions concerning the use of this model are well known.^{18,19} The volume of the solution is divided by the number of fullerene particle to obtain the average volume of the solution per fullerene particle. This volume is assumed to be spherical, and the spherical fullerene ion, which we shall call macroion, is located in the center of the cell of radius R . The fullerene macroion of radius a carries ν negative ionized groups which are supposed to be uniformly smeared over its surface. The cell contains the neutralizing number of counterions B and C with radii r_B and r_C and with the charge numbers z_B and z_C , respectively. The exclusion radii from the center of the macroion to the center of the smaller and larger counterions are denoted by b ($= a + r_B$) and c ($= a + r_C$), or according to eqn. (4) by dimensionless quantities $t_1 = \ln(b/a)$ and $t_2 = \ln(c/a)$. The Poisson-Boltzmann equation for this model has three domains:

$$\nabla^2 \Phi_1 = 0, \quad a \leq r \leq b \quad (1)$$

$$\nabla^2 \Phi_2 = 4\pi l_B z_B n_B^0 \exp(z_B \Phi_2), \quad b \leq r \leq c \quad (2)$$

$$\nabla^2 \Phi_3 = 4\pi l_B \sum_i z_i n_i^0 \exp(z_i \Phi_3), \quad c \leq r \leq R \quad (3)$$

where i in eqn. (3) stand for B or C, and dimensionless quantities Φ , t , and γ and the charge parameter Θ , are given by

$$\Phi = -e_0 \psi / kT, \quad r = a \exp(t), \quad R = a \exp(\gamma). \quad (4)$$

$$\Theta = \nu e_0^2 / \epsilon k T a = \nu l_B / a \quad (5)$$

In these equations ψ is the electrostatic potential, e_0 is the proton charge, ϵ is the dielectric constant of the solvent, n_i^0 is the number density of counterions i at $\psi(R) = 0$, l_B ($= e_0^2 / \epsilon k T$) is the Bjerrum length, r ($a \leq r \leq R$) is the radial distance from the center of the cell and k and T have their usual significance.

The boundary conditions are

$$(d\Phi_1 / dt)_{t=0} = -\Theta \quad (6)$$

$$\Phi_1(t_1) = \Phi_2(t_1), \quad (d\Phi_1 / dt)_{t_1} = (d\Phi_2 / dt)_{t_1} \quad (7)$$

$$\Phi_2(t_2) = \Phi_3(t_2), \quad (d\Phi_2 / dt)_{t_2} = (d\Phi_3 / dt)_{t_2} \quad (8)$$

$$\Phi_3(\gamma) = 0, \quad (d\Phi_3 / dt)_{t=\gamma} = 0 \quad (9)$$

Equation (1) can be solved analytically, with the result

$$\Phi_1 = \Phi_1(0) - \Theta(1 - \exp(-t)), \quad d\Phi_1 / dt = -\Theta \exp(-t) \quad (10)$$

where $\Phi_1(0)$ is the dimensionless potential at the surface of the macroion.

The differential eqn. (2) and (3) cannot be solved analytically and are transformed into eqn. (11) and (12) which are appropriate for numerical computation

$$d^2 \Phi_2 / dt^2 + d\Phi_2 / dt - k_B \exp(2t + z_B \Phi_2) = 0 \quad (11)$$

$$d^2 \Phi_3 / dt^2 + d\Phi_3 / dt - \sum_i k_i \exp(2t + z_i \Phi_3) = 0 \quad (12)$$

where i in eqn. (12) stand for B or C and the constants k_B and k_C are given by

$$k_B = \frac{4\pi e_0^2 a^2 z_B n_B^0}{\epsilon k T}, \quad k_C = \frac{4\pi e_0^2 a^2 z_C n_C^0}{\epsilon k T}. \quad (13)$$

For later use we introduce the equivalent fraction X_i of the species i , i.e. the fraction of the macroion charge compensated by the species i :

$$X_i = z_i N_i / \nu = z_i \bar{n}_i V_i / \nu = (z_i / \nu) \int_V \bar{n}_i dV \quad (14)$$

In eqn. (14) N_i is the total number of counterion species i , \bar{n}_i is its average number density, and V_i is the volume accessible to the species i , i.e. $V_B = 4\pi(R^3 - b^3)/3$ and $V_C = 4\pi(R^3 - c^3)/3$. It follows from eqn. (14) that the equivalent fractions X_B and X_C are related to the constants k_B and k_C by eqn. (15) and (16):

$$k_B \left[\int_{t_1}^{t_2} \exp(3t + z_B \Phi_2) dt + \int_{t_2}^{\gamma} \exp(3t + z_B \Phi_3) dt \right] = \Theta X_B \quad (15)$$

$$k_C \left[\int_{t_2}^{\gamma} \exp(3t + z_C \Phi_3) dt \right] = \Theta X_C \quad (16)$$

In all computations we used for the radius of the fullerenehexamalonate macroion the value⁸ $a = 0.77$ nm, which gives for water solutions at 25 °C ($\epsilon = 78.54$) and for $\nu = 12$ the value of the charge parameter $\Theta = 11.12$. The analytical concentration c and the concentration parameter γ are related by

$$c \exp(3\gamma) = 3\nu / 4\pi a^3 N_A \quad (17)$$

where N_A is the Avogadro constant. From this relation we get $c \exp(3\gamma) = 10.42$ mol COO⁻dm⁻³.

3. Fraction of Bound Counterions

Figure 1 shows the radial distribution function of counterions throughout the elementary cell for the equal equivalent fractions of monovalent and divalent counterions, i.e. for mixtures of two monovalent and one divalent counterions, for various values of their radii. The fraction of the total number of counterion species i , N_i , per spherical shell of thickness dr is $dN_i/N_i dr = n_i(r)dV/N_i dr$. Taking into account eqs. (4), (5), (13), and (14), and since $dr = rdt$, and the ratio $k_i/\Theta = 4\pi a^3 z_i n_i^0/v$, we get for the radial distance $b \leq r \leq c$, accessible only to the smaller counterions B, the expression

$$\frac{1}{N_B} \frac{dN_B}{dt} = k_B \exp(3t + z_B \Phi_2) / X_B \Theta \quad (18)$$

For the radial distance $c \leq r \leq R$, accessible to both counterions B and C we get

$$\frac{1}{N_B} \frac{dN_B}{dt} = k_B \exp(3t + z_B \Phi_3) / X_B \Theta \quad (19)$$

and

$$\frac{1}{N_C} \frac{dN_C}{dt} = k_C \exp(3t + z_C \Phi_3) / X_C \Theta \quad (20)$$

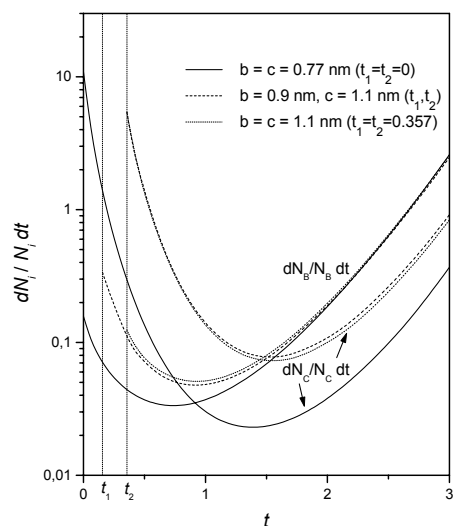


Figure 1. The radial distribution functions of counterions around the spherical macroion of radius $a = 0.77$ nm vs. the reduced radial distance t , for a mixture of two monovalent and one divalent counterions. Parameters: $v = 12$, $z_B = 1$, $z_C = 2$, $\gamma = 3$, $X_B = 0.5$.

Figure 1 shows that the distribution functions given by eqs. (18)–(20), have minima at $r_m = a \exp(t_m)$. The value of t_m can be indirectly determined from eqn. (19) and (20) by applying the analytical condition for the minimum, $d(dN_i/N_i dt)/dt = 0$, which gives

$$\left(\frac{d\Phi_3}{dt} \right)_{t_m} = -\frac{3}{z_i} \quad (21)$$

The osmotic coefficient, φ , and the fraction of free counterions, f_i , are measures of the total and

individual concentrations of counterions, respectively, at the surface of the cell.^{2,18} By analogy, with the practice adopted in the field of polyelectrolyte solutions containing only one counterion species,¹⁸ we can define the osmotic coefficient of solutions with a mixture of counterions by

$$\varphi = \frac{\sum_i n_i^0}{\sum_i \bar{n}_i} \quad (22)$$

which for the mixture of two counterionic species B and C yields

$$\varphi = \frac{(z_B k_C + z_C k_B) [\exp(3\gamma) - 1] V_B V_C}{3\Theta (z_B V_B X_C + z_C V_C X_B) V} \quad (23)$$

The fraction of free counterions has been defined^{2,7,18} by

$$f_i = \frac{n_i^0}{\bar{n}_i} = \frac{n_i^0}{v X_i / z_i V_i} \quad (24)$$

Taking into account eqs. (5), (13) and (14) and dimensionless quantities t_1 and t_2 we get

$$f_B = \frac{k_B [\exp(3\gamma) - \exp(3t_1)]}{3\Theta X_B} \quad (25)$$

and

$$f_C = \frac{k_C [\exp(3\gamma) - \exp(3t_2)]}{3\Theta X_C} \quad (26)$$

Evidently, the degree of binding, b_i , is

$$b_i = 1 - f_i \quad (27)$$

The influence of the radius and charge of counterions on the osmotic coefficient of the mixed fullerene electrolyte solutions is illustrated in Fig. 2–4. It can be seen from Fig. 2 that φ is not very sensitive to the size of counterions of the same charge. On the other hand, the dependence of φ on the charge of counterions is considerable (Fig. 3 and 4). All curves in Fig. 4 show distinct maxima, which are shifting to lower values of the equivalent fraction of the monovalent counterion B with the increasing charge of the multivalent counterion C. It has to be mentioned that such behavior of φ has been observed experimentally as well as theoretically also with solutions of linear polyelectrolytes containing mixtures of counterions.^{3,4} The osmotic coefficient increases with the increasing z_C for all values of X_B except for the values of X_B close to zero.

The corresponding values for the degree of binding of counterions calculated from eqn. (25)–(27) are presented in Figs. 5 and 6 for the same mixtures as before. It can be seen in Fig. 5 that the degree of binding of the less bound monovalent ions B decreases and consequently that of the more bound divalent ions C increases with increasing the ionic radius of monovalent counterions, keeping the radius of divalent counterions constant. The influence of the charge of counterion on b_i

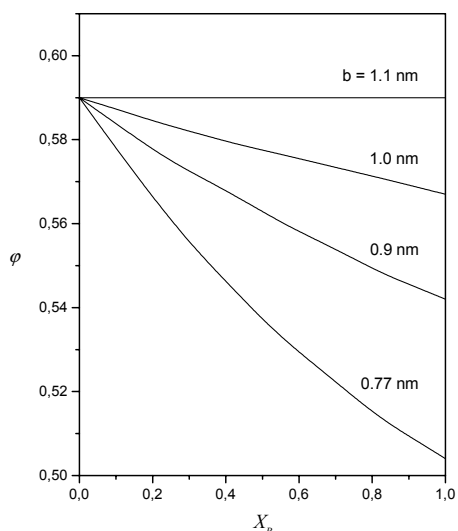


Figure 2. Dependence of the osmotic coefficient, ϕ , on the mole fraction X_B , for a mixture of two monovalent counterions B and C, calculated for the exclusion radii from the center of the macroion to the center of the smaller and larger counterions, b and c , respectively, as indicated. Parameters: $c = 1.1$ nm, $z_B = z_C = 1$, $\gamma = 2$.

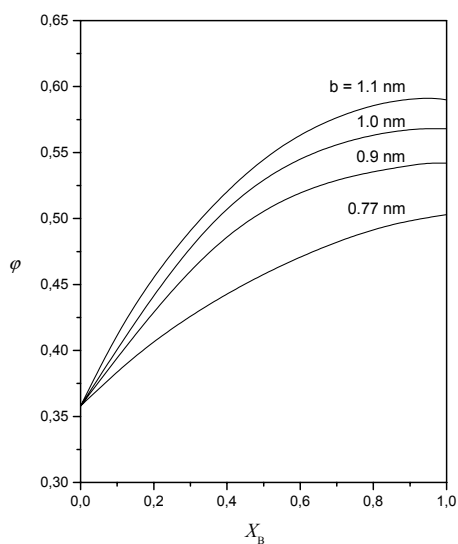


Figure 3. Osmotic coefficient of a fullerene electrolyte solution containing a mixture of monovalent and divalent counterions, B and C, respectively, vs. the mole fraction X_B , for the values of b as indicated. Parameters: $c = 1.1$ nm, $z_B = 1$, $z_C = 2$, $\gamma = 2$.

is for mixtures of monovalent and z_C -valent counterions C presented in Fig. 6. As expected the degree of binding of monovalent ions, b_B , decreases and of the multivalent ions, b_C , increases with the valency of the multivalent counterions. Also, it can be seen that the degree of binding of the less bound monovalent ionic species increases and of the more bound multivalent ionic species decreases with increasing the corresponding equivalent fractions, a situation observed also with polyelectrolyte solutions.

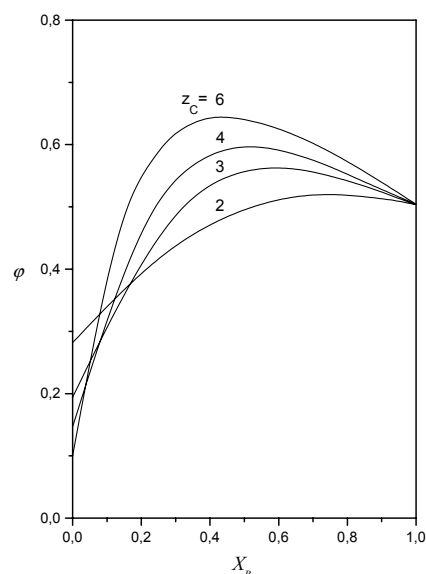


Figure 4. Osmotic coefficient of a fullerene electrolyte solution containing a mixture of monovalent and z_C -valent counterions vs. X_B . Parameters: $b = c = 0.77$ nm, $z_B = 1$, $\gamma = 2$.

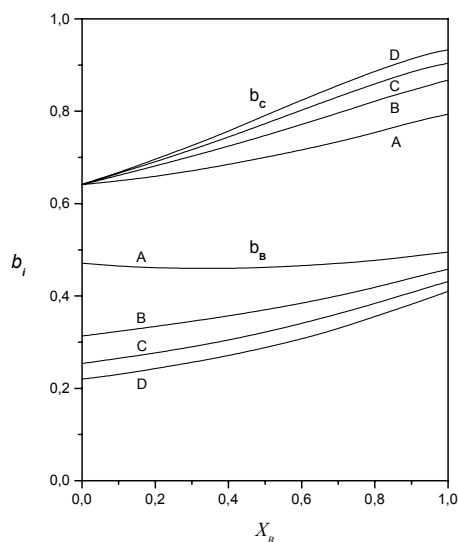


Figure 5. Degrees of binding, b_B and b_C , of the monovalent and divalent counterions B and C, respectively, against X_B for series of distances b and c . Parameters: A ($b = 0.77$ nm), B ($b = 0.9$ nm), C ($b = 1.0$ nm), D ($b = 1.1$ nm); $c = 1.1$ nm, $z_B = 1$, $z_C = 2$, $\gamma = 2$.

It has been shown for polyelectrolyte solutions²⁰ that the fraction of free counterions f_i obtained from transport measurements can be approximated by the ratio D_i/D_i^0 , where D_i and D_i^0 are the macroscopic self-diffusion coefficients of counterions in the presence and absence of the polyion, respectively. It can be estimated^{21,22} from eqn. (28)

$$\frac{D_i}{D_i^0} = 1 / \left[\frac{1}{V_i} \int_V \exp(z_i \Phi) dV \right] \left[\frac{1}{V_i} \int_V \exp(-z_i \Phi) dV \right] \quad (28)$$

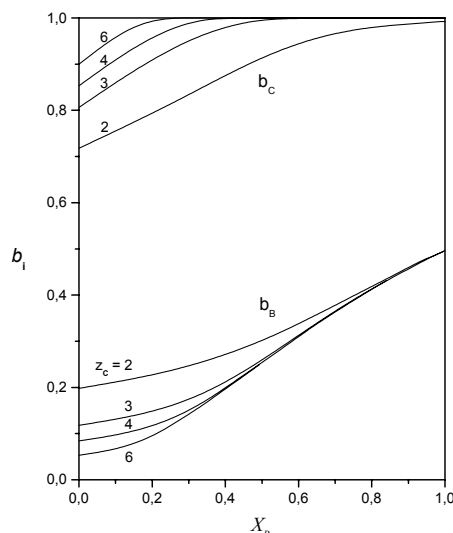


Figure 6. Degrees of binding, b_B and b_C , of the monovalent and multivalent counterions B and C, respectively, against X_B . Values of parameters as in Figure 4.

applying to the i -th ion in the counterion mixture. Supposing that the same relation holds also for counterions in the high electrostatic field of the fullerene macroion, we get

$$\frac{D_B}{D_B^0} = \frac{\int_{t_1}^{\gamma} \exp(3t + z_B \Phi_2) dt}{\int_{t_1}^{\gamma} \exp(3t - z_B \Phi_2) dt} \quad (29)$$

and

$$\frac{D_C}{D_C^0} = \frac{\int_{t_2}^{\gamma} \exp(3t + z_C \Phi_3) dt}{\int_{t_2}^{\gamma} \exp(3t - z_C \Phi_3) dt} \quad (30)$$

Equations (33) and (34) have been used in the interpretation of the experimental data presented recently in our paper¹² on the molar conductivity of fullerenehexamalonate aqueous solutions containing mixtures of sodium and calcium counterions. All details have been given there.

4. Electrostatic Energy and Free Energy

The electrostatic energy of the solution, U , calculated per macroion is related to the electrostatic potential, ψ , by the expression

$$U = \frac{\epsilon}{8\pi} \int_V (\text{grad } \psi)^2 dV \quad (31)$$

which upon insertion of dimensionless quantities Φ and t from eqn. (4) transforms into

$$U = \frac{\nu kT}{2\Theta} \int_0^{\gamma} \left(\frac{d\Phi}{dt} \right)^2 \exp(t) dt \quad (32)$$

The integral in eqn. (32) is the sum of three integrals in accordance with the three domains of the

model [cf. eqn. (1) – (3)]:

$$\begin{aligned} \int_0^{\gamma} \left(\frac{d\Phi}{dt} \right)^2 \exp(t) dt &= \int_0^{t_1} \left(\frac{d\Phi_1}{dt} \right)^2 \exp(t) dt \\ &+ \int_{t_1}^{t_2} \left(\frac{d\Phi_2}{dt} \right)^2 \exp(t) dt \\ &+ \int_{t_2}^{\gamma} \left(\frac{d\Phi_3}{dt} \right)^2 \exp(t) dt \quad (33) \end{aligned}$$

The first integral can be solved analytically by applying for the derivative $d\Phi/dt$ eqn. (10):

$$\int_0^{t_1} \left(\frac{d\Phi_1}{dt} \right)^2 \exp(t) dt = \Theta^2 [1 - \exp(-t_1)] \quad (34)$$

whereas the second and third integral must be solved numerically. The final expression for U reads

$$U = \frac{\nu kT}{\Theta} u \quad (35)$$

where

$$\begin{aligned} u &= \frac{1}{2} \Theta^2 [1 - \exp(-t_1)] + \frac{1}{2} \int_{t_1}^{t_2} \left(\frac{d\Phi_2}{dt} \right)^2 \exp(t) dt \\ &+ \frac{1}{2} \int_{t_2}^{\gamma} \left(\frac{d\Phi_3}{dt} \right)^2 \exp(t) dt \quad (36) \end{aligned}$$

The electrostatic energy of the system U is simply related²³ to the total electrostatic internal energy U_e

$$U_e = U(1 + d \ln \epsilon / d \ln T) \quad (37)$$

which can be compared with the experiment.

The electrostatic contribution A_e to the Helmholtz free energy can be obtained by the method^{24,25} that combines the electrostatic energy U with the configurational entropy S_{conf}

$$A_e = U - TS_{conf} \quad (38)$$

where S_{conf} represents the entropy change due to the ordering of counterions in a charged system. The final result reads

$$A_e = -U + \nu kT v = \frac{\nu kT}{\Theta} f \quad (39)$$

where

$$v = \Phi_1(0) + \sum_i \frac{X_i}{z_i} \ln f_i \quad (40)$$

$$f = -u + \Theta v \quad (41)$$

and the dimensionless potential at the surface of the macroion, $\Phi_1(0)$, can be calculated from

$$\Phi_1(0) = \Phi_1(t_1) + \Theta [1 - \exp(-t_1)] \quad (44)$$

Fig. 7 and 10 represent the electrostatic energy and free energy functions, u and f , respectively, for mixtures of monovalent B and divalent C counterions as a function of equivalent fraction X_B , for various values

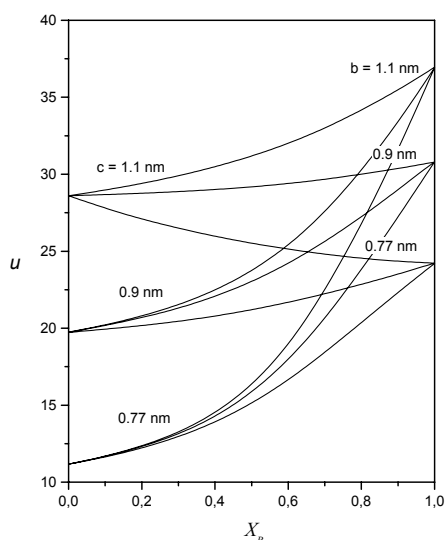


Figure 7. Dependence of the electrostatic energy function u of a fullerene electrolyte solution containing a mixture of monovalent and divalent counterions, on the mole fraction X_B for series of distances b and c . Parameters: $z_B = 1$, $z_C = 2$, $\gamma = 2$.

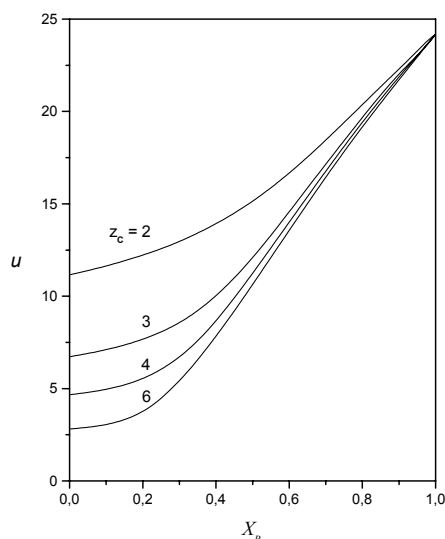


Figure 8. Dependence of the electrostatic energy function u on X_B for mixtures of monovalent and z_C -valent counterions. Parameters as in Fig. 4.

of distances b and c , the exclusion radii of counterions from the center of the macroion. The influence of the charge number of counterions on the electrostatic energy function u is for mixtures of monovalent and z_C -valent point-charged counterions demonstrated in Fig. 8. It is seen that with the increasing z_C the electrostatic energy u decreases for all values of X_B . Fig. 9 presents Δu ($\gamma : 1 \rightarrow 3$), the electrostatic contribution to the heat of dilution from $\gamma = 1$ to $\gamma = 3$, i.e., from the initial to final concentrations 0.519 to 0.00129 mol $\text{COO}^- \text{dm}^{-3}$, respectively. The most remarkable feature

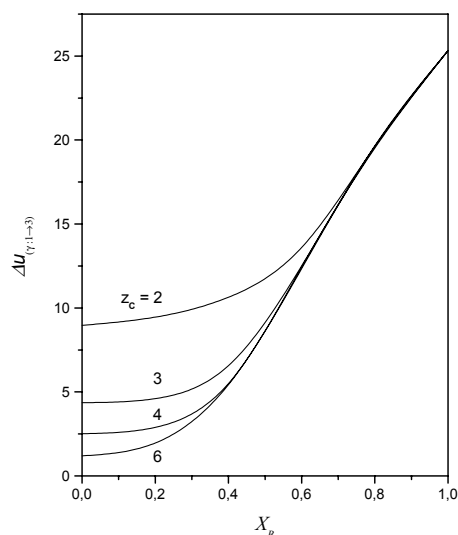


Figure 9. Electrostatic contribution to the enthalpy of dilution Δu vs. X_B for mixtures of monovalent and z_C -valent counterions. Concentration parameters $\gamma = 1$ and $\gamma = 3$ correspond to the initial to final concentrations 0.519 and 0.00129 mol $\text{COO}^- \text{dm}^{-3}$, respectively. Parameters: $b = c = 0.77$ nm, $z_B = 1$.

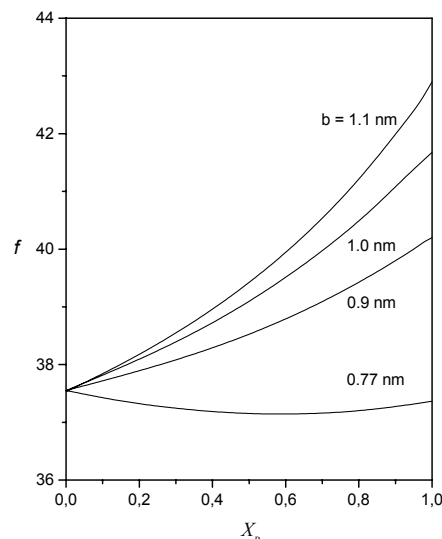


Figure 10. Electrostatic free energy function f vs. X_B of a fullerene electrolyte solution containing a mixture of monovalent and divalent counterions, for a series of the distances of closest approach b . Parameters as in Figure 3.

of the results in Fig. 9 is the fact that the enthalpy of dilution is practically the same for various counterion mixtures when X_B exceeds a given value. This critical value decreases with the increasing charge number z_C , so that for $z_C > 4$ the differences in the values of Δu become insignificant and are lying within the limit of the expected experimental errors. We mentioned in the introduction of this paper, that experimentally observed as well as theoretically predicted curves for the heat of dilution of solutions of linear polyelectrolytes containing mixtures of counterions, display well-defined sigmoidal

shapes.^{4,5} Contrary to those observations, we can see in Fig. 9 that in the case of spherical fullerene electrolytes the inflection point is only slightly indicated.

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Povzetek

Z rešitvijo Poisson-Boltzmannove enačbe za sferični celični model smo izračunali elektrostatski potencial okrog fulerenove molekule, na kateri so pripete nabite funkcionalne skupine. Fulerenov makroion obdajajo majhni protioni, ki se razlikujejo tako po velikosti kot po naboju. Izračunali smo elektrostatsko notranjo in prsto energijo, stopnjo vezanja protionov, osmozni koeficient in porazdelitev protionov okrog nabite fulerenove molekule. Prikazali smo odvisnost teh količin od velikosti, naboja in molskega ulomka protionov.