

CONTRIBUTIONS OF THE MACROION AND COUNTERIONS TO THE INTERNAL ENERGY OF FULLERENE ELECTROLYTE SOLUTIONS***Jože Škerjanc***Faculty of Chemistry and Chemical Technology, University of Ljubljana, 1000 Ljubljana, Slovenia**Dedicated to Professor Davorin Dolar on his 80th birthday*Received 29-05-2001***Abstract**

From the solution of the Poisson-Boltzmann equation for the spherical cell model of a fullerene electrolyte solution, the contributions of the fullerene macroion and counterions to the electrostatic energy of the solution are calculated. Computations are made for solutions containing mixtures of counterions differing in size and charge. The results are presented as functions of the macroion concentration and mole fractions of the counterions.

Introduction

Theoretical predictions for behavior of charged particles in solutions have been tested by various experimental properties that are related to various derivatives of the electrostatic free energy of the solution. Relevant thermodynamic properties are activity and osmotic coefficients, enthalpies of dilution, apparent molar volumes, *etc.* Although theoretical expressions for simple electrolytes demonstrate very distinctly the contribution of individual ionic species to the absolute value of these properties, in the relevant theoretical formulas for polyelectrolyte solutions the contributions of counterions and the polyion are not so explicitly evident. It has been demonstrated¹ that for high molecular weight polyelectrolytes only counterions contribute to the osmotic and activity coefficients. On the other hand, we have shown² that both the polyion and the counterions contribute to the enthalpy of dilution. So for anionic polyelectrolytes the positive polyion contribution to the electrostatic energy of the solution is partly compensated by the negative counterion contribution.

In this paper we present the relevant theoretical results for solutions of fullerene electrolytes, a new type electrolytes that fill up the gap between simple electrolytes and polyelectrolytes. Thus far we have reported³⁻⁶ on the first thermodynamic and transport studies of aqueous solutions of T_h symmetric derivative of fullerene C_{60} , at which six malonic acid molecules have been attached, $T_h-C_{60}(C(COOH)_2)_6$, and its sodium salt, $T_h-C_{60}(COONa)_6$, which has the properties of a highly charged ideally-spherical strong electrolyte. For this macroelectrolyte we shall show that contributions of the macroion and counterions to the internal energy of the solution is similar as those found for linear polyelectrolytes, although not so explicitly expressed.

Electrostatic Potential

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.^{7,8} 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 dimensionless quantities Φ , t , and γ and the charge parameter Θ , are given by

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

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

In these equations ψ is the electrostatic potential, e_0 is the proton charge, ε is the relative permittivity of the solvent, n^0 is the number density of counterions at $\psi(R) = 0$, $l_B (= e_0^2 / \varepsilon k T)$ 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

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

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

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

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

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) stands for B or C and the constants k_B and k_C are given by

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

For later use we introduce the equivalent fraction \bar{N}_i of the species i

$$\bar{N}_i = z_i \bar{n}_i V_i / \sum_i z_i \bar{n}_i V_i \quad (14)$$

where V_i is the volume accessible to counterion species i , i.e., $V_B = 4\pi (R^3 - b^3)/3$ and $V_C = 4\pi (R^3 - c^3)/3$, and \bar{n}_i is its average number density. The equivalent fraction \bar{N}_B and \bar{N}_C are related to the constants k_B and k_C by eqn. (15) and (16):

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

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

that follow from the electroneutrality condition

$$v \bar{N}_i = \int_V z_i \bar{n}_i dV. \quad (17)$$

In all computations we used for the radius of fullerenehexamalonates macroion the value^{3,5} $a = 0.77$ nm, which gives for water solutions at 25 °C ($\epsilon = 78.54$) the value of the charge parameter $\Theta = 11.12$. The analytical concentration c and the concentration parameter γ are related by

$$c \exp(3\gamma) = 3v / 4\pi a^3 N_A \quad (18)$$

where N_A is the Avogadro constant. From this relation we get $c \exp(3\gamma) = 10.42$ mol COO⁻/dm³.

Results and Discussion

The electrostatic energy of the system U calculated per macroion, which is the sum of the macroion and counterion contributions, U_m and U_c , respectively, is related to the potential by the expression

$$U = U_m + U_c = \frac{\epsilon}{8\pi} \int_V (\text{grad } \psi)^2 dV \quad (19)$$

where U_m and U_c are given by

$$U_m = \frac{1}{2} \int_S \sigma \psi(a) dS \quad (20)$$

and

$$U_c = \frac{1}{2} \int_V \rho \psi dV \quad (21)$$

Here, $\sigma (= -ve_0/S)$ and ρ are the surface and volume charge densities, and S and V are the surface and volume per macromolecule, respectively. Evidently, $\rho = e_0 \rho_n$, where ρ_n , the number density of charges, is given by the sum expression in eqn. (3). Upon insertion of dimensionless quantities Φ , t , and γ from eqn. (4) we get

$$U_m = \frac{vkT}{2} \Phi_1(0) \quad (22)$$

The contribution U_c is the sum of the contributions of the smaller and larger counterions, U_{cB} and U_{cC} . According to eqn. (21) we get

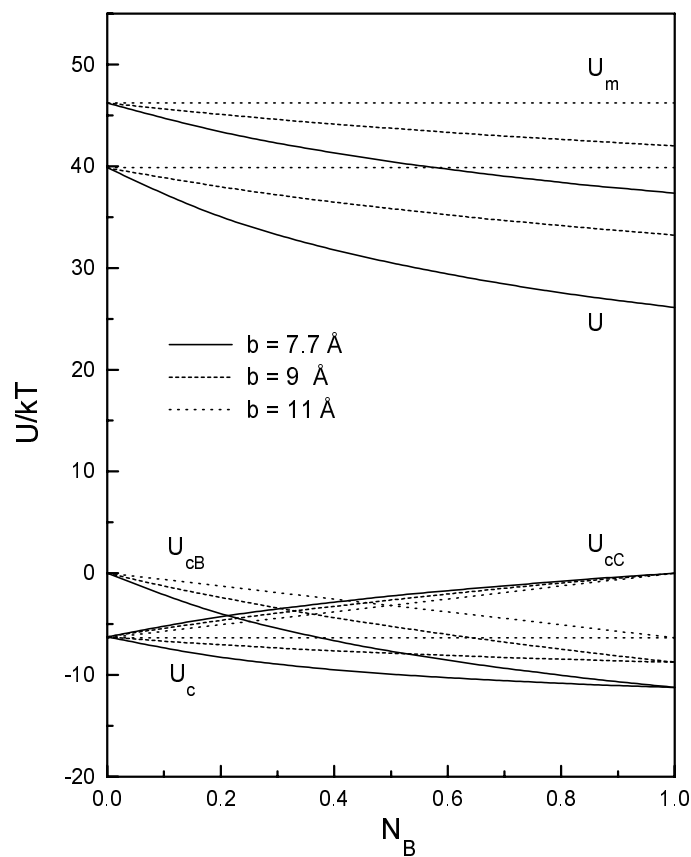


Figure 1. Contributions U_c , U_{cB} , and U_{cC} to the electrostatic energy U vs. \bar{N}_B , the mole fraction of counterions B, for a mixture of two kinds of monovalent counterions B and C differing in size. The exclusion radius from the center of the macroion to the center of the larger counterion C is $c = 11 \text{ \AA}$, the concentration parameter $\gamma = 2$ corresponds to the concentration about $0.026 \text{ mol COO}^-/\text{dm}^3$.

$$U_{cB} = -\frac{vkT}{2\Theta} k_B \left[\int_{t_1}^{t_2} \Phi_2 \exp(3t + z_B \Phi_2) dt + \int_{t_2}^{\gamma} \Phi_3 \exp(3t + z_B \Phi_3) dt \right] \quad (23)$$

and

$$U_{cC} = -\frac{vkT}{2\Theta} k_C \int_{t_2}^{\gamma} \Phi_3 \exp(3t + z_C \Phi_3) dt \quad (24)$$

Dependence of U_m , U_{cB} , U_{cC} , U_c , and U on the equivalent fraction \bar{N}_B is presented in Figure 1 for a mixture of two kinds of monovalent counterions B and C differing in size. In all computations we used for the charge parameter Θ the value:⁵ $\Theta = 11.12$, typical for fullerenehexamalonates. Figure shows that for any value of \bar{N}_B , U_m and U become more positive, and U_{cB} and U_c less negative, by increasing the radius of the smaller counterion B, and keeping the radius of the larger counterion C constant. It is

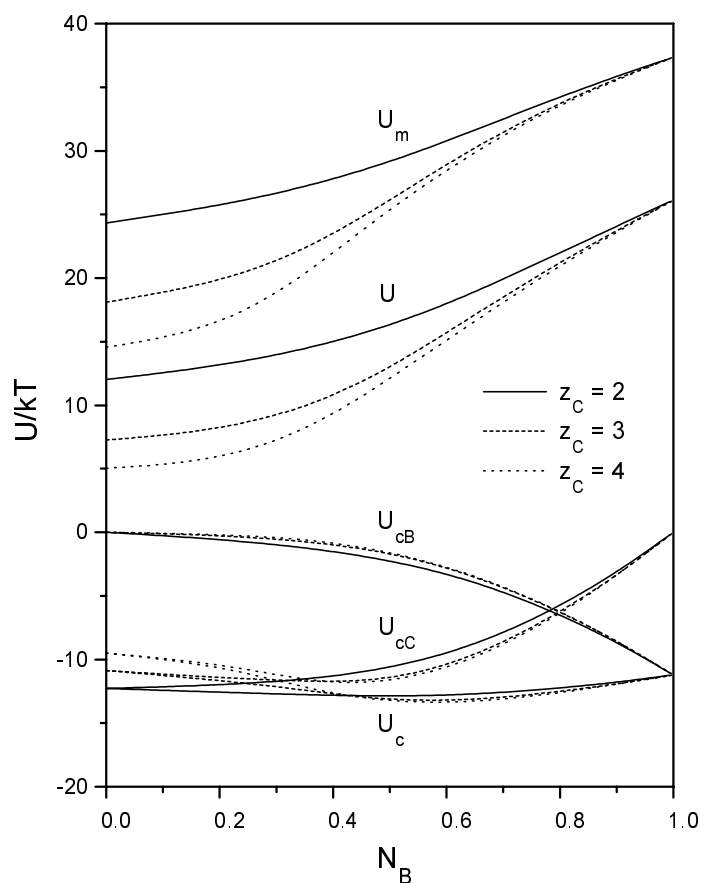


Figure 2. Dependence of U_m , U_c , U , and the electrostatic energies of monovalent and multivalent point-charged counterions, B and C, respectively, on the equivalent fraction of the monovalent counterion species \bar{N}_B , for a fullerenehexamalonate solution with a mixture of monovalent and z_c valent counterions.

well known that the degree of binding of counterions decreases by increasing their radius.⁹ Hence, the bulkier counterions are spread to larger distances from the macroion domain, *i.e.*, to the regions of weaker electrostatic field which are energetically less favored (*cf.* discussion below). As a consequence, the absolute value of the electrostatic energy of these counterions U_{cB} and thus also of all counterions becomes smaller and of the less screened macroion U_m larger.

Figure 2 represents various contributions to U as functions of \bar{N}_B for mixtures of

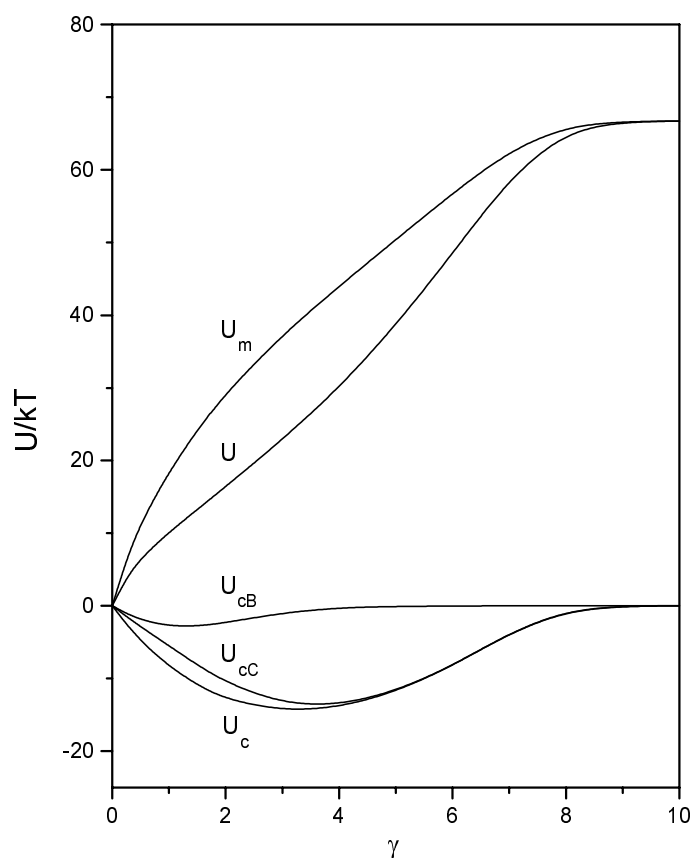


Figure 3. Variation of the contributions U_m , U_c , U_{cB} , and U_{cC} to the electrostatic energy U , of a mixture of two monovalent and one divalent point-charged counterions, B and C, respectively, with the concentration parameter γ .

monovalent counterions B and multivalent counterions C with the charge number z_C . It is seen that the values of counterion contributions U_{cB} , U_{cC} , and U_c depend only slightly on the charge number z_C , whereas dependence of the electrostatic energy of the macroion U_m , and consequently, of the entire system U on z_C is more explicit.

Concentration dependence of various contributions to U is presented in Figure 3 for mixtures of two monovalent and one divalent counterions. It can be seen that electrostatic contributions of monovalent as well as divalent counterions become negligible at concentrations at which the binding of counterions become insignificant (for monovalent counterions B at $\gamma \approx 4$, and for divalent counterions C at $\gamma \approx 8$). As a consequence, U_m and U join each other at extremely dilutions, and tend to the limiting value,⁶ $U/kT = 66.7$.

Interesting is the distribution of counterion energy among the counterion species throughout the elementary cell. Evidently, the radial counterion-energy distribution functions around the spherical macroion are given by

$$\frac{1}{U_{cB}} \frac{dU_{cB}}{dt} = \frac{\Phi_2 \exp(3t + z_B \Phi_2) + \Phi_3 \exp(3t + z_B \Phi_3)}{\int_{t_1}^{t_2} \Phi_2 \exp(3t + z_B \Phi_2) dt + \int_{t_2}^{\gamma} \Phi_3 \exp(3t + z_B \Phi_3) dt} \quad (25)$$

and

$$\frac{1}{U_{cC}} \frac{dU_{cC}}{dt} = \frac{\Phi_3 \exp(3t + z_C \Phi_3)}{\int_{t_2}^{\gamma} \Phi_3 \exp(3t + z_C \Phi_3) dt} \quad (26)$$

a results that follow from eqn. (23) and (24).

The results of computations are presented in Fig. 4 for a mixture of two monovalent and one divalent counterions, B and C, respectively, and for various ionic radii. It can be seen that 99% of the energy of divalent counterions is possessed by the ions which are laying within the radial distances $0.13 R$ ($t = 1$), from the surface of the macroion. This volume element represents only 0.2% of the total cell volume $4\pi R^3/3$. Due to the exclusion of the monovalent counterions B to regions farther from the macroion their energy distribution function is not so sharp. We can thus conclude that the contribution of so-called “osmotically active” counterions to the total energy U is negligible. Obviously, the overall energy change accompanying for example the dilution process, that is experimentally demonstrated as the heat of dilution, is governed by the

energy of ions in the immediate vicinity of the macroion, and not by the energy of “free

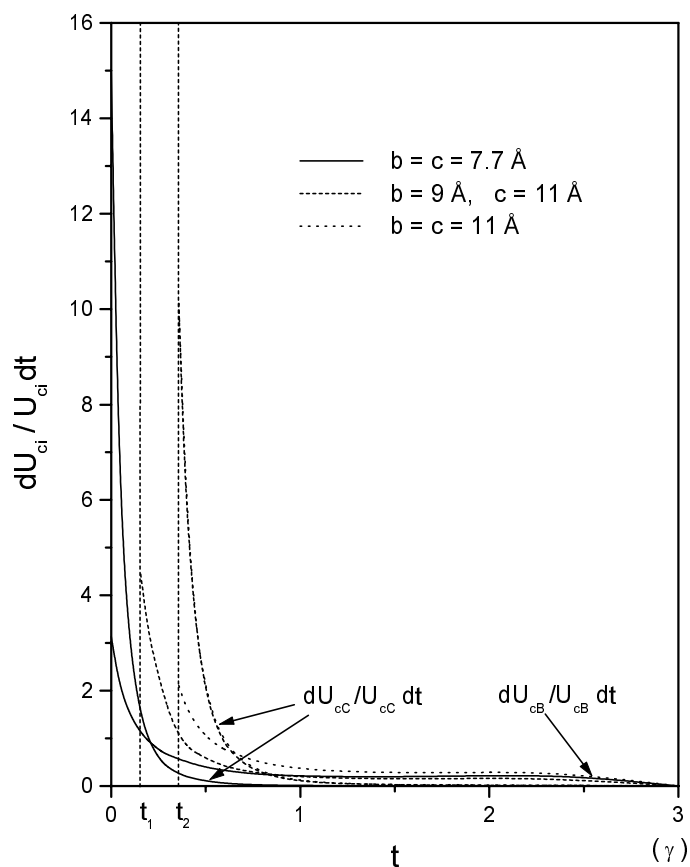


Figure 4. The radial electrostatic energy distribution functions of counterions around the spherical macroion, for a mixture of two monovalent and one divalent counterions, B and C, respectively, vs. the dimensionless radial distance t . The concentration parameter $\gamma=3$.

counterions” that determine the values of the osmotic and activity coefficients. Similar finding has been found also for linear polyelectrolytes.²

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Povzetek

Z rešitvijo Poisson-Boltzmannove enačbe za sferični celični model raztopine fulerenovega elektrolita smo izračunali prispevek fulerenskega makroiona in protiionov k elektrostatski energiji raztopine. Račune smo naredili za raztopine z mešanico protiionov, ki se ločijo tako po velikosti kot tudi po naboju. Rezultate podajamo v odvisnosti od koncentracije makroelektrolita in molskega ulomka protiionov.