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**WATER-SOLUBLE FULLERENE ELECTROLYTES.  
LIMITING VALUES OF THERMODYNAMIC FUNCTIONS\***

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**Abstract**

In a previous paper from this laboratory results from the solution of the Poisson-Boltzmann equation for the spherical cell model of a fullerene molecule at which charged groups are attached have been presented. The electrostatic internal and free energies, degree of binding of counterions, osmotic coefficient, and distribution of counterions around the charged fullerene shell have been calculated. Numerical computations have shown that some properties tend to the well-defined limiting values for vanishing concentrations. In this paper it is shown that limiting values of these properties can be predicted by the analytical solution of the Poisson-Boltzmann equation.

**Introduction**

Recently we have reported on the first experimental<sup>1</sup> and theoretical<sup>2</sup> results on aqueous solutions of  $T_h$  symmetric derivative of fullerene  $C_{60}$ , at which six malonic acid molecules have been attached,  $T_h-C_{60}(C(COOH)_2)_6$ . It has been found that fullerenehexamalononic acid,  $C_{66}(COOH)_{12}$ , has properties of a diprotic acid. The first carboxylic group,  $COOH_{(1)}$ , of the malonic acid functional group behaves as an almost strong acid, whereas the second  $COOH_{(2)}$  group is a weak acid with  $pK_2$  of about 5.5.

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\* Dedicated to Professor Drago Leskovšek on his 80<sup>th</sup> birthday.

We may expect that the salts of  $C_{66}(\text{COOH})_{12}$  with strong bases should have the properties of a strong electrolyte, and could serve therefore as a good example of a highly asymmetric electrolyte due to the high charge number of the bulky ion.

In the second article on this subject<sup>2</sup> the theoretical results for some fundamental thermodynamic properties of fullerenehexamalonate solutions have been presented: the electrostatic internal and free energies, degree of binding, osmotic coefficient, and the distribution function of counterions around the fullerene shell. The nonlinearized Poisson-Boltzmann equation has been used for this purpose which is still a popular and practical method of describing the electrical double layers in ionic solutions. Theoretical computations have shown that in the limit of high dilution various properties studied tend to the well defined limiting values. In this contribution we show that limiting values can be elucidate also by the analytical solution of the theoretical expressions.

### Theoretical model

The general equations derived here refer to a spherical cell model of a fullerene electrolyte solution. The volume of the solution is divided by the number of fullerene particles to obtain the average volume of solution per fullerene particle. This volume is assumed to be spherical, and the spherical fullerene ion, which we shall call macroion, is situated in the center of this cell.

The macroion of radius  $a$  carries  $P$  ionizable groups, and of these  $P$  groups  $\nu$  are actually ionized, so that  $\alpha = \nu/P$  is degree of ionization. It is supposed that the charges on the macroion are negative and that they are uniformly smeared over its surface. The spherical cell of radius  $R$  contains  $\nu/z$  positive counterions of radius  $r_c$  and with the charge number  $z$ . The exclusion radius from the centre of the macroion to the centre of the counterion is denoted by  $b$  ( $= a + r_c$ ), or according to the equations below by a dimensionless quantity  $t_l = \ln(b/a)$ . The Poisson-Boltzmann equation for this model has two domains: model has two domains:

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

$$\nabla^2 \Phi_2 = 4\pi l_B z^2 n_0 \exp(\Phi_2), \quad b \leq r \leq R \quad (2)$$

where dimensionless quantities  $\Phi$ ,  $t$  and  $\gamma$  are given by

$$\Phi = -ze_0\psi/kT, \quad r = a \exp(t), \quad R = a \exp(\gamma) \quad (3)$$

In these equations  $\psi$  is the electrostatic potential,  $e_0$  is the proton charge,  $\varepsilon$  is the relative permittivity of the solvent,  $n_0$  is the number density of counterions at  $\psi(R) = 0$ ,  $l_B (= e_0^2/\varepsilon kT)$  is the Bjerrum length,  $r$  ( $a \leq r \leq R$ ) is the radial distance from the centre of the cell, and  $k$  and  $T$  have their usual significance.

For the later use we introduce the charge parameters,  $\Theta_0$  and  $\Theta$ :

$$\Theta_0 = ve_0^2/\varepsilon kTa = vl_B/a, \quad \Theta = z\Theta_0 \quad (4)$$

The boundary conditions are

$$(d\Phi_1/dt)_{t=0} = -\Theta \quad (5)$$

$$\Phi_1(t_1) = \Phi_2(t_1); \quad (d\Phi_1/dt)_{t_1} = (d\Phi_2/dt)_{t_1} \quad (6)$$

$$\Phi_2(\gamma) = 0; \quad (d\Phi_2/dt)_{t=\gamma} = 0 \quad (7)$$

Eq. (1) can be solved analytically, with the result

$$\Phi_1 = \Phi_1(0) - \Theta(1 - \exp(-t)); \quad d\Phi_1/dt = -\Theta \exp(-t) \quad (8)$$

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

### Limiting Values

The analytical concentration  $c$  and the concentration parameter  $\gamma$  are related by

$$c \exp(3\gamma) = 3/4\pi a^3 N_A \quad (9)$$

where  $c$  is the concentration of the fullerene macroion, FM, in mol FM/L, and  $N_A$  is the Avogadro constant. In the limit of high dilution when  $c \rightarrow 0$  ( $\gamma \rightarrow \infty$ ) the number density of counterions  $n_0 \rightarrow 0$ . In this case Eq. 2 resembles the form of Eq. 1 and can be solved analytically, with the result

$$\Phi_2 = \Theta (\exp(-t) - \exp(-\gamma)) = \Theta \exp(-t); \quad d\Phi_2/dt = -\Theta \exp(-t) \quad (10)$$

Considering the boundary condition Eq. 6, we find from Eqs. 8 and 10 that

$$\lim_{\gamma \rightarrow \infty (c \rightarrow 0)} \Phi_1(0) = \Theta \quad (11)$$

or

$$\lim_{c \rightarrow 0} \psi(a) = -\frac{ve_0}{\epsilon a} \quad (12)$$

which is the potential of the macroion itself in the absence of the ionic atmosphere contribution.

The degree of counterion binding can be defined on various ways.<sup>3</sup> The most common property used for this purpose is the osmotic coefficient,  $\varphi$ , which is the measure of the amount of free counterions and has been defined by<sup>4</sup>

$$\varphi = \frac{n_0}{\bar{n}} \quad (13)$$

where  $\bar{n}$  is the average number density of counterions. Obviously, in the limit when  $c \rightarrow 0$  the number density  $n_0 \rightarrow \bar{n}$ , and the osmotic coefficient tends to one.

Following the idea of Bjerrum<sup>5</sup> we can consider as bound counterions those ions which are located in the region between the distance of closest approach of counterions to the fullerene macroion,  $b$ , and the distance  $r_m$ , at which the radial distribution function of counterions has its minimum,<sup>2</sup> *i.e.*, for  $t_1 \leq t \leq t_m$ :

$$b = \frac{\int_{t_1}^{t_m} \exp(3t + \Phi_2) dt}{\int_{t_1}^{\gamma} \exp(3t + \Phi_2) dt} \quad (14)$$

Evidently, the fraction of free counterions,  $f_c$ , is

$$f_c = 1 - b \quad (15)$$

When  $c \rightarrow 0$  ( $\gamma \rightarrow \infty$ ) the integral in the denominator tends to infinity, and consequently  $b \rightarrow 0$  and  $f_c \rightarrow 1$ .

The fraction of free counterions obtained from transport properties can be approximated<sup>6</sup> by the ratio  $D_c/D_c^0$ , where  $D_c$  and  $D_c^0$  are the macroscopic self-diffusion coefficients of the counterion in the presence and absence of the macroion, respectively. In the previous paper<sup>2</sup> we have obtained the following expression for  $D_c/D_c^0$ :

$$\frac{D_c}{D_c^0} = \frac{\varphi(\exp(3\gamma) - \exp(3t_1))}{3 \int_{t_1}^{\gamma} \exp(3t - \Phi_2) dt} \quad (16)$$

It can be shown that in the limit when  $\gamma \rightarrow \infty$  the integral in Eq. 16 equals  $1/3 [\exp(3\gamma) - \exp(3t_1)]$  and the ratio  $D_c/D_c^0$  equals to 1.

Numerical results<sup>2</sup> have also pointed out that for highly diluted solutions of the salts of fullerenehexamalononic acid, the distance  $r_m$  or relative distance  $t_m$ , at which the radial distribution function of counterions  $dN/N dt$  has its minimum, tend to a definite limiting value. The condition for the minimum has been found to be

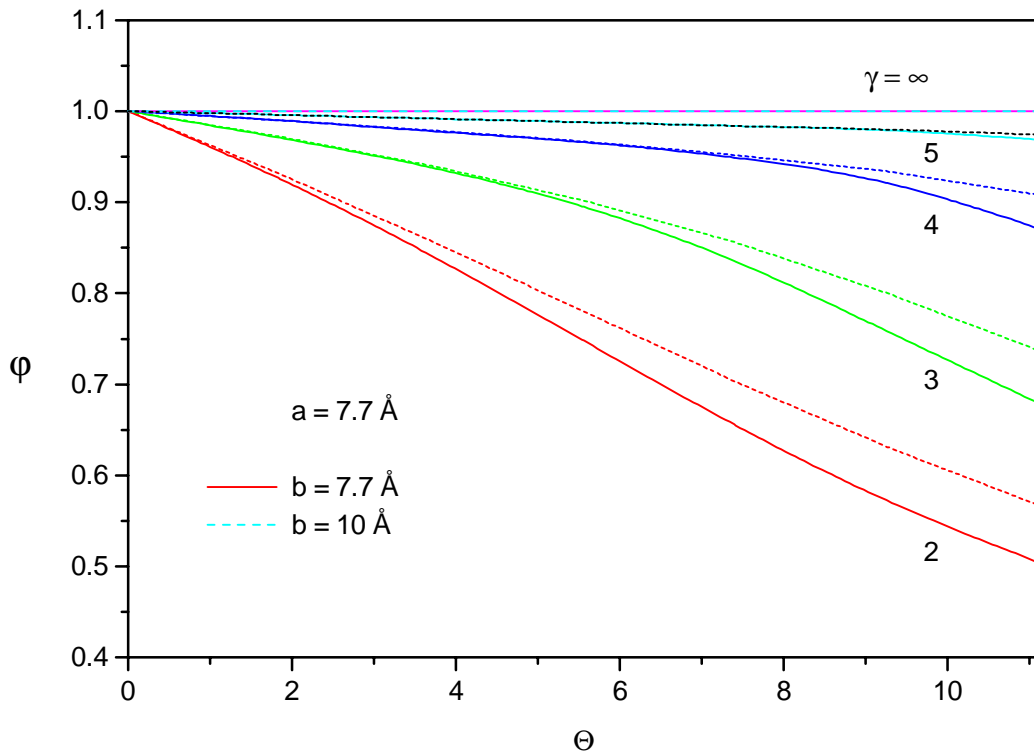
$$\left( \frac{d\Phi_2}{dt} \right)_{t_m} = -3 \quad (17)$$

which according to Eq. 10 gives

$$\lim_{\gamma \rightarrow \infty (c \rightarrow 0)} t_m = \ln \frac{\Theta}{3} \quad (18)$$

Similarly we can calculate the limiting values of the electrostatic energy function  $u$  and free energy function  $f$  of the solution. By applying the limiting values for the gradient  $d\Phi_2/dt$  (Eq. 10) and for the dimensionless potential at the surface of the macroion  $\Phi_1(0)$  (Eq. 11) to Eqs. 30, 34 and 35 of Ref. 2 we find

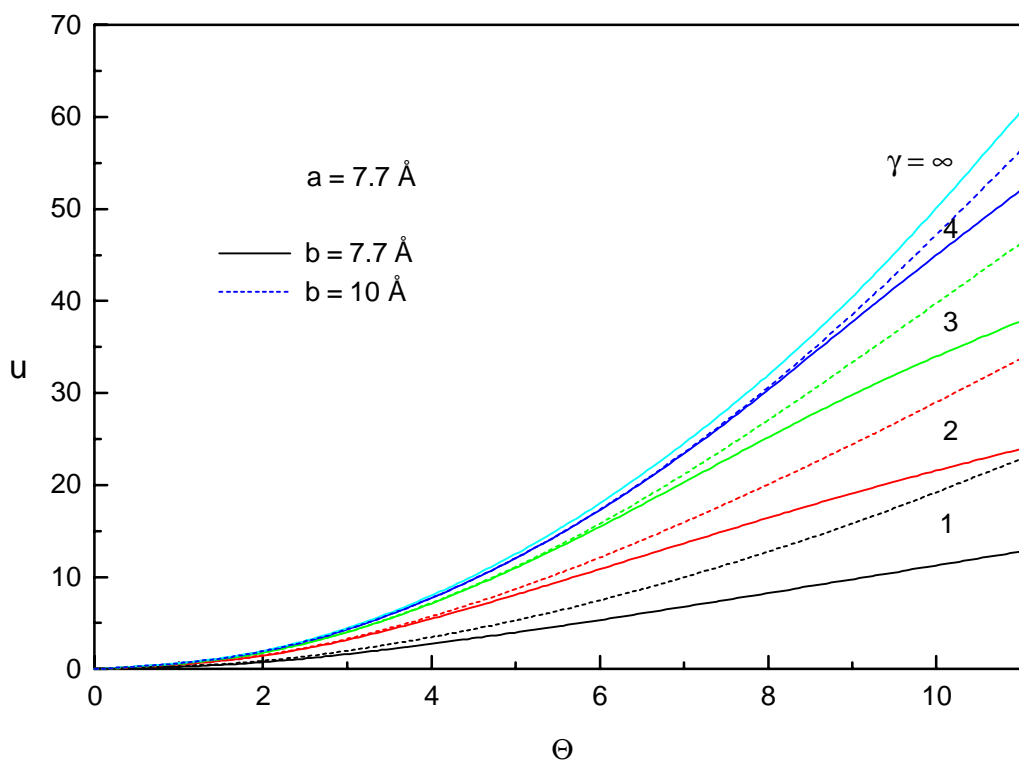
$$\lim_{\gamma \rightarrow \infty (c \rightarrow 0)} u = \lim_{\gamma \rightarrow \infty (c \rightarrow 0)} f = \frac{1}{2} \Theta^2 \quad (19)$$



**Figure 1.** Dependence of the osmotic coefficient  $\phi$  on the charge parameter  $\Theta$  for various values of the concentration parameter  $\gamma$ .

Figures 1 and 2 show the dependence of the osmotic coefficient  $\phi$  and the electrostatic energy  $u$ , respectively, on the charge parameter  $\Theta$  for various values of the concentration parameter  $\gamma$  and for two values of the counterion radius (for point charges

and for  $r_c = 2.3 \text{ \AA}$ , which corresponds to the radius of the sodium counterion). The highest value of the charge parameter,  $\Theta = 11.12$ , is typical for fullerenehexamalonates.



**Figure 2.** Dependence of the electrostatic energy function  $u$  on the charge parameter  $\Theta$  for various values of the concentration parameter  $\gamma$ .

It can be seen that dependence of  $\varphi$  and  $u$  on the counterion radius is more significant at higher concentrations (lower values of  $\gamma$ ), and as expected, vanishes in the limiting curve for  $\gamma = \infty$  given for the osmotic coefficient by  $\varphi = 1$  and for the electrostatic energy by Eq. 19.

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### **Povzetek**

V prejšnjem prispevku smo predstavili rezultate računov, ki so bili dobljeni z rešitvijo Poisson-Boltzmannove enačbe za sferični celični model vodne raztopine fulerena, na katerega so vezane ionske skupine. Izračunali smo elektrostatsko notranjo in prosto energijo raztopine, stopnjo vezanja protiionov, osmozni koeficient ter porazdelitev protiionov okrog nabitega fulerenovega skeleta. Numerični računi so pokazali, da težijo pri nizkih koncentracijah nekatere lastnosti k dobro definiranim limitnim vrednostim. V tem prispevku smo pokazali, da lahko limitne vrednosti teh količin napovemo z analitično rešitvijo Poisson-Boltzmannove enačbe.