

Scientific paper

The Mean Activity Coefficients of Fullerenehexamalonates $T_h-C_{66}(COO^-M^+)_{12}$ in Aqueous Solutions

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Dedicated to Prof. Dr. Gorazd Vesnaver on the occasion of his 70th birthday

Abstract

The Poisson-Boltzmann equation has been solved for the spherical cell model of a fullerenehexamalonate solution to obtain the contributions of the macroion and its counterions to the total electrostatic free energies. The contribution of the macroion is large and positive, whereas the contribution of the counterions is small and negative. From these data the concentration dependence of the activity coefficients of the macroion and counterions have been calculated, as well as the mean activity coefficient of the fullerenehexamalonate electrolyte. Calculated values for the mean activity coefficient have been compared with the existing experimental data and a good agreement has been observed.

Keywords: Mean activity coefficients, fullerenehexamalonate solutions

1. Introduction

In the interpretation of the experimental properties of a solution the most effective way is that of finding a theoretical expression for the nonideal part of the chemical potential. Once this excess function is obtained, all colligative and thermal properties of a solution can readily be calculated. In practice, it is much easier to deal with the activity coefficient of the solute than with the chemical potential, and consequently the problem reduces to obtain the theoretical expression for the activity coefficient. From the theoretical expression for the chemical potential one may formally calculate the activity coefficients of the single ions in the solution, but since the individual ion activity coefficients are inaccessible to exact thermodynamic measurements,⁵ the mean activity coefficient is calculated to obtain an expression that can be compared with experimental data.

In this contribution we present the relevant theoretical expressions for solutions of fullerene electrolytes,^{1–3} water soluble solutes that fill up the gap between simple electrolytes and polyelectrolytes. We shall present the contributions of the fullerene macroion, $T_h-C_{60}C(COO^-)_2)_6$, and its counterions to the total electrostatic free energy. For this purpose we adopted the charging process⁴ of Lifson and Katchalsky, used for the

cylindrical cell model of a polyelectrolyte solution, to the spherical cell model. From relevant expressions the activity coefficients of the macroion and its compensating counterions have been calculated and from them the mean activity coefficient which has been compared with the existing experimental data.

1.1. Electrostatic Free Energies of Macroion and Counterions

The 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 the solution per fullerene molecule. This volume is assumed to be spherical, and the spherical fullerene macroion is situated in the centre of this cell. The approximations and assumptions concerning the use of the cell model are well known.^{6,7}

Various methods may be used to calculate the electrostatic contribution, A_e to the Helmholtz free energy.⁸ In this contribution we shall use a reversible isothermal charging process, which is performed in a manner such that at any stage all ions have the same fraction of their final charge.

Electrostatic free energy of the system, A_e , consisting of one macroion and the pertaining counterions, may

be formally divided into the contributions of counterions, A_c , and the macroion, A_m . According to Ref. 4 the free energy of the macroion is given by

$$A_m = \int_{e'=0}^{e_0} \int_S \psi_a' \sigma' \frac{de'}{e'} dS \quad (1)$$

where ψ_a' , σ' and e' are the variable surface potential, surface charge density, and the charge, respectively, e_0 is the proton charge and S is the surface of the macroion. In the following we apply the symbols and the formalism used previously.² We introduce the dimensionless potential Φ_1 , and the charge parameter, Θ

$$\Phi_1 = -ze_0\psi_a' / kT \quad (2)$$

$$\Theta = \nu ze_0^2 / \varepsilon kTa \quad (3)$$

In these equations ν is the number of ionized groups on the macroion, z is the charge number of counterions of radii r_c , ε is the relative permittivity of the solvent, a is the radius of the macroion, and k and T have their usual significance.

Since $\sigma' = -ve'/S$ and $de'/e' = d\Theta'/2\Theta'$, the solving of the second integral of eq 1 yields

$$A_m = \frac{\nu kT}{2z} \int_{\Theta'=0}^{\Theta} \Phi_1(0) d \ln \Theta' = \frac{\nu kT}{2z} I \quad (4)$$

$$I = \int_{\Theta'=0}^{\Theta} \Phi_1(0) d \ln \Theta' \quad (5)$$

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

The electrostatic contribution, A_e to the Helmholtz free energy is related⁸ to the electrostatic energy of the system, U , by the expression:

$$A_e = A_c + A_m = T \int_{T=\infty}^T U d\left(\frac{1}{T}\right) \quad (6)$$

The electrostatic energy of the solution, calculated per macroion can be expressed as²

$$U = \frac{\nu kT}{z\Theta} u \quad (7)$$

where

$$u = \frac{1}{2} \Theta^2 [1 - \exp(-t_1)] + \frac{1}{2} \int_0^{t_1} \left(\frac{d\Phi_2}{dt}\right)^2 \exp(t) dt \quad (8)$$

The subscripts 1 and 2 refer to the first and second domains² of the cell model, respectively, and the dimensionless quantity t_1 is given by $t_1 = \ln(b/a)$, where b ($= a + r_c$) is the exclusion radius from the center of the macroion to the center of the counterion. The concentration parameter γ is defined by $\gamma = \ln(R/a)$ where R is the radius of the spherical cell.

Marcus⁸ has shown that eq (6) is equivalent to eq (9)

$$A_e = \int_{\lambda=0}^1 2U \frac{d\lambda}{\lambda} \quad (9)$$

where λ is the fraction of the final charge of all ions at any stage of the charging process, i.e., $0 \leq \lambda \leq 1$.

Since $d\lambda/\lambda = de'/e' = d\Theta'/2\Theta'$, as stated above, it follows

$$A_e = \int_{\Theta'=0}^{\Theta} U d \ln \Theta' \quad (10)$$

Inserting eq (7) we get the final expression

$$A_e = \frac{\nu kT}{z} \int_{\Theta'=0}^{\Theta} \frac{u}{\Theta'} d \ln \Theta' = \frac{\nu kT}{z} J \quad (11)$$

$$J = \int_{\Theta'=0}^{\Theta} \frac{u}{\Theta'} d \ln \Theta' \quad (12)$$

Eqs (4), (6), and (11) yield A_c , the contribution of the counterions to the electrostatic free energy of the system

$$A_c = \frac{\nu kT}{z} \left(J - \frac{1}{2} I \right) \quad (13)$$

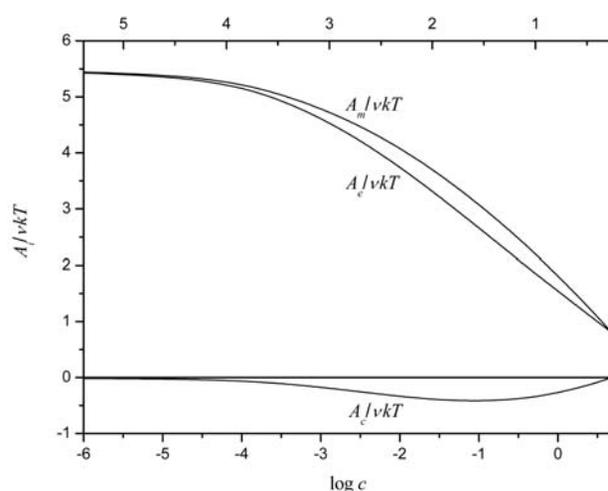


Figure 1. Dependence of the electrostatic free energy A_e and contributions of counterions A_c and macroion A_m to A_e on the concentration for the solution of fullerenehexamalonates with monovalent counterions of radius 0.23 nm.

In Figure 1 the dependences of A_c , A_m , and A_e on the logarithm of concentration are presented for the charge parameter $\Theta = 11.12$, typical for fullerenehexamalonates, and for monovalent counterions of radius 0.23 nm, i.e., $a = 0.77 \text{ nm}^1$, $b = 1 \text{ nm}$, $t_1 = 0.26$. It can be seen that the contribution of the macroion to the electrostatic free energy of the solution is prevailing over the negative contribu-

tion of counterions at all concentrations. Our recent studies¹¹ have shown that in the limit of high dilutions various properties tend to the well defined limiting values. In the limit as $c \rightarrow 0$ ($\gamma \rightarrow \infty$) it has been found that

$$\lim_{\gamma \rightarrow \infty (c \rightarrow 0)} \Phi_1(0) = \Theta \quad (14)$$

and

$$\lim_{(c \rightarrow 0)} \mu = \frac{1}{2} \Theta^2 \quad (15)$$

From eqs (4) and (5) it follows

$$\lim_{c \rightarrow 0} I = \Theta \quad (16)$$

$$\lim_{c \rightarrow 0} A_m = \frac{v k T}{2z} \Theta \quad (17)$$

and consequently from eqs (11) and (12)

$$\lim_{c \rightarrow 0} J = \frac{1}{2} \Theta \quad (18)$$

and

$$\lim_{c \rightarrow 0} A_c = 0 \quad (19)$$

1. 2. Activity Coefficients

Formally we can obtain the activity coefficients of an ionic species by differentiation the expression for the electrostatic free energy with respect to its number in a solution.¹⁰ If N_m is the number of macroions in a solution of volume V and N_c the number of the corresponding counterions ($N_c = vN_m/z$) the electrostatic free energy, \mathcal{A}_e , can be expressed by⁹

$$\mathcal{A}_e = N_m A_e = N_m (A_c + A_m) \quad (20)$$

$$\mathcal{A}_e = N_c k T \left(J - \frac{1}{2} I \right) + N_m \frac{v k T}{2z} I \quad (21)$$

The activity coefficients of the counterions, f_c , and the macroion, f_m , are defined by

$$k T \ln f_c = \frac{\partial \mathcal{A}_e}{\partial N_c} \quad (22)$$

$$k T \ln f_m = \frac{\partial \mathcal{A}_e}{\partial N_m} \quad (23)$$

In differentiation we must take into account the dependence of the functions I and J on the concentration, i.e., on the concentration parameter γ . Since $V/N_m = 4\pi R^3/3$ we get

$$\gamma = \ln \frac{R}{a} = \frac{1}{3} \ln \frac{3V}{4\pi a^3 N_m} \quad (24)$$

Supposing,⁹ that the ratio R/a is not influenced by the addition of counterions to the solution, $\partial \gamma / \partial N_c = 0$,

while $\partial \gamma / \partial N_m = -1/3N_m$. From eqs (20) – (23) we obtain

$$\ln f_c = J - \frac{1}{2} I \quad (25)$$

and

$$\ln f_m = \frac{v}{z} \left[\frac{1}{2} I - \frac{1}{3} \left(\frac{\partial J}{\partial \gamma} \right)_\Theta \right] \quad (26)$$

Experimentally accessible are only mean activity coefficients, f_{\pm} . By definition, f_{\pm} is written as

$$\left(1 + \frac{v}{z} \right) \ln f_{\pm} = \frac{v}{z} \ln f_c + \ln f_m \quad (27)$$

From eqs (25) – (27) we thus obtain

$$\ln f_{\pm} = \frac{v}{z+v} \left[J - \frac{1}{3} \left(\frac{\partial J}{\partial \gamma} \right)_\Theta \right] \quad (28)$$

2. Results and Discussion

In Figure 1 we have seen that the contribution of the macroion to the electrostatic free energy of the solution is prevailing over the negative contribution of counterions at all concentrations. This unusual finding is reflected also in the activity coefficients.

The concentration dependence of the coefficients f_c , f_m , and f_{\pm} , is presented in Figures 2 and 3 according to eqs (5), (12), and (25) – (28) for the value^{1,2} of the charge parameter $\Theta = 11.12$, and for monovalent counterions of radius 0.23 nm. The dependence of the osmotic coefficient, ϕ , on the concentration^{1,2} is included for comparison.

Referring for a moment to solutions of linear polyelectrolytes, we find that one of their most unique proper-

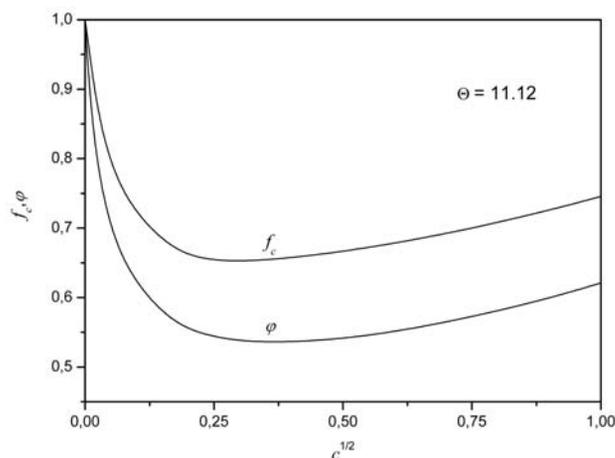


Figure 2. Concentration dependence of the activity coefficient of counterions and the osmotic coefficient for aqueous solutions of fullerenehexamalonates with monovalent counterions of radii 0.23 nm at 25 °C.

ties results from interactions of the charged polyion with its compensating counterions. These strong interactions have been clearly demonstrated by measuring the activity coefficients of counterions, determined usually potentiometrically by using counterion-selective electrodes. Although the evaluation of the activity coefficients of counterions, f_c , requires nonthermodynamic assumptions, the extensive amount of data have been accumulated.⁶ The activity coefficients f_c in the salt free polyelectrolyte solutions has been often approximated⁶ with the osmotic coefficient, ϕ , however, accurate experimental^{6,12} and theoretical⁹ studies have shown that ϕ is always smaller than f_c . Figure 2 demonstrates that this finding is observed also with solutions of spherical macroelectrolytes. In Figure 2, which represents the behavior of these two properties for aqueous solutions of fullerenehexamalonates with monovalent counterions of radii 0.23 nm, it can be seen that the osmotic coefficient ϕ appreciable differ from the activity coefficient f_c at all concentrations.

Dependence of the coefficients f_c , f_m , and f_{\pm} on the log of concentration is shown in Figure 3 for the fullerenehexamalonate solution with monovalent counterions ($\nu = 12$ and $z = 1$). The most attractive features of results presented in Figure 3 are the extremely high values of f_m , and f_{\pm} at high dilution. Analysis of the present theoretical data has shown that

$$\lim_{\gamma \rightarrow \infty (c \rightarrow 0)} \left(\frac{\partial J}{\partial \gamma} \right)_{\Theta} = 0 \quad (29)$$

After combining eqs (16) and (18) with eqs (25)–(28) one obtains

$$\lim_{c \rightarrow 0} f_c = 1 \quad (30)$$

and with $\Theta = 11.12$

$$\lim_{c \rightarrow 0} f_m^{z/\nu} = \lim_{c \rightarrow 0} f_{\pm}^{(z+\nu)/\nu} = \exp\left(\frac{\Theta}{2}\right) = 259.8 \quad (31)$$

With $z = 1$ and $\nu = 12$ we get the limiting values at zero concentration $f_{\pm} = 169.4$ and $f_m = 9.465 \cdot 10^{28}$. This sharp increase of f_m and f_{\pm} with the decreasing concentration has been observed also with linear polyelectrolytes,^{9,13–16} and good agreement between experimental values and those predicted by the Poisson-Boltzmann equation has been observed.^{14,15}

For the present no experimental data exist for f_c and f_{\pm} for solutions of fullerenehexamalonates. Similarly, as with solution of linear polyelectrolytes, they could be obtained electrochemically by using a concentration cell with transference with counterion-selective electrodes. Another method is indirect, by integrating the Gibbs-Duheme equation, which yields the relation between the osmotic coefficient, ϕ , and the mean activity coefficient

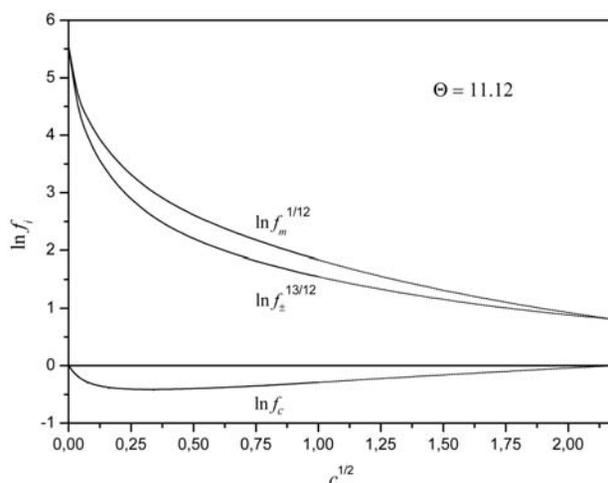


Figure 3. Activity coefficients of the macroion and counterions and the mean activity coefficient as functions of concentration for the aqueous fullerenehexamalonate solution with monovalent counterions of radii 0.23 nm at 25 °C.

$$d \ln f_{\pm} = (\phi - 1) d \ln m + d \phi \quad (32)$$

where m is the molality of the macroion, which can be at concentrations for which the experimental data for ϕ exist³ approximated with the monomolar concentration c .

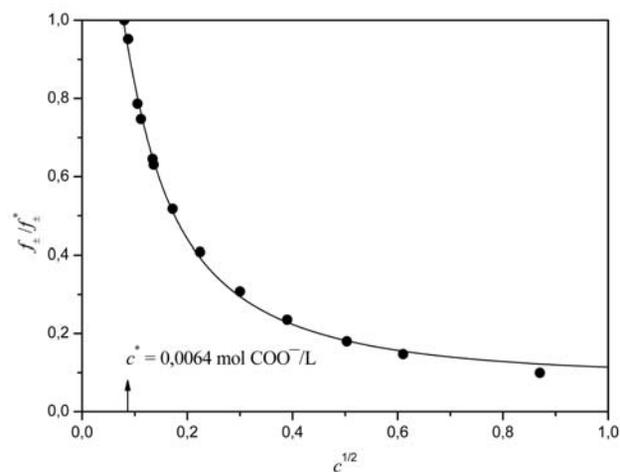


Figure 4. Comparison of the experimental (points) and from eq (28) computed (line) mean activity coefficient ratio f_{\pm}^*/f_{\pm}^* of the sodium fullerenehexamalonate in aqueous solution at 25 °C. Values of the experimental points were calculated from the experimental data for the osmotic coefficient.³ The coefficient f_{\pm}^* refers to the lowest concentration reached in the osmotic coefficient measurements.³

Comparison of the experimental and from eq (28) computed mean activity coefficients for the sodium fullerenehexamalonate is presented in Figure 4. From the experimental data³ for ϕ calculated values of f_{\pm} are presented relative to the value f_{\pm}^* , obtained at the lowest concentration reached in the osmotic coefficient measurements,

$c^* = 0.0064 \text{ mol COO}^-/\text{L}$. A good agreement between measured and calculated values can be observed, a finding which is not surprising, since also experimental data for ϕ , from which the values of f_{\pm} were calculated, displayed a reasonable agreement³ with predictions of the Poisson-Boltzmann equation.

3. References

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Povzetek

Z rešitvijo Poisson-Boltzmannove enačbe za celični model s sferično simetrijo smo dobili prispevek fulerenheksamalonatnega makroiona in prispevek pripadajočih protiionov k celotni elektrostatski prosti energiji fulerenheksamalonatne raztopine. Prispevek makroiona je velik in pozitiven, medtem ko je prispevek protiionov majhen in negativen. Iz teh podatkov smo izračunali koncentracijsko odvisnost aktivnostnih koeficientov makroiona in protiionov ter srednji aktivnostni koeficient fulerenheksamalonatnega elektrolita. Izračunane vrednosti za srednji aktivnostni koeficient smo primerjali z obstoječimi eksperimentalnimi podatki in dobili dobro ujemanje.