Water-Soluble Fullerenes. 3. Alkali Salts of Fullerenehexamalonic Acid $T_h-C_{66}(COOH)_{12}$[†]

Janez Cerar and Jože Škerjanc*

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

Received: November 21, 2002; In Final Form: May 16, 2003

The electrical conductivity, the osmotic coefficient, the apparent molar volume, and the enthalpy of dilution of aqueous solutions of the lithium and cesium salts of fullerenehexamalonic acid, $C_{66}(COOH)_{12}$, were measured at 25 °C in a wide concentration range. The data for the sodium salt published previously were included for comparison. Following the idea of association of counterions with the macroion we estimated the values of the molar conductivity of the fullerene macroion constituent and its transport numbers in solutions of the three alkali fullerenehexamalonates, assuming for the fraction of apparently free counterions the theoretical values based on the solution of the Poisson−Boltzmann equation for the spherical cell model. The mean value of the limiting molar conductivity of the macroion constituent was $\Lambda_0 \left[^{1}/_{12} C_{66} (COO^-)_{12}\right] = (104.8 \pm 5)\ \Omega^{-1}\ cm^2\ mol^{-1}$. The curves of the apparent molar volumes and the enthalpies of dilution display minima at low concentrations, a finding which is characteristic for hydrolyzing electrolytes. Comparison of experimental data with predictions of the spherical cell model shows a semiquantitative agreement.

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.[1−3] It has been observed that the osmotic coefficient of polyelectrolyte solutions slightly depends on the ionic radius of counterions, whereas the enthalpy of dilution, the apparent molar volume, the electrical conductivity, and the transport number of macroion constituent display an explicit dependence on the nature of counterions.

Recently, we have reported[4−7] 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}-$(C(COOH)_2)_6$, and its sodium salt, $T_h-C_{66}(COONa)_{12}$, have been isolated and characterized by some fundamental data and properties. Fullerenehexamalonic acid, $C_{66}(COOH)_{12}$, 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. The sodium salt, C_{66}-$(COONa)_{12}$, 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 because of the high charge number of the bulky ion. Another one is the perfect spherical symmetry of the fullerene macroion that justifies the use of the spherical model for theoretical interpretation of this system.

In this paper, we extended our studies with fullerenehexamalonic acid to its lithium and cesium salts. The properties of the first can usually be satisfactorily interpreted in the light of pure electrostatic theories, whereas solutions of the cesium salts

in addition to electrostatic contribution frequently show more or less expressed nonelectrostatic effects. The results for the sodium salt, published previously,[5] are included for comparison.

Experimental Section

Materials. The sodium and the lithium salt of fullerenehexamalonic acid $T_h-C_{66}(COOH)_{12}$ (FHMA) were obtained by neutralization of the acid with aqueous solution of corresponding alkaline hydroxide.[5] The cesium salt, $T_h-C_{66}(COOCs)_{12}$ (Cs-FHM), was prepared by adding extra pure crystalline Cs_2CO_3 (Merck) into concentrated aqueous solution of fullerenehexamalonic acid until the pH of the solution was about 6. During the neutralization, the solution was stirred and released CO_2 was removed by a flow of pure nitrogen. The solution of CsFHM was concentrated by freeze-drying and the final concentration of the stock solution was determined spectrophotometrically. Solutions of lower concentrations were prepared by weighing.

Apparatus. The measurements of osmotic coefficients, densities of aqueous solutions, enthalpies of dilution, and electrical conductivities have been described before in detail.[7]

Results and Discussion

Experimental electrical conductivity, Λ, of the lithium, sodium, and cesium salts is plotted against the square root of the concentration, c, in Figure 1. For the sodium salt, the data from previous measurements[5,7] are presented. Curves typical for strong multivalent electrolytes are observed. Recent theoretical treatment[8] of electrical conductivity of simple electrolyte solutions explained such behavior at low and moderate concentrations not only for symmetrical but also asymmetrical 2−1 and 3−1 electrolytes. As discussed previously,[4,5] the salts of fullerenehexamalonic acid with strong bases should be treated as highly asymmetric strong 1−12 valent electrolytes. The experimental data in Figure 1 can be represented by the
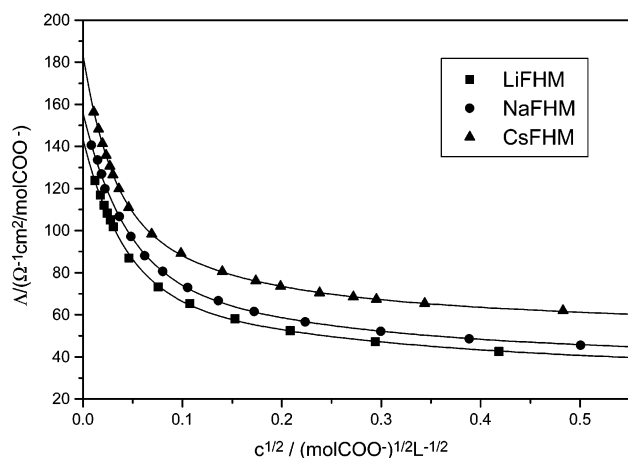

Figure 1. Concentration dependence of the molar conductivity of alkali fullerenehexamalonates in water at 25 °C.

empirical equation

$$\Lambda = \Lambda_0 - Ac^{1/2} + Bc - Cc^{3/2} + \cdots \quad (1)$$

which fairly well represents the conductivity data for strong electrolytes at moderate concentrations.[9]

Using eq 1 with the experimental data in Figure 1, the following values of Λ_0, the molar conductivity at infinite dilution, were obtained: 142.5, 155.1, and 183.0 Ω^{-1} cm^2 mol^{-1}, for the Li, Na, and Cs salts, respectively. Subtracting from the limiting values of Λ the corresponding molar conductivities of the alkali ions[9] at $c = 0$, Λ_0 (Li$^+$) = 38.7, Λ_0 (Na$^+$) = 50.1, and Λ_0 (Cs$^+$) = 77.3 Ω^{-1} cm^2 mol^{-1}, we get the following values for the molar conductivity of the fullerene-hexamalonate anion: Λ_0 [$^1/_{12}$ C$_{66}$ (COO$^-$)$_{12}$] = 103.8, 105.0, and 105.7 Ω^{-1} cm^2 mol^{-1}, respectively, giving the mean value 104.8 Ω^{-1} cm^2 mol^{-1}. This value is comparable to the equivalent ionic conductivities of multivalent ions, such as $^1/_3$ Fe(CN)$_6{}^{3-}$ or $^1/_4$ Fe(CN)$_6{}^{4-}$, at infinite dilution.[9]

From measured transport properties of polyelectrolyte solutions, the fraction of free counterions has been frequently calculated following the idea of association of counterions with the macroion.[10−13] The relation between the molar conductivity and the fraction of free counterions, f, is given by

$$f = \Lambda/(\Lambda_p + \Lambda_c) \quad (2)$$

where Λ_c is the molar conductivity of free counterions and the molar conductivity of the polyion constituent,[11] Λ_p, has been obtained from T_p, the transport number of the polyion[10] without any approximation, $\Lambda_p = \Lambda T_p$. Equation 2 has been used for calculation of the fraction of apparently free counterions, f, in cases when conductivity as well as transference data were known. Since thus far no transference experiments with solutions of fullerene electrolytes have been performed, we adopted in the present case eq 2 to estimate the molar conductivity and transport number of the fullerene macroion constituent, Λ_p and T_p, respectively. By a phenomenological approach, it has been shown[14] for polyelectrolyte solutions that f can be approximated 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 polyion, respectively. Experimental data have justified this approximation.[15,16] We suppose that this approximation holds also for counterions in the high field of the fullerene macroion.
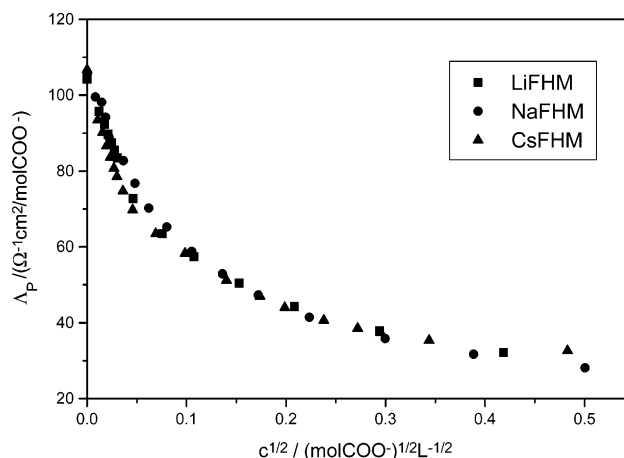

Figure 2. Calculated values of Λ_p, the molar conductivity of the fullerene macroion constituent, for alkali fullerenehexamalonates at 25 °C (see text) as functions of concentration.

Since a reasonable agreement between some experimental and theoretical data, on the basis of the solution of the Poisson−Boltzmann equation, has been observed in our previous work[4] with solutions of fullerenehexamalonates, we have applied for the calculation of $D_c/D_c{}^0$ this classical electrostatic theory. In the case of the fullerene electrolyte, the spherical cell model can be used. Basic assumptions and equations for such a model have been reported recently.[5,6] The ratio $D_c/D_c{}^0$ and thus f can be estimated from[17,18]

$$f \approx D_c/D_c{}^0 = 1/<\exp \Phi_2> <\exp - \Phi_2> \quad (3)$$

where the brackets denote volume averages of the reduced electrostatic potential, Φ_2, over the macroion cell. A detailed description of numerical computations of $D_c/D_c{}^0$ has been given recently.[6,7] In eq 2, Λ_c is still an unknown and may be, to a good approximation,[12] equated to the corresponding value for the same counterion in a solution of simple electrolyte at a concentration equal to that of the free counterions, fc. In the computation of Λ_c, the data[19] for the molar conductivities and transport numbers of LiCl, NaCl, and CsCl solutions were used.

The values of Λ_p calculated from eqs 2 and 3 for all three fullerenehexamalonates are presented as functions of concentration in Figure 2. It is seen that Λ_p decreases sharply with increasing c. As expected, the values for the three salts are practical equal within the experimental errors and assumptions made in computations. On the other hand, the transport numbers of the fullerenehexamalonate macroion constituent, T_p ($=\Lambda_p/\Lambda$), presented in Figure 3, display expected differences, depending if the macroion competes in electrical transport with the large lithium or the smaller cesium counterions. We also see that in all cases T_p rises to a maximum and then decreases with increasing concentration.

The osmotic coefficient, which is the ratio of the real and ideal osmotic pressure,

$$\varphi = \pi/\pi_{id} \quad (4)$$

is plotted in Figure 4 against concentration. The ideal osmotic pressure was calculated from

$$\pi_{id} = \frac{\nu + 1}{\nu} cRT \quad (5)$$

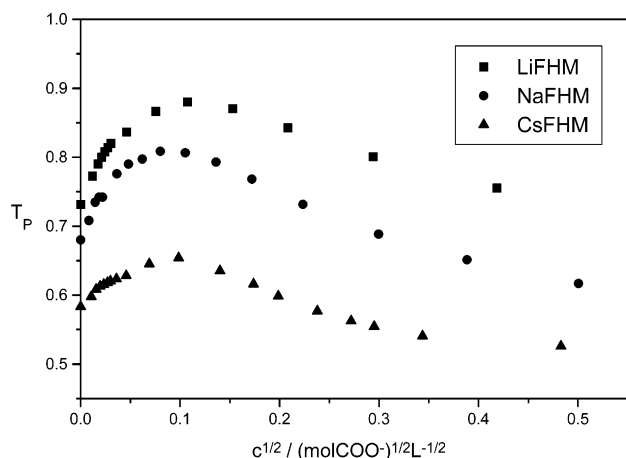taking for the number of the carboxylate groups on the fullerene

Figure 3. Concentration dependence of the fullerene macroion constituent transport number, T_p, in aqueous solutions of alkali fullerenehexamalonates at 25 °C.
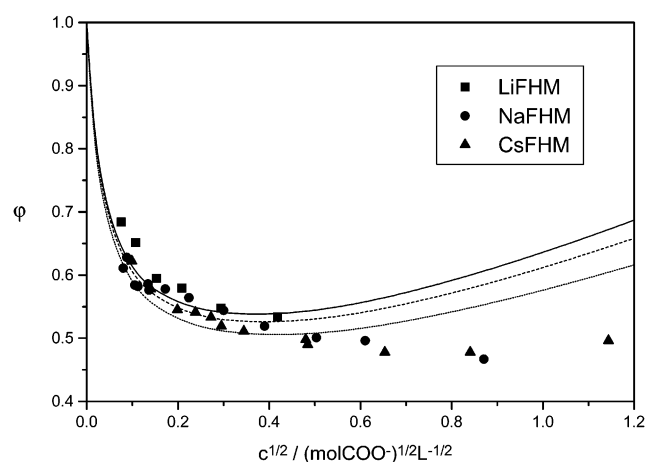

Figure 4. Comparison of the experimental (symbols) and from the solution of the Poisson−Boltzmann equation for the spherical cell model calculated osmotic coefficients (lines) of alkali fullerenehexamalonates in water at 25 °C. In computations, the following values for the radii of hydrated ions were used:[29] 0.25 nm (solid line), 0.21 nm (dashed line), and 0.15 nm (dotted line) for the lithium, sodium, and cesium counterions, respectively.
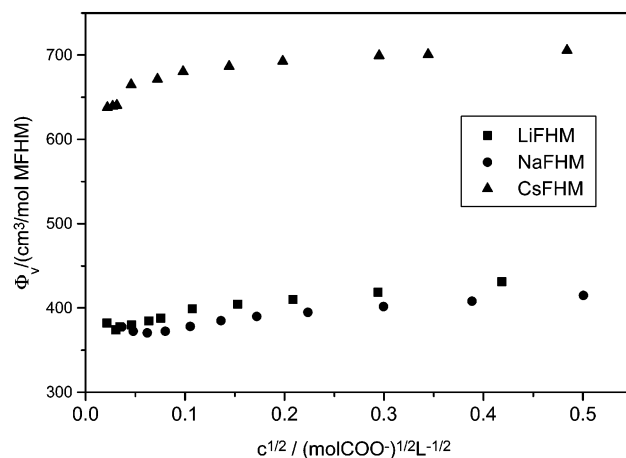

Figure 5. Concentration dependence of the apparent molar volume of alkali fullerenehexamalonates in water at 25 °C.
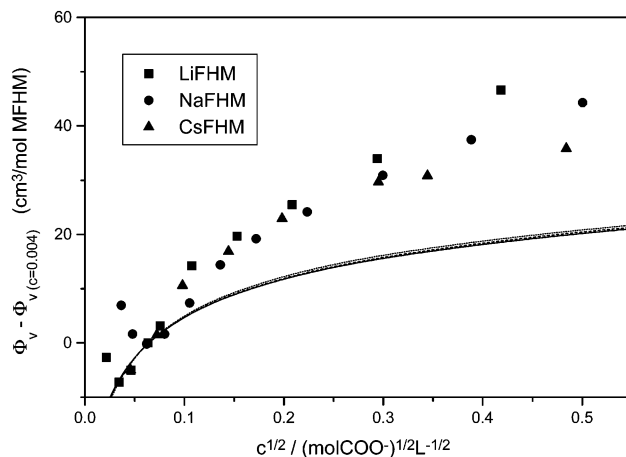

Figure 6. Comparison of the concentration dependence of the relative apparent molar volumes of alkali fullerenehexamalonates in water at 25 °C (points) with that predicted by theory (lines; ionic radii as in Figure 4). See text.

skeleton the value $\nu = 12$. Lines show the theoretical values obtained by the solution of the Poisson−Boltzmann equation for the spherical cell model. It can be seen that the osmotic coefficient indicates a tendency to decrease with the decreasing ionic radius of the counterion, in consequence of the stronger binding of smaller ions to the macroion. The decrease is predicted also by the theory. The agreement between theory and experiment is good at low concentrations; however, an increasing deviation of the observed values from the predicted ones can be noticed at higher concentrations. Such discrepancies have been observed also in studies of solutions of linear polyelectrolytes[1−3] and have been attributed to the increasing nonelectrostatic interactions between the polyion and counterions at higher concentrations, not taking into account by pure electrostatic theories.

The results of density measurements are shown in Figure 5. The apparent molar volumes were calculated from measured densities of the solvent and fullerenehexamalonate solutions, ρ_o and ρ, respectively, according to eq 6, where M_2 is the molar mass of alkali metal (M) fullerenehexamalonate, $C_{66}(COOM)_{12}$,

and c_F is the concentration expressed in moles of $C_{66}(COOM)_{12}$ per liter.

$$\phi_V = \frac{1}{\rho_o}\left(M_2 - \frac{\rho - \rho_o}{c_F}\right) \qquad (6)$$

It can be seen that the absolute values of ϕ_V reflect the size of counterions (at 25 °C the conventional molar volumes at infinite dilution are −0.88, −1.21, and 21.34 cm³/mol for the Li⁺, Na⁺, and Cs⁺ counterions,[20] respectively). We also see that the measured values display minima at low concentrations, a situation observed with hydrolyzing electrolytes.[21,22] Figure 6 shows the concentration dependence of the apparent molar volume relative to its value ϕ_V^f at a selected low concentration, c_f (in this case at 0.004 mol COO⁻/L), which is related to the volume change on dilution[23] between concentration c and the final concentration c_f:

$$\Delta V_{D(c \to c_f)}/n_p = (\phi_V^f - \phi_V) \qquad (7)$$

In eq 7, n_p is the amount of the solute in moles of $C_{66}(COOM)_{12}$. The concentration dependence of the apparent molar volume (and also the enthalpy of dilution, ΔH_D) may be compared[9,24] with the electrostatic contribution to the volume and enthalpy changes on dilution, ΔV_e and $\Delta H_e \approx \Delta U_e$, respectively. They are related[23−25] to the electrostatic energy
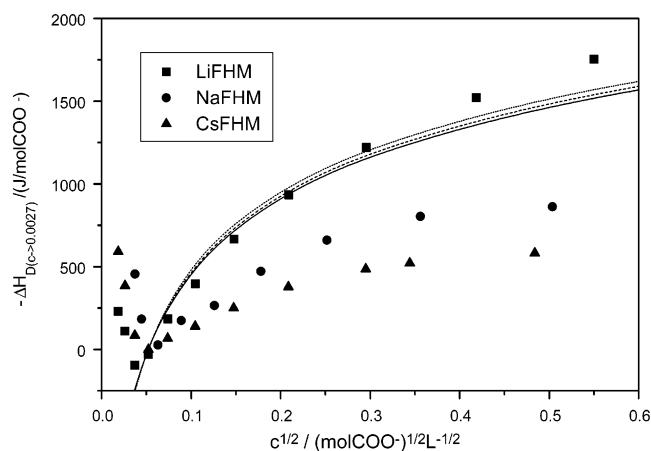
Figure 7. Comparison of the experimental intermediate enthalpies of dilution to the final concentration 0.0027 mol COO⁻/L of alkali fullerenehexamalonates in water at 25 °C (points) with predictions based on the solution of the Poisson−Boltzmann equation for the spherical cell model (lines; ionic radii as in Figure 4).

of the solution, U, which can be obtained from the theory, by

$$U_e = U(d \ln \epsilon / d \ln T) \qquad (8)$$

$$V_e = - U(d \ln \epsilon / dP) \qquad (9)$$

In these equations, ϵ is the relative permittivity of the solvent, while T and P have their usual significance. Details of the computations and theoretical expressions have been given previously.[5,6] We can see in Figure 6 that the theoretical curves show practically no dependence on the radius of the counterion and that they increase much gentler than the experimental values. Such discrepancies of the experimental and theoretical slopes of ϕ_V have been observed also with other hydrolyzing electrolytes.[9]

Figure 7 represents the concentration dependence of the relative apparent molar enthalpy, more often called the intermediate enthalpy of dilution, $\Delta H_{D(c \rightarrow c_f)}$. It is defined as the enthalpy change on dilution from the initial concentration c to the final concentration c_f (in this case 0.0027 mol COO⁻/L). We can see that the curves of ΔH_D display a similar behavior to those of ϕ_V. The measured heat effects are exothermic above minima (between 0.0015 and 0.004 mol COO⁻/L), while below them they become endothermic. The appearance of minima for hydrolyzing electrolytes[26] and polyelectrolytes[27] has been attributed to the endothermic enthalpy of hydrolysis that overweights the exothermic enthalpy of dilution at high dilutions. A brief discussion concerning fullerenehexamalonate solutions has been given recently.[5]

Figure 7 shows also the comparison of the experimental enthalpies of dilution with predictions based on the solution of the Poisson−Boltzmann equation for the spherical cell model. Similarly, as found for the apparent molar volumes, the theoretical values of ΔH_D are very insensitive to the ionic radii of counterions. We see that above the minimum the agreement between theory and experiment is good for the lithium salt, whereas negative deviations from the theoretical predictions are noticed for the sodium and cesium salts. Such deviations have been observed also with other simple electrolytes[26] and polyelectrolytes[28] and have been attributed to the increasing non-Coulombic interactions at higher concentrations, not taken into account by simple electrostatic theories.

Concluding Remarks

Fullerenehexamalonic acid, $C_{66}(C(COOH)_2)_6$, behaves as a diprotic acid.[4] The first carboxylic group is a rather strong acid, whereas the second COOH group behaves as a weak electrolyte. The salts of $C_{66}(C(COOH)_2)_6$ with strong bases have properties of highly charged hydrolyzing electrolytes. The equilibrium and transport properties of aqueous solutions of alkali salts of fullerenehexamalonic acid presented in this paper show a usual and therefore expected dependence on the size of counterions, observed also with other high molecular weight electrolytes.[1−3] The influence of the ionic radii on the osmotic coefficient, which is the measure of free counterions, is small. On the other hand, the electrical conductivity and the apparent molar volume, which are directly determined by the size of ionic species, show a definite dependence on the ionic radii of counterions. The concentration dependence of the molar conductivity of the fullerene macroion constituent is practically the same for all three salts when the contribution of counterions is taken into account.

It has been shown before[30,31] that the overall energy change accompanying the dilution process that is experimentally demonstrated as the enthalpy of dilution is governed by the energy of ions in the immediate vicinity of the macroion and not by the energy of free counterions that determine the values of the osmotic coefficient. Consequently, the heat of dilution usually shows much more explicit dependence on the size of counterions than the osmotic coefficient.[1,3]

Similar to some other water-soluble fullerene derivatives, the possibility has been indicated[32] that also lower malonic acid derivatives of C_{60}, such as monoadduct $C_{60}C(COO^-)_2$, may form small aggregates. We believe that because of the electrostatic repulsion, this possibility is much less probable for higher adducts, for example, $C_{60}(C(COO^-)_2)_6$, with the surface charge density of about 1 charge/60 Å² that is two times higher than the corresponding value of a highly charged polyion, such as poly(styrenesulfonate) anion. Although the possibility that fullerenehexamalonates $C_{60}(C(COO^-)_2)_6$ in aqueous solutions form clusters is small, especially when counterions are monovalent, it is not excluded. Recent small-angle X-ray scattering (SAXS) measurements from this laboratory[33] with cesium fullerenehexamalonate pointed out evidence for a possible dimer formation at the concentration limit of the present measurements. Confirmation of this indication would to a certain degree explain the discrepancy between observed and theoretically predicted values at high concentration and certainly should demand an improved theoretical treatment at the highest concentrations of these studies.

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