

Electric Transport and Ion Binding in Solutions of Fullerenehexamalononic Acid T_h -C₆₆(COOH)₁₂ and Its Alkali and Calcium Salts

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The transport numbers of the macroion constituent in aqueous solutions of fullerenehexamalononic acid, C₆₆-(COOH)₁₂, and its lithium, sodium, cesium, and calcium salts were determined by the indirect moving boundary method. By combining the transport data with the literature data for the electrical conductivity of the same solutions, the fraction of bound counterions to the fullerenehexamalonate macroion was calculated. It was found that about 20–40% of counterions are associated with the macroion in the concentration range from about 0.1 to 0.002 mol COO[−]/L. Consequently, under the influence of a potential field, these counterions move toward the anode as an integral part of the migrating macroion in opposition to the electrical field. Therefore, the absolute values of the macroion constituent transport numbers are relatively high. The experimental values of the fractions of bound counterions were compared with the theoretical predictions based on the solution of the Poisson–Boltzmann equation for the spherical cell model, and a reasonable agreement was obtained.

Introduction

In recent papers from this laboratory,^{1–4} we have reported on some physicochemical properties of aqueous solutions of fullerene electrolytes, new type spherical electrolytes that fill up the gap between low molecular weight electrolytes and polyelectrolytes. A T_h symmetric derivative of fullerene C₆₀, at which six malonic acid molecules have been attached, C₆₀-(C(COOH)₂)₆, and some its salts have been synthesized and characterized. These studies have shown that the degree of binding of monovalent counterions to fullerene macroion, determined by the osmotic coefficient measurements, is about 0.5 at moderate concentrations,⁴ and that it sharply decreases at concentrations below 0.01 mol COO[−]/L. The value of 0.5 is much lower than that found with linear polyelectrolytes, such as poly(styrenesulfonates),⁵ where the association of counterions with the polyion is almost 80% at the same concentrations.

On the basis of their studies on self-diffusion and conductivity of linear polyelectrolytes, Wall and his co-workers⁶ postulated that a fraction of the counterions is free to move in the solution, whereas the rest of counterions are firmly associated with the polyion. These immobilized counterions should not contribute to either transport or colligative properties. Consequently, the degrees of binding derived from equilibrium and that from transport measurements should be in the first approximation equal. Extensive studies with various polyelectrolyte solutions disclosed, however, that degrees of immobilization obtained from equilibrium properties are usually higher than those derived from transport experiments.

In the previous articles,^{2–4} we published the concentration dependence of the molar conductivity of fullerenehexamalononic acid, C₆₆(COOH)₁₂, and its alkali and calcium salts. In the present contribution, these studies were supplemented by measuring the transport number of the fullerenehexamalonate polyion in the same solutions. From the experimental transport numbers and measured electrical conductivities, the fraction of

free counterions, f , was calculated, following the method proposed by Wall and co-workers.⁶ From electrical transport measurements, calculated fractions of free counterions were compared with the theoretical values of the coefficient of self-diffusion of counterions,^{7–9} which were obtained by the solution of the Poisson–Boltzmann equation for the spherical cell model. A reasonable agreement between experimental and theoretically predicted values was obtained.

Experimental Section

Materials. Ethyl ester of T_h symmetric fullerenehexamalononic acid, T_h -C₆₆(COOEt)₁₂, was prepared and purified according to the literature.¹⁰ A minor change in the hydrolysis of water-insoluble ethyl ester to water-soluble sodium salt containing an excessive amount of sodium ions was made¹¹ with regard to the original procedure.¹² In order to obtain T_h symmetric fullerenehexamalononic acid C₆₆(COOH)₁₂ (FHMA), all of the sodium ions were exchanged by the protons as already reported.¹ The stock solutions of stoichiometric sodium (NaFHM) and the lithium (LiFHM) salt of FHMA were prepared by neutralization of the acid with an aqueous solution of corresponding alkaline hydroxide and consequent concentration by freeze-drying. The concentrations of the final solutions were obtained spectrophotometrically.¹ The cesium salt, T_h -C₆₆(COOCs)₁₂ (CsFHM), was prepared by adding extra pure crystalline Cs₂CO₃ (Merck, Darmstadt) into a concentrated aqueous solution of fullerenehexamalononic acid until the pH of the solution was about 6. During the neutralization, the solution was stirred and released CO₂ 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.

For the preparation of leading solutions, hydrochloric acid (Titrisol), LiCl (p.a.), NaCl (p.a.), and CsCl (p.a.), all from Merck, Darmstadt, were used. Concentrations of these solutions

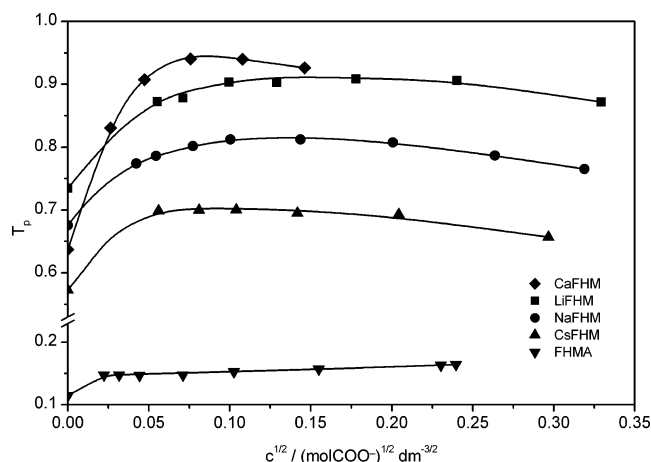


Figure 1. Concentration dependence of the fullerenehexamalonate macroion constituent transport number, T_p , in aqueous solutions of fullerenehexamalononic acid, $C_{66}(COOH)_{12}$, and its lithium, sodium, cesium, and calcium salts at 25 °C.

were precisely determined by potentiometric neutralization titrations (HCl) or by potentiometric precipitation titrations with $AgNO_3$ solution (LiCl, NaCl, and CsCl). Solutions of lower concentrations were prepared from the more concentrated solutions of known concentrations by weighing.

Apparatus. The macroion constituent transference numbers were determined by the indirect moving boundary method.¹³ A conventional cell for the rising type boundaries was described in detail elsewhere.¹⁴ It consisted of a 14 cm long tube with an internal diameter of 3 mm, a stopcock on each end of the tube, the platinum mesh cathode, and the anode of silver wire. The cell was immersed in the water bath with the temperature 25.00 °C (± 0.01 °C). The adjusted Kohlrausch solution was formed during the experiment in the tube upward from the lower stopcock. The upper stopcock enabled the closing of the tube after the end of the experiment. As leading solution, the corresponding chloride salt (in transference number experiments with fullerenehexamalonate salts) or hydrochloric acid (for fullerenehexamalononic acid itself) was used. The concentration of Kohlrausch solution was determined spectrophotometrically¹ at 334 nm using a Cary 1 spectrophotometer.

Results and Discussion

Experimentally obtained macroion constituent transport numbers, T_p , in solutions of fullerenehexamalononic acid and its lithium, sodium, cesium, and calcium salts are plotted against the square root of the concentration of carboxylic groups, c , in Figure 1. Due to the unfavorable ratio of the specific conductivities of the leading and following solutions, we could not obtain by the indirect moving boundary method reliable experimental data at concentrations below about 0.0015 mol COO^-/L . Nevertheless, it is possible to estimate the transport numbers of the macroion constituent at infinite dilution, T_p^0 , from the limiting molar conductivities of the macroion constituent, Λ_p^0 , and fullerenehexamalonate solutions, Λ^0

$$T_p^0 = \Lambda_p^0 / \Lambda^0 \quad (1)$$

From the reported values⁴ of $\Lambda_0 [^{1/12} C_{66}(COO^-)_{12}]$ and $\Lambda_0 [^{1/12} C_{66}(COOM)_{12}]$, where M represents the lithium, sodium, or cesium, the following values of T_p^0 in the Li, Na, and Cs salt solutions, consequently, were obtained: 0.735, 0.676, and 0.573. Similarly, the limiting values obtained for T_p^0 in the acid¹ and the calcium salt³ solutions are 0.114 and 0.637. It can be seen

in Figure 1 that the experimental flat bell-shaped curves show only slight concentration dependence. As could be predicted, the transport number of the fullerenehexamalonate macroion constituent decreases with the increasing molar conductivity of the counterion ($\Lambda_{Li^+} < \Lambda_{Na^+} < \Lambda_{Cs^+} < \Lambda_{H^+}$). Also, the values of the transport number of the fullerenehexamalonate constituent are smaller than those observed with “true” high molecular weight polyions, such as poly(styrenesulfonate) polyion.¹⁵ In the case of divalent calcium salt, a similar bell-shaped curve is observed with the value of T_p somewhat higher than that for the alkali metal salts. Again, an analogous situation has been observed in solutions of poly(styrenesulfonates).¹⁶ The polyion transport numbers in solutions of the acid are considerably lower. It can be ascribed to the fact that the mobility of the H^+ ion is much higher than the mobilities of the alkali and calcium counterions.

In the field of linear polyelectrolytes, one of the frequently studied properties was the degree of counterion binding to the polyion. The most illustrative historical evidence, on which the classification of counterions into bound and free ones is based, was provided by the transport studies of Wall and co-workers.⁶ They showed that under the influence of a potential field a considerable part of the positive counterions moved toward the anode in opposition to the electrical field. This finding was explained by the hypothesis that bound counterions are an integral part of the migration macroion. In the following, we shall use the approach of Wall and co-workers,⁶ later adapted by Kurucsev and Steel.¹⁷ The fraction of free counterions, f , can be related to the equivalent conductivity by the equation

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

where Λ_p and Λ_c are the equivalent conductivities of the polyion constituent and free counterions, respectively. The former one can be obtained without any approximation from T_p , the measured transport number of the macroion constituent, and the measured equivalent conductivity, Λ ($\Lambda_p = \Lambda T_p$). The mobility of the free counterions is assumed to be equal to their mobility in a simple salt solution at a concentration equal to that of the free counterions, $f \times c$.¹⁸ Data for the transport numbers and equivalent conductivities of lithium, sodium, cesium, hydrogen, and calcium chloride solutions were used¹⁹ in the computations of f , while, for the values of equivalent conductivities of fullerenehexamalonate salts and fullerenehexamalononic acid, we referred to the results of our previous studies.^{1–4} Since at the beginning of calculation the fraction of free counterions, f , was unknown, in the first step, the equivalent conductivity of the counterion was calculated assuming f was equal to 1. In the subsequent steps, better and better estimations of f were calculated by iterative procedures until a constant value for f was obtained.

The calculated fractions of free counterions, f , are plotted in Figure 2 as a function of the square root of concentration. It can be seen that the concentration dependence of f is similar for all three alkali salts studied. In their studies with real carboxylic polyelectrolytes, De Jong et al.²⁰ found a linear relationship between Λ of alkali polyacrylate solutions and Λ_0 of the lithium, sodium, and potassium counterions. It follows from eq 2 that this could be possible only in the case where the fraction of the free counterions is equal for all salts studied. Such a situation is expected to occur if the counterions are bound nonspecifically, that is, purely electrostatically, and their dependence on the ionic radius could be neglected. According to the present studies, the dependence of the fraction of free counterions on the ionic radius of the counterion is definitely

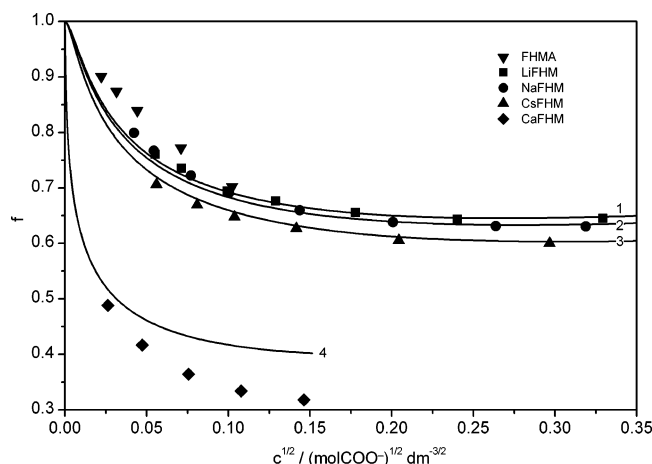


Figure 2. Concentration dependence of the fraction of free counterions in fullerenehexamalonate solutions at 25 °C. Points, experimental values; lines, theoretical predictions based on the solution of the Poisson–Boltzmann equation for the spherical cell model for the following ionic radii: (1) $r_{\text{Li}^+} = 0.18$ nm, (2) $r_{\text{Na}^+} = 0.15$ nm, (3) $r_{\text{Cs}^+} = 0.08$ nm, (4) $r_{\text{Ca}^{2+}} = 0.20$ nm.

expressed. We can see in Figure 2 that f decreases with the increasing crystallographic radius of the counterion in the order $\text{Li}^+ > \text{Na}^+ > \text{Cs}^+$.

A similar concentration dependence of f , as found experimentally, is predicted also by theoretical computations based on the solution of the Poisson–Boltzmann equation for the spherical cell model.²¹ We shall apply the phenomenological approach of Schmitt and Varoqui,⁷ who showed that f may be approximated by the ratio D_c/D_c^0 , where D_c and D_c^0 are the average self-diffusion coefficient of the counterion in the presence and absence of the polyion, respectively. The details of numerical calculations have already been described.^{3,21} As could be seen from Figure 2, the ratio D_c/D_c^0 rather satisfactorily predicts the behavior of f in the whole concentration range studied. Calculated fractions of the free counterions are plotted for different radii of the hydrated counterions. In the absence of specific interactions of alkali counterions with the fullerenehexamalonate macroion, supposed in our model, the fraction of free counterions should decrease with the decreasing radius of the hydrated counterion. Such binding order was found also in our experiments presented in Figure 2.

Figure 2 represents also the calculated fractions of free calcium and hydrogen counterions in solutions of the Ca salt and pure fullerenehexamalononic acid. While the prediction of the fraction of the free counterions, based on the solution of the Poisson–Boltzmann equation for the spherical cell model, is rather good for the case of monovalent alkali counterions, it can be seen that the agreement is worse for the divalent calcium salt. This is not a surprise since it is well-known that the major weaknesses of the used approach (neglecting of electrostatic forces among counterions) are much more pronounced in the cases of di- and higher valent counterions.

It is interesting to compare calculated and experimentally determined values of the potential at the boundary of the electrokinetic entity comprising a macroion partially screened by adsorbed counterions, usually called ζ -potential or electrokinetic potential, ζ . At this point, one has to mention that the use of the notion of ζ -potential is still accompanied with some ambiguities²² and that two major comprehensions of ζ -potential are used. In the first one,²³ the ζ -potential is equal to (or is very close to) the potential characterizing the diffuse part of the double layer, ψ_d , while in the second one,²⁴ the ζ -potential is the potential at the shear plane, which may not necessarily

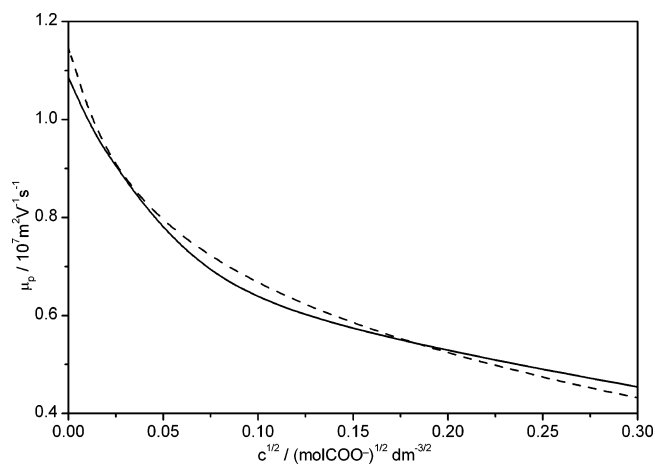


Figure 3. Comparison of the experimental (full line) and calculated (dotted line) electrophoretic mobilities of the fullerenehexamalonate constituent in the aqueous solutions of the cesium salt, $\text{C}_{66}(\text{COOCs})_{12}$, at 25 °C.

coincide with the outer Helmholtz plane²² but is rather displaced from the latter one for a distance Δ into the diffuse layer. For our understanding and modeling of the fullerenehexamalonate system, the second comprehension seems physically more appropriate since it includes finite sizes of the bound solvated counterions, so we are going to use it in our calculations.

On a spherical macroion of radius a , with the plane of shear at the radius r_{sp} , bearing effective central point charge Q , in an external homogeneous electric field of magnitude E , the system acts with electric force $F_E = QE$. If we consider that the surface potential of the electrokinetic entity at the plane of shear $\psi(r_{\text{sp}})$ is equal to the ζ -potential, it follows from Coulomb's law $\zeta = \psi(r_{\text{sp}}) = Q/4\pi\epsilon_0\epsilon r_{\text{sp}}$ where ϵ_0 and ϵ are the permittivity of a vacuum and the dielectric constant, respectively. For a steady motion with a velocity v , the electric force F_E is counterbalanced by the Stokes drag $F_\eta = 6\pi\eta r_{\text{sp}}v$, where η is the viscosity of the solution. Equating the electric force with the Stokes drag and introducing the electrophoretic mobility, μ_E , which is defined as v/E , leads to the Hückel's equation²⁵

$$\mu_E = \frac{2\epsilon_0\epsilon\zeta}{3\eta} \quad (3)$$

In the calculations according to the equation above, we used ϵ of pure water as an approximation for the dielectric constant of the solution, the measured viscosity of cesium fullerenehexamalonate solutions (at the moment, the only available data concerning the viscosity of fullerenehexamalonates²⁶) and for ζ the potential $\psi(r_{\text{sp}})$, which was calculated by solving the Poisson–Boltzmann equation for the spherical cell model.²¹ In view of the discussion above, we took for the distance r_{sp} the radius of the spherical outer Helmholtz plane, encompassing the exclusion radius from the center of the fullerenehexamalonate macroion to the center of the cesium counterion, $b = a + r_c$, and the distance Δ , for which we took an arbitrary value 0.15 nm. This figure is close to those applied by Smith to a number of systems.^{24,27} With the values¹ $a = 0.77$ nm and $r_{\text{Cs}^+} = 0.08$ nm, we obtained for the radius of the shear plane a value $r_{\text{sp}} = b + \Delta = a + r_{\text{Cs}^+} + \Delta = 0.77$ nm + 0.08 nm + 0.15 nm = 1.0 nm.

The experimental values of the mobility of the fullerenehexamalonate constituent can be calculated straightforwardly from the measured data

$$\mu_E = \frac{\Lambda_p}{F} = \frac{\Lambda T_p}{F} \quad (4)$$

where F is Faraday's constant.

Comparison of the calculated and experimental mobilities is shown in Figure 3. As can be seen, a reasonable agreement between the experimental and calculated mobilities has been obtained.

Conclusion

Our previous studies on thermodynamic and transport properties on aqueous solutions of fullerenehexamalonate electrolytes, a new type of electrolytes that fill up the gap between simple electrolytes and macromolecular electrolytes—polyelectrolytes, were supplemented by measuring the transport number of the fullerenehexamalonate macroion constituent in solutions of the acid, $C_{66}(\text{COOH})_{12}$, and its lithium, sodium, cesium, and calcium salts. By combining transference experiments with the results of the previous electrical conductivity measurements of the same solutions, the fraction of counterions bound to the macroion was obtained. It was found that degrees of immobilization obtained from transport experiments are lower than those derived from equilibrium properties,⁴ a situation which was observed also in physicochemical studies of classical polyelectrolyte solutions.

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