Water-Soluble Fullerenes. 1. Fullerenehexamalonic Acid T_h-C$_{66}$(COOH)$_{12}$, an Intermediate Spherical Electrolyte

Janez Cerar,[†] **Janez Cerkovnik, and Jože Škerjanc***

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

Following the procedure given in the literature, we prepared water-soluble T_h symmetric derivative of fullerene C$_{60}$, at which six malonic acid molecules have been attached, T_h-C$_{60}$(C(COOH)$_2$)$_6$. The sample has been characterized by some fundamental physicochemical data and properties: ^{13}C NMR chemical shifts for the acid and its sodium salt, solubility data, potentiometric and conductometric titration curves, the electrical conductivity, the osmotic coefficient, and the apparent molar volume. It has been found that fullerenehexamalonic acid (FHMA), C$_{66}$(COOH)$_{12}$, behaves as 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. The molar conductivity extrapolated to zero concentration yielded $\Lambda_0 = 395.0$ Ω^{-1} cm^2 mol^{-1} COOH$_{(1)}$ and the molar conductivity of half-ionized fullerenehexamalonate ion Λ_0 ($^1/_6$C$_{66}$(COOH)$_6$(COO$^-$)$_6$) = 45.2 Ω^{-1} cm^2 mol^{-1}. Due to the low solubility of the acid (about 11.8 g/L) the measurements were restricted to a narrow concentration range from about 0.0018 to 0.000 01 mol FHMA/L. In this concentration range, the apparent molar volume was found to be constant and equal to $\phi_V = 557$ mL/mol FHMA. The osmotic coefficient, which we succeeded in determining only at the highest concentration, is comparable to the fraction of free hydrogen ions calculated from conductivity data and pH measurements.

Introduction

Over the past several years, after the bulk preparation method of fullerenes was discovered, fullerene chemistry became progressively attractive for many scientists and engineers, and the number of publications in this new field is still rapidly increasing.[1−3] This attraction may be ascribed to fullerenes' enchanting symmetry, and outstanding chemical and physical properties, and their potential application in technology and biologically important areas. Many of the biological activity investigations have thus far focused on the water-soluble fullerene derivatives. This can be achieved by the attachment of polar functional groups. Specially attractive are derivatives of C$_{60}$ since C$_{60}$ is the most symmetrical as well as the most abundant fullerene. Following the procedure given in the literature,[4,5] we therefore prepared T_h symmetric a malonic acid hexaadduct of C$_{60}$, C$_{60}$(C(COOH)$_2$)$_6$. We could expect that the salts of this acid with strong bases would have the properties of a strong electrolyte. In view of the experimental and theoretical studies with solutions of simple electrolytes and polyelectrolytes performed hitherto in this laboratory,[6] studies of such water-soluble highly charged fullerene derivatives could be attractive not only per se but also for the reason of their eventual indices of polyelectrolyte character. In this paper, we report on physicochemical studies with aqueous solutions of fullerenehexamalonic acid, T_h-C$_{66}$(COOH)$_{12}$. As far as we could ascertain, these are the first studies of that kind. Therefore, special care was taken to prepare a pure sample of this acid and characterize it by some fundamental data and properties, such as ^{13}C NMR data for the acid and its sodium salt, solubility

data, potentiometric and conductometric titration curves, the electrical conductivity, the osmotic coefficient, and the apparent molar volume.

Experimental Section

Materials. All solvents were purified according to the literature procedures before use. Other chemicals were supplied as follows: C$_{60}$ (gold grade, Hoechst), NaH (60% in mineral oil, Merck), 9,10-dimethylanthracene (99%, Aldrich), 1,8-diazabicyclo[5,4,0]undec-7-ene (98%, Aldrich), diethyl bromomalonate (95%, Merck), 1,1-cyclopropanedicarboxylic acid (≥98%, Fluka).

Ethyl ester of T_h-fullerenehexamalonic acid, T_h-C$_{66}$(COOEt)$_{12}$, was prepared and purified according to the literature.[5] Purity was checked by HPLC analysis using Milton Roy Model 3100 instrument with silica column (Nucleosil-100, 3 μm, 50 mm × 4 mm i.d.) and toluene/ethyl acetate (98/2) mobile phase (flow rate 2 mL/min). UV detection was monitored at 330 nm.

Water-insoluble ethyl ester, T_h-C$_{66}$(COOEt)$_{12}$, was converted into the water-soluble sodium salt, T_h-C$_{66}$(COONa)$_{12}$, according to the Hirsch method.[4]

The sodium salt was converted into acidic form by ion exchange. The majority of T_h-fullerenehexamalonic acid was collected as T_h-C$_{66}$(COOH)$_{12}$ at the outlet of column. However, due to the lower solubility of acid, a minor part was deposited on the ion-exchange resin as a yellow precipitate. By final flushing of column with water this precipitate was dissolved and collected as separate fraction.

The acid and the corresponding sodium salt were analyzed by ^{13}C NMR spectroscopy:

T_h-C$_{66}$(COONa)$_{12}$, ^{13}C NMR (δ, ppm): 172.79 (12C), 144.42 (24C), 144.25 (24C), 75.46 (12C), 59.75 (6C).

* Corresponding author.
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T_h-$C_{66}(COOH)_{12}$, ^{13}C NMR (δ, ppm): 168.61 (12C), 146.04 (24C), 142.60 (24C), 71.22 (12C), 50.15 (6C).

The solubility of T_h-$C_{66}(COOH)_{12}$ was estimated to be 11.8 mg/mL. It was determined by potentiometric titration of the saturated solution with CO_2-free NaOH solution.

The concentration of the stock solution of T_h-$C_{66}(COOH)_{12}$ was determined by potentiometric and conductometric titrations with NaOH. Solutions of lower concentrations were prepared by weighing. Throughout the paper the following symbols will be used for concentrations: c_F is expressed in moles of C_{66}-$(COOH)_{12}$, c in moles of all COOH groups, and c_1 in moles of the stronger COOH groups of the malonic acid functional groups per liter, *i.e.*, $c = 2c_1 = 12c_F$.

Apparatus. NMR spectra were performed at 29 °C on Bruker AVANCE DPX 300 and Varian VXR 300 NMR instruments at 75.47 MHz in D_2O using acetone-d_6 as internal standard.

Titration curves were recorded at 25 °C by a Metrohm automatic titrator 736 GP Titrino using glass and calomel electrodes.

Densities of the solutions were measured with a Paar digital density meter DMA 60 with external measuring cell DMA 602. An ultrathermostat attached to the instrument controlled the temperature at 25.00 ± 0.002 °C. The accuracy of density measurements was within $\pm 4.5 \times 10^{-6}$ g cm^{-3}.

The conductivity measurements used a Jones conductivity bridge, Leed & Northrup Co. 4666, at frequency 20 kHz. The measuring cell was immersed in a glycerol thermostat controlled within 25 ± 0.01 °C.

The osmotic coefficient measurements were performed at 25 °C with a Knauer vapor pressure osmometer. The instrument was calibrated using an aqueous KCl solution (0.005 mol kg^{-1}). Measurements were made only for the highest concentration. Due to the low concentration of the sample the accuracy of the osmotic coefficient determination was estimated to be $\pm 10\%$.

UV−visible absorption spectra were recorded at 25 ± 0.2 °C on a Cary 1 (Varian) spectrophotometer. The extinction coefficient determined at 334 nm using 1.00, 0.50, 0.20, and 0.10 cm cells was $\epsilon_{334\ nm} = 4.19 \times 10^4$ L/(cm mol) FHMA.

Results and Discussion

Potentiometric titration curve for aqueous solutions of C_{66}-$(COOH)_{12}$ (FHMA) is presented in Figure 1. Titration curves for malonic acid (MA), 1,1-cyclopropanedicarboxylic acid (ethylenemalonic acid, EMA), and equimolar mixture of HCl and CH_3COOH are included for comparison. For all acids the value $\alpha = 1$ corresponds to complete neutralization of both carboxylic groups. It is seen that EMA and MA exhibit two points of inflection, corresponding to the end points of titration of the first and second acid hydrogen. The pK values corresponding to the half titration points for the two stages of ionization are comparable to the literature values. On the other hand, the pH titration curve for $C_{66}(COOH)_{12}$ shows only one inflection point at the degree of ionization $\alpha = 1$, where all carboxylic groups on the fullerene skeleton have been neutralized. This finding can be ascribed to the fact that the first acid hydrogen in a $\rangle C(COOH)_2$ group is strongly ionized. Since the measurements were performed with solutions in which the solute concentration was small, the distinction between the degree of ionization, α, and neutralization, α_n

$$\alpha = \alpha_n + ([H^+] - [OH^-])/c \qquad (1)$$

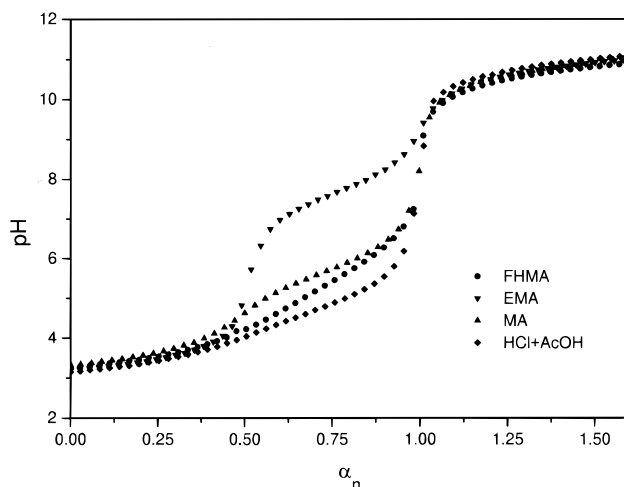needed to be taken into account. In eq 1, which follows from

Figure 1. Potentiometric titration of aqueous solutions of fullerene-hexamalonic acid (FHMA), ethylenemalonic acid (EMA), malonic acid (MA), and an equimolar mixture of HCl and CH_3COOH with approximately 0.1 mol/L NaOH at 25 °C. For all acids the concentration is $c = 0.00138$ mol H^+/ L.
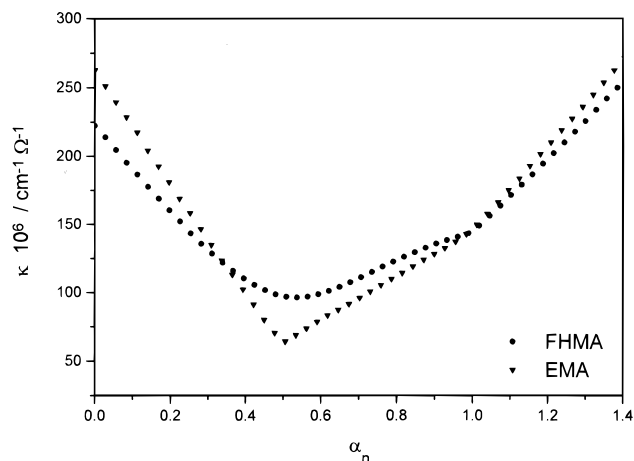

Figure 2. Conductometric titration of aqueous solutions of FHMA and EMA at 25 °C with approximately 0.1 mol/L NaOH.

the electroneutrality condition, the concentration of H^+ ions, $[H^+]$, was calculated from the measured pH. In most cases the concentration of OH^- ions, $[OH^-]$, can be neglected. Applying eq 1 to pure $C_{66}(COOH)_{12}$ ($\alpha_n = 0$) at $c = 0.0138$ mol COOH/ L, one gets the degree of ionization as $\alpha = 0.31$, indicating that the first COOH group of the malonic acid functional group is a rather strong acid. In the context of this discussion it is interesting that the equimolar mixture of a strong acid HCl and a weak acid CH_3COOH (Figure 1) shows a similar pH titration curve with only one point of inflection.

The results of the conductometric titration are shown in Figure 2 for fullerenehexamalonic acid, FHMA, and for ethylenemalonic acid, EMA. It is seen that the specific conductivity first decreases with the increasing degree of neutralization until $\alpha_n \approx 0.5$, then increases until $\alpha_n = 1$, and after $\alpha_n = 1$ a sharper rise of the curve is observed. The added NaOH first reacts with the strong $COOH_{(1)}$ groups producing a break in the curve at the first equivalent point, followed by another break in the curve when the weak $COOH_{(2)}$ groups of the malonic acid functional group are neutralized. As shown, the first break for FHMA is far from being sharp. This is due to the beginning of the ionization of the second $COOH_{(2)}$ groups before all first $COOH_{(1)}$ groups have been neutralized. It has to be mentioned that a similar conductometric titration curve has been observed[7]

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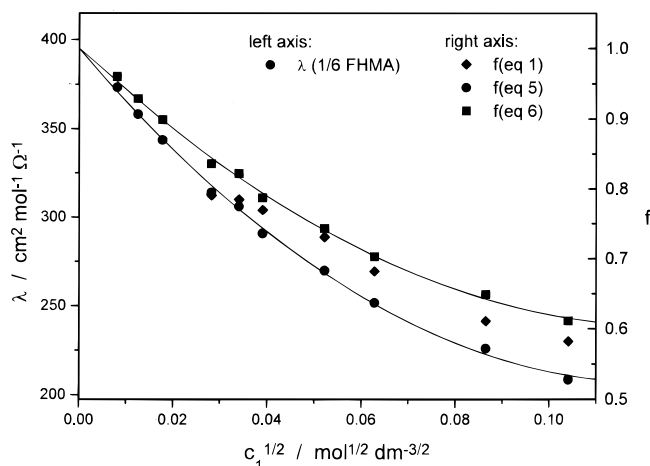*J. Phys. Chem. B, Vol. 102, No. 38, 1998* **7379**

Figure 3. Concentration dependence of the molar conductivity of C_{66}-$(COOH)_{12}$ (left axis), and of the fraction of free hydrogen ions (right axis) in water at 25 °C. The conductivity Λ is expressed per mole of the stronger carboxylic groups. See text.

for the mixture of strong and weak acids, HCl and CH_3COOH. Contrary to these observations, the titration curve for the EMA shows two sharp breaks in the titration curve, since the two ionization constants are of quite different orders of magnitude:[8] $pK_1 = 1.82$ and $pK_2 = 7.43$. It has to be mentioned that for fullerenehexamalonic acid the first break is observed at about $\alpha_n = 0.48$, presumably indicating that the number ratio of COOH$_{(1)}$ to COOH$_{(2)}$ is about 5.5 to 6. This finding is to some extent supported by the NMR observations. Until more information on this matter is accumulated we shall treat the sample as an electrolyte containing 12 COOH groups.

The pK_2 value for the second COOH group of the fullerene-hexamalonic acid read from Figure 1 at $\alpha_n = 0.75$ is about $pK_2 = 5.5$, indicating that even at concentrations much below the experimentally accessible concentrations the ionization of the second COOH group can be neglected.[7] The problem is then reduced to that of a monoprotic acid. It is very likely that the hydrogen of the second COOH group is bound to the adjacent COO$^-$ group by the intramolecular hydrogen bond. In Figure 3 we therefore plotted the molar conductivity, calculated per mole of the first COOH$_{(1)}$ groups, against the square root of the concentration, c_1. A curve typical for strong electrolytes is observed. A steep increase of Λ at high dilutions is characteristic for electrolytes of higher valence. Thus, the fullerene-hexamalonate anion should be treated as a highly charged anion, especially when both carboxylic groups on the functional group are ionized. As already discussed above, the full ionization of FHMA could only be achieved by titrating it with a strong base. The experimental data in Figure 3 can be represented by the empirical equation

$$\Lambda = \Lambda_0 - Ac^{1/2} + Bc \qquad (2)$$

which has been found to fairly well represent the conductivity data for strong electrolytes at moderate concentrations. The line in Figure 3 is represented by the following values of the constants: $\Lambda_0 = 395.0 \ \Omega^{-1} \ cm^2 \ mol^{-1}$, $A = 3086 \ \Omega^{-1} \ cm^2 \ mol^{-3/2} \ dm^{3/2}$, and $B = 12641 \ \Omega^{-1} \ cm^2 \ mol^{-2} \ dm^3$. Subtracting from the limiting value Λ_0 the molar conductivity of the hydrogen ion at $c = 0$, $\Lambda_0(H^+) = 349.82 \ \Omega^{-1} \ cm^2 \ mol^{-1}$, we get the molar conductivity of the half-ionized fullerenehexa-malonate anion $\Lambda_0[^1/_6 C_{66}(COOH)_6(COO^-)_6] = 45.2 \ \Omega^{-1} \ cm^2 \ mol^{-1}$. This value is comparable to the ionic conductivities of low molecular weight carboxylates at infinite dilution.[9] The

value of the limiting slope A can be compared to the predicted value δ in Onsager's theoretical equation for strong electrolytes:

$$\Lambda = \Lambda_0 - \delta\sqrt{c} \qquad (3)$$

By using the theoretical expressions of Onsager[9,10] the value of δ for 1−6-valent electrolyte can be expressed as

$$\delta = \frac{7.519}{1 + 5t_0^+ + 0.926\sqrt{1 + 5t_0^+}} \Lambda_0 + 394.1 \qquad (4)$$

where t_0^+ is the limiting transference number of the cation, in our case of H^+ ion. Upon insertion for $t_0^+ = \Lambda_0^+/\Lambda_0$ the value 0.886 we get $\delta = 0.9913\Lambda_0 + 394.1 = 786 \ \Omega^{-1} \ cm^2 \ mol^{-3/2} \ dm^{3/2}$. As expected, the theoretical value δ differs considerably from the experimental one A, a finding which has been usually observed for polyvalent strong electrolytes or incompletely dissociated electrolytes. Onsager pointed out that completely ionized electrolytes should approach the limiting tangent asymptotically from above, whereas incompletely dissociated electrolytes should approach it from below, a situation observed in our case. The degree of ion association to the polyvalent ion can be expressed on various ways. The simplest one is to define the fraction of electrolyte present as free ions, f, by the well-known expression

$$f = \Lambda/\Lambda_0 \qquad (5)$$

This equation has been frequently used for weak electrolytes, for which f is identical to the degree of ionization, $f \equiv \alpha$. Any exact determination of the fraction of free ions must, however, take into account the dependence of the ion mobilities upon concentration. Therefore the method has been perfected[9,11,12] by defining f as

$$f = \Lambda/\Lambda_f \qquad (6)$$

where Λ_f is the molar conductivity of the hypothetical completely ionized electrolyte at the ion concentration equal to that of the free ions, fc_1. This equation has been often used in the field of polyelectrolytes, where Λ_f was estimated from $\Lambda_f = \Lambda T_p + \Lambda_c$, T_p being the transport number of the polyion constituent, and Λ_c the molar conductivity of free counterions.[13] Owing to the lack of experimental data, in the present case the idea of Fuoss[9,14] and Shedlowsky[9,15] will be applied. Fuoss assumed that the hypothetical completely ionized electrolyte would obey the Onsager's limiting law, eq 3, at low concentrations. However, Shedlovsky proposed an extension of the Onsager's equation, which allows small departures above the limiting law in the experimental concentration range, and has the advantage of avoiding the empirical parameters:

$$\Lambda_f = \Lambda_0 - \delta c_f^{1/2} + \frac{\delta^2}{\Lambda_0} c_f - \frac{\delta^3}{\Lambda_0^2} c_f^{3/2} + \ldots \qquad (7)$$

In this relation, $c_f = fc_1$. The values of f obtained from eqs 6 and 7 by iteration are presented in Figure 3. We see that these values are somewhat higher than those calculated from the Arrhenius relation, eq 5. The use of eq 3 instead of eq 7 gives still slightly larger values of f (about 5% at the highest concentration). At this point it has to be stressed that thus far we have no evidence about the nature of association of hydrogen ions to the fullerenemalonate ion. Some ions may bind covalently to the bulky anion, effectively discharging it, whereas other ionized ions are bound in the general electrostatic field

of the anion. This "ionic atmosphere binding" is very difficult to prove absolutely, since most experiments do not distinguish between the effects of ions bound to the specific sites on the bulky ion and those which are simply trapped electrostatically within the domain of the oppositely charged bulky ion. The experimental data indicate that the first carboxylic group of the fullerenehexamalonic acid behaves as an intermediate electrolyte, that is, neither as a typical weak nor as a typical strong acid. In Figure 3 we present also the values of the degree of ionization of the stronger carboxylic groups, α_1, calculated from measured pH values and eq 1. We see that they are lying between the curves calculated from eqs 5 and 6.

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

$$\varphi = \pi/\pi_{id} \qquad (8)$$

was calculated from eq 8 using for

$$\pi_{id} = (\nu + 1)c_F RT \qquad (9)$$

with $\nu = 12$. Only the value of the osmotic coefficient at the highest concentration ($c_F = 0.001\,813$ mol FHMA/L), $\varphi = 0.38$, is reliable. With the value of $\nu = 7$, which corresponds to the first step of ionization, we get the value of $\varphi = 0.71$. In the limits of the estimated experimental error ($\pm 10\%$) this value is in qualitative agreement with the values of f at the same concentration.

Density measurements showed that the density of fullerene-hexamalonic acid solutions, ρ, varies linearly with the concentration in the concentration range below 0.002 mol FHMA dm^{-3}, i.e., $\rho = \rho_0 + bc_F$, with the constant $b = 0.778\,09$ kg/mol FHMA. Within the limits of the experimental uncertainty is thus the apparent molar volume of FHMA, ϕ_V, calculated from

$$\phi_V = \frac{1}{\rho_0}\left(M_2 - \frac{\rho - \rho_0}{c_F}\right) \qquad (10)$$

constant, and given by

$$\phi_V = \frac{M_2 - b}{\rho_0} \qquad (11)$$

where M_2 ($=1.332\,95$ kg/mol), is the molar mass of C_{66}-$(COOH)_{12}$. From eq 11 calculated value of ϕ_V is 557 cm^{3}mol^{-1}. This value corresponds to the degree of neutralization zero, $\alpha_n = 0$, or degree of ionization $\alpha = 0.30$ at the concentration $c = 0.0180$ mol COOH/L (eq 1). We determined also the apparent molal volumes for solutions with partly neutralized FHMA, and found for degrees of ionization 0.5 and 1.0 the values of ϕ_V equal to 497 and 371 cm^3 mol^{-1}, respectively, at the same concentration $c = 0.0180$ mol/L. From these data we can estimate the apparent molal volume, ϕ_u, of undissociated acid.

The conductivity measurements have disclosed that the ionization reaction

$$C_{66}(COOH)_{12} \rightarrow C_{66}(COOH)_6(COO^-)_6 + 6H^+ \qquad (12)$$

proceeds far at experimental concentrations. Therefore, the ions must contribute to the measured apparent molar volume, ϕ_V. It is well-known that the additivity principle[9]

$$c\phi_V = \sum_i c_i \phi_i \qquad (13)$$

may be expected to be fulfilled very closely at high dilutions, and to be a reasonable approximation at moderate concentra-

tions. By applying eq 13 to the process 12 we obtain

$$c_F \phi_V = c_F(1 - \alpha_1)\phi_u + c_F \alpha_1 \phi_{d1} + 6c_F \alpha_1 \phi_{H^+} \qquad (14)$$

where α_1 is the degree of ionization of the first carboxylic groups, i.e., $\alpha_1 = 2\alpha$, and ϕ_{d1} stands for the apparent molar volume of the $C_{66}(COOH)_6(COO^-)_6$ constituent. Equation 14 can be written in the form

$$\phi_u = \frac{\phi_V}{1 - \alpha_1} - \frac{\alpha_1}{1 - \alpha_1}(6\phi_{H^+} + \phi_{d1}) \qquad (15)$$

The value of ϕ_{d1} was obtained from the measured ϕ_V at $\alpha_1 = 1$ ($\alpha = 0.5$), which is ϕ_V of the $C_{66}(COOH)_6(COONa)_6$ species, taking into account the value of the apparent molar volume[9,16] of Na$^+$ ion at experimental concentration. From eq 15 calculated value of ϕ_u is $\phi_u = 632$ mL /mol FHMA.

We can calculate also the volume change of ionization of the first carboxylic groups, ΔV_1, from

$$\Delta V_1 = 6\phi_{H^+} + \phi_{d1} - \phi_u \qquad (16)$$

considering the ϕ_{H^+} value at experimental concentration.[9,16] The resulting value is -125 mL/mol FHMA. For one carboxylic group we get $\Delta V_1 = -21$ mL/mol COOH$_{(1)}$. Similarly, we can calculate the ionization volume, ΔV_2, for the second ionization step

$$C_{66}(COOH)_6(COO^-)_6 \rightarrow C_{66}(COO^-)_{12} + 6H^+ \qquad (17)$$
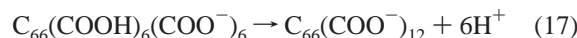
$$\Delta V_2 = 6\phi_{H^+} + \phi_{d2} - \phi_{d1} \qquad (18)$$

The apparent molar volume of $C_{66}(COO^-)_{12}$ species, $\phi_{d2} = 380$ mL/mol FHMA, was obtained from the experimental value of ϕ_V at $\alpha = 1$ ($\alpha_2 = 1$), taking into account $\phi_{V(Na^+)}$. The resulting value is $\Delta V_2 = -20$ mL/mol COOH$_{(2)}$. We see that both ionization volumes are negative, a situation that is normal because of the electrostriction of water produced by the ions resulting in a ionization process. Contrary to the two ΔV_i values found for FHMA, which are practically equal, in the case of ethylenemalonic acid[17] ΔV_2 exceeds ΔV_1 by a factor of about 4. Finally, we can calculate the radius of the fullerenehexamalonate anion, a, from ϕ_{d2}. Taking for the radius of the fullerene shell the value[18] 3.53 Å, and approximating the six malonate groups by six spheres attached to the fullerene globe, we get from ϕ_{d2} the value $a = 7.7$ Å, which is the distance from the center of the FHMA molecule to the negative charge.

Conclusion

Fullerenehexamalonic acid, T_h-$C_{66}(COOH)_{12}$, behaves as a diprotic acid. The second carboxylic group is a weak acid with a pK_2 value of about 5.5. The first COOH group has properties of an intermediate electrolyte; i.e., it behaves as neither a typical strong nor a typical weak electrolyte. We may expect that the salts of $C_{66}(COOH)_{12}$ with strong bases will have the properties of a highly charged strong electrolyte.

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