MOLAR CONDUCTIVITY OF AQUEOUS SOLUTIONS OF LITHIUM FULLERENEHEXAMALONATE, T_h-$C_{66}(COOLi)_{12}$, AS A FUNCTION OF TEMPERATURE[#]

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[#]This paper is dedicated to Prof. Dr. Davorin Dolar on his 80th birthday

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Abstract

Electrical conductivity measurements on aqueous solutions of the lithium salt of fullerenehexamalonic acid, T_h-$C_{66}(COOLi)_{12}$, were carried out at four temperatures: 5, 15, 25, and 35°C, and in the concentration range from about 0.2 to 0.00014 mol $(COO^-)/dm^3$. The limiting equivalent conductivities of the fullerenehexamalonate anion were estimated at the temperatures of our measurements. Temperature dependence of the molar conductivity of T_h-$C_{66}(COOLi)_{12}$ can be satisfactorily explained by changed viscosity of the solution. Molar conductivities of lithium fullerenehexamalonate are compared with those of sodium and calcium fullerenehexamalonates.

Introduction

Fullerenes, their chemistry and potential applications have stimulated numerous studies in chemistry, physics, biology and other natural sciences over the past several years.[1,2] Due to increased interest in biologically active compounds in recent years, more and more research is done in the field of water-soluble fullerene compounds.[3,4] In view of the experimental and theoretical studies with solutions of electrolytes, taking advantage of the discovery of fullerenehexamalonic acid[5], T_h-$C_{66}(COOH)_{12}$, and its derivatives displaying properties of strong electrolyte, physico-chemical studies of these compounds are especially attractive since they fill up the gap between simple electrolytes and macromolecular electrolytes - polyelectrolytes.[6,7] Electrolyte of this kind might be interesting at least for two reasons. One of them is the enchanting spherical symmetry of the fullerene ion. Another one is that this solute is a good example of a highly asymmetric electrolyte due to the high charge number of the bulky ion.

In a series of recent papers[6,8-11] from our laboratory we have reported on the first physicochemical studies of aqueous solutions of T_h symmetric fullerenehexamalonic acid, T_h-$C_{60}(C(COOH)_2)_6$, and its sodium salt, T_h-$C_{66}(COONa)_{12}$. Compounds have been isolated and characterized by some fundamental data and properties: ^{13}C NMR chemical shifts, solubility data, potentiometric and conductometric titration curves, the electrical conductivity, the osmotic coefficient, and the apparent molar volume.

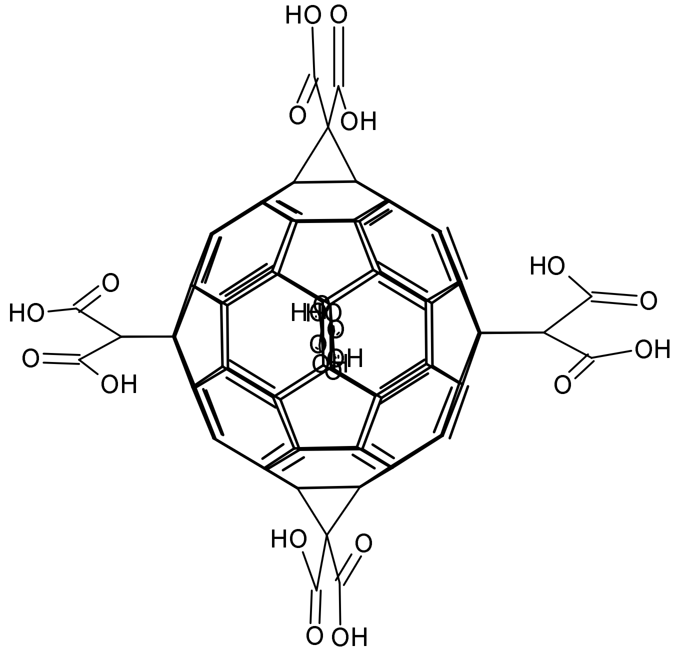

Figure 1: Structural drawing of fullerenehexamalonic acid, T_h-$C_{66}(COOH)_{12}$.

It has been found that 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.

In the present paper we report on studies of electrical conductivity in aqueous solutions of the lithium salt, T_h-$C_{66}(COOLi)_{12}$, at four temperatures: 5, 15, 25, and 35 °C, and at concentrations from about 0.2 to 0.00014 mol $(COO^-)/dm^3$. Experimental data are fitted into empirically proven equation to obtain molar conductivities at infinite dilution. A reasonable agreement between equivalent ionic conductivity of fullerenehexamalonate anion obtained from limiting molar conductivity of the lithium and sodium salts has been observed.[11] Dependence of the molar conductivity of aqueous solutions of lithium fullerenehexamalonate on temperature is examined against dependence of solvent viscosity on temperature. Molar conductivity of lithium fullerenehexamalonate is compared with those of sodium and calcium fullerenehexamalonate.[11]

Experimental

Materials. The T_h-fullerenehexamalonic acid, T_h-$C_{66}(COOH)_{12}$ (FHMA), has been synthesized according to already described procedure.[6] The product was checked by ^1H and ^{13}C NMR spectroscopy, UV-VIS spectroscopy and ion-chromatography.

The lithium salt, T_h-$C_{66}(COOLi)_{12}$ (LiFHM), was prepared from the acid solution by adding aqueous solution of LiOH until the pH was about 6. For the preparation of the aqueous solution of LiOH we used triple distilled water and $LiOH{\cdot}H_2O$ (SigmaUltra, Sigma). Prepared solution of LiFHM was concentrated by freeze drying. The solubility of $C_{66}(COOLi)_{12}$ is estimated to be, as in the case of sodium salt $C_{66}(COONa)_{12}$, over 400 mg $C_{66}(COOLi)_{12}$ per 1 g of H_2O.

The concentration of the concentrated solution of $C_{66}(COOLi)_{12}$ was determined spectrophotometrically, using for the extinction coefficient at 334 nm the value $\varepsilon_{334\ \mathrm{nm}} = 4.54 \cdot 10^4\ \mathrm{dm^3/(cm\ mol\ LiFHM)}$.

Solutions of lower concentrations were prepared by weighing. Densities of the aqueous solutions were measured with a Paar digital density meter DMA 60 with an external measuring cell DMA 602. The concentration c is expressed in moles of COO^- groups/dm^3.

Apparatus. Measurements of electrical conductivity of aqueous solutions were carried out with measuring assembly consisting of a cold bath (Lauda WK 1400), a precision glycerol thermostat (Lauda UB 40J) with immersed conductance cell (or a set of cells) and a highly precise conductance bridge (Leeds & Northrup Co. 4666). The temperature of the thermostat was set to the desired value with a reproducibility of less than 0.003 K.

In our experiments we used demineralized water which was two times distilled in a quartz. The final product with specific conductance $< 6{\cdot}10^{-7}\ \Omega^{-1}\ \mathrm{cm^{-1}}$ was transferred into the measuring cell under an atmosphere of nitrogen. The conductivities of dilute solutions were determined with the help of three-electrode measuring cell, described elsewhere.[12,13] At the beginning of every measuring cycle, the cell was filled with a weighed amount of water. After measurement of the water conductivity at all selected temperatures, weighed amounts of a stock solution were added using a gas-tight syringe.

Conductivity measurements at concentrations higher than 0.002 mol/dm^3 were performed with a set of nine capillary cells for concentrated solutions[14] of different cell constants ($3 \leq B$/cm$^{-1} \leq 83$) as these are required for concentrated solutions.

The measuring cells were calibrated with aqueous potassium chloride solutions according to standard procedure.[15]

Resistant measurements were made at different frequencies from which the value at infinite frequency was obtained by linear extrapolation.[12-15]

Taking into account the sources of error (calibration, measurements, impurities) the specific conductivities are certain within 0.05% at dilute and 0.2% at high concentrations.

Results and discussion

Experimental molar conductivity of the lithium fullerenehexamalonate, Λ, at temperatures 5, 15, 25, and 35 °C, is shown as a function of the square root of the concentration, c (Figure 2). A steep increase of Λ at high dilution can be seen. Such behaviour is characteristic for strong electrolytes of higher valence. It has to be stressed, that the salts of fullerenehexamalonic acid with strong bases should be treated as highly

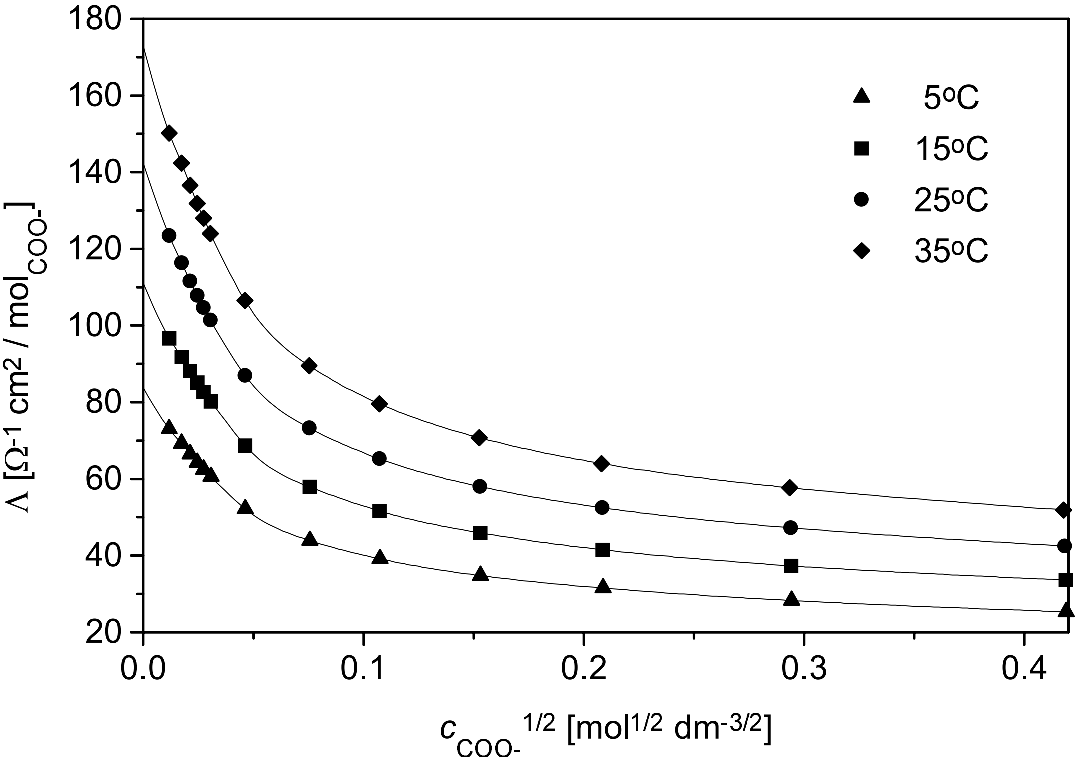

Figure 2: Concentration dependence of the molar conductivity of lithium fullerenehexamalonate, Λ [$^1/_{12}$ $C_{66}(COOLi)_{12}$], in aqueous solutions at 5, 15, 25 and 35°C.

asymmetric strong 1–12 valent electrolytes.[6,9] Although some progress in theoretical explanation[16] of electrical conductivity of simple electrolyte solutions at low and moderate concentrations for asymmetrical electrolytes, such as $BaCl_2$ or $LaCl_3$, has been made recently, the theory still fails to describe concentration dependence at the quantitative level. Therefore we used the empirical equation:

$$\Lambda = \Lambda_0 - A\,c^{\frac{1}{2}} + B\,c - Cc^{\frac{3}{2}} + \cdots \qquad (1)$$

which has been found that fairly well represents the conductivity data for strong electrolytes at moderate concentrations.[17]

In our case we tried to represent experimental data by the first four terms of eqn. (1). As a result we got the following values of Λ_0, the molar conductivity of LiFHM at infinite dilution: 83.8, 111.2, 142.5, and 173.0 $\Omega^{-1}cm^2mol^{-1}$ at 5, 15, 25, and 35 °C, respectively. The ionic limiting conductivities of the fullerenehexamalonate anion at temperatures of our measurements, Λ_0 $[{}^1/_{12}\ C_{66}\ (COO^-)_{12}]$, can be obtained if corresponding molar conductivities of the lithium ion (Λ_0 $[Li^+]$ = 22.76, 30.20, 38.68, and 48.0 $\Omega^{-1}cm^2mol^{-1}$) are subtracted from the limiting values of Λ_0 for LiFHM. According to this procedure we got the following values for the molar conductivity of the fullerenehexamalonate anion: Λ_0 $[{}^1/_{12}\ C_{66}\ (COO^-)_{12}]$ = 61.0, 81.0, 103.8, and 125.0 $\Omega^{-1}cm^2mol^{-1}$ at 5, 15, 25, and 35 °C, respectively. These values are approximately 10 % lower than those obtained previously from the conductivity measurements of NaFHM (Λ_0 $[{}^1/_{12}\ C_{66}\ (COO^-)_{12}]$ = 68.9, 91.4, 115.4, and 137.2 $\Omega^{-1}cm^2mol^{-1}$).[11] It should be stressed that extrapolation of molar conductivity to infinite dilution is delicate due to steep and non-linear increase of molar conductivity when square root of concentration is decreasing. Another possible experimental error is partial adsorption of fullerenehexamalonate ion to glassy surfaces – the phenomenon presumably caused by active hydroxyl groups in glass, a prevision which has to be proven.

Better agreement between molar conductivity of NaFHM and LiFHM is obtained at the lowest concentrations. In this concentration region degrees of association between fullerenehexamalonate and counterions (in the first case Li^+ ions and in the second case Na^+ ions) do not differ significantly.

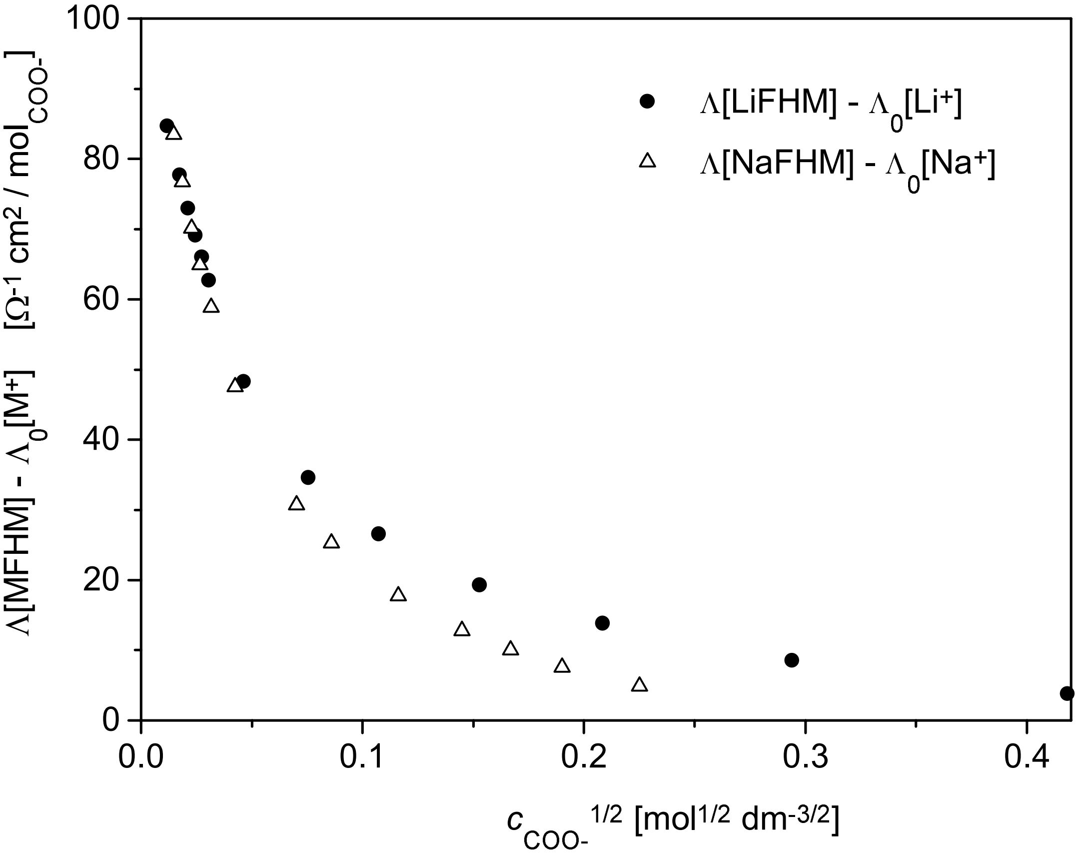

Figure 3: Comparison between $\Lambda[\mathrm{LiFHM}] - \Lambda_0[\mathrm{Li}^+]$ and $\Lambda[\mathrm{NaFHM}] - \Lambda_0[\mathrm{Na}^+]$ at 25°C.

In Figure 3 the comparison of $\Lambda[\mathrm{LiFHM}] - \Lambda_0[\mathrm{Li}^+]$ and $\Lambda[\mathrm{NaFHM}] - \Lambda_0[\mathrm{Na}^+]$ is shown. It can be seen that in the concentration region between $c_{\mathrm{COO^-}} = 0.0002$ mol/dm^3 and $c_{\mathrm{COO^-}} = 0.001$ mol/dm^3 both values are practically equal. However, both values should be identical at infinite dilution ($\Lambda_0[\mathrm{FHM}^-] = \Lambda_0[\mathrm{LiFHM}] - \Lambda_0[\mathrm{Li}^+] = \Lambda_0[\mathrm{NaFHM}] - \Lambda_0[\mathrm{Na}^+]$).

The increased molar conductivity at higher temperatures can be satisfactorily explained with decreased viscosity of solvent and therefore increased ionic mobility. Approximate constancy of the product of the limiting equivalent ionic conductivity, Λ_i^0, and solvent viscosity, η, was empirically discovered by Walden. It is known that the product $\Lambda_i^0 \cdot \eta$ is practically independent of the temperature. The Walden's rule is a direct consequence of the application of Stokes' law to the motion of ions:[17]

$$\Lambda_i^0 \cdot \eta = \frac{z_i e_0 F}{6\pi r_i} \tag{2}$$

where e_o is the proton charge, F is the Faraday constant, and z_i is the charge number of the ith ion of radius r_i. Equation 2 is originally postulated only at infinite dilution but with diminished validity can be extended to finite concentrations. In order to check whether increased molar conductivity at higher temperatures is a consequence of decreased solution viscosity, we multiply viscosity of solvent at different temperatures with corresponding molar conductivities. As can be seen on Figure 4, the extended Walden's rule is practically valid at all temperatures of our measurements and in the whole concentration range studied. It is therefore reasonably to adopt that the difference in molar conductivity of LiFHM at different temperatures studied is influenced almost exclusively by the viscosity of solution.

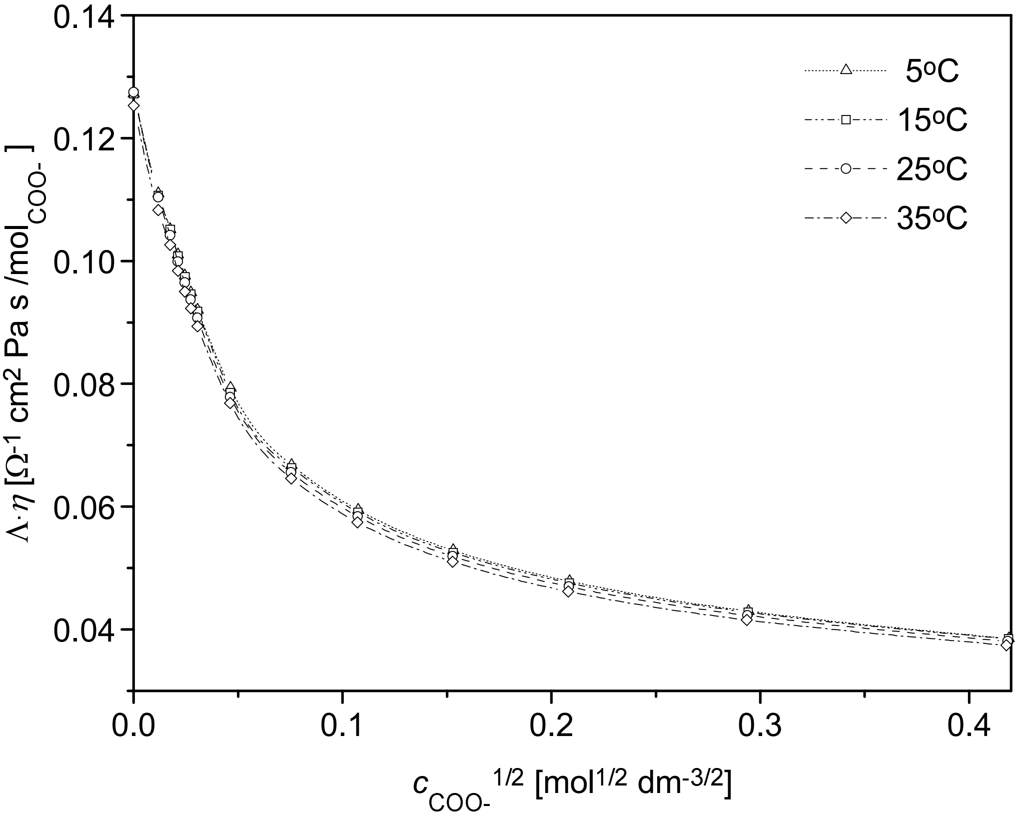

Figure 4: Product of molar conductivity of LiFHM and solvent viscosity, $\Lambda\cdot\eta$, as a function of temperature and a square root of concentration.

Comparison of molar conductivities of lithium, sodium and cesium salts in Figure 5 shows, as expected, that molar conductivity, Λ, for the divalent calcium salt is much lower than Λ for monovalent salts, due to the more extensive binding of divalent counterions.

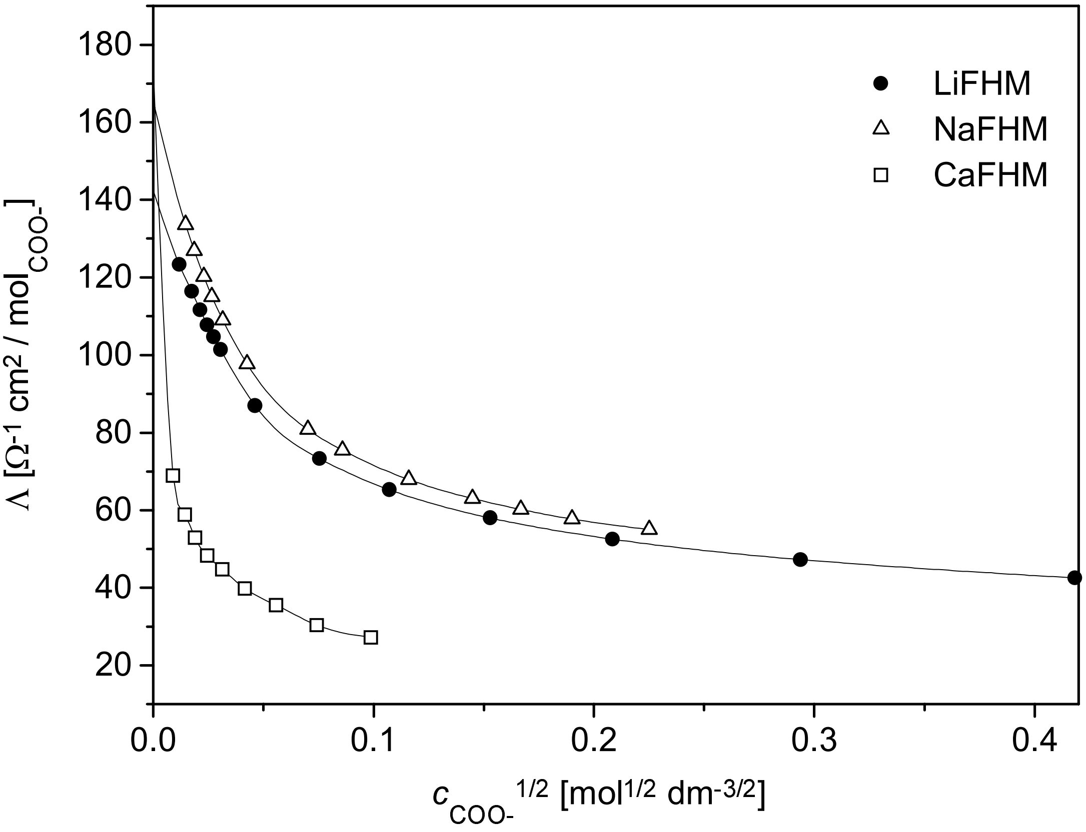

Figure 5: Molar conductivities of lithium, sodium and calcium salts of fullerenehexamalonic acid at 25°C. Molar conductivities at infinite dilution for LiFHM and NaFHM were obtained by extrapolation.

Conclusions

Dependence of the molar conductivity of lithium fullerenehexamalonate, $C_{66}(COOLi)_{12}$, on concentration shows features which are characteristic for strong electrolytes of higher valence. Furthermore, concentration dependence of molar conductivity on concentration observed for monovalent salts of fullerenehexamalonates is distinctively different from that of corresponding divalent salt.

Temperature dependence of the molar conductivity of lithium fullerenehexamalonate can be almost exclusively ascribed to the temperature dependent viscosity of the solvent.

Limiting equivalent conductivity of fullerenehexamalonate ion, Λ_0 [$^1/_{12}$ $C_{66}(COO^-)_{12}$], obtained from the measurements of the lithium fullerenehexamalonate, is about 10 % lower than that, obtained from the sodium salt. Additional efforts will be needed to collect more data and establish more accurate values.

Acknowledgements

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References and Notes

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Povzetek

Izmerili smo molske prevodnosti vodnih raztopin litijeve soli fulerenheksamalonske kisline, T_h-$C_{66}(COOLi)_{12}$, pri temperaturah 5, 15, 25 in 35°C ter v območju koncentracij med približno 0,2 in 0,00014 mol (COO^-)/dm^3. Ocenili smo molske prevodnosti pri neskončnem razredčenju pri vseh štirih temperaturah. Temperaturno odvisnost molske prevodnosti LiFHM je mogoče zadovoljivo pojasniti z vplivom temperature na viskoznost raztopine. Molske prevodnosti litijevega fulerenheksamalonata smo primerjali z molskimi prevodnostmi natrijevega in kalcijevega fulerenheksamalonata, ki smo jih določili že pri prejšnjih raziskavah.