

# Viscosity and Electrophoretic Mobility of Cesium Fullerenehexamalonate in Aqueous Solutions—Comparing Experiments and Theories on Nanometer-Sized Spherical Polyelectrolyte

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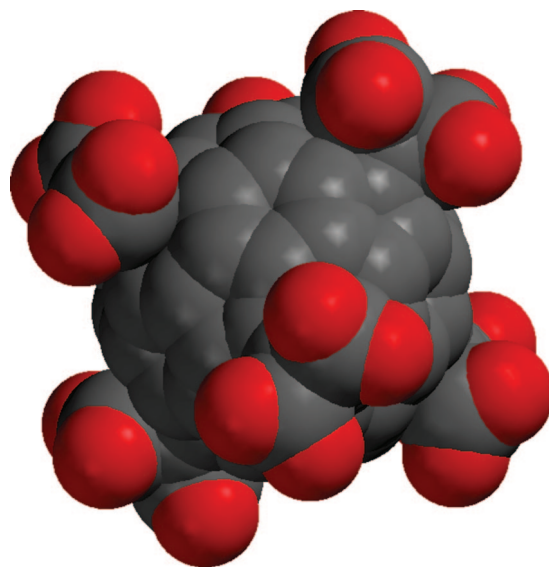
The viscosity of aqueous solutions of cesium fullerenehexamalonate  $T_h\text{-C}_{66}(\text{COOCs})_{12}$ , a rigid spherical nanometer-sized polyvalent salt, was measured by the Ubbelohde-type viscometer. The measurements were performed without added salt at 25 °C in the concentration range between 7 and 320 g/dm<sup>3</sup>. The concentration dependence of the obtained reduced viscosity was compared with the theoretical prediction, taking into account contributions stemming from the intrinsic viscosity, hydrodynamic perturbations of the hypothetically bare fullerenehexamalonate macroion, the primary electroviscous effect, and the secondary electroviscous effect. Using the geometric radius of the bare macroion from the previous measurements of the estimated effective charge of the macroion and from the small-angle X-ray scattering data of the estimated thickness of the compact shell of counterions electrostatically bound to the macroion, a good agreement between theory and the experiment was obtained in the range of the lowest and of the highest concentrations. Electrostatic interactions are identified as the main cause of the increased reduced viscosity at the lowest measured concentrations. At the highest concentrations, electrostatic interactions are effectively screened, and the influence of binary hydrodynamic interactions and perturbations of the hypothetical bare macroion prevails over electrostatic contributions to the increased viscosity. The electrophoretic mobility of the fullerenehexamalonate ion in aqueous salt-free medium was computed with the same value for the radius of the fullerenehexamalonate macroion as that used in the calculation of viscosity. The numerical solution of Ohshima's equation agreed well with the experimental values.

## 1. Introduction

Although in past decades numerous theoretical and experimental studies on polyelectrolytes were done, some fundamental questions still lack definite answers. One such topic is certainly the understanding of the concentration dependence of reduced viscosity in solutions and suspensions of macroions. Whereas plentiful experimental data are available for the case of linear polyelectrolytes, interpretation of their viscous properties is difficult because their conformational changes during dilution are still not well understood.<sup>1,2</sup> In order to eliminate the concentration-dependent rod–coil transition of polyelectrolytes and thus simplify the analysis, well-defined spherical polyelectrolytes are sought to be used in model studies.

Another subject in the field of polyelectrolytes where there is a need for experimental data for well-characterized macroions with narrowly distributed radius and charge is the investigation of electrophoretic mobility. Again, application of the sphere-shaped particles<sup>3,4</sup> facilitates interpretation of experimental results and comparisons with theoretical calculations.<sup>5,6</sup> A lack of suitable model systems for such studies is once more the reason for the scarceness of experimental data that could be used for the verification of the theories.

As the model polyelectrolyte to help understand these topics, we used  $T_h\text{-C}_{66}(\text{COOCs})_{12}$ ,  $T_h$  symmetric and highly water-soluble cesium fullerenehexamalonate (CsFHM), a salt with the asymmetry  $-12: +1$  in charge where all 12 charged carboxyl



**Figure 1.** Structure of the  $T_h\text{-C}_{66}(\text{COO}^-)_{12}$  ion space-filling model. Carbon atoms are gray, and oxygen atoms are red.

groups on the polyion are attached equiradially with respect to the center of the fullerene C-60 (Figure 1). The advantages of employing fullerenehexamalonate salts for this purpose are the well-defined and rigid structure that does not allow conformational changes, easily obtained geometric dimensions, chemical stability in neutral and basic aqueous solutions at room temperature, the known charge of the macroion, the impenetrable

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molecular core, the high surface charge density, and regular distribution of carboxyl groups over the macroion surface. In addition, no specific interactions between the fullerenehexamalonate macroion and alkali cations that could not be explained by the radius of the hydrated cation have been detected so far. As such, fullerenehexamalonates are very close to the ideal model system for testing intermolecular interactions among charged colloidal particles.<sup>7,8</sup> In this respect, use of fullerenehexamalonates in testing theories may overcome problems encountered with the use of other sphere-like charged particles such as latex particles and colloidal silica spheres (particles are usually relatively large in comparison to linear polyelectrolytes, sedimentation may occur, experiments are limited to low concentrations, the charge of the macroion is not exactly known) and may be employed when a better-defined and smaller system than microgels<sup>9,10</sup> and dendrimers<sup>11,12</sup> is required. Thus, it is possible that fullerenehexamalonates could expand the frontier in research of polyelectrolytes from the mesoscopic to nanoscopic scale. Such an attempt was already tested in the examination of thermodynamic properties where the use of the Poisson–Boltzmann equation for the spherical cell model proved to be useful in the theoretical predictions.<sup>13,14</sup>

In the present work, an attempt to explain some transport properties of cesium fullerenehexamalonate as a representative of a small spherical polyelectrolyte in salt-free aqueous solutions will be made. In the case of viscosity, the approach of Antonietti,<sup>10</sup> where reduced viscosity is taken to be a sum of intrinsic viscosity, electrostatic contribution, and hydrodynamic perturbations, will be followed. Because the incorporation of hydrodynamic interactions among uncharged particles through the Huggins equation could be questionable at the highest concentrations measured, this is done in this work via the expression that Simha derived from the cell model.<sup>15</sup> A small change is proposed also in the calculation of the Debye–Hückel parameter,  $\kappa$ , for the solutions of relatively low charged polyelectrolytes in salt-free solutions, taking into account that only free counterions and a portion of the electrical charge of the macroions that is not screened by associated counterions contribute to the ionic strength. Electrophoretic mobility will be calculated according to Ohshima's formula,<sup>6</sup> based on the numerical solution of the Poisson–Boltzmann equation for the spherical cell model, and compared to the data obtained on the basis of former measurements of the electrical conductivity of CsFHM solutions, transport numbers of the fullerenehexamalonate ion, and the measured viscosity. The rationale for choosing cesium salt is that the (nonhydrated) cesium counterion has the smallest possible diameter of all monovalent counterions, and thus, such a macroion–counterion system offers the closest match with the premise of the cell model used in the theoretical calculations.

## 2. Experimental Section

**2.1. Materials.** CsFHM was prepared by adding extra pure crystalline Cs<sub>2</sub>CO<sub>3</sub> (supplied by Merck) into an aqueous solution of fullerenehexamalononic acid,  $T_h$ -C<sub>66</sub>(COOH)<sub>12</sub>, synthesized as already described.<sup>14,16</sup> During the neutralization, the acidic solution was stirred, and released CO<sub>2</sub> was removed by a flow of pure nitrogen. The final degree of the neutralization with Cs<sub>2</sub>CO<sub>3</sub> was approximately 99% in order to keep the pH value of the obtained CsFHM solution slightly below 7. The stock solution was prepared by dissolving freeze-dried CsFHM in triple distilled water, and its concentration was determined spectrophotometrically.<sup>17</sup> Solutions of lower concentrations were prepared from the stock solution by weighing.

**2.2. Viscosity Measurements.** The measurements were performed with a Micro-Ubbelohde (suspended ball level) capillary viscometer. This kind of viscometer is especially suitable for measurements of small liquid quantities and for particularly short running times. The capillary used (Schott 536 10/I) had diameter of 0.40 mm and an approximate constant of 0.01 mm<sup>2</sup>/s<sup>2</sup> intended for the measurements of liquids with the kinematic viscosity between 0.4 and 6 mm<sup>2</sup>/s. The viscometer was immersed in a water thermostat controlled within (25.00 ± 0.01) °C. The passing meniscus was monitored by a naked eye. The calibration and, thus, the precise determination of the viscometer constant were made with the solvent (triple distilled water). Before filling the viscometer, all of the solutions and the solvent were filtered through a 1 μm polytetrafluoroethylene (PTFE) filter. The measurements were carried out under an air atmosphere because, even in the solution with the lowest CsFHM concentration, the estimated error due to CO<sub>2</sub>, possibly present in the solution, was lower than the error of measuring the time of flow. The contribution of the Hagenbach correction to the calculated viscosity was examined by measuring times of flow of the triple distilled water at 10.00, 15.00, 20.00, and 25.00 °C. We found that, for our case, this correction lies within the experimental error of the determination of viscosity by this kind of viscometer and is therefore ignored.

For the 5 lowest concentrations of CsFHM, the measurements were repeated 20 times, while for the higher concentrations, at least 5 measurements were done. The relative standard deviation of the time measurement was 0.25% at the lowest concentration, while that for the others in the lowest concentration regime was smaller. At the lowest concentration, a systematic decrease of flow times during consecutive measurements was observed. An adsorption of highly charged fullerenehexamalonate ions to the glassy walls of the viscometer may be a possible explanation for such a time drift.<sup>1</sup> Taking in account all possible errors, including the calibration of the viscometer, an uncertainty of the experimentally obtained reduced viscosity is estimated to be around 10% at the lowest concentration and diminishes rapidly with the increased concentration, reaching around 1% at the highest concentration.

**2.3. Small-Angle X-ray Scattering (SAXS) Measurements.** Measurements were performed with an evacuated Kratky compact camera system (Anton Paar, Graz, Austria) with a block collimating unit, attached to a conventional X-ray generator (Bruker AXS, Karlsruhe, Germany) equipped with a sealed X-ray tube (Cu anode target type), producing Ni-filtered Cu Kα X-rays with a wavelength of 0.154 nm. Further details can be found elsewhere.<sup>18</sup>

## 3. Results and Discussion

**3.1. Viscosity. Hydrodynamic Interactions.** The simplest theoretical expression that describes the viscosity of spherical particles is Einstein's equation for the specific viscosity,  $\eta_{sp}$ , of dilute suspensions of noninteracting spheres

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = 2.5\phi \quad (1)$$

where  $\eta$  and  $\eta_0$  denote the viscosity of the solution and that of the solvent, respectively, while  $\phi$  is the volume fraction of spheres. The reason for the increased viscosity with the increased particle fraction is the distortion of the applied flow field in the neighborhood of the particles. Although this equation was derived for the neutral spheres, it may be used as a rough approximation also for the charged spheres, where electrostatic interactions are screened enough.

Einstein's equation is, strictly speaking, valid only in the limit of the infinite dilution. In order to extend its validity to higher concentrations, one has to take into consideration hydrodynamic perturbations among particles. Classically, this is done by using Huggins equation

$$\eta_{\text{red}} = [\eta]_0 + k_H [\eta]_0^2 c_p \quad (2)$$

where  $\eta_{\text{red}} (= \eta_{\text{sp}}/c_p)$  represents the reduced viscosity,  $c_p$  denotes the polymer concentration in  $\text{g/dm}^3$ ,  $[\eta]_0$  is the intrinsic viscosity, and  $k_H$  is the Huggins constant, which depends on the molecular architecture and interactions; it has a value of  $k_H = 0.69$  for noninteracting hard spheres.<sup>19</sup> The intrinsic viscosity, which is a property of a given polymer–solvent pair, can be evaluated from the concentration dependence of  $\eta_{\text{red}}$  as

$$\lim_{c_p \rightarrow 0} \eta_{\text{red}} = [\eta]_0 = \frac{10}{3} \pi N_A \frac{R_\eta^3}{M_p} \quad (3)$$

where  $N_A$  is Avogadro's number,  $R_\eta$  the viscometric radius of the particle, and  $M_p$  the molecular weight of the colloid. The Huggins equation (eq 2) is, what is often forgotten, actually a limiting expression and should be used only at low concentrations.<sup>20</sup> At higher concentrations, one should prefer the equation<sup>20</sup>

$$\eta_{\text{red}} = [\eta]_0(1 + k_H \eta_{\text{sp}}) = [\eta]_0(1 + k_H \eta_{\text{red}} c_p) \quad (4)$$

The equation of this type was experimentally proven by Schulz and Blaschke.<sup>21</sup>

More exact approaches, valid for the suspensions of rigid spheres, were proposed by Simha<sup>15</sup> and Happel.<sup>22</sup> They both followed and extended the idea of Einstein, using as the starting point the cell model. Here, each spherical particle is surrounded by a concentric shell of a solution, having such an outer radius that the particle/cell volume ratio in the cell is equal to the particle volume fraction throughout the entire suspension. The difference between the approaches of Simha and Happel lies in the applied boundary conditions. While Simha used a hypothesis that there is no velocity disturbances at the cell boundary, Happel assumed that only the normal component of the perturbation velocity vanishes at the surface of the cell.

Simha's treatment of hydrodynamic interactions was recently used by Ruiz-Reina et al. in a theoretical model for calculation of the electroviscous effect of salt-free suspensions of spherical colloidal macroions, based on the solution of the Poisson–Boltzmann equation for the spherical cell model.<sup>23</sup> They obtained a solution which includes both electrostatic and hydrodynamic interactions. Unfortunately, their solution is too complex to be readily used by nonspecialists; it is suitable for the cases where ordering of macroions occurs. For this reason, we will rather use the already mentioned approach of Antonietti et al.<sup>10</sup> and replace Huggins's equation in their expression with Simha's formula, that is, the limiting solution of Ruiz-Reina et al.<sup>23</sup> for the noncharged particles.

According to Simha's equation,<sup>15</sup> the concentration dependence of viscosity can be expressed as

$$\eta = \eta_0 \left[ 1 + \frac{5}{2} \phi S(\phi) \right] \quad (5)$$

and the Simha function,  $S(\phi)$ , is calculated as

$$S(\phi) = \frac{4(1 - \phi^{7/3})}{4(1 + \phi^{10/3}) - 25\phi(1 + \phi^{4/3}) + 42\phi^{5/3}} \quad (6)$$

As followed from the geometry, for the case of a spherical macroion with the nominal charge number  $Z_p$  and the ap-

**TABLE 1: Viscosity and Reduced Viscosity of CsFHM in Water at 25.00 °C As a Function of the Molar Concentration of Carboxyl Groups on the Polyion ( $c_c'$ ) (= molar concentration of counterions) and the Weight Concentration of CsFHM ( $c_p$ )**

$c_c'$ (mol/dm <sup>3</sup> )	$c_p$ (g/dm <sup>3</sup> )	$\eta$ (centipoise)	$\eta_{\text{red}}$ (dm <sup>3</sup> /kg)
0.0302	7.34	0.909	2.8
0.0566	13.8	0.914	1.9
0.0739	18.0	0.924	2.1
0.118	28.7	0.938	1.9
0.233	56.7	0.9749	1.68
0.236	57.7	0.9723	1.56
0.427	104	1.036	1.57
0.7063	171.6	1.148	1.69
1.308	317.8	1.454	1.99

purtenant point monovalent counterions, the volume fraction  $\phi$  is related to the concentration of macroion via eq 7

$$\phi = \frac{4\pi a^3 N_A c_p}{3M_p} = \frac{4\pi a^3 N_A c_c'}{3|Z_p|} \quad (7)$$

where  $a$  is the radius of the particle, and  $c_c'$  is the molar concentration of the monovalent counterions, which is equivalent to the molar concentration of the macroion expressed in monomer units per volume unit. In terms of the reduced viscosity, eq 5 can be written for the case of rigid spheres (by taking into account eqs 3 and 7) also as

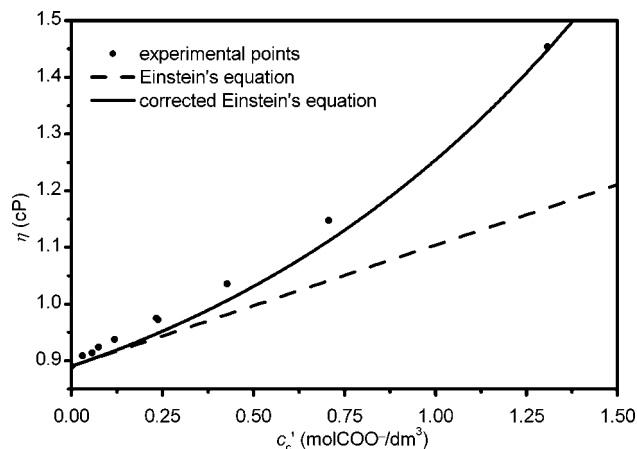
$$\eta_{\text{red}} = \frac{5}{2} \frac{\phi S(\phi)}{c_p} = [\eta]_0 + [\eta]_0 (S(\phi) - 1) \quad (8)$$

where the term  $[\eta]_0 (S(\phi) - 1)$  represents the contribution of hydrodynamic interactions to the reduced viscosity.

When the nondrained rigid spherical particles are considered, the geometric radius  $a$  is usually taken as a good approximation of the viscometric radius.<sup>10</sup> In order to compare the measured reduced viscosity of CsFHM solutions (Table 1) with Einstein's and Simha's equations, we have to determine the geometric radius  $a$ . To be consistent with our previous studies, we shall set  $a = 7.7$  Å, a radius obtained from the effective volume of the  $T_h\text{-C}_{66}(\text{COO}^-)_{12}$  ion by the semiempirical calculations with the Spartan program;<sup>24</sup> a similar value can be derived also from the measurements of the apparent molar volumes.<sup>17</sup> The graph of the concentration dependence of the viscosity of CsFHM solutions and theoretical predictions for uncharged spheres are plotted in Figure 2. As can be seen, such a rough approximation predicts the viscosity in the given concentration range with an error of less than 4%. The agreement is especially good at the highest concentration ( $c_p = 317.8$  g/dm<sup>3</sup>) where electrostatic interactions are obviously screened enough that the increase of the reduced viscosity can be explained solely by the hydrodynamic perturbations caused by a rigid sphere having dimensions of the bare fullerenehexamalonate macroion. According to calculations, the Debye–Hückel screening length in CsFHM solution with the highest concentration is 1.9 Å (equivalent to 2.6 M 1–1 electrolyte solution), which confirms, taking into account the estimated distance between two fullerenehexamalonate macroions at this concentration (27 Å), that the contribution of electrostatic interactions to increased viscosity is significantly smaller than that of hydrodynamic interactions.

**Electrostatic Interactions.** When electrostatic contributions to viscosity are concerned, these can, in general, arise at least from three sources. According to the mechanism, they are classified as the primary, the secondary, and the tertiary electroviscous effect. The last one emerges in solutions of





**Figure 2.** Prediction of the Einstein's equation (eq 1) and the corrected Einstein's equation (eq 5) in comparison to the measured viscosity of the aqueous solutions of CsFHM. In the calculations, the geometric radius of fullerenehexamalonate was taken to be 7.7 Å. Here, the macroion is supposed to be sufficiently electrostatically screened by the counterions to be approximated by the uncharged sphere.

flexible polyelectrolytes due to conformational changes of the polyelectrolyte backbone caused by changes of polyelectrolyte concentration or by an addition of a salt. Because the fully ionized fullerenehexamalonate ion is a very rigid molecule, the third electroviscous effect can be ruled out and will not be discussed here.

**The Primary Electroviscous Effect.** It arises from the formation of the double layer of (counter)ions around the macroion. This double layer, whose thickness is dependent on the concentration of the polyelectrolyte as well as on the concentration of the eventually added salt, exerts Stokesian friction when it is moved through the medium. This additional friction is superimposed to the friction of the bare macroion and is the main cause of increased viscosity due to electrostatic interactions at low concentrations. Since this effect apparently increases the radius of the macroion moving through the medium, this phenomenon is of first order in  $\phi$ . It is then easy to understand that when it has to be theoretically considered, one usually adds to the geometric radius  $a$  of the bare macroion an extra distance  $\Delta r$  that is a measure of a viscous drag of the double layer formed around the macroion. This value, representing, in fact, an effective rather than a true distance, is however difficult to estimate. One of the possibilities is to equate  $\Delta r$  with the thickness of a Bjerrum shell, a shell that contains all of the counterions whose electrostatic energy exceeds their thermal energy  $kT$ . This concept overestimates the contribution of the primary electroviscous effect to the viscosity because such a shell is certainly less effective in exerting Stokesian drag than the rigid particle of the equivalent size. For our case, a failure of such an approach is quite obvious, and the predicted reduced viscosity is several times larger than the measured one in the certain concentration range. We had referred also to some other simple estimations<sup>10</sup> of  $\Delta r$ , but none of them gave reasonable results, and more complex theories<sup>25</sup> were left aside. Instead, we decided to use the radii of gyration  $R_g$ , obtained from a Guinier plot of the small-angle X-ray spectroscopy (SAXS) data of CsFHM solutions, as the starting point for estimation of  $\Delta r$ . In analysis of these data, an increase of  $R_g$  upon dilution of salt-free solutions of CsFHM was noticed. Since the conformation of the rigid fullerenehexamalonate macroion cannot change upon dilution and also the obtained  $R_g$  is too large to be explained solely from the scattering of X-rays on the fullerene-

hexamalonate macroion, the only possible explanation is that also counterions contribute to  $R_g$ . According to definition,  $R_g$  is equal to

$$R_g = \sqrt{\frac{\sum_i m_i r_i^2}{\sum_i m_i}} \quad (9)$$

where  $m_i$  is the mass of the  $i$ th atom in the particle and  $r_i$  is the distance from the center of mass to the  $i$ th particle. In the first step,  $R_g$  was calculated from the positions of all carbon and oxygen atoms in the fullerenehexamalonate macroion by the Spartan program,<sup>24</sup> while for the electrostatically bound cesium counterions, it was assumed that they are located adjacent to the fullerene core, surrounded by three malonic groups. The rationale for presuming that electrostatically bound cesium counterions are located close to the fullerene skeleton is based on the radius of the shear plane (10 Å), which satisfactorily explains the calculated electrophoretic mobility of CsFHM,<sup>27</sup> as well as the fact that a macroion constituent radius of 7.7 Å quite well reproduces also the reduced viscosity at higher concentrations, where electrostatic interactions are strongly screened. More direct experimental evidence that electrostatically bound Cs<sup>+</sup> can be located in the hydrophilic layer of colloid particles was found by other researchers.<sup>28</sup> Then, a common distance from the center of mass for all of the free counterions (their number is equal to the effective charge of the macroion) was used as an adjustable parameter in eq 9 in order to get experimental  $R_g$  as the result of the calculation. The obtained distances of free counterions for the measured 1, 2, 5, and 9.6% (w/w) aqueous solutions of CsFHM (calculated from corresponding  $R_g$  values of 7.5886, 7.282, 7.227, and 7.185 Å, respectively) are 10.59, 9.98, 10.00, and 10.00 Å, respectively. Similarly to  $R_g$  also, the calculated apparent distance of free counterions diminishes with increased concentration within experimental error, an effect that, in the absence of conformational changes of the macroion, can be attributed only to the influence of electrostatic interactions between the macroion and counterions. We consider that the concentration dependence of the distance of free counterions, as obtained from the radii of gyration, is more a reliable measure of the change of the effective radius of the macroion constituent than the calculated Bjerrum shell since it is related to the experimental evidence. Because the fraction of free counterions is quite constant in this concentration range, the influence of the number of free counterions in the diffuse layer on  $\Delta r$  applied in the estimation of the primary electroviscous effect is neglected here. In absolute terms, the apparent distance of free counterions, calculated from  $R_g$ , is not suitable for estimation of the effective radius  $r_{\text{eff}}$  of the macroion constituent since it predicts a far too high reduced viscosity. For example, taking  $r_{\text{eff}} = 10.0$  Å for the solution with  $c_p = 103.8$  g/dm<sup>3</sup> would give, after considering also hydrodynamic perturbations of such a particle,  $\eta_{\text{red}} = 3.56$  dm<sup>3</sup>/kg instead of an experimental value of 1.56 dm<sup>3</sup>/kg. Additionally, it has to be said that such a calculated value could be even higher due to an eventual secondary electroviscous effect. In order to avoid such unrealistic values for  $\Delta r$  of the double layer contributing to the viscous drag, the absolute increment of the apparent distance of free counterions at a given concentration  $c_p$  in comparison to the apparent distance of free counterions, assumed to be also at the highest concentration ( $c_p = 317.8$  g/dm<sup>3</sup>) equal to 10.0 Å, is used. The choice of 10.0 Å as a reference point is supported also from the calculation of the apparent distance of free counterions from  $R_g$ , which was

obtained from an extrapolation to the highest concentration. The calculated value was only slightly below 10.0 Å. The effective volume fraction  $\phi_{\text{eff}}$  of the macroion constituent is then expressed as

$$\phi_{\text{eff}} = \frac{4\pi(a + \Delta r_{\text{cp}})^3 N_A c_p}{3M_p} \quad (10)$$

where  $\Delta r_{\text{cp}}$  denotes an increment of the effective radius at the given concentration  $c_p$  in comparison to that at the highest concentration, and consequently, the contribution of the primary electroviscous effect to the reduced viscosity  $\eta_{\text{red(1EE)}}$  can be written as

$$\eta_{\text{red(1EE)}} = \frac{5(\phi_{\text{eff}} S(\phi_{\text{eff}}) - \phi S(\phi))}{2c_p} \quad (11)$$

Regarding the choice of the apparent distance of free counterions at the highest concentration as the referential point, we consider that the calculated Debye–Hückel screening length (1.9 Å) justifies this decision. It is however interesting that the apparent distance of free counterions is more or less equal to 10.0 Å (within an experimental error) in the concentration range from 20 g CsFHM/dm<sup>3</sup> upward (Debye–Hückel screening length of 7 Å; an equivalent of 0.2 M 1–1 electrolyte solution), which suggests that both from the constant apparent distance of free counterions and the calculated ionic strength that no significant contribution of the primary electroviscous effect to the viscosity is expected in this concentration range. It has to be stressed again that SAXS data were used mainly to detect a digression of free counterions from the macroion and thus the onset of the primary electroviscous effect upon dilution. The calculated contribution of the primary electroviscous effect to the reduced viscosity at the concentrations below  $c_p = 15$  g CsFHM/dm<sup>3</sup> is more or less a guess for which we think it is much more reasonable in the case studied than the use of other criteria.

**The Secondary Electroviscous Effect.** According to this mechanism, the viscosity is increased due to repulsive electrostatic particle–particle interactions during flow-induced encounters of such colloidal particles. While the primary electroviscous effect dominates at very low  $\phi$ , the secondary one is more accentuated at higher concentrations. In the rather comprehensive work, Hess and Klein<sup>29</sup> tackled among the other ones also the problem of viscosity of low-concentrated systems of strongly charged particles. They derived, making some simplifications, a closed set of nonlinear equations that have to be solved numerically. Such a solution is not readily obtained, and it is not suitable for everyday work. Therefore, we decided to use a simplified form, derived in the same paper by assuming a weak-coupling approximation where the static structure factor may only slightly deviate from the ideal value of 1. As stated by Hess and Klein, this approximation is expected to give reliable results only in the case of a dilute solution of macroions with sufficient additional salt where practically all of the electrostatic screening is obtained by the salt ions alone.<sup>29</sup> Their result, rearranged to the form of

$$\frac{\eta - \eta_0}{\eta_0} = \frac{1}{160} (4\pi l_B N_A)^2 r_H \frac{Z_{\text{eff}}^4 c_p^2 \exp[2\kappa a]}{\kappa^3 (1 + \kappa a)^2} \quad (12)$$

was used by Antonietti et al.<sup>10</sup> for describing the viscosity of small spherical polyelectrolytes in aqueous solutions with and without added salt in the concentration regime up to  $c_p \approx 5$  g/dm<sup>3</sup>. In the upper equation,  $l_B$  is the Bjerrum length,  $Z_{\text{eff}}$  is the effective charge number per macroion,  $r_H$  and  $a$  are the

hydrodynamic and the geometric radius of the particle, and  $c_p'$  is molar concentration of the polyion. The Debye–Hückel parameter is in the Debye–Hückel theory connected to the thickness of the atmosphere-like cloud of ions of the opposite kind that surround the given ion and is defined as

$$\kappa^2 = 4\pi l_B N_A \sum_i Z_{i(\text{eff})}^2 c_i' \quad (13)$$

where  $c_i'$  and  $Z_{i(\text{eff})}$  are the molar concentrations and effective charge numbers of all ionic species present in the solution, respectively.

Since the Debye–Hückel theory was developed for describing thermodynamic properties of solutions of the low-charged simple ions where no ionic association is expected, the equation should be used with caution in cases where ions are electrostatically bound one to another. In the cases of salt-free solutions of real polyelectrolytes, where the charge of the polyion is, to a good extent, effectively screened by the associated monovalent counterions, one usually replaces eq 13 by the expression

$$\kappa^2 = 4\pi l_B N_A |Z_p| c_p' \quad \text{or} \quad \kappa^2 = 4\pi l_B N_A Z_c^2 c_c' \quad (14)$$

where  $Z_c$  denotes nominal charge number of the counterion and  $c_c'$  is its molar concentration.

When  $\kappa a \ll 1$ , eq 12 can be, using the definition of  $\kappa^2$  from eq 14, reduced to<sup>10,29</sup>

$$\eta_{\text{red}} = \frac{1}{160} \left( \frac{4\pi l_B N_A}{M_p} \right)^{1/2} r_H \frac{Z_{\text{eff}}^4 c_p}{\left( \frac{2M_p}{M_s} c_s + |Z_{\text{eff}}| c_p \right)^{3/2}} \quad (15)$$

where  $M_s$  and  $c_s$  denote the molecular weight of the (possibly) added salt and its concentration in g/dm<sup>3</sup>, respectively.

In our opinion, approximations given by eq 14 might be reasonable in the cases where the polyion has the nominal charge number of several hundreds or even several thousands, while this cannot be necessarily true for macroions with lower charge in salt-free solutions. Following this rationale, we define, following polyelectrolyte and Debye–Hückel theories

$$Z_{\text{eff}} = Z_p f \quad (16)$$

and

$$c_{\text{cf}}' = c_c' f \quad (17)$$

where  $f$  is fraction of free (= not (electrostatically) bound to macroions) counterions while  $c_{\text{cf}}'$  is the molar concentration of free counterions. Having in mind that  $c_c' = c_p |Z_p| / |Z_c|$  and that in the calculation of the  $\kappa^2$  only the concentration of active (free) ions is important, we may in our notation rewrite  $\kappa^2$  for salt-free polyelectrolyte solution as

$$\kappa^2 = 4\pi l_B N_A (Z_{\text{eff}}^2 c_p' + Z_c^2 c_{\text{cf}}') \quad (18)$$

which, taking into account the above written relations, leads to

$$\kappa^2 = 4\pi l_B N_A c_p' |Z_{\text{eff}}| (|Z_{\text{eff}}| + |Z_c|) \quad (19)$$

In the low concentration range, where the relation  $\kappa R \ll 1$  holds, we may then divide both sides of eq 12 by  $c_p$  and write the contribution of the secondary electroviscous effect of  $\eta_{\text{red(2EE)}}$  to  $\eta_{\text{red}}$ , expressing  $\kappa^2$  according to eq 19, as

$$\eta_{\text{red(2EE)}} = \frac{1}{160} \left( \frac{4\pi l_B N_A}{M_p} \right)^{1/2} a \frac{|Z_{\text{eff}}|^{5/2}}{c_p^{1/2} (|Z_{\text{eff}}| + |Z_c|)^{3/2}} \quad (20)$$

In the upper equation, intended for our case, the hydrodynamic radius  $r_H$  was substituted by the geometric radius of the

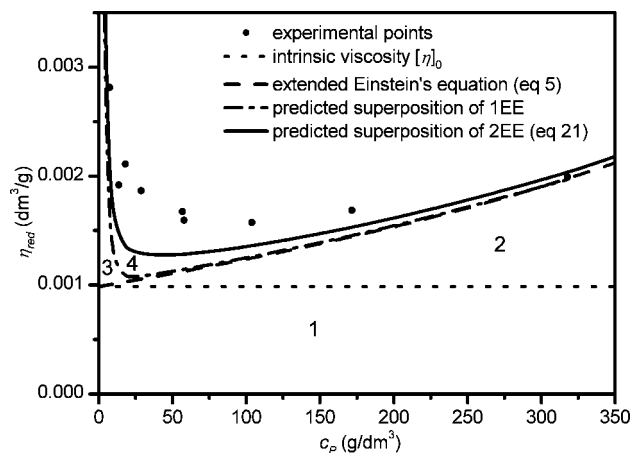
macroion  $a$  because they are practically equal, as was already discussed above. The equation obtained should now account for interparticle electrostatic perturbations (= the secondary electroviscous effect). In our opinion, this expression more faithfully follows the idea of the Debye–Hückel screening parameter than the term used by Antonietti et al.<sup>10</sup> and should be used at least in the cases when the charge of the macroions is relatively small. The question that remains now is whether as a fraction of free ions,  $f$ , which is used in the calculation of  $\kappa^2$ , one should take the value obtained from the measurements of the transport properties (e.g., fraction of free ions from the combined measurements of electric conductivity and transport number) or that from the measurements of the thermodynamic properties (e.g., fraction of osmotically active counterions). Although intuitively one may think that since viscosity is a transport property the value obtained from the transport measurements is more significant, thermodynamic properties of polyelectrolytes are more closely related with the charge screening. Even though numerous studies and our recent research<sup>27</sup> showed that the values derived from the transport properties are usually somewhat higher, the difference in this case is probably irrelevant considering a rough estimate of the electrostatic interactions among charged particles.

For the interested reader, however, it might be useful to know the range of  $f$  and  $Z_{\text{eff}}$  used in the calculations. The osmotic coefficient (as an approximation of the fraction of the free ions) in CsFHM solutions at 25 °C has, in the concentration range examined, values between 0.56 (at  $c_p \sim 7.3 \text{ g/dm}^3$ ) and 0.50 (at  $c_p \sim 320 \text{ g/dm}^3$ ).<sup>14</sup> On the other hand, recent measurements of transport numbers,<sup>27</sup> combined with the electrical conductivity data,<sup>14</sup> gave values for  $f$  between 0.62 (at  $c_p \sim 7.3 \text{ g/dm}^3$ ) and 0.60 (at  $c_p \sim 22 \text{ g/dm}^3$ ). These values are rather constant in the concentration range studied and are, on average, about 12% higher than those obtained from thermodynamic properties, which are also only modestly concentration dependent. If we take  $f$  as the arithmetic average of the thermodynamic and transport values, then we see that  $Z_{\text{eff}} (=12f)$  in the studied concentration range varies between 7.1 and 6.1.

**Comparison of Theory with Experiment.** In order to compare theory with the experimental viscosity of salt-free CsFHM solutions, all of the terms representing contributions stemming from the intrinsic viscosity of the bare fullerenehexamalonate macroion  $[\eta]_0$ , hypothetical hydrodynamic perturbations of the bare macroion, the primary electroviscous effect  $\eta_{\text{red(1EE)}}$ , and the secondary electroviscous effect  $\eta_{\text{red(2EE)}}$  should be summed up

$$\eta_{\text{red}} = [\eta]_0 + [\eta]_0(S(\phi) - 1) + \frac{5(\phi_{\text{eff}}S(\phi_{\text{eff}}) - \phi S(\phi))}{2c_p} + \frac{1}{160} \left( \frac{4\pi l_B N_A}{M_p} \right)^{1/2} a \frac{|Z_{\text{eff}}|^{5/2}}{c_p^{1/2}(|Z_{\text{eff}}| + |Z_c|)^{3/2}} \quad (21)$$

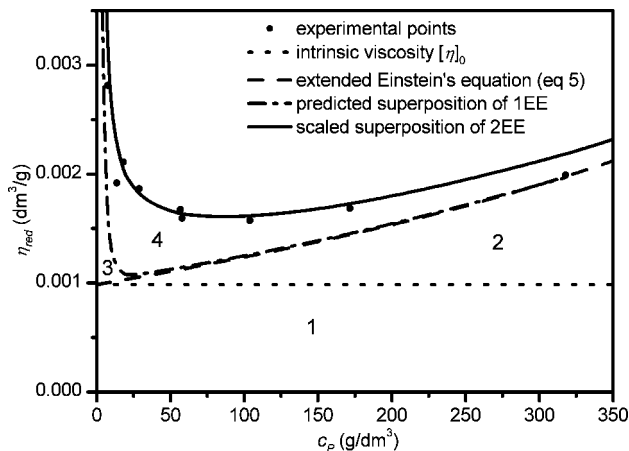
In Figure 3, a graphically represented comparison is made. It is appropriate to say here that for a macroion with the nanometer dimensions, evaluation of the magnitude of the primary electroviscous effect is difficult since it is extremely dependent on the estimate of the contribution of the diffuse layer and is probably impossible without having additional data about the structure of the macroion surface structure. As can be seen, agreement between theory and the experiment is good at the lowest concentration, where the primary and the secondary electroviscous effects play important roles, and at the highest concentration, where the hydrodynamic perturbations attributed solely to the macroion are practically the only effect superim-



**Figure 3.** Concentration dependence of the reduced viscosity of CsFHM solutions in comparison with the estimated contributions from the various sources; (1) intrinsic viscosity of the bare macroion, (2) hydrodynamic perturbations of the hypothetically bare macroion, (3) the primary electroviscous effect (1EE), and (4) the secondary electroviscous effect (2EE). Discrepancy between the theory and the experiment is attributed mainly to the failure of the term predicting the secondary electroviscous effect. For the details, see the text.

posed on the intrinsic viscosity. The latter fact is hardly a surprise since the electrostatic interactions are strongly screened. Agreement is only qualitative immediately after the lowest concentration, where steep decrease of the contribution from the primary electroviscous effect is estimated from the SAXS measurements while the contribution from hydrodynamic perturbations is still relatively small. This discrepancy actually could be expected since the presumptions of the weak-coupling approximation used in the evaluation of the applied equation are not valid here. Obviously, the electrostatic interactions among fullerenehexamalonate macroions are too poorly screened, and the repulsion is therefore much stronger than the one taken into account in the applied equation. An impression of how strongly this repulsion changes the structure of the solution can be obtained from the macroion–macroion distribution function, calculated on the basis of Monte Carlo simulations made for the electrolyte with the asymmetry in charge  $-12: +1$  and with the very similar dimensions of the macroion and counterions to those met in CsFHM (Figures 1 and 2 in ref 30). It would be interesting to test whether more a rigorous solution than that obtained on the basis of the weak-coupling approximation would give better agreement with the experimental data. It has to be said that such an analysis that was performed here is possible only when the macroion is well-defined, possibly spherical, rigid, homogeneous, and well-characterized in charge as well as in dimensions. Since the number of such compounds is extremely limited, it might be, in the majority of cases when only detection of the primary and the secondary electroviscous effect is required, sufficient to use appropriate formulas and involve some adjustable parameters. Such an approach would give practically quantitative agreement of experiment and theory with the existing formula also in our case. For example, if only the term representing the contribution of the secondary electroviscous effect in eq 20 is multiplied by a factor of  $(4\pi)^{1/2}$  (a lapsus calami that occurred in the last term of eq 16 from ref 10), an almost perfect agreement is obtained, as shown in Figure 4. Because we do not know which form of this term was used by Antonietti et al.<sup>10</sup> nor do we know their experimental data that could be used in the analysis as was done here, we cannot judge whether the agreement shown in Figure 4 is accidental or not.





**Figure 4.** The same as that for Figure 3, but the contribution from the secondary electroviscous effect is multiplied by  $(4\pi)^{1/2}$ .

Until more evidence is gathered, we will consider this agreement as a pure coincidence.

**3.2. Electrophoretic Mobility.** The same geometric radius of the bare fullerenehexamalonate ion as that considered in the analysis of viscosity can be applied and tested also in another example of transport properties, the electrophoretic mobility.<sup>5</sup> One of the recent attempts that describes movement of a charged spherical macroion under the influence of the external electrostatic field in the salt-free solution in the frame of the spherical cell model, based on the solution of the Poisson–Boltzmann equation, is that of Ohshima.<sup>6,31,32</sup>

Here, a spherical polyion (fullerene) with a nominal charge number  $Z_p$  is immersed in a salt-free medium containing only counterions. It is assumed that each macroion is surrounded by a spherical volume in which counterions compensating the macroion charge are distributed. The particle volume fraction  $\phi$  is then defined as  $\phi = (b/R)^3$ , where  $b$  is the distance of the closest approach of the macroion and counterions (equal to the sum of radii of the macroion and the counterion) while  $R$  is the radius of the spherical volume around the macroion. The latter one can be calculated from the electroneutrality condition

$$Z_p e_0 = \frac{4}{3} \pi (R^3 - b^3) n e_0 \quad (22)$$

where  $e_0$  and  $n$  denote the elemental charge and the average number density of counterions in the cell, respectively. The equilibrium electric potential distribution,  $\Psi$ , around the macroion in the absence of an applied external electric field can be calculated by solving the Poisson–Boltzmann equation

$$\frac{d^2 \Psi(r)}{dr^2} + \frac{2}{r} \frac{d\Psi(r)}{dr} = -\frac{\rho(r)}{\epsilon \epsilon_0} \quad (23)$$

In this equation  $\epsilon_0$  is the permittivity of the vacuum,  $\epsilon$  is the relative permittivity, and  $\rho(r)$  is the volume charge density obtained from the counterion distribution around the polyion. The last one is a function of the ratio between the electrostatic energy at a given radius ( $e_0 \Psi(r)$ ) and thermal energy, calculated as the product of the Boltzmann constant,  $k$ , and the absolute temperature,  $T$

$$\rho(r) = e_0 n e^{-e_0 \Psi(r)/kT} \quad (24)$$

Defining the scaled potential as

$$y = \frac{e_0 \Psi(r)}{kT} \quad (25)$$

we can write the Poisson–Boltzmann equation as

$$\frac{d^2 y(r)}{dr^2} + \frac{2}{r} \frac{dy(r)}{dr} = \frac{e_0^2 n e^{-y(r)}}{\epsilon \epsilon_0 kT} \quad (26)$$

The boundary conditions are

$$\left. \frac{dy}{dr} \right|_{r=b} = \frac{Z_p e_0^2}{4\pi \epsilon \epsilon_0 b^2 kT} \quad (27)$$

and

$$\left. \frac{dy}{dr} \right|_{r=R} = 0 \quad (28)$$

Let us now imagine that the particles are moving with velocity  $\vec{u}$  in an applied electric field  $\vec{E}$ . If the origin of the spherical polar coordinate system is held fixed at the center of the particle and the polar axis is set parallel to electric field, then the fundamental electrokinetic equations can be transformed into the coupled equations for two functions,  $f(r)$  and  $\Phi(r)$ , as<sup>6</sup>

$$f(r) = \int_b^R \left[ -\frac{r^3}{30} + \frac{b^2 r}{18} - \frac{b^5}{45 r^2} + \left( \frac{r}{9b} - \frac{1}{6} + \frac{b^2}{18 r^2} \right) r^3 \right] g(r') dr' + \int_b^r \left( \frac{r^3}{30} - \frac{r r'^2}{6} + \frac{r'^3}{6} - \frac{r'^5}{30 r^2} \right) g(r') dr' - \frac{R^2 \rho(R) Y(R)}{9 \eta b} \left[ \left( 1 + \frac{\phi}{2} \right) r - \frac{3b}{2} + \frac{b^3}{2 r^2} \left( 1 - \frac{2\phi}{5} \right) - \frac{3\phi r^3}{10 b^2} \right] \quad (29)$$

$$\Phi(r) = \frac{1}{1-\phi} \left( r + \frac{b^3}{2r^2} \right) + \frac{1}{3(1-\phi)} \left( r + \frac{b^3}{2r^2} \right) \times \int_b^R \left( 1 + 2\phi \frac{r'^3}{b^3} \right) \left( -\frac{dy}{dr'} \right) \left( \frac{d\Phi}{dr'} + \frac{2\lambda f}{e_0 r'} \right) dr' - \frac{1}{3} \int_b^r \left( r - \frac{r'^3}{r^2} \right) \left( -\frac{dy}{dr'} \right) \left( \frac{d\Phi}{dr'} + \frac{2\lambda f}{e_0 r'} \right) dr' \quad (30)$$

where  $\rho(R)$  is the counterion charge at the boundary of the cell while  $Y(r)$  is related to the deviation of the potential  $\Psi(r)$  and can be for diluted cases set to  $R$ . The drag coefficient  $\lambda$  of the counterions may be obtained from the limiting conductance  $\Lambda^0$  by  $\lambda = N_A e_0^2 / \Lambda^0$ . Function  $g(r)$  can be calculated as

$$g(r) = -\frac{e_0 n}{\eta r} \frac{dy}{dr} e^{-y} \Phi(r) \quad (31)$$

The electrophoretic mobility  $\mu = u/E$  is expressed as<sup>6</sup>

$$\mu = \frac{b^2}{9} \int_b^R \left[ 1 - \frac{3r^2}{b^2} + \frac{2r^3}{b^3} - \phi \left( \frac{2}{5} - \frac{r^3}{b^3} + \frac{3r^5}{5b^5} \right) \right] g(r) dr - \frac{2b^2 \rho(R) Y(R)}{9 \eta R \phi} \Omega \quad (32)$$

with

$$\Omega = 1 - \frac{9\phi^{1/3}}{5} + \phi - \frac{\phi^2}{5} \quad (33)$$

The set of equations for  $f(r)$  and  $\Phi(r)$  can be solved numerically with iteration. For the initial approximation, we used

$$f^0(r) = -\frac{R^2 \rho(R) Y(R)}{9 \eta b} \left[ \left( 1 + \frac{\phi}{2} \right) r - \frac{3b}{2} + \frac{b^3}{2 r^2} \left( 1 - \frac{2\phi}{5} \right) - \frac{3\phi r^3}{10 b^2} \right] \quad (34)$$

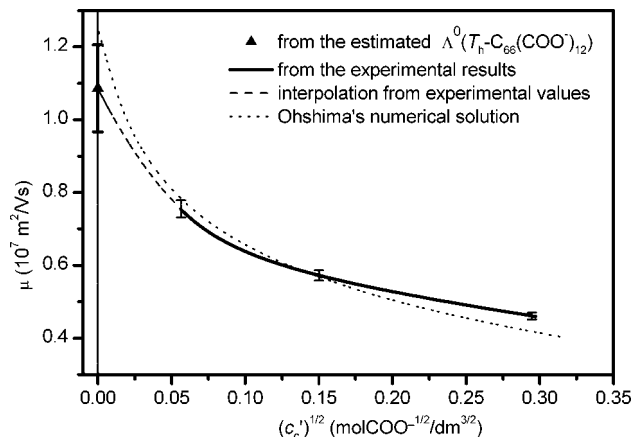
and

$$\Phi^0(r) = \frac{1}{1-\phi} \left( r + \frac{b^3}{2r^2} \right) \quad (35)$$

The comparison between the calculated and measured electrophoretic mobility is shown in Figure 5. The agreement is rather good in the concentration range between 0.0006 and 0.05 mol carboxyl groups/dm<sup>3</sup>. While the weakness of the use of the cell model at higher concentrations is known,<sup>33</sup> the reasons for the widening gap between calculated and measured values toward lower concentrations are less clear and can be sought both in the theoretical insufficiencies and experimental errors. For the theoretical side, the errors are believed to be inherent to the use of the cell and the standard electrokinetic model,<sup>5</sup> both forming the base for the Ohshima's model. More can be said about possible experimental inaccuracies. The experimental electrophoretic mobility of the macroion was calculated from the relation<sup>27</sup>

$$\mu_E = \frac{\Lambda_p}{F} = \frac{\Lambda T_p}{F} \quad (36)$$

where  $F$ ,  $T_p$ ,  $\Lambda$ , and  $\Lambda_p$  denote the Faraday constant, the transport number of the macroion, the equivalent electric conductivity of the electrolyte composed of the macroion and corresponding counterions, and the electric conductivity of the macroion, respectively. While experimental  $\Lambda$  and  $T_p$  can be rather accurately determined at concentrations greater than 0.005 mol carboxyl groups/dm<sup>3</sup>, their errors increase at least for two reasons when the concentration is approaching infinite dilution. First, as it was already said in the Experimental Section of this paper, the adsorption of the fullerenehexamalonate species on the glass is believed to be the reason for the diminishing of the flow time during consecutive measurements of the viscosity at the lowest concentration. Even more, during measurements of the electrolytic conductance of fullerenehexamalonate salts,<sup>14,34</sup> a downward deviation from the expected trend of molar conductivity values was observed when approaching the infinite dilution regime. Although the experimental points, where this shift was unambiguously identified, were discarded and therefore not used in the extrapolation of molar conductivity to infinite dilution, it is quite possible that also the points at the lowest concentrations reported<sup>14</sup> as well as the reported extrapolated values of the molar conductivities at infinite dilutions  $\Lambda^0$  for alkali fullerenehexamalonates were affected by the adsorption on the glassy wall of the measuring cell, thus giving values which are too low. Second, regarding the values of  $\Lambda^0$  itself, one cannot exclude neither uncertainty in the extrapolation procedure. Because CsFHM is a highly asymmetric electrolyte, a steep increase of molar conductivity occurs when approaching infinite dilution, thus making the choice of an appropriate extrapolation function difficult. Besides the complexity of the ideal multiparameter function for unassociated electrolytes,<sup>35</sup> a further obstacle presents substantial change of the extent of the association of the counterions<sup>27</sup> to the macroion in the concentration regime from which the extrapolated value was obtained. In reality, it is practically impossible to obtain  $\Lambda^0$  for polyelectrolytes in such a way, and instead, a polynomial function was used.<sup>14</sup> Despite the fact that extrapolations for three alkali fullerenehexamalonate salts<sup>14</sup> gave a rather consistent value at around 105  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  for the equivalent limiting molar conductivity of the macroion constituent,  $\Lambda_p^0$  [1/12  $T_h$ -C<sub>66</sub>(COO<sup>-</sup>)<sub>12</sub>], the extrapolation for two sets of measurements for one salt (e.g., for NaFHM)<sup>34,36</sup> can differ significantly one from the other. Taking then the higher value of  $\Lambda_p^0$  [1/12  $T_h$ -C<sub>66</sub>(COO<sup>-</sup>)<sub>12</sub>] obtained from the measurements of sodium



**Figure 5.** Concentration dependence of the experimental electrophoretic mobility of the fullerenehexamalonate macroion stemming from CsFHM in aqueous solutions in comparison to the Ohshima's numerical solution for the spherical cell model. The estimated uncertainty of the experimental data is presented by the error bars. For other details, see the text.

fullerenehexamalonate<sup>36</sup> ( $\Lambda_p^0 = 115.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) leads to considerably better agreement between experiment and theory also in the regime of the lowest concentrations. This hypothesis is very difficult to check because additional measurements of the electric conductivity of highly diluted solutions would require suppression of the adsorption sites on the glassy walls of the measuring cell. Such an experimental setup is hardly believed to be successful because at these concentrations chemical blocking of the adsorption sites could easily produce an additional source of unwanted impurities in the measuring cell.

#### 4. Conclusions

The general theories for the calculation of the viscosity and electrophoretic mobility as the examples of the transport properties appear to be valid also on the nanometer scale. This is in the line with the recent theoretical study of Sharma and Yashonath<sup>37</sup> that the Stokes–Einstein relationship concerning self-diffusivity of the solute is valid up to the dimensions where the radius of the solute is only one-half of that of the solvent. A good agreement at the lowest concentrations measured was obtained by taking into account the intrinsic viscosity of the bare fullerenehexamalonate macroion and the contribution of electrostatic interactions (the primary and the secondary electroviscous effect). Conformity between theory and the experiment at the upper concentration range was achieved by considering contributions from the intrinsic viscosity of the bare fullerenehexamalonate macroion and hydrodynamic perturbations attributed only to the macroion. At the highest concentrations, the electrostatic screening is so strong that the contribution stemming from the secondary and especially from the primary electroviscous effect can be in the first approximation neglected. The reason for the observed discrepancy between theoretical prediction and experimental data in the middle of the concentration range studied, where the agreement is only qualitative, is the use of the term that assumes weak repulsive interactions among macroions when the secondary electroviscous effect has to be taken into account. These interactions are in the solutions of CsFHM obviously too strong to be correctly described by the here-used approximation. To improve this theoretical prediction, probably a very tedious and lengthy procedure that includes calculation of the static structure factors and finding solution for a closed set of nonlinear equations should be applied.



A good agreement between experiment and theoretical calculations for the electrophoretic mobility of CsFHM was obtained using Ohshima's numerical solution of the Poisson–Boltzmann equation for the spherical cell model in the range of moderate concentrations. It is not improbable that a large portion of difference between experimental and theoretical values at the lowest concentrations is due to experimental uncertainties in this concentration regime.

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