FEATURE ARTICLE

Analytical Theories of Transport in Concentrated Electrolyte Solutions from the MSA

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Ion transport coefficients in electrolyte solutions (e.g., diffusion coefficients or electric conductivity) have been a subject of extensive studies for a long time. Whereas in the pioneering works of Debye, Hückel, and Onsager the ions were entirely characterized by their charge, recent theories allow specific effects of the ions (such as the ion size dependence or the pair association) to be obtained, both from simulation and from analytical theories. Such an approach, based on a combination of dynamic theories (Smoluchowski equation and mode-coupling theory) and of the mean spherical approximation (MSA) for the equilibrium pair correlation, is presented here. The various predicted equilibrium (osmotic pressure and activity coefficients) and transport coefficients (mutual diffusion, electric conductivity, self-diffusion, and transport numbers) are in good agreement with the experimental values up to high concentrations (1−2 mol L^{-1}). Simple analytical expressions are obtained, and for practical use, the formula are given explicitly. We discuss the validity of such an approach which is nothing but a coarse-graining procedure.
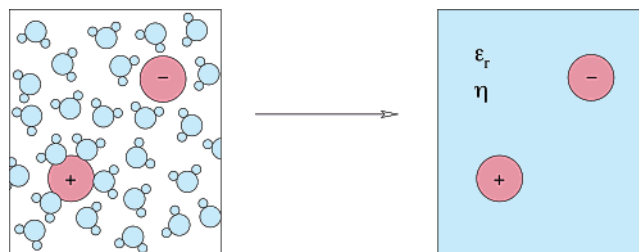
1. Introduction

The transport of ions in electrolyte solutions[1−7] has remained an active area of research in physical chemistry for a long time. Yet, at first sight, such systems are very complex media. However, the problem is simplified if one uses a continuous solvent model (see Figure 1), as it is commonly done since the early works of Debye, Hückel, and Onsager.[8]

Ion transport properties such as the electric conductivity are a very important source of information on charge transport and structure of electrolyte solutions. Conductivity measurements can be easily carried out with commercially available equipments at precisions of 1−2%. The classical transport theories of Debye, Hückel, and Onsager (DHO) correctly explain the rise of diffusion, conductivity, and viscosity of electrolytes at very low concentration. These transport models for continuous solvent were based on the point ion model of the Debye Hückel theory.[8,9] The only ingredients of the model are as follows: (i) for the static part, the charges Z_i of the ions, the temperature T, and the macroscopic dielectric constant of the solvent ϵ_r; (ii) for the transport, the viscosity η of the solvent and the individual ionic diffusion coefficients at infinite dilution D_i^0 which are related to the individual limiting molar conductivities λ_i^o by the Nernst Einstein relation

$$\frac{D_i^0}{\lambda_i^0} = \frac{k_{\mathrm{B}}T}{Z_i \mathcal{N}_{\mathrm{A}} e^2} \tag{1}$$

where $k_{\mathrm{B}}T$ is the thermal factor, $\mathcal{N}_{\mathrm{A}}$ is the Avogadro number, and e is the elementary charge.

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Figure 1. In discrete solvent models (left), the degrees of freedom of the solvent are treated explicitly. For continuous solvent models, the latter is considered as a continuum described by its dielectric constant ϵ_r and its viscosity η.

From these data, Onsager et al. were able to derive exact limiting laws for the variation of electrical conductance, mutual diffusion and self-diffusion.[8,10] Laws for mixtures of electrolytes were also derived.[11] Unfortunately, these laws are restricted to the domain of very dilute electrolyte solutions ($C < 10^{-2}$ mol L^{-1} for the best cases).

The influence of the size of the ions has been taken into account more recently. Taking into account the finite size of the ions as boundary conditions in the integration of transport equations, Onsager and Fuoss[12] have found extended laws for the variation of conductance. Turq and Micheletti[13,14] used the same approach for self-diffusion. The variation of thermodynamic quantities as a function of electrolyte concentration can be understood with the help of Hamiltonian models at the McMillan−Mayer level.

The development of modern theories of fluids[15,16] allowed the description of electrolyte solutions to be improved. The use of solvent-averaged potentials in integral equations with closure relations such as the mean spherical approximation (MSA) or the hyper netted chains (HNC) gives a fair description of the

Model	Microscopic Variables	Equation in the Phase Space	Equation of the Trajectories	Simulation Method
Discrete Solvent	$\{\mathbf{r}_{solvent}, \mathbf{p}_{solvent}$ $\mathbf{r}_{solute}, \mathbf{p}_{solute}\}$	Liouville	Newton	Molecular Dynamics
Continuous Solvent	$\{\mathbf{r}_{solute}, \mathbf{p}_{solute}\}$	Fokker-Planck	Langevin	Brownian Dynamics
	$\{\mathbf{r}_{solute}\}$ $t > \tau_{vit}$	Smoluchowski	Ermak Algorithm	Brownian Dynamics

Figure 2. Various level of descriptions for the transport of ions in electrolyte solutions. In the Fokker−Planck level of description, the simulation method is sometimes called "Langevin dynamics" in order to distinguish it from the Brownian dynamics in the Smoluchowski level.

variation of thermodynamic properties such as osmotic and activity coefficients in simple electrolyte solutions until 1 or 2 mol L^{-1}. MSA is especially interesting because it can be solved analytically. On the other hand, since the solvent-averaged Hamiltonian used at the McMillan Mayer level does not include the solute−solvent interactions in a direct way, the transport properties of the solute at infinite dilution in the solvent cannot be deduced from first principles.

The description of the dynamical properties of ions is historically based on the concept of friction forces. They balances the thermal motion of the solute, and they can mimic the effects of the solute−solvent interactions at long time. This idea is now understood in terms of Brownian motion theory (see Figure 2). From the modern point of view, the fundamental equations of Onsager (for example the Fuoss−Onsager equation), which have been initially obtained semi-phenomenologically, are direct consequences of Brownian motion theory when it is applied to electrolyte solutions.[4] The dynamics of these Brownian solutes can be studied by using either the Langevin's equation or the Smoluchowski equation. The first Brownian dynamics simulations of electrolyte solutions were based on the Langevin equation.[17] However, the hydrodynamic interactions between the ions are included more easily at the Smoluchowski level.[18−21]

Apart from the simulations which can only give numerical values of the transport coefficients, different attempts have been made to obtain extended laws for transport coefficients of electrolyte solutions. Thus, Smoluchowski-level solution theories, in which the dynamical variables are the locations of the solute particles, seems to be a natural way of calculating the solute transport coefficients for the same models of electrolyte solutions.[22−28] Ebeling et al.[29] using a Smoluchowski level theory recovered and generalized the DHO theory. At last, mode-coupling theory (MCT), (combined with time-dependent density functional theory)[30−35] leads to self-consistent expressions of the relaxation and allows the time dependence to be obtained.

When the Smoluchowski theory is coupled to the MSA, analytical expressions which are especially interesting for practical use can be obtained. Taking into account the excluded volume effect of the ions with the MSA, Ebeling and Rose[36] have given extended laws for conductance with an averaged ionic radius. Bernard et al.[37] have extended that with different ionic radii and for self-diffusion. Durand-Vidal et al.[100] have used this approach for conductance in ionic mixtures. Dufrêche et al. obtained a self-consistent description of the mutual diffusion coefficients with other transport and equilibrium properties.[38] Being linear in the correlation functions, MSA is limited to weakly interacting systems. For associated electrolytes, the association concept introduced by Bjerrum[39] were applied to conductance and other transport phenomena.[40]

The objective of this article is to summarize and discuss the MSA approach to the transport properties of electrolyte solutions. In the next section, we introduce the basic elements of the continuous solvent description and especially the MSA. The collective transport properties are given in section 3. Section 4 contains the theory of self-diffusion (which is an individual transport coefficient) from an alternative MCT approach. The validity and the consequences of such theories are analyzed in sections 5 and 6.

We have tried to make this article self-contained. One of the most important advantage of the MSA transport theory presented here lies in the fact that the final results are obtained analytically. Thus, the analytical formula of the various transport coefficients are given explicitly for practical use.

2. Continuous Solvent Description of Electrolyte Solutions

2.1. Primitive Model and Effective Potential. The continuous solvent description is characterized by the effective potential between the solute particles. Since the early works of Debye, Hückel, and Onsager,[8] the so-called primitive model (PM) has been the valuable tool for the description of the properties of electrolyte solutions. In that case, the ions are modeled by charged hard-spheres.

The validity of such an approach can be clarified. The solvent-averaged effective potential between the ions can be defined without any ambiguity from the statistical mechanics of multicomponent systems, as it has been done by McMillan and Mayer:[41]

$$V_{\text{eff}}(\{\mathbf{r}_i\}) = -k_B T \ln g_{N_i}(\{\mathbf{r}_i\}) \tag{2}$$

where k_B is the Boltzmann constant and T the temperature. $g_{N_i}(\{\mathbf{r}_i\})$ stands for the N body correlation function of particle i in the infinite dilution limit. The effective potential is therefore a complex function of the ion positions. It is not pair additive, even if the microscopic potential (where the solvent molecules are taken into account explicitly) is pair additive. The continuous solvent models have been proved to be useful for dilute solutions, though. Within this limit, it is not too bad an approximation to account for the 2 particles' terms only which is the low-density limit.

The calculation of the effective potential between the ions can be carried out from Monte Carlo and molecular dynamics simulations.[42−44] The three-body effects are found to be negligible for simple electrolytes if the concentration is not too high (namely $c < 2$ mol L^{-1} roughly), the 2 particles effective potential reproducing well the basic features of the high-order structure. The (2 particles') effective potential between i and j reads

$$V_{\text{eff}}(r) = \frac{Z_i Z_j e^2}{4\pi\epsilon_0 \epsilon_r r} + V_{\text{SR}}(r) \tag{3}$$

where the first term corresponds to the long-range electrostatic interactions between two charges Z_i and Z_j. e is the elementary charge, ϵ_0 is the permittivity of vacuum, ϵ_r is the dielectric constant of the solvent, and r is the distance between i and j. The actual effective pair potential between two ions is therefore similar to the potential of the PM. Within the PM, the short-range part $V_{\text{SR}}(r)$ is modeled by a hard sphere repulsion. It is worth noting that in fact[43] $V_{\text{SR}}(r)$ makes oscillations which reflect the molecular nature of the solvent. Then the validity of the PM seems to be surprising. In fact, the situation is not that bad: at infinite dilution, $V_{\text{SR}}(r)$ is negligible, the Debye−Hückel

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theory being exact.[45] Thus, the short-range term is a kind of perturbation to the electrostatic term, and it can be modeled by a simple hard sphere repulsion. For very concentrated solutions, this assumption does not hold, but anyway the effective potential between the ions is not pair additive anymore.

2.2. Mean Spherical Approximation. The calculation of transport coefficients is based on an accurate description of equilibrium. For electrolyte solutions, the PM can be solved by different techniques based for example on integral equations.[15,46] Among these methods, the mean spherical approximation (MSA) is especially interesting since it yields to analytical formula. The MSA applied to the PM has been solved initially by Waisman and Lebowitz.[47] The solution has also been obtained by further authors.[48] We used the solution by Blum[49−51] because the formula are the most simple: they generalize the Debye−Hückel theory with a screening parameter which is not anymore the inverse Debye length κ_D but Γ. Γ is defined implicitly by

$$\Gamma = \left[\pi L_B \sum_i C_i \left(\frac{Z_i}{1 + \Gamma \sigma_i} \right)^2 \right]^{1/2} \tag{4}$$

where C_i (SI unit: m^{-3}) and σ_i are respectively the concentration and the diameter of ion i. $L_B = e^2/4\pi\epsilon_0\epsilon_r k_B T$ is Bjerrum length. Thus, 2Γ generalizes $\kappa_D = (4\pi L_B \sum Z_i C_i^2)^{1/2}$. The inverse Debye screening length is replaced by 2Γ because we account for the size of the ions in the ionic atmosphere.

The various thermodynamic quantities can be expressed as a function of Γ. The osmotic coefficient ϕ of an electrolyte solution which is defined by the equation

$$\phi = \beta P_{osmo} \Big/ \sum_{i=1}^n C_i \tag{5}$$

where $P_{osmo} = P$ is the osmotic pressure. In the MSA,[51,50] P_{osmo} is given by

$$P_{osmo} = P^c + P^{HS} \tag{6}$$

The electrostatic contribution P^c reads

$$\beta P^c = -\frac{\Gamma^3}{3\pi} \tag{7}$$

similarly to the Debye−Hückel theory. The second term corresponds to the osmotic coefficient of an hard-sphere mixture[52]

$$\beta P^{HS} = \frac{6}{\pi} \left[\frac{X_0}{1 - X_3} + \frac{3X_1 X_2}{(1 - X_3)^2} + \frac{3X_2^3}{(1 - X_3)^3} + \frac{X_3 X_2^2}{(1 - X_3)^3} \right] \tag{8}$$

with $X_k = \pi/6 \sum_i C_i \sigma_i^k$. The MSA theory used here is valid only if the diameters of the ions are not too different. This approximation[53] has been checked numerically; it does not hold only for very dissymmetrical electrolytes (ratio 5 for the sizes for example). Another advantage of such an assumption comes from the fact that the correlation functions $g_{ij}(r)$ are also the sum of two terms (electrostatic term and hard sphere term), similarly to eq 6. It strongly simplifies the calculations, and this assumption has been made for the derivation of the transport coefficient given in this article, unless otherwise stated.

The MSA is a McMillan−Mayer (MM) theory of solutions. The thermodynamic functions are calculated at constant solvent chemical potential.[54] Thus, if comparison is made with experi-

TABLE 1: Ion Diameters (Å) for the Different Electrolytes[a]

	$\sigma_{Pauling}$	σ_{PM}	h_{PM}	h_{litt}
K$^+$	2.66	2.95	0.7	1.9,[b] 1.3[c]
Na$^+$	1.96	3.05	2.1	3.5,[b] 2[c]
Li$^+$	1.56	4.35	8.0	7.1,[b] 4.7[c]
Ca^{2+}	1.98	5.00	12.0	12[b]
Br$^-$	3.90	3.90	0.0	0.5[b]
Cl$^-$	3.62	3.62	0.0	0

[a] $\sigma_{Pauling}$ is the bare pauling diameter. σ_{PM} is hydrated diameter used in the MSA-Smoluchowski theory based on the primitive model. h_{PM} is the hydration number which can be deduced from σ_{PM} and from the formula $h_{PM} = \alpha(\sigma_{PM}^3 - \sigma_{Pauling}^3)$, α being conventionally chosen to yield $h_{PM} = 12$ for Ca^{2+}. $h_{Cl^-} = 0$ are conventional ionic hydration numbers calculated from activity coefficients and from transport numbers. The calculation is based on the assumption $h_{Cl^-} = 0$. [b] See ref 111. [c] See ref 112.

mental data carried out at constant external pressure, a correction factor has to be taken into account.[55,56] This conversion, known under the name of MM to Lewis−Randall (LR) conversion can be obtained by neglecting the effect of compressibility from the following approximate but very accurate expression[57]

$$\phi_{LR} = \Phi \phi_{MM} \tag{9}$$

where Φ is the volume fraction of the solvent which can be calculated from the density of the solution.

The MSA does not take into account the electrostatic association of ions.[58] Indeed, the MSA holds only if the electrostatic interaction between two ions is less than the thermal energy $k_B T$. It is the simplest theory accounting correctly for the finite diameter of the ions and fulfilling the local and global electroneutrality condition, namely the Stillinger−Lovett sum rules.[59] For low dielectric constant solvents or high charge electrolytes (2−2 electrolyte in water for example), it does not yield proper results. In that case, a part of the cations are associated to the anions and the MSA is unable to describe this association phenomenon. This difficulty can be overcome if one considers a chemical model:[60,61] a third particle (the pair) is then taken into account, as it has been initially proposed by Bjerrum.[39] The equilibrium constant of the mass action law between the free ions and the pair can be obtained by several criteria. We have chosen the Ebeling constant[62] because of its consistency for the calculation the transport properties.[63] For the sake of simplicity, the formula given in this article stand for dissociated electrolytes; thus, there are only two solute particles, the (free) cation and the (free) anion. An alternative method consists of introducing the pair in the integral equation itself. This associative or binding MSA theory[64−67] accounts for the electrostatic interactions between the pair and the free particles. It is in agreement with experimental data for equilibrium properties,[68,69] but it has not been used for the calculation of transport properties for the time being, the equations for the pair correlation functions being rather complicated.

The (simple) MSA theory has been found to be in agreement with experimental values for dissociated electrolyte solutions up to 2 mol L^{-1}.[70−72] The only unknown parameters are the diameters of the ions. We have retained the values σ_{PM} given in Table 1. They correspond to the value of Ebeling.[72] The diameters are the only parameters of the model. Once they are fixed, there are no more adjustable parameters. The transport properties calculated from this model obtained in the next paragraph are therefore real predictions.

2.3. Ion Transport Coefficient and Reference Frame. Before entering into the dynamic theories, it may be useful to characterize the transport properties which will be considered

in this article. A continuous solvent model takes explicitly into account only the motion of the ions. As a matter of fact, it is especially appropriate for the calculation of the transport coefficients associated to the *ion* degrees of freedom. The thermodynamics of irreversible processes[73] applied to electrolyte solutions[74,75] is the general macroscopic framework to define the various transport coefficients. The Onsager coefficients L_{ij}^R are defined from the flux of particles i $\mathbf{J}_i^R$

$$\mathbf{J}_i^R = \sum_j \frac{L_{ij}^R}{T}(-\mathbf{grad}\mu_j + Z_j e\mathbf{E}) \tag{10}$$

where μ_i is the chemical potential of i and $\mathbf{E}$ is the (internal or external) electric field. The definition of L_{ij}^R depends on the reference frame R which characterizes the linear relation between the fluxes.[76] For an open system, the flux are calculated in the mass fixed frame of reference R = M where

$$\sum_i m_i \mathbf{J}_i^M = 0 \tag{11}$$

m_i is the mass of i. The flux of every species is the sum of this diffusion flow $\mathbf{J}_i^M$ and the convection flow which can be calculated from the hydrodynamic Navier−Stokes equation. These equations are valid for every species, including the solvent. The solvent-fixed frame of reference S is defined by

$$\mathbf{J}_0^S = 0 \tag{12}$$

where 0 denotes the solvent. In the volume-fixed frame V, no net flows of volume occurs

$$\sum_{i=0}^n V_i \mathbf{J}_i^V = 0 \tag{13}$$

where V_i is the partial specific volume of component i. The significance of this frame of reference comes from the fact that the experimental diffusion coefficients can be identified with the volume-fixed ones (if the concentration gradients are small). Most of the time, the transport coefficients obtained from continuous solvent models are calculated in the solvent-fixed frame of reference. The Onsager coefficients L_{ij}^R are defined in any reference frame R and the conversion from one reference frame to another[77] is carried out by writing down the various linear relations (e.g. eqs 12 and 13). The specific conductivity

$$\chi = e^2 \sum_{i,j} C_i Z_i Z_j \frac{L_{ij}}{T} \tag{14}$$

does not depend on the reference frame because of the electroneutrality condition.[24] Transference (transport) numbers

$$t_i = \frac{Z_i \sum_j Z_j L_{ij}}{\sum_{i,j} Z_i Z_j L_{ij}} \tag{15}$$

are defined as the fraction of the total current carried by an ion.[3] Experimental transport numbers (Hittorf transport numbers) are commonly defined and measured in the solvent-fixed frame of reference.

There are several kinds of diffusion in electrolyte solutions. The mutual diffusion corresponds to the case where there is a concentration gradient for the two ions. Then the diffusion of cations and anions occurs simultaneously, even if the mobilities of the two ions are different. There is no macroscopic charge separation because of the intensity of the electrostatic force. Everything happens as if there was just one kind of solute particles (representing the salt) and an effective diffusion coefficient called the mutual diffusion coefficient D_m of the electrolyte. This simultaneous motion of cations and anions is controlled by the electroneutrality condition. The force on the particles corresponds to a gradient of chemical potential.[74] Thus, the calculation of D_m requires an analysis of the diffusion equations, which can be performed from the normal-mode technique.[5] The final result is[38]

$$D_m = \frac{Q_{11}D_{21}^* + Q_{22}D_{12}^*}{Q_{11} + Q_{22}} \tag{16}$$

with

$$Q_{ij} = Z_j Q_i = \frac{Z_j e^2 C_i}{k_B T \epsilon_0 \epsilon_r} k_B \sum_{k=1}^2 Z_k L_{ik} \tag{17}$$

and

$$D_{ij}^* = k_B \sum_{k=1}^2 L_{ik} \frac{\partial \beta P}{\partial C_k} \tag{18}$$

where P is the osmotic pressure of the solution which can be calculated from the MSA.[50]

This theory described in the next paragraph will be established in the solvent-fixed frame of reference. The measurements of D_m being performed in the volume-fixed frame of reference, a correction factor has to be taken into account. The relationship between the calculated value D_m^{calc} in the solvent fixed frame of reference and the experimental value D_m^{exp} in the volume fixed is[38,74,75]

$$D_m^{calc} = \Phi D_m^{exp} \tag{19}$$

where Φ is the volume fraction of the solvent which can be calculated from the density of the solution.[38] It is worth noting that this conversion factor is the same as the conversion factor of the osmotic coefficient. The calculation of the thermodynamics force effect (16) should be rigorously performed in the volume-fixed frame of reference. However, beyond the electrostatic Debye time, there is no charge separation anymore, the two ions behave as a single solute particle and (16) is valid in the solvent-fixed frame of reference as well. Thus, the previous formula are exact.

The self-diffusion coefficient D_i corresponds to the individual diffusion of a tracer i in the electrolyte solution. i can be a tracer of the cation or of the anion of the electrolyte. The concentration of the tracer tends to zero and the thermodynamic force $-\mathbf{grad}\mu_i$ can be identified to the gradient of chemical potential without any activity corrections. Furthermore, the self-diffusion coefficient does not depend on the frame of reference. The expressions of the L_{ij} obtained from microscopic theories are given in the next section.

3. Smoluchowski-MSA Theory of Electrolyte Solutions

3.1. Smoluchowski Equation and Its Hierarchy. The Smoluchowski equation governs the Brownian motion of N particles. It is a continuity equation for the N particles density

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$\mathscr{P}(\{\mathbf{r}_i\}, t)$ with $\mathbf{r}_i$ the position of the ith particle

$$\frac{\partial \mathscr{L}}{\partial t} + \operatorname{div} \mathscr{P}\mathbf{U} = 0 \tag{20}$$

The $3N$ vector $\mathbf{U} = \{\mathbf{U}_1, \mathbf{U}_2, ..., \mathbf{U}_N\}$ stands for the hydrodynamic velocities of the N particles

$$\mathbf{U} = \beta\bar{\mathbf{D}}\mathbf{F} = \beta\bar{\mathbf{D}}\left(\mathbf{F}_{\text{ext}} + \mathbf{F}_{\text{int}} - \frac{1}{\beta}\mathbf{grad} \ln \mathscr{P}\right) \tag{21}$$

where $\beta = 1/k_{\text{B}}T$. $\bar{\mathbf{D}} = \bar{\mathbf{D}}(\{\mathbf{r}_i\})$ is the hydrodynamic diffusion tensor. It depends on the model used for the description of the hydrodynamics interactions. $\mathbf{F}_{\text{ext}}$ represents the external forces on the solute particles (e.g., the external electric force for the conductivity experiments), and $\mathbf{F}_{\text{int}}$ represents the solvent-averaged internal forces.

For classical systems with N particles, the Liouville equation implies that the nonequilibrium n body reduced probability densities are coupled together by a set of $N - 1$ equations called the BBGKY hierarchy. A similar hierarchy exists for the Smoluchowski equation.[29] The final result for the 1 body densities $n_i = n_i(\mathbf{r})$ (=local concentration $C_i(\mathbf{r})$) is

$$\frac{\partial n_i(\mathbf{r}_1, t)}{\partial t} + \operatorname{div}_1 \mathbf{J}_i(\mathbf{r}_1, t) = 0 \text{ with } \mathbf{J}_i(\mathbf{r}_1, t) = n_i(\mathbf{r}_1, t) \, \mathbf{u}_i(\mathbf{r}_1, t) \tag{22}$$

where $\mathbf{u}_i$ reads

$$\mathbf{u}_i(\mathbf{r}_1, t) = \omega_i^0 \mathbf{F}_i(\mathbf{r}_1, t) +$$
$$\sum_j \int \bar{\mathbf{T}}_{ij}(\mathbf{r}_1, \mathbf{r}_2) \, \mathbf{F}_j^i(\mathbf{r}_1, \mathbf{r}_2) \frac{n_{ij}(\mathbf{r}_1, \mathbf{r}_2)}{n_i(\mathbf{r}_1)} d\mathbf{r}_2 \tag{23}$$

The eqs 22 and 23 are valid if the hydrodynamic interactions are pairwise. That is the reason $n_i(\mathbf{r})$ depends only on the two particles density $n_{ij}(\mathbf{r}_1, \mathbf{r}_2)$. More precisely $\bar{\mathbf{D}}$ is made of N^2 3×3 under-matrixes $\bar{\mathbf{D}}_{ij}$ which correspond to the influence of the force j on particle i because of the hydrodynamic motion of the solvent

$$\bar{\mathbf{D}}_{ij} = \delta_{ij}D_i^0\bar{\bar{\Pi}} + (1 - \delta_{ij})k_{\text{B}}T\bar{\mathbf{T}}_{ij} \tag{24}$$

where $D_i^0 = \omega_i^0 k_{\text{B}}T$ is the self-diffusion coefficient of i at infinite dilution and $\bar{\mathbf{T}}_{ij}$ is the hydrodynamic interaction tensor between j and i. The latter can be for example the Rotne-Prager or the Oseen mobility tensors.[78,79] $\mathbf{F}_i$ is the mean force acting on particle of type i, $\mathbf{F}_j^i(\mathbf{r}_1, \mathbf{r}_2)$ is the mean force acting on particle of type j at $\mathbf{r}_2$ when particle i is at $\mathbf{r}_1$, and $n_{ij}(\mathbf{r}_1, \mathbf{r}_2)$ is the two particles density related to the probability to find particle i at position $\mathbf{r}_1$ and particle j at $\mathbf{r}_2$. The force $\mathbf{F}_i$ is given by

$$\mathbf{F}_i(\mathbf{r}_1) = \mathbf{F}_i^{\text{ext}}(\mathbf{r}_1) - k_{\text{B}}T \, \mathbf{grad}_1 \ln n_i(\mathbf{r}_1) + \mathbf{F}_i^{\text{int}}(\mathbf{r}_1) \tag{25}$$

where $\mathbf{F}_i^{\text{ext}}$ and $\mathbf{F}_i^{\text{int}}$ are respectively the external force and the internal force acting on a

$$n_i(\mathbf{r}_1)\mathbf{F}_i^{\text{int}}(\mathbf{r}_1) = -\sum_j \int \mathbf{grad}_1 V_{ij}(\mathbf{r}_1, \mathbf{r}_2) \, n_{ij}(\mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_2 \tag{26}$$

$\mathbf{F}_j^i$ is given by

$$\mathbf{F}_j^i(\mathbf{r}_1, \mathbf{r}_2) = \mathbf{F}_j^{\text{ext}}(\mathbf{r}_2) - k_{\text{B}}T \, \mathbf{grad}_2 \ln n_{ji}(\mathbf{r}_1, \mathbf{r}_2) + \mathbf{F}_{ji}^{\text{int}}(\mathbf{r}_1, \mathbf{r}_2) \tag{27}$$

with the internal contribution

$$\mathbf{F}_{ji}^{\text{int}}(\mathbf{r}_1, \mathbf{r}_2) = -\mathbf{grad}_2 V_{ji}(\mathbf{r}_1, \mathbf{r}_2) -$$
$$\sum_k \int \mathbf{grad}_1 V_{jk}(\mathbf{r}_2, \mathbf{r}_3) \frac{n_{ijk}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)}{n_{ij}(\mathbf{r}_1, \mathbf{r}_2)} d\mathbf{r}_3 \tag{28}$$

In the same way, the next level of the hierarchy of equations corresponds to the continuity equation for the two particles densities n_{ij}

$$\frac{\partial n_{ij}(\mathbf{r}_1, \mathbf{r}_2, t)}{\partial t} + \operatorname{div}_1 \mathbf{J}_i^j(\mathbf{r}_1, \mathbf{r}_2, t) + \operatorname{div}_2 \mathbf{J}_j^i(\mathbf{r}_2, \mathbf{r}_1, t) = 0 \tag{29}$$

$\mathbf{J}_i^j$ being given by a similar equation.

If the external force on i is constant ($\mathbf{F}_i^{\text{ext}}(\mathbf{r}_1) = \mathbf{F}_i^{\text{ext}}$) and if the system is roughly homogeneous, the two and three particles densities can be expressed as follows:

$$n_{ij}(\mathbf{r}_1, \mathbf{r}_2) = n_i(\mathbf{r}_1) \, n_j(\mathbf{r}_2) \, g_{ij}(\mathbf{r}_1, \mathbf{r}_2)$$
$$\simeq \bar{n}_i \, \bar{n}_j \, g_{ij}(\mathbf{r}_1, \mathbf{r}_2) \tag{30}$$

where $\bar{n}_i$ is the mean value of n_i and

$$n_{ijk}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = n_i(\mathbf{r}_1) \, n_j(\mathbf{r}_2) \, n_k(\mathbf{r}_3) \, g_{ijk}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$$
$$\simeq \bar{n}_i \, \bar{n}_j \, \bar{n}_k \, g_{ij}(\mathbf{r}_1, \mathbf{r}_2) \, g_{ik}(\mathbf{r}_1, \mathbf{r}_3) \, g_{kj}(\mathbf{r}_2, \mathbf{r}_3) \tag{31}$$

where g_{ij} and g_{ijk} are respectively the two and three particles distribution functions in the nonequilibrium case. The two particles distribution function g_{ij} can be separated into an equilibrium part g_{ij}^0 and a nonequilibrium part h_{ij}^1. Neglecting the hydrodynamic interactions, the Fuoss-Onsager continuity equation for h_{ij}^1 can be derived from the two particles diffusion-like eq 29. Then the relaxation force can be derived from (26)

$$\mathbf{F}_i^{\text{rel}} = \mathbf{F}_i^{\text{int}} = -\sum_j \bar{n}_j \int \mathbf{grad}_1 V_{ij}(\mathbf{r}_1, \mathbf{r}_2) \, g_{ij}(\mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_2$$
$$= -\sum_j \bar{n}_j \int \mathbf{grad}_1 V_{ij}(\mathbf{r}_1, \mathbf{r}_2) \, h_{ij}^1(\mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_2 \tag{32}$$

Using eq 23, we get the final expression of the velocity of an ion of type i

$$\mathbf{u}_i = \omega_i^0(\mathbf{F}_i^{\text{ext}} + \mathbf{F}_i^{\text{rel}}) +$$
$$\sum_j \bar{n}_j \int \bar{\mathbf{T}}_{ij}(\mathbf{r}_1, \mathbf{r}_2) \, \mathbf{F}_j^i(\mathbf{r}_1, \mathbf{r}_2) \, g_{ij}(\mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_2 \tag{33}$$

3.2. Hydrodynamic Interactions. The last eq 33 allows the various effects to be quantified. The first term $\omega_i^0\mathbf{F}_i^{\text{ext}}$ corresponds to the ideal velocity at infinite dilution. The second term $\omega_i^0\mathbf{F}_i^{\text{rel}}$ stands for the relaxation effect, whereas the last one corresponds to the hydrodynamic interactions (i.e., the electrophoretic effect).

For the sake of simplicity, the two effects (hydrodynamic interactions and relaxation effect) can be uncoupled. Then we

neglect the influence of the relaxation for the calculation of the electrophoretic term

$$\sum_j \bar{n}_j \int \bar{\mathbf{T}}_{ij}(\mathbf{r}_1, \mathbf{r}_2)\, \mathbf{F}_j^i(\mathbf{r}_1, \mathbf{r}_2)\, g_{ij}(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_2 =$$
$$\sum_j \bar{n}_j \int \bar{\mathbf{T}}_{ij}(\mathbf{r}_1, \mathbf{r}_2)\, \mathbf{F}_j\, g_{ij}^0(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_2 \quad (34)$$

with $\mathbf{F}_j = \mathbf{F}_i^{\text{ext}} + \mathbf{F}_i^{\text{int}}$. Various hydrodynamic tensor $\mathbf{T}_{ij}$ can be taken into account. The simplest one is the Oseen tensor

$$\bar{\mathbf{T}}_{ij} = \frac{1}{8\pi\eta \mathbf{r}_{ij}}\left(\overline{\overline{\Pi}} + \frac{\mathbf{r}_{ij} \otimes \mathbf{r}_{ij}}{\mathbf{r}_{ij}^2}\right) \quad (35)$$

which is the Green function of the Stokes equation. Within this model, the hydrodynamic diameter of the particles is zero. Equation 34 becomes ($C_i = \bar{n}_i$)

$$\sum_j \bar{n}_j \int \bar{\mathbf{T}}_{ij}(\mathbf{r}_1, \mathbf{r}_2)\, \mathbf{F}_j\, g_{ij}^0(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_2 =$$
$$\frac{2}{3\eta} \int_0^\infty \sum_j C_j r g_{ij}^0(r)\, dr\, \mathbf{F}_j \quad (36)$$

Unfortunately the last integral does not converge if $\sum_j C_j \mathbf{F}_j \neq 0$. This problem can be overcome if the hydrodynamic velocity of the solvent is removed. Then the equation becomes[38,80]

$$\frac{2}{3\eta} \int_0^\infty \sum_j C_j r h_{ij}^0(r)\, dr\, \mathbf{F}_j \quad (37)$$

where $h_{ij}^0(r) = g_{ij}^0(r) - 1$. If the Oseen tensor is replaced be the Rotne−Prager tensor,[78] we get the same final formula (37). This expression of the electrophoretic term is obtained if one removes the averaged velocity of the solvent. Thus, the result is obtained in the solvent-fixed frame of reference.

Recently, Felderhof[81] criticized the use of such a formula by pointed out that the size of the solute particle is not properly taken into account. However, the ions are *not* considered to be hard spheres[82] for the calculations of the hydrodynamic interactions. Microscopic ions are not macromolecules. They are neither greater nor heavier than the solvent. A Brownian motion theory is not a priori justified. Its greatest interest is furnishing *soluble models* which imitate the real microscopic world. However, it must not yield parameters which are not physically relevant. For example a microscopic ion does not have any intrinsic shape. The only relevant diameter of the ions is the equilibrium one; it models the short-range repulsion between the ions averaged over the configurations of the solvent but it cannot be identified to the hydrodynamic diameter (since it does not follow the Stokes−Einstein law). Thus, the hydrodynamic diameter and the volume of microscopic ions cannot be defined properly. Hydrodynamic Brownian theory of concentrated hard spheres suspensions[83,84] are relevant for mesoscopic solute particles but they are less interesting for electrolyte theory. It is probably not to bad an approximation to neglect the exact detail of the solvent motion in the vicinity of a microscopic ion which is anyway not correctly described by a macroscopic Navier−Stokes equation with spherical boundary conditions. Ions in electrolyte solutions interact mainly via the long ranged electrostatic force. The dominant hydrodynamic interaction term is then long ranged and the Oseen tensor is microscopically justified, especially in the range of concentration we consider which does not correspond to very concentrated solutions.

Equations 33 and 37 can than be combined to yield the following expression of the Onsager coefficients (calculated in the solvent-fixed frame of reference)

$$\frac{L_{ij}}{T} = (\omega_i^0 \delta_{ij} + \Omega_{ij})\left(1 + \frac{\delta F_j^{\text{rel}}}{F_j^{\text{ext}}}\right) \quad (38)$$

where $\omega_i^0 = D_i^0/k_B T$ is the mobility at infinite dilution and C_i is the concentration of the ith species. The coefficient Ω_{ij} in eq 38 are related to the hydrodynamic interactions between the particles. They can be obtained from the equilibrium distribution function $h_{ij}^0(r)$

$$\Omega_{ij} = \frac{2}{3\eta} C_j \int_0^\infty r h_{ij}^0(r)\, dr \quad (39)$$

where η is the pure solvent viscosity.

The distribution functions can be calculated with the help of the solution of the MSA.[50] h_{ij} is obtained as the sum of three contributions

$$h_{ij}^0(r) = h_{ij}^{\text{HS}}(r) + h_{ij}^{\text{c1}}(r) + h_{ij}^{\text{c2}}(r) \quad (40)$$

where $h_{ij}^{\text{HS}}(r)$ is an hard sphere term given by the corresponding Percus Yevick approximation; $h_{ij}^{\text{c1}}(r)$ is the electrostatic part deduced from the MSA theory, and $h_{ij}^{\text{c2}}(r)$ is a second-order electrostatic contribution, approximated by

$$h_{ij}^{\text{c2}}(r) \simeq \frac{Z_i^2 Z_j^2 L_B^2}{2(1 + \Gamma\sigma_i)^2(1 + \Gamma\sigma_j)^2 r^2} e^{-2\kappa_D(r-\sigma_{ij})} \quad (41)$$

σ_i is the diameter of the ion i and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$. Γ is the screening parameter of the MSA and it is defined by (4). κ_D is the inverse Debye length. The hydrodynamic coefficients Ω_{ij} are then obtained as the sum of three contributions too

$$\Omega_{ij} = \Omega_{ij}^{\text{HS}} + \Omega_{ij}^{\text{c1}} + \Omega_{ij}^{\text{c2}} \quad (42)$$

The hard sphere electrophoretic contribution can be analytically calculated by taking an average diameter for the low volume fractions typical of ionic solutions[58]

$$\sigma_{\text{HS}} = \sqrt[3]{\frac{3X_1 X_2/X_0 + X_3}{4X_0}} \quad (43)$$

with $X_n = \pi/6 \sum C_i \sigma_i^n$. Integration of the function h_{ij}^0 deduced from the Percus−Yevick theory yields the following hard-sphere electrophoretic term:

$$\Omega_{ij}^{\text{HS}} = -\frac{(\sigma_i + \sigma_j)^2}{12\eta} C_j \frac{1 - \tilde{X}_3/5 + \tilde{X}_3^2/10}{1 + 2\tilde{X}_3} \quad (44)$$

where $\tilde{X}_3 = \pi/6 \sum C_i \sigma_{\text{HS}}^3$. The MSA electrostatic term is

$$\Omega_{ij}^{\text{c1}} = -\frac{1}{3\eta} \frac{Z_i Z_j L_B C_j}{(1 + \Gamma\sigma_i)(1 + \Gamma\sigma_j)\left(\Gamma + \sum_k C_k \dfrac{\pi L_B Z_k^2 \sigma_k}{(1 + \Gamma\sigma_k)^2}\right)} \quad (45)$$

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The second-order electrostatic term is

$$\Omega_{ij}^{c2} \simeq \frac{L_B^2 Z_i^2 C_j Z_j^2}{3\eta(1+\Gamma\sigma_i)^2(1+\Gamma\sigma_j)^2} e^{\kappa_D(\sigma_i+\sigma_j)} \int_{\kappa_D(\sigma_i+\sigma_j)}^{\infty} \frac{e^{-u}}{u} du \quad (46)$$

3.3. Relaxation Effect. The force, $\mathbf{F}_i$, is the sum of two terms, the external force ($\mathbf{F}_i^{ext} = Z_i e \mathbf{E}^{ext}$ for the conductivity) and the relaxation force $\mathbf{F}_i^{rel}$ acting on charged particles i. $\mathbf{E}^{ext}$ is the applied electric field. The relaxation force is related to the deformation of the ionic atmosphere owing to the external force

$$\mathbf{F}_i^{rel}(\mathbf{r}_1) = -\sum_j \rho_j \int \mathbf{grad}_1 V_{ij}(r_1, r_2) \, h_{ij}^1(\mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_2 \quad (47)$$

The external forces $\mathbf{F}_i^{ext}$ are uniform and constant. The Fuoss-Onsager equation[2] which corresponds to the second level of the BBGKY like hierarchy of the Smoluchowski equation can be used to evaluate the functions h_{ij}^1. In the linear response regime, the first-order equation is for a binary salt solution[37]

$$\Delta h_{ij}^1 - \kappa_q^2 h_{ij}^1 = \frac{\omega_i^0 \mathbf{F}_i^{ext} - \omega_j^0 \mathbf{F}_j^{ext}}{k_B T(\omega_i^0 + \omega_j^0)} \mathbf{grad} \, g_{ij}^0 \quad (48)$$

where κ_q^2 is given by

$$\kappa_q^2 = \frac{1}{\epsilon_0 \epsilon_r k_B T} \frac{C_1 e_1^2 \omega_1^0 + C_2 e_2^2 \omega_2^0}{\omega_1^0 + \omega_2^0} \quad (49)$$

We note that the term $\omega_i^0 \mathbf{F}_i^{ext} - \omega_j^0 \mathbf{F}_j^{ext}$ appearing in eq 48 is proportional to the difference of current density $J_i - J_j$ when hydrodynamic correction terms Ω_{ik} are neglected. The solution of eqs 48 and 47 can be obtained by using the MSA theory for the equilibrium pair distribution function g_{ij}^0. Thus, the relaxation term obtained for the conductivity is

$$\frac{\delta F_1^{rel}}{F_1^{ext}} = \frac{\delta F_2^{rel}}{F_2^{ext}} = \frac{\delta E}{E} = -\frac{\kappa_q^2}{3} \frac{\sinh(\kappa_q \sigma_{12})}{\kappa_q \sigma_{12}} \int_{\sigma_{12}}^{\infty} dr \, r h_{12}^0(r) \, e^{-\kappa_q r} \quad (50)$$

where $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ is the distance of least approach between ions 1 and 2. The integral of the indirect correlation function h_{12}^0 in the preceding equation are deduced from one part of the MSA expressions and from an other part of a second-order term in order to be consistent with the similar integrals calculated in the hydrodynamic terms

$$\frac{\delta E^{(1)}}{E} = \frac{-\kappa_q^2 e^2 |Z_1 Z_2|}{\epsilon_0 \epsilon_r k_B T \sigma_{12}(1+\Gamma\sigma_1)(1+\Gamma\sigma_2)} \times$$
$$\frac{1 - e^{-2\kappa_q \sigma_{12}}}{\left[\kappa_q^2 + 2\Gamma\kappa_q + 2\Gamma^2 - 2\pi L_B \sum_k C_k \frac{Z_k^2}{(1+\Gamma\sigma_k)^2} e^{-\kappa_q \sigma_k}\right]} \quad (51)$$

$$\frac{\delta E^{(2)}}{E} = \frac{-\kappa_q L_B^2 Z_1^2 Z_2^2 \sinh(\kappa_q \sigma_{12})}{6\sigma_{12}(1+\Gamma\sigma_1)^2(1+\Gamma\sigma_2)^2} e^{\kappa_D(\sigma_1+\sigma_2)} \int_{(\kappa_q+2\kappa_D)\sigma_{12}}^{\infty} \frac{e^{-u}}{u} du \quad (52)$$

4. Mode-Coupling Theory

4.1. Nonequilibrium Calculation. The ion self-diffusion coefficients can be obtained similarly from the MSA too.[85] For dilute solutions, the hydrodynamic interactions are negligible.

They decrease the relaxation force, and this second-order effect can be neglected up to 1 mol L^{-1} for simple electrolytes, as it can be shown from Brownian dynamics simulations.[21] However, the calculation of the relaxation force based on the Fuoss−Onsager equation is more complicated because the tracer is actually a further species. We propose there an alternative approach based on mode-coupling theory (MCT)[30,35] which can be deduced from the Smoluchowski equation formalism.

The Smoluchowski equation describes the system in the ion configuration space. The velocities of the particles are considered as fast variables and they have been eliminated. Thus, the classical Kubo formula for transport coefficients[15,86] have to be generalized to the Smoluchowski equation formalism.[21,87] If the hydrodynamic interactions are neglected the corresponding linear-response theory formula for the self-diffusion coefficient of species i reads

$$D_i^s = D_i^0 - \frac{1}{3}\int_0^{\infty} dt \left(\frac{D_i^0}{k_B T}\right)^2 \langle \mathbf{F}_i(0) \cdot \mathbf{F}_i(t)\rangle \quad (53)$$

where $\mathbf{F}_i(t)$ is the force on one particle i at time t. The calculation of D_i^s requires the calculation of the time dependent friction

$$\delta\zeta(t) = \frac{1}{3k_B T}\langle \mathbf{F}_i(0) \cdot \mathbf{F}_i(t)\rangle \quad (54)$$

At the thermodynamic limit, the system is uniform and

$$\delta\zeta(t) = \frac{V}{3k_B T}\int d\mathbf{r} \, \langle F(\mathbf{r}, t)F(\mathbf{r}, 0)\rangle \quad (55)$$

where $F(\mathbf{r}, t)$ is the time dependent force per unit of volume exerted on the tagged ion due to its interaction with the other ions of the solution.

An expression for $F(\mathbf{r}, t)$ can be obtained from time dependent density functional theory[88−90]

$$\mathbf{F}(\mathbf{r}, t) = k_B T C_s(\mathbf{r}, t) \, \mathbf{grad} \sum_i \int c_{si}(\mathbf{r}, \mathbf{r}')\delta C_i(\mathbf{r}, t) \, d\mathbf{r}' \quad (56)$$

where c is the direct correlation function between the particles and C is the concentration. s denotes the tracer, and i (or j) denotes one of the two ionic species. Use of eq 56 together with eq 55 leads to

$$\delta\zeta(t) =$$
$$\frac{k_B T}{3(2\pi)^3}\sum_{i,j}\sqrt{C_i C_j}\int q^2 c_{si}(q)G_{ij}(q, t)c_{sj}(q)F_s(q, t)4\pi q^2 \, dq \quad (57)$$

Thus, the electrostatic friction can be formally expressed as an integral over the wave-vector space q. $F_s(q, t)$ is the self-dynamic structure factor of the tagged ion. $c_{ij}(q)$ is the Fourier transform of the direct correlation function and $G_{\alpha\beta}(q, t)$ is the ionic van Hove function defined by

$$G_{ij}(q, t) = (N_i N_j)^{-1/2}\langle C_i(\mathbf{q}, t)C_j(-\mathbf{q}, 0)\rangle \quad (58)$$

Note that the derivation of eq 57 uses the Gaussian approximation commonly used in MCT.[91] This implies that 4 particles correlation functions can be identified to the product of 2 particles correlation functions.

The time Fourier transform of $G_{\alpha\beta}(q, t)$ can be calculated from a Mori projector technique[30,35]

$$G_{\alpha\beta}(q, \omega) = [-i\omega + D_\alpha q^2]^{-1} S_{\alpha\beta}(q) +$$

$$\frac{D_\alpha q^2}{-i\omega + D_\alpha q^2}\sum_{\gamma=1}^{2} \sqrt{C_\alpha C_\gamma} c_{\alpha\gamma}(q) G_{\gamma\beta}(q, \omega) \quad (59)$$

where i is there the imaginary number $i^2 = -1$. This expression, eq 59, corresponds to the Brownian approximation because the memory effects have been removed. $S_{\alpha\beta}(q) = G_{\alpha\beta}(q, t = 0)$ is the partial static structure factor between species α and β.

4.2. Practical Calculation. The calculation of $\delta\zeta(t)$ requires $G_{ij}(q, t)$ and $F_s(q, t)$. The four ($\alpha, \beta = 1, 2$) linear coupled eqs 59 can be solved analytically to obtain the frequency dependence of the ionic van Hove functions. For $F_s(q, t)$, we used the long time limit[15]

$$F_s(q, t) = e^{-D_s q^2 t} \quad (60)$$

The difficulty of the practical calculation comes from the fact that the formula are implicit since $F_s(q, t)$ and $G_{ij}(q, t)$ depend on the self-diffusion coefficients. Thus, the MCT equations need to be solved self-consistently.

The equilibrium terms $S_{\alpha\beta}(k)$ $c_{\alpha\beta}(k)$ have been obtained from the solution of the MSA.[51,50] The calculation of $h_{ij}(q)$ can use the method described in the case of hard sphere mixtures.[92,93] We considered the whole analytical solution of the MSA with different sizes ($P_n \neq 0$) so that the Stillinger-Lovett sum-rule is exactly verified. It should be noted that the calculation of the self-diffusion coefficients for a given concentration takes time. The MSA theory for the conductivity or the mutual diffusion coefficient is completely analytical and the numerical calculation is practically instantaneous. Conversely, the theory for self-diffusion is only semianalytical; there are several numerical integrations and the self-consistency requires a loop. On modern computers, the calculation of the two D_i of a electrolyte for a given concentration lasts several seconds (almost one minute for very *dilute* solutions). The theory of self-diffusion presented here is not valid at very high concentration: if C is too high (typically 1 mol L^{-1}) the hydrodynamic interactions reduce the relaxation effect, as it can be shown from Brownian dynamics simulations[21] and they have to be taken into account.[94]

5. Results and Discussion

In the two previous sections, we have generated expressions for the various ion transport coefficients of electrolyte solutions (self-and mutual diffusion coefficient, conductivity and transference numbers) under the Smoluchowski/MSA approximation. In this section, these analytical (or semianalytical) expressions are compared to the experimental values for seven dissociated electrolytes in water: NaCl, KCl, LiCl, NaBr, KBr, LiBr, and CaCl$_2$. The various ions are characterized by their charges, their diameters σ_i, and their self-diffusion coefficients at infinite dilution D_i^0. The diameters are given in Table 1. The self-diffusion coefficients at infinite dilution have been tabulated from the Nernst−Einstein relation.[3,95] The size of the ions have been obtained[72] from the equilibrium properties, as it is shown in Figure 3. The value of the osmotic coefficient calculated from the MSA is in agreement with the experimental values taken from refs 96 and 3. For dilute solutions, the osmotic coefficient decreases because of the strong electrostatic interactions whereas
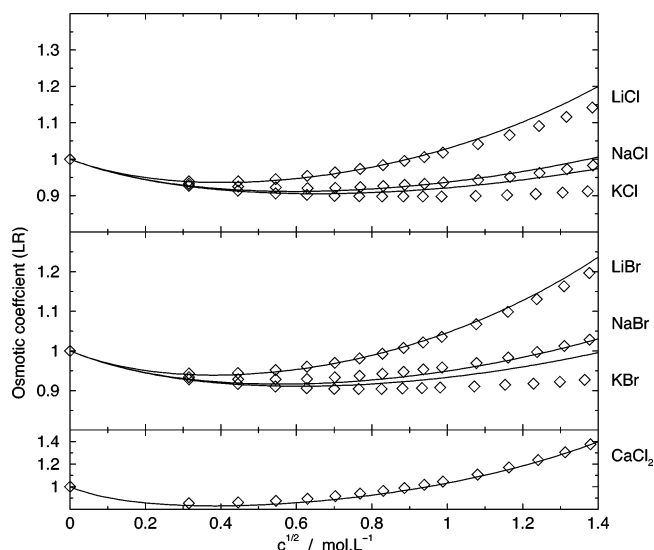
Figure 3. Lewis−Randall osmotic coefficient of aqueous electrolyte solutions at 25 °C as a function of the square root of concentration. Solid lines, MSA theory; ◇, experimental values.

it increases at high concentration because of the repulsion between the ions. There is actually a small discrepancy between MSA and the experiments for very concentrated solutions of KCl and KBr. MSA overestimates the osmotic coefficient. It is probably a consequence of the structure breaking effect of K$^+$ [97] which reduces the effective size of that cation. The electrolyte activity coefficients are similarly in agreement with the experimental data. The have not been reproduced, because the activity coefficient is solely deduced from the osmotic pressure[6] because of the Gibbs−Duhem relation. Thus, it is not a real independent parameter.

It should be noted that the various Smoluchowski/MSA theories have been compared to Brownian dynamics,[21,80,98] and they have been found to be in close agreement with this simulation method. Thus the various approximations we used (MSA and uncoupling approximations) are mathematically justified. If the theory is in agreement with the experimental values as well, it should not come from compensating errors. The comparison of the Smoluchowski/MSA theory to the experiments is then a crude test of the primitive model and of the relevance of Brownian motion theory for electrolyte solutions.

In Figure 4, we have plotted the equivalent conductivity of the various electrolytes as a function of the square root of the concentration. The theory is still in agreement with the experimental values, even if they are some small discrepancies. The equivalent conductivity decreases in the whole concentration range we have considered because of the relaxation and the electrophoretic effects. However, at high concentration, the two effects are proportionally less important. It comes from the repulsion between the particles which brings down the electrostatic relaxation field and the hydrodynamic interactions.

Figure 5 exhibits a similar agreement between the theory and the experimental values for the mutual diffusion coefficient. This transport coefficient does not vary a lot and the values are close to the Nernst-Hartley expression $D_m^{NH} = (Z_2 D_2^0 D_1^0 - Z_1 D_1^0 D_2^0)/(Z_1 D_1^0 - Z_2 D_2^0)$ which is the value at infinite dilution. In fact, at high concentration, there is a competition between the effect of the activity coefficients which increases D_m and the electrophoretic effect which slows down the diffusion process. Thus the plateau obtained comes from the fact that the two

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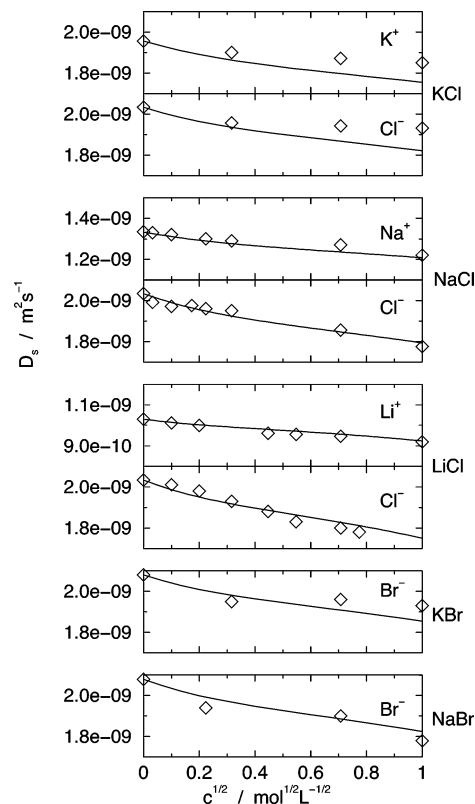*J. Phys. Chem. B, Vol. 109, No. 20, 2005* **9881**
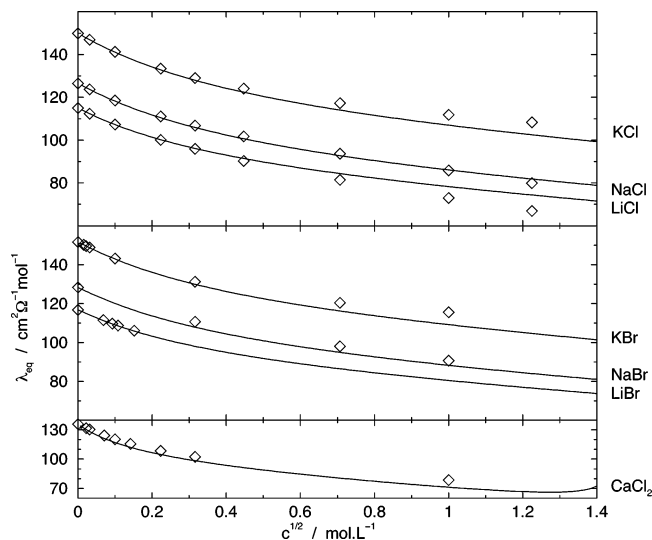
Figure 4. Molar conductivity of aqueous electrolyte solutions at 25 °C as a function of the square root of concentration. Solid lines, Smoluchowski−MSA theory; ◇, experimental values.
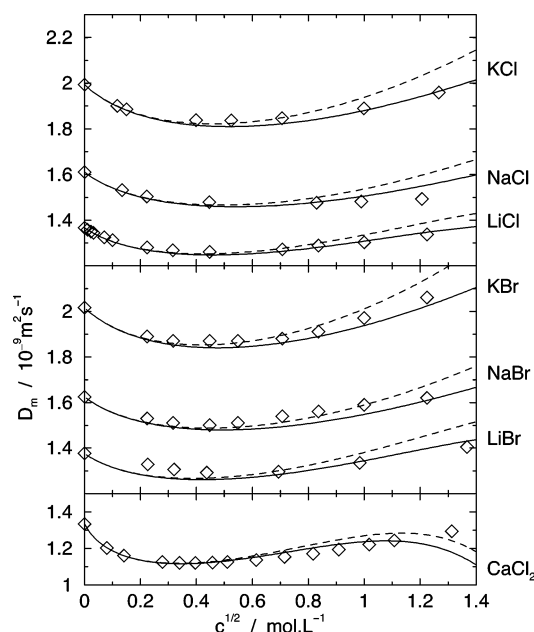

Figure 5. Mutual diffusion coefficients of aqueous electrolyte solutions at 25 °C as a function of the square root of concentration. Solid lines, Smoluchowski−MSA theory; ◇, experimental values. Dashed lines, Smoluchowski-MSA theory in the solvent-fixed frame of reference.

Figure 6. Self-diffusion coefficients of various ions in aqueous electrolyte solutions at 25 °C as a function of the square root of concentration. Solid lines, MCT−MSA theory; ◇, experimental values.
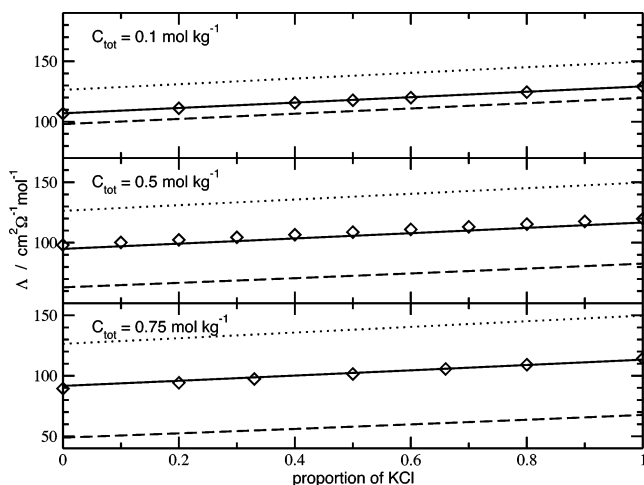
Figure 7. Molar conductivity of NaCl/KCl mixture aqueous solutions at 25 °C for different molalities. Solid line, Smoluchowski−MSA theory; ◇, experimental values. Dashed line, Onsager−Kim limiting law. Dotted line, ideal conductivity.

effects (and the reference frame correction) cancel each other out. The experimental values in Figures 4 and 5 have been taken from ref 96.

The experimental data of Figure 6 have been taken from the critical analysis given in ref 95. The MSA theory is able to reproduce the self-diffusion coefficients for the various electrolyte (when the experimental values are available) as well. This transport coefficient decreases because of the relaxation effect. It is worth noting that this MCT/MSA theory also allows the *time dependent* self-diffusion coefficients to be calculated.[35] The characteristic time of the relaxation effect is roughly the Debye time $\tau_D = (4\pi L_B \sum_i Z_i^2 C_i D_i^0)^{-1}$ whose order of magnitude is close to 1 ns for the simple electrolytes we have considered. This result can explain the discrepancy between the self-diffusion coefficients measured by time-of-flight neutron scattering and NMR or tracer methods.[99] The values measured by neutron scattering whose characteristic time is 20 ps do not

take into account the whole relaxation effect and there are greater than the values measured by long times method.

The MSA approach has been generalized to the mixtures of electrolyte solutions.[100] This approach extends the theoretical study by Onsager and Kim[11] which is valid in the limiting law domain ($C < 10^{-2}$ mol L^{-1} for 1−1 electrolytes). The calculation is more complicated because the calculation of the relaxation effect requires the diagonalization of 3 × 3 tensors. The molar conductivity of KCl/NaCl mixtures is plotted in Figure 7. The experimental values have been taken from ref 101. The agreement is still good. The Onsager−Kim limiting law underestimates the molar conductivity. Indeed, the repulsion

TABLE 2: Influence of the Three Effects on the Various Ion Transport Coefficients[a]

	molar conductivity	mutual diffusion		self-diffusion		transport number
	low c and high c	low c	high c	low c	high c	low c and high c
hydrodynamic interactions	dec	0 or dec	dec	0	inc	inc if $t > 0.5$
						dec if $t < 0.5$
relaxation effect	dec	0		dec		0
activity coefficients	0	dec	inc	0		0

[a] dec (respectively, inc) means that the corresponding effect decreases (respectively increases) the transport coefficient. 0 means that the effect is zero or negligible. c is the concentration. The low concentration domain corresponds to the Onsager limiting law. At low concentration, the hydrodynamic interactions do not influence the mutual diffusion coefficient of a *symmetrical* electrolyte. Note that there is a another effect for the mutual diffusion coefficient: the reference frame correction which decreases this transport coefficient unless the partial volume is negative.

between the ions reduces the relaxation effect. Thus, the Smoluchowski/MSA approach seems to be valid for the mixtures too.

This approach allows the influence of the various effects to be clarified (see Table 2). The hydrodynamic interactions (i.e., the electrophoretic effect), the (electrostatic) relaxation effect, and the activity coefficients drive the values of the transport coefficients. Their influence depends on the concentration, though. For example the activity coefficients decrease D_m at low concentration but they increase this quantity at high concentration. They are in fact two regimes: at low concentration, the Coulombic interaction between the ion is predominant, whereas the repulsion between the particles becomes significant at high concentration. The Onsager limiting laws are valid in the first domain only. On the other hand, the MSA approach takes into account the repulsion by a hard-sphere interaction, and it can be applied up to concentrated solutions (typically $1-2$ mol L^{-1}).

The only parameters of the model are the ion diameters (see Table 1). They do not correspond to the bare Pauling diameters for all of the ions. The difference between σ_{PM} and $\sigma_{Pauling}$ represents the hydration which is zero for the anions we have considered. We can then deduce hydration numbers that are found to be consistent with the values given in the literature. It should be noted that the smaller a bare ion is, the biggest it is in aqueous solution, because of the hydration. The size, the charge, and the self-diffusion coefficient at infinite dilution are the only specific parameter of an ion within our model, and it seems that they are enough to describe the various equilibrium and transport properties of electrolyte solutions if the concentration is not too high.

6. Conclusion

We have presented a review of our recent work on the transport of electrolyte solutions. The theory is based on a combined MSA/Smoluchowski approach, and it uses the primitive model: the ions are charged hard spheres. The expression of the various transport coefficients has been obtained analytically for dissociated electrolyte and their results are in agreement with the experimental values up to $1-2$ mol L^{-1}. Furthermore, all of the coefficients are calculated with the same level of approximation, and the results have been found to be in agreement with Brownian dynamics simulations. The theory recovers the exact Debye−Hückel−Onsager limiting law at low concentration, and it seems to yield interesting results for the mixtures as well. The agreement with the experimental results may differ depending on the ion and on the transport coefficient, but it is in any case quite impressive. For example, the data of this article have been calculated for 7 electrolytes, $5 \times 7 = 35$ properties have been compared to the experimental values (even

if sometimes the whole concentration range has not been checked because of the lack of experimental data), and they have been found to be in agreement with the experiments. The validity and the simplicity of the final results makes this approach specially interesting for chemical engineering.[102−104] It may sometimes be less accurate than phenomenological theories[105] with many adjustable parameters, but it gives a clear picture of the electrolyte solution which may be useful. For practical use, programs are freely available in the Web site of our laboratory.[106] The self-consistency and the reliability of this approach comes from the fact that it is based on a well-established physical picture.

First, we use a continuous solvent description (McMillan− Mayer level of description). This approach is *in principle* always justified. However, we use pair potentials, and the theory does not hold at very high concentration. Hence the concentration range $C < 1-2$ mol L^{-1}.

Second, we consider the primitive model of electrolyte solutions. The Coulombic part of the model is exact, but the short-range repulsion is modeled by simple hard sphere interactions. This assumption may be at first sight questionable, but the short-range term is a kind of perturbation to the electrostatic long-range term (since for dilute solution the Debye−Hückel theory is exact) and the precise description of the short-range interactions can be neglected.

Third, we use the MSA, which is a very accurate approximation for dissociated electrolytes.

Fourth, the dynamics of the solutions is obtained from the Smoluchowski equation which is a Brownian motion theory. Strictly speaking, this theory is valid only if the ions have a large mass relative to the mass of the solvent molecules.[4] This assumption is doubtful for bare ions, but it is probably valid for electrolyte solutions because the ions are hydrated. Also, the hydration is all the more important since the ion is small.

Fifth, the approximation used to calculate the various transport coefficient are justified as it can be shown from the comparison with Brownian dynamics simulations.

This approach is very satisfactory for simple electrolytes but its domains of validity could be improved. The case of very concentrated electrolyte solutions is much more complicated. There is no accurate microscopic theory for the equilibrium properties. The calculation of the transport coefficients could be based on simple semiphenomenological assumptions. For example, it is possible to describe the properties of concentrated electrolyte solutions self-consistently from the MSA by considering that the dielectric constant and the size of the ions vary,[107−109] and this idea could be extended to the transport coefficients.

The description of further transport coefficients such as the viscosity is also challenging. The MCT may be the best

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method.[32] However, the situation is much more complicated. Beyond the Falkenhagen−Onsager limiting law of viscosity, continuous solvent models predict an increase of the viscosity as a function of C. Unfortunatly, this prediction is not correct for several electrolytes (such as KCl). The discrepancy may arise from the solvent structure breaking effect which characterizes some of the ions (K^+, for example). The description of such an effect requires the calculation of the ion−solvent configurations, which is far from being simple.

However, the most important enhancement of this method to bulk solutions would be to extend the results to associated electrolytes. A MSA theory of transport coefficients for such systems has been proposed[40,63,110] but the theory is less conclusive. The problem comes from the fact that they are many unknown parameters, such as the size and the mobility of the pair of ions.

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