

# Influence of Ion Properties on the Equilibrium and Transport Properties of Electrolyte Solutions

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Strong electrolytes are described in the framework of the primitive model in which the solvent is regarded as a dielectric continuum, using the mean spherical approximation. The analytical solution of the equilibrium and transport properties is dependent on the ions' diameters and valencies. For hydrated or nonspherical ions, an effective diameter must be fitted. A sensitivity study of the osmotic coefficient and the transport coefficients is performed on theoretical 1–1, 2–1, and 3–1 electrolytes, up to a total ion concentration of 2 mol/L.

## Introduction

The mean spherical approximation (MSA)<sup>1,2</sup> solved for the primitive model of electrolytes (in which the ions are modeled as charged hard spheres) represents a promising method to describe departures from ideality in electrolytes. It is fundamentally connected to the popular Debye–Hückel theory: the solvent is regarded as a dielectric continuum, but the neutralizing ion cloud around a central ion is composed of finite-sized ions instead of point ions. The main attractive feature of the MSA is that it proposes analytical formulas for the electrolyte properties,<sup>2,3</sup> whereas better approximations such as the hypernetted-chain (HNC)<sup>4</sup> must be solved numerically for each individual system. The MSA can be applied for dissociated electrolytes up to molar concentrations (1–2 mol/L).

The only slightly adjustable parameters in the MSA are the diameters of the hydrated ions. The consistency of the MSA, i.e., its ability to predict the various equilibrium and transport properties with the same set of diameters, was verified by Dufrêche et al.<sup>3,5</sup> The extent to which the calculated properties are dependent on the chosen diameters has not been investigated yet. Therefore, the sensitivity of the osmotic coefficient and the transport coefficients, with respect to the diameters, is studied in this paper. The study will be performed on symmetrically and asymmetrically charged electrolytes.

This work will further the understanding of electrolyte properties beyond the limiting laws—e.g., Debye–Hückel's law for the osmotic coefficient and Onsager's law for the conductivity—where the size of the ions becomes important.

## Theory

The MSA has been solved for the primitive model with equal diameters by Waisman et al.<sup>1</sup> and with unequal diameters by Blum.<sup>2</sup> Similar to the Debye length  $\lambda_D$  in the Debye–Hückel theory, the thickness of the neutralizing ion cloud around a

central ion is characterized by  $(2\Gamma)^{-1}$  in the MSA. The screening parameter  $\Gamma$  is defined by the implicit equation

$$\Gamma^2 = \pi L_B \sum_i c_i \left( \frac{z_i - \Psi \sigma_i^2}{1 + \Gamma \sigma_i} \right)^2 \quad (1)$$

where

$$L_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T} \quad (2)$$

$$\Psi = \frac{\pi}{2\Delta\Omega} \sum_i \frac{c_i \sigma_i z_i}{1 + \Gamma \sigma_i} \quad (3)$$

$$\Omega = 1 + \frac{\pi}{2\Delta} \sum_i \frac{c_i \sigma_i^3}{1 + \Gamma \sigma_i} \quad (4)$$

$$\Delta = 1 - \frac{\pi}{6} \sum_i c_i \sigma_i^3 \quad (5)$$

and  $c_i$  is the concentration of the  $i$ th species, which has a diameter  $\sigma_i$  and a valency  $z_i$ . Analytical expressions have been derived for the osmotic coefficient,<sup>2,3,5,6</sup> the activity coefficients,<sup>6</sup> the conductivity,<sup>3,7,8</sup> the mutual diffusion coefficient,<sup>5,9</sup> and the transport numbers.<sup>5</sup>

**The Osmotic Coefficient.** The osmotic coefficient of an electrolyte describes the difference in stability between a hypothetical solution, where the ions only interact with the solvent, and the real solution, where the ions also interact with each other. Within the MSA, the osmotic coefficient is the sum of an electrostatic interaction (E) term and a hard sphere repulsion (HS) repulsion term:

$$\phi = \phi^{(E)} + \phi^{(HS)} \quad (6)$$

The electrostatic interaction dominates at low concentration and has a tendency to decrease the osmotic coefficient, according to<sup>2,6</sup>

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$$\phi^{(E)} = -\frac{\Gamma^3}{3\pi c_t} - \frac{2L_B\Psi^2}{\pi c_t} \quad (7)$$

where  $c_t$  is the total ion concentration ( $c_t = \sum_k c_k$ ). The second term is present only for asymmetric ion sizes and is negligible if the sizes are not too different. The hard sphere term in eq 6 corresponds to the osmotic coefficient of a hard sphere mixture:<sup>10</sup>

$$\phi^{(HS)} = \frac{6}{\pi c_t} \left[ \frac{X_0}{1-X_3} + \frac{3X_1X_2}{(1-X_3)^2} + \frac{(3-X_3)X_2^3}{(1-X_3)^3} \right] \quad (8)$$

where

$$X_p = \frac{\pi}{6} \sum_k c_k \sigma_k^p \quad (9)$$

Its value is always  $>1$  and dominates at high concentration.

**Ion Transport Coefficients.** Ion transport in a solution can be described either by directly measurable quantities—e.g., conductivity, mutual diffusion coefficient, and transport number—or by the Onsager coefficients  $l_{ij}$ .<sup>11,12</sup> Two types of interaction affect ion transport:<sup>13</sup> (i) the relaxation of the ion cloud around a central ion to restore local electroneutrality, and (ii) the drag of ions by the motion of other ions, the velocity being hydrodynamically transmitted by the solvent. For a binary electrolyte, the Onsager coefficients in the solvent-fixed reference frame are given by

$$l_{ij} = \frac{c_1 c_2 l_{ij}^0 - \alpha(l_{11}^0 l_{22}^0 - l_{12}^0 l_{21}^0) c_i c_j}{c_1 c_2 - \alpha(c_1^2 l_{22}^0 + c_2^2 l_{11}^0 - 2l_{12}^0 c_1 c_2)} \quad (10)$$

where

$$l_{ij}^0 = (\delta_{ij} \omega_i^0 + \Omega_{ij}) c_i \quad (11)$$

$\omega_i^0$  is the mobility of ion  $i$  and is related to its diffusion coefficient  $D_i^0$  at infinite dilution by  $\omega_i^0 = D_i^0/(k_B T)$ ,  $\alpha$  represents the relaxation effect, and  $\Omega_{ij}$  are the hydrodynamic interaction coefficients. Given the complexity of eq 10, it is difficult to analyze the sensitivity of the Onsager coefficients, with respect to the ion diameters beyond the limiting law. The general expression for the Onsager coefficients of a multi-ion solution is even more complex. Therefore, the hydrodynamic interaction coefficients and the relaxation effect will be discussed separately.

The hydrodynamic interaction coefficients are obtained from an integral of the equilibrium pair distribution functions  $h_{ij}^0$ .<sup>3,5</sup>

$$\Omega_{ij} = \frac{2}{3\eta} c_j \int_0^\infty r h_{ij}^0(r) dr \quad (12)$$

where  $\eta$  is the pure solvent dynamic viscosity. In the absence of relaxation effects,  $\Omega_{ii}$  describes the change in the “intrinsic mobilities” of the ions and  $\Omega_{ij}$  represents “interaction mobilities”. Under the approximation  $\Psi = 0$ , which is valid if the ion sizes are not too different,  $\Omega_{ij}$  can be decomposed to an electrostatic part and a hard sphere part. The electrostatic part consists of two terms. The first-order term,

$$\Omega_{ij}^{(E1)} = -\frac{L_B}{3\eta} \frac{z_i z_j c_j}{(1 + \Gamma \sigma_i)(1 + \Gamma \sigma_j)} \left[ \Gamma + \pi L_B \sum_k \frac{z_k^2 c_k \sigma_k}{(1 + \Gamma \sigma_k)^2} \right] \quad (13)$$

is positive for ions of opposite sign and negative for ions of like sign, describing electrostatic entraining and restraining, respectively. The second-order term is

$$\Omega_{ij}^{(E2)} = \frac{L_B^2}{3\eta} \frac{z_i^2 z_j^2 c_j}{(1 + \Gamma \sigma_i)^2 (1 + \Gamma \sigma_j)^2} e^{2\kappa_D \sigma_{ij}} \int_{2\kappa_D \sigma_{ij}}^\infty \frac{e^{-u}}{u} du \quad (14)$$

where

$$\kappa_D = \sqrt{4\pi L_B \sum_k z_k^2 c_k} \quad (15)$$

is the inverse Debye length and

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (16)$$

is the distance of closest approach between ions  $i$  and  $j$ . It is always positive. The hard sphere term is calculated from an average diameter,

$$\sigma_{HS} = \sqrt[3]{\frac{3X_1X_2 + X_0X_3}{4X_0^2}} \quad (17)$$

and is expressed as

$$\Omega_{ij}^{(HS)} = -\frac{\sigma_{ij}^2 c_j}{3\eta} \frac{1 - \tilde{X}_3/5 + \tilde{X}_3^2/10}{1 + 2\tilde{X}_3} \quad (18)$$

where

$$\tilde{X}_3 = \frac{\pi}{6} \sum_k c_k \sigma_{HS}^3 \quad (19)$$

is the volume fraction occupied by the ions. It is always negative and accounts for obstruction effects.

The relaxation effect can be obtained from linear response theory. The calculation has been performed for the conductivity of binary electrolytes<sup>3,7</sup> and ternary electrolytes<sup>8</sup> and involves another integral of the equilibrium pair distribution functions:

$$G_{ij}(\kappa_q) = -\frac{\sinh(\kappa_q \sigma_{ij})}{\kappa_q \sigma_{ij}} \int_{\sigma_{ij}}^\infty r h_{ij}^0(r) \exp(-\kappa_q r) dr \quad (20)$$

where the parameter  $\kappa_q$  is a function of the concentrations and is dependent on the diffusion constants at infinite dilution and the valencies, but not on the diameters. In accordance with the electrostatic portion of the hydrodynamic interaction, the relaxation factor is also written as the sum of two terms:

$$G_{ij}^{(1)} = \left[ \frac{L_B |z_i z_j| \sinh(\kappa_q \sigma_{ij})}{\sigma_{ij} (1 + \Gamma \sigma_i) (1 + \Gamma \sigma_j)} \right] \left[ \frac{\exp(-\kappa_q \sigma_{ij})}{\kappa_q^2 + 2\Gamma \kappa_q + 2\Gamma^2 - 2\pi L_B \sum_k \frac{z_k^2 c_k}{(1 + \Gamma \sigma_k)^2} \exp(-\kappa_q \sigma_k)} \right] \quad (21)$$

and

$$G_{ij}^{(2)} = \left[ \frac{L_B^2 z_i^2 z_j^2 \sinh(\kappa_q \sigma_{ij})}{2\kappa_q \sigma_{ij} (1 + \Gamma \sigma_i)^2 (1 + \Gamma \sigma_j)^2} \right] \exp \left[ (2\kappa_D \sigma_{ij}) \int_{(\kappa_q + 2\kappa_D) \sigma_{ij}}^{\infty} \frac{\exp(-u)}{u} du \right] \quad (22)$$

For a binary electrolyte, the complete relaxation factor is

$$\alpha = \frac{4\pi L_B}{3} \frac{z_1 z_2}{\omega_1^0 + \omega_2^0} G_{12}(\kappa_q) \quad (23)$$

where

$$\kappa_q = \sqrt{4\pi L_B \left( \frac{c_1 D_1^0 z_1^2 + c_2 D_2^0 z_2^2}{D_1^0 + D_2^0} \right)} \quad (24)$$

## Results and Discussion

Theoretical strong binary electrolytes with different ion diameters and valencies are investigated for total ion concentrations ranging from  $10^{-3}$  mol/L to 2 mol/L. Beyond this upper limit, the primitive model fails, because the average number of water molecules between the ions becomes too low to consider it as a dielectric continuum. The diameters are chosen to be 2.5, 5.0, and 7.5 Å, to cover the range from weakly hydrated cations to strongly hydrated cations or complex anions. The study is performed on 1–1, 2–1, and 3–1 electrolytes to vary the relative contribution of the electrostatic and hard sphere interaction. For each electrolyte, the osmotic coefficient, the hydrodynamic interaction coefficients, and the relaxation factor has been calculated as a function of the total ion concentration. To save space, only the results for the 1–1 and 3–1 electrolyte will be shown; the 2–1 electrolyte has an “intermediate” behavior. The sensitivity of each quantity, i.e., the change in the calculated value for a given change in diameter, will be

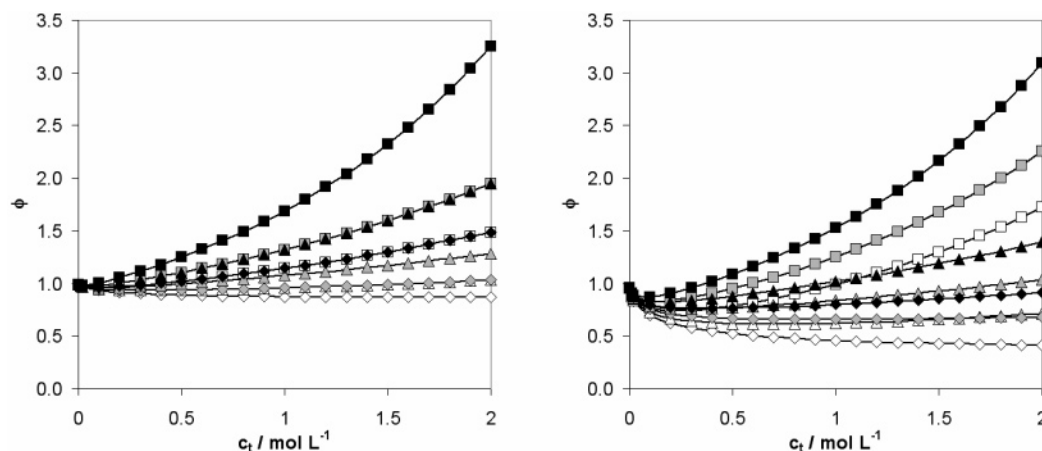
discussed. Because eqs 7, 8, 13, 14, 18, 21, and 22 are applicable to multi-ion solutions, the conclusions will have general validity.

**The Osmotic Coefficient.** In Figure 1, the osmotic coefficient is plotted for the 1–1 and 3–1 electrolyte. Increasing an ion's diameter results in a higher osmotic coefficient, which is in agreement with the notion that stronger hard sphere repulsion destabilizes the solution. The hard sphere term naturally contributes to this behavior, but the electrostatic term also contributes. Bigger ions have lesser screening capability, because they cannot get close to the central ion; hence,  $\Gamma$  decreases. Its effect on the electrostatic term can be counteracted by the second term in eq 7, if increasing the diameter leads to significantly more asymmetric ion sizes.

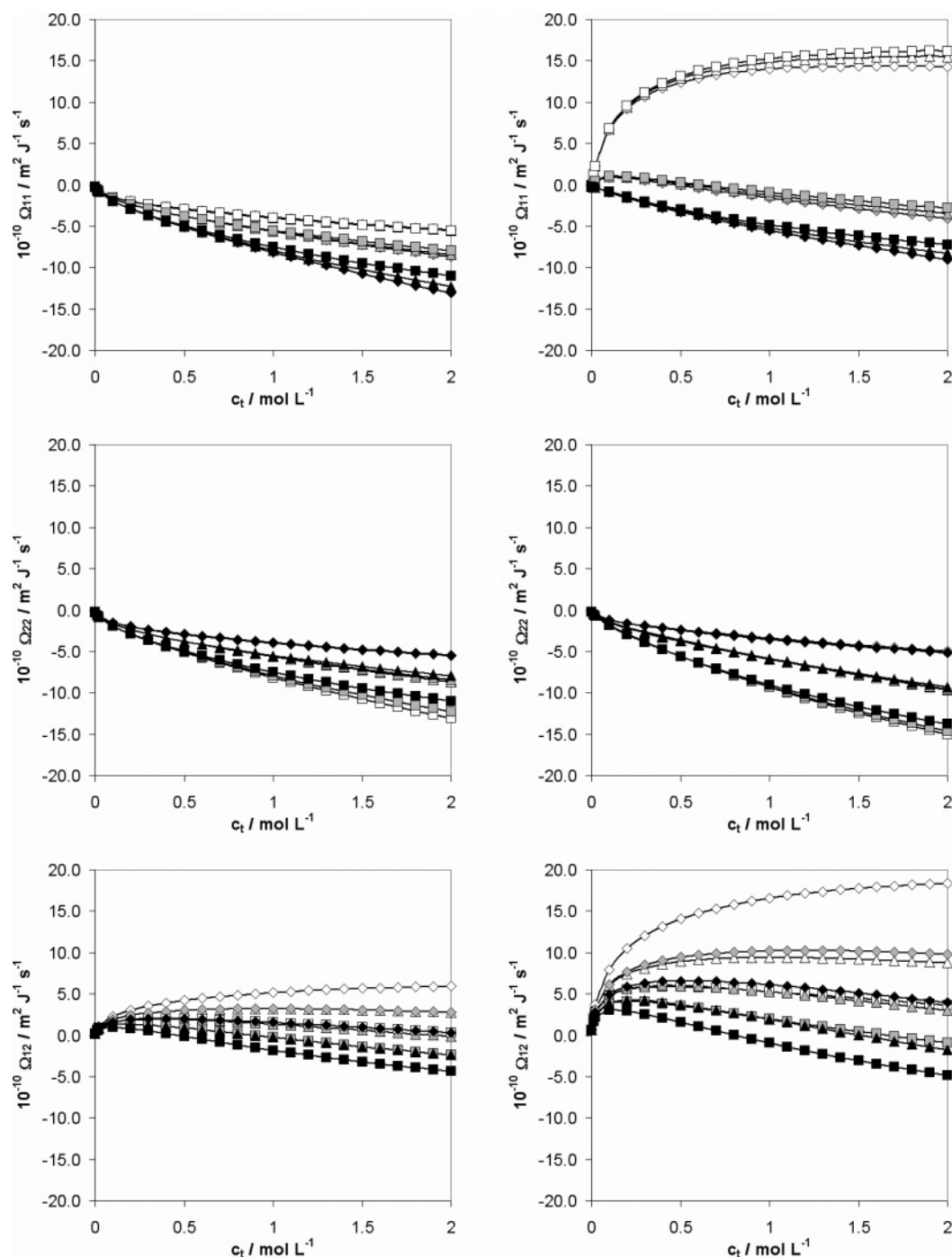
An analogue reasoning for the valency does not always hold. Increasing an ion's valency strengthens the electrostatic interaction and would reduce the osmotic coefficient. However, at constant total ion concentration, a change in valency implies a change in relative ion concentrations. Consequently, if the smaller ion's valency is increased, the hard sphere contribution will increase, because the balance tips to the side of the bigger ion and can overcome the stabilizing effect. This phenomenon is more likely to occur at high concentration, where the hard sphere repulsion is more important. In the theoretical examples, it is observed for  $\sigma_2 = 7.50$  Å,  $z_2 = -1$ , and  $\sigma_1 = 2.50$  Å when  $z_1$  is increased (the white squares curve in Figure 1).

The osmotic coefficient is an interesting quantity to fit effective diameters, because extensive data are available. The graphs clearly indicate that its sensitivity toward the diameter is enhanced at higher concentration and becomes better for bigger diameters. In practice, this would mean that the effective diameter of the more strongly hydrated  $\text{Li}^+$  ion can be more accurately fitted than the effective diameter of the  $\text{Na}^+$  ion. Sensitivity to the size is also improved if the counterion is large, so bromides would give more-accurate fittings than chlorides. Finally, if the counterion has a high valency, the osmotic coefficient is more sensitive, so sulfates would make more-suitable electrolytes than halides. However, care should always be taken for additional effects. For high valencies, ion association<sup>14</sup> may become important. In addition, bigger ions may have a high polarizability, which introduces an additional short-range attraction.

The effective diameter of an ion may slightly differ between electrolytes, because the molecular nature of the solvent is not taken into account by the hard sphere repulsion.<sup>3</sup> If the solvation shells of ions A and B can interpenetrate more than those of ions A and C, the effective diameter of ion A will be smaller in



**Figure 1.** Osmotic coefficient  $\phi$  of a 1–1 electrolyte (left) and a 3–1 electrolyte (right), as a function of the total ion concentration  $c_t$ . Legend is as follows:  $\sigma_1 = 2.5$  Å (white),  $\sigma_1 = 5.0$  Å (gray),  $\sigma_1 = 7.5$  Å (black);  $\sigma_2 = 2.5$  Å (diamonds),  $\sigma_2 = 5.0$  Å (triangles),  $\sigma_2 = 7.5$  Å (squares).



**Figure 2.** Hydrodynamic coefficients  $\Omega_{11}$ ,  $\Omega_{22}$ , and  $\Omega_{12}$  of a 1–1 electrolyte (left) and a 3–1 electrolyte (right), as a function of the total ion concentration  $c_t$ . Legend is the same as that described in Figure 1.

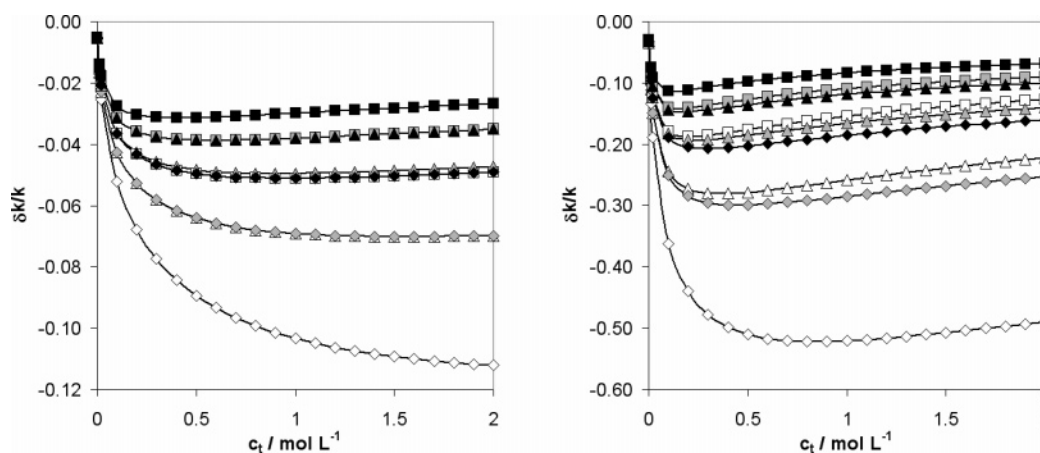
electrolyte AB than in AC. Still, a fitted diameter in one electrolyte will be acceptable in another electrolyte.

**The Hydrodynamic Interaction Coefficients.** The hydrodynamic interaction coefficients are plotted in Figure 2. At low concentrations, all hydrodynamic interaction coefficients go to zero, because the ions are far apart. Bigger ions have a lower  $\Omega_{12}$  and the same holds for  $\Omega_{ii}$ , with respect to the size of ion  $i$ . Both observations agree with the increased obstruction. The electrostatic component of  $\Omega_{12}$  intensifies this effect, because the electrostatic entraining fades as the centers of ions are prevented from getting close to each other. Similarly, the electrostatic terms of  $\Omega_{ii}$  are reduced. The lesser electrostatic restraining counteracts the stronger obstruction effect, but the change in the second-order term acts in accordance with it. The relative contribution of each term at different diameter, valency,

and total ion concentration is visualized in Table 1 for  $\Omega_{12}$  and in Table 2 for  $\Omega_{ii}$ . The parameter  $\Omega_{ii}$  is rather insensitive to the other ion's diameter. This phenomenon is because of the fact that  $\Omega_{ii}$  corresponds to the correlations between ions  $i$ : the influence of the other ions through the screening parameter  $\Gamma$  and the excluded volume fraction  $\tilde{X}_3$  is weak.

**The Relaxation Factors.** The relaxation factor  $-\kappa_q^2 G_{12}(\kappa_q)/3$  is examined (note that  $G_{12}(\kappa_q)$  diverges for  $c_t \rightarrow 0$ ). It equals the relaxation correction  $\delta k/k$  for the conductivity of a binary electrolyte.<sup>3,7</sup> In Figure 3, this relaxation correction is plotted for  $\kappa_q = \kappa_D/\sqrt{2}$ , which corresponds to the case of  $D_1^0 = D_2^0$ . The relaxation correction rapidly increases between  $10^{-3}$  mol/L and  $10^{-1}$  mol/L, because the neutralizing ion cloud becomes more compact and more effectively prevents the displacement





**Figure 3.** Relaxation correction  $\delta k/k$  of a 1–1 electrolyte (left) and a 3–1 electrolyte (right) as a function of the total ion concentration  $c_t$ . Legend is the same as that described in Figure 1.

**TABLE 1: Sign and Relative Magnitude<sup>a</sup> of the Electrostatic Terms ( $E_1$  and  $E_2$ ) and the Hard Sphere (HS) Terms of the Hydrodynamic Self-Interaction Coefficients**

$c_t^b$	$z_i^b$	$d_i^b$	$\Omega_{ii}^{(E_1)}$	$\Omega_{ii}^{(E_2)}$	$\Omega_{ii}^{(HS)}$
low	low	low	---	++	-
		high	---	+	--
	high	low	---	+++	-
high	low	high	---	++	-
		low	---	++	-
	high	high	---	+	---
		low	---	+++	-
	high	high	---	+	--

<sup>a</sup> The presence of one symbol indicates that it is the smallest term (in absolute value); the presence of three symbols indicates that it is the largest term. <sup>b</sup> The terms “high” and “low” should be viewed within the investigated range (see text).

**TABLE 2: Sign and Relative Magnitude<sup>a</sup> of the Electrostatic Terms ( $E_1$  and  $E_2$ ) and the Hard Sphere (HS) Terms of the Hydrodynamic Cross-Interaction Coefficients**

$c_t^b$	$z_i^{b,c}$	$d_i^{b,c}$	$\Omega_{ij}^{(E_1)}$	$\Omega_{ij}^{(E_2)}$	$\Omega_{ij}^{(HS)}$
low	low	low	+++	++	-
		high	+++	+	--
	high	low	+++	++	-
high	low	high	+++	+	--
		low	+++	++	-
	high	high	+++	+	---
		low	+++	++	-
		high	++	+	---

<sup>a</sup> The presence of one symbol indicates that it is the smallest term (in absolute value); the presence of three symbols indicates that it is the largest term. <sup>b</sup> The terms “high” and “low” should be viewed within the investigated range (see text). <sup>c</sup> Quantity of either ion  $i$  or  $j$ .

of the central ion. Beyond  $10^{-1}$  mol/L, the relaxation correction gradually levels off. Increasing the valency of the ions increases the relaxation correction in a similar manner. Bigger ions reduce the relaxation correction by expanding the neutralizing ion cloud. Analogue behavior was observed when  $D_1^0 \neq D_2^0$  and is also expected for multi-ion solutions, because the relaxation corrections involve terms similar to  $-\kappa_q^2 G_{12}(\kappa_q)/3$ .

## Conclusions

The present study provides a better understanding of the dependence of the equilibrium and transport properties of strong electrolytes on the ion diameters. The behavior of the osmotic coefficient, the hydrodynamic interaction coefficients, and the relaxation factors is explained for diameters in the range of 2.5–

7.5 Å, thereby covering most simple ions. It is shown that the osmotic coefficient makes a suitable quantity to fit effective diameters (e.g., for hydrated ions) at high total ion concentration, and guidelines are given to obtain more-accurate fittings.

All the curves clearly indicate that there are two concentration regimes. At very low concentration, the electrostatic interaction is predominant. This domain corresponds to the limiting laws, where the departures from the infinite dilution limit of the various ionic quantities are proportional to the square root of the electrolyte concentration. At higher concentration, the finite size of the ions must be taken into account. It strongly modifies the concentration dependence of the various equilibrium and transport coefficients: sometimes, it simply moderates the effect of the electrostatic interaction, but in many cases, it reverses it.

This study underlines the need of modern theories of electrolytes for concentrated solutions. Knowledge of the behavior of the equilibrium and transport properties, as a function of the concentrations, is essential to process optimization in electrochemical engineering. Because the concentrations are frequently on the order of 1 mol/L, limiting laws will be inadequate.

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