

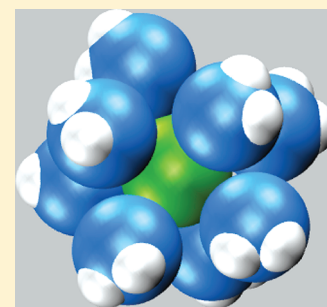
A Set of Molecular Models for Alkaline-Earth Cations in Aqueous Solution

Stephan Deublein,[†] Steffen Reiser,[†] Jadran Vrabec,[‡] and Hans Hasse^{*,†}

[†]Lehrstuhl für Thermodynamik, Technische Universität Kaiserslautern, 67653 Kaiserslautern, Germany

[‡]Lehrstuhl für Thermodynamik und Energietechnik, Universität Paderborn, 33098 Paderborn, Germany

ABSTRACT: New Lennard-Jones plus point charge models are developed for alkaline-earth cations. The cation parameters are adjusted to the reduced liquid solution density of aqueous alkaline-earth halide salt solutions at a temperature of 293.15 K and a pressure of 1 bar. This strategy is analogous to the one that was recently used for developing models for alkali and halide ions so that both model families are compatible. The force fields yield the reduced liquid solution density of aqueous alkaline-earth halide solutions in good agreement with experimental data over a wide range of salinity. Structural microscopic properties (i.e. radial distribution function and hydration number) are predicted in good agreement with experimental and quantum chemical data. The same holds for dynamic properties (i.e., hydration dynamics, self-diffusion coefficient and electric conductivity). Finally, the enthalpy of hydration of the salts in aqueous solution was favorably assessed.



1. INTRODUCTION

Aqueous electrolyte solutions play an important role in many natural processes and industrial applications. Their thermodynamic properties are dominated by the strong electrostatic interactions between the ions and the solvent molecules. In technical applications, however, not only the charges and ionic strengths are relevant, but the individual nature of the different ions is important, as well. Thus, most electrolyte solutions are outside of the regime that can be described with the approach by Debye and Hückel.¹ Therefore, different empirical extensions of the Debye–Hückel limiting law have been suggested,^{2–6} which consider the nonelectrostatic interactions between the ions. These models introduce a large number of adjustable parameters so that they often serve as correlation tools only. Molecular simulations of electrolyte solutions go far beyond these models. They allow for detailed insights into the properties of electrolyte solutions and for predictions of their properties. The prerequisites are accurate molecular force fields. The goal of the present study is the development of such models for alkaline-earth cations.

Force fields for alkaline-earth cations have been developed since the 1980s by different groups and have been used in various types of studies.^{7,8} The most common model type is a Lennard-Jones (LJ) sphere with the unit charge of magnitude +2e in its center. These models, hence, only differ with respect to their LJ parameters. Ion models for magnesium⁹ and calcium¹⁰ were developed from ab initio calculations and were evaluated regarding their ability to predict structural properties of solutions. Guardia et al.¹¹ extended the analysis to the potential of mean force, and Koneshan et al.¹² studied some of these models with respect to transport properties. Åqvist¹³ derived force fields for alkaline-earth cations on the basis of free energy perturbation theory. These force fields were further

improved under the label ff99¹⁴ and are part of the AMBER¹⁵ package.

Spangberg et al.¹⁶ developed two different molecular models for magnesium from ab initio calculations: one model explicitly considers three-body interactions, the other one explicitly considers polarization effects. For aqueous MgCl₂ solutions, both models describe the first hydration shell around the ions in good agreement with experimental data, but only the three-body model yields a reliable solvation enthalpy of the salt.¹⁶ Jiao et al.¹⁷ developed force fields for magnesium and calcium from ab initio calculations using a polarizable potential. For chloride solutions, these models reproduce the solvation free energy in good agreement with experimental data. For an aqueous CaCl₂ solution, the self-diffusion coefficient of the cation was also well predicted, whereas with the magnesium model, it was significantly underpredicted.¹⁷ Megyes et al.¹⁸ developed a simple LJ-based model for calcium in aqueous CaCl₂ solutions that yields the structural properties in good agreement with experimental values. Gavryushov et al.¹⁹ published effective ion potentials for all alkaline-earth chloride salts, neglecting the long-range contributions of the electrostatic interactions between the ions. These models were used for the calculation of thermodynamic properties (e.g. the activity coefficient¹⁹) describing the solvent implicitly.

This short literature survey shows that significant effort was spent on the development of force fields for some alkaline-earth cations; however, a comprehensive approach is still lacking.

In the present work, a set of molecular models for all non-radioactive alkaline-earth cations (i.e. Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺) was developed for aqueous solutions. The models follow

Received: February 10, 2012

Revised: April 3, 2012

Published: April 6, 2012



the classical approach; that is, they describe the ions by one LJ sphere with one superimposed point charge with a magnitude of +2e. This simple model type is supported by all common molecular simulation codes.^{20,21}

The LJ model parameters were adjusted to experimental data on the reduced liquid solution density of aqueous alkaline-earth halide solutions. This approach was used in preceding work for developing a set of molecular models for alkali and halide ions.²² Throughout the present study, the halide ion models were taken from that work,²² and water was described by the SPC/E model.²³ However, the results from our previous study²² suggest that the simulation results for the reduced liquid solution density do not strongly depend on the choice of the water model, and hence, the ion models presented here should also be applicable in combination with other water models. Section 2 introduces the parametrization method; in Section 3, details on the simulations of the studied properties are given. In Section 4, simulation results are shown for the density, structural, dynamic and caloric properties. Section 5 concludes the work.

2. FORCE FIELD DEVELOPMENT

The force field type employed in this study was the standard LJ 12-6 potential plus Coulombic interactions

$$u_{ij} = 4\epsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right) + \sum_{l=1}^{N_{C,i}} \sum_{m=1}^{N_{C,j}} \frac{q_l q_m}{4\pi\epsilon_0 r_{lm}} \quad (1)$$

where u_{ij} is the potential energy between the particles i and j with a distance r_{ij} between their LJ sites. σ_{ij} and ϵ_{ij} are the LJ parameters for size and energy, respectively; q_l and q_m are the charges of the solute or the solvent molecules that are at a distance r_{lm} ; and ϵ_0 is the vacuum permittivity. The indices l and m count the point charges, and the total number of charges of molecule i is denoted by $N_{C,i}$. Note that eq 1 is given in a form that includes the interactions with water. Throughout the present simulations, the Lorentz–Berthelot combining rules^{24,25} were applied for the unlike LJ interactions. Technical details of the employed simulation methods are given in the Appendix. Note that the employed simple force field does not explicitly capture the physical effect of polarization. This effect, however, is included in the force field by the parametrization strategy that was used for the force field development and that is introduced in detail the last part of this section.

The solvent water was modeled by the rigid, nonpolarizable force field SPC/E,²³ which consists of one LJ sphere and three point charges. It is widely used for molecular simulations of biomolecules, often in combination with the GROMOS force field.²⁶ The SPC/E water model yields decent agreement with the experimental liquid density of pure water at ambient conditions of $T = 293.15$ K and $p = 1$ bar.²²

The ions were modeled by one LJ sphere with one point charge of magnitude +2e in their center. The halide anion force fields are of the same type and were taken from preceding work.²² For the molar mass of all particles, the experimental values were used. For parametrization, the cation LJ size parameter σ_c was adjusted to reproduce the reduced liquid solution density, $\tilde{\rho}$, over salinity x at the temperature $T = 293.15$ K and the pressure $p = 1$ bar. Here, $\tilde{\rho}$ is defined by the density of the electrolyte solution, ρ , and the density of the pure solvent water, ρ_0 , at the same temperature, T , and pressure, p

$$\tilde{\rho} = \frac{\rho}{\rho_0} \quad (2)$$

These data were taken from the literature and were typically measured by vibrating tube densimeter or hydrometer. It was shown recently²² that the reduced density, $\tilde{\rho}$, depends only very weakly on the LJ energy parameter. Following the same approach here, the cation LJ energy parameter, ϵ_c , was set to $\epsilon_c/k_B = 200$ K for all models. This choice yields reasonable values for the osmotic coefficient of various alkali halide solutions.²⁷

The dependence of $\tilde{\rho}$ on x was approximated by a first-order Taylor expansion around the pure water ($x = 0$) state point

$$\tilde{\rho}(x) = \tilde{\rho}(x = 0) + \left. \frac{d\tilde{\rho}}{dx} \right|_{x=0} x + O^2 = 1 + mx + O^2 \quad (3)$$

The short notation m stands for the derivative of $\tilde{\rho}$ with respect to the salinity x (i.e. the mass fraction of the salt in solution) at infinite dilution and O^2 contains all higher order terms of the expansion. The quantity m is well accessible from experimental solution density data by simple derivation. Plots of these data show an almost linear behavior of $\tilde{\rho}(x)$ up to high salinities (cf. Figure 1). The mass fraction was used in the present work to specify the salinity rather than other common measures such as molality or ion strength because the linear range turns out to be particularly large when the mass fraction is used. Other advantages of this force field parametrization with respect to the reference $\tilde{\rho}$ were discussed in more detail before²² and are not repeated here.

For the present parametrization, the cation LJ size parameter, σ_c , was systematically varied between 1.5 and 4.5 Å with increments of 0.5 Å and regressed using a polynomial function. By molecular simulation with varying low salinity, the increase of the reduced density with increasing salinity in aqueous alkaline-earth solutions was determined. The parameter σ_c for the cations was subsequently adjusted to the derivative m of five solutions, namely, BeCl₂ (the only water-soluble beryllium salt), MgBr₂, CaBr₂, SrBr₂, and BaBr₂. Fluoride salts were not considered, since they are not soluble in water. Bromide salts were selected for the adjustment, since the employed bromide anion model was found to be very accurate for aqueous alkali bromide solutions.²² Mathematically, the adjustment leads to a single solution for all five cations. Although the ion force fields contain experimental information on only the five solutions mentioned above, they show good predictive capabilities with respect to other salt combinations containing alkaline-earth cations and halide anions (cf. Section 4). Note that a different parametrization strategy, a global fit of all ion parameters, was also feasible, but was not performed here (cf. Section 4).

3. STRUCTURAL, DYNAMIC AND CALORIC PROPERTIES

The electrolyte solutions were analyzed regarding structural properties of the solution, that is, the radial distribution function (RDF), $g_{i-o}(r)$, of water around the cation i ;²⁸ the hydration number, n_{i-o} ;²⁹ as well as the potential of mean force, w_{i-o} ,²⁸ between cation i and water. To study the dynamics in the liquid, the residence time, τ_o ; the self-diffusion coefficient, D_i ; and the electric conductivity, σ , of aqueous alkaline-earth solutions were evaluated. In addition, the enthalpy of hydration for the ions in solution was determined.

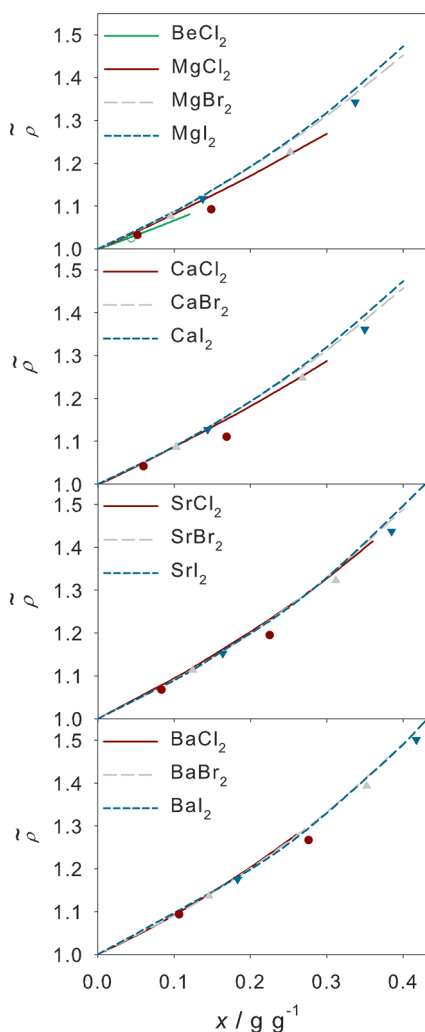


Figure 1. Reduced liquid solution density $\tilde{\rho}$ of aqueous solutions of different alkaline-earth halide salts over salinity at $T = 293.15\ K$ and $p = 1\ bar$. Present simulation data (symbols) are compared with correlations of experimental data³⁸ (lines).

Throughout these analyses, the position of water molecules was represented by the position of the oxygen site, O.

The RDF $g_{i-O}(r)$ of water around the ion i indicates the structure that the ion imposes onto the solution. This quantity is well-known from the literature²⁸ and is not further discussed here. The hydration number, n_{i-O} , quantifies the number of solvent molecules within a given distance around the ion i . It is defined by

$$n_{i-O} = 4\pi\rho_O \int_0^{r_{\min}} r^2 g_{i-O}(r) dr \quad (4)$$

where ρ_O is the number density of water and r_{\min} is the distance up to which the hydration number is calculated. To determine the hydration number within the first shell around the ion, the value $r_{\min,1}$ was chosen to be the distance of the first minimum of the RDF.²⁹

The residence time, τ_O , defines the average time span that a water molecule remains within a given distance, r_{i-O} , around an ion i . It is related to the following autocorrelation function¹²

$$\tau_O = \frac{1}{n_{i-O}} \int_0^\infty \sum_{k=1}^{n_{i-O}} \Theta_k(t) \Theta_k(0) dt \quad (5)$$

where Θ is the Heavyside step function which yields unity if a water molecule is paired with an ion, and t is the time. In this study, the residence time of water in the first hydration shell was determined. A water molecule and an ion were considered as paired when their mutual distance, r_{i-O} , was lower than the distance of the first RDF minimum, that is, $r_{i-O} < r_{\min,1}$. Following a proposal by Impey et al.,³⁰ unpairing was assumed when the separation $r_{i-O} > r_{\min,1}$ lasts more than 2 ps. However, a short-time pairing of two particles with $\tau_O < 2\ ps$ was fully accounted for in the calculation of τ_O .

The dynamics of water molecules leaving the first hydration shell was also characterized by the rate coefficient, k , which is simply the inverse of the residence time $k = 1/\tau_O$.

The potential of mean force, w_{i-O} , between the ion i and water can be derived from the orientationally averaged ion–water RDF by^{12,31,32}

$$w_{i-O}(r) = -\beta^{-1} \ln g_{i-O}(r) \quad (6)$$

where $\beta^{-1} = 1/(k_B T)$ and k_B is the Boltzmann constant. The energy difference between the first minimum of the potential of mean force and its first maximum, where the transition state is located, is the energy barrier that a water molecule has to overcome to leave the first hydration shell of the ion. Using transition state theory, the maximum rate coefficient, k^T , for water molecules leaving this shell can be determined according to^{12,31}

$$k^T = \sqrt{\frac{k_B T}{2\pi\mu}} \frac{\exp(-\beta w_{i-O}^{\text{eff}}(r^*))}{\int_0^{r^*} \exp(-\beta w_{i-O}^{\text{eff}}(r)) dr} \quad (7)$$

where $\mu = m_i m_O / (m_i + m_O)$ is the reduced mass of the ion–water pair and w_{i-O}^{eff} is the effective potential of mean force between ion and solvent. The distance r^* is set to the distance of the first maximum of the potential of mean force, since the hydration dynamics in the first hydration shell around the cation was targeted in this work. The effective potential of mean force is linked to w_{i-O} by an additional term that accounts for the increase of the potential of mean force with increasing volume and, hence, r according to^{12,31}

$$w_{i-O}^{\text{eff}}(r) = w_{i-O}(r) - 2k_B T \ln \frac{r}{r^*} \quad (8)$$

The maximum rate coefficient, k^T , from transition state theory is related to the rate coefficient, k , by the transmission coefficient, κ .

$$\kappa = \frac{k}{k^T} \quad (9)$$

In addition to hydration dynamics, the self-diffusion coefficient of the ions and the electric conductivity of the aqueous solutions were determined via equilibrium molecular dynamics (MD) simulations by means of the Green–Kubo formalism.³³ This formalism offers a direct relationship between transport coefficients and the time integral of the autocorrelation function of the corresponding fluxes within a fluid. Hence, the Green–Kubo expression for the self-diffusion coefficient, D_i , is based on the individual ion velocity autocorrelation function,³³

$$D_i = \frac{1}{3N_i} \int_0^\infty \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle dt \quad (10)$$

where $\mathbf{v}_k(t)$ is the center of mass velocity vector of ion k of species i at some time t . Equation 10 is an average over all N_i ions.

The electric conductivity, σ , is related to the time autocorrelation function of the electric current flux, $\mathbf{j}(t)$, and is given by³⁴

$$\sigma = \frac{1}{3Vk_B T} \int_0^\infty \langle \mathbf{j}(t) \cdot \mathbf{j}(0) \rangle dt \quad (11)$$

where V is the volume. The electric current flux is defined by the charge, q_k , of ion k and its velocity vector, \mathbf{v}_k , according to

$$\mathbf{j}(t) = \sum_{k=1}^{N_{\text{ion}}} q_k \cdot \mathbf{v}_k(t) \quad (12)$$

where N_{ion} is the number of ions in solution. Note that all ions in solutions have to be considered, but not the water molecules. For better statistics, σ was sampled over all three independent spatial elements of $\mathbf{j}(t)$. The electric current time autocorrelation function may be decomposed into the sum³⁵

$$\begin{aligned} \langle \mathbf{j}(t) \cdot \mathbf{j}(0) \rangle &= Z(t) + \Delta(t) \\ &= \sum_{k=1}^{N_{\text{ion}}} \langle q_k^2 \cdot \mathbf{v}_k(t) \cdot \mathbf{v}_k(0) \rangle \\ &\quad + \sum_{k=1}^{N_{\text{ion}}} \sum_{\substack{n=1 \\ n \neq k}}^{N_{\text{ion}}} \langle q_k q_n \cdot \mathbf{v}_k(t) \cdot \mathbf{v}_n(0) \rangle \end{aligned} \quad (13)$$

where $Z(t)$ is an autocorrelation function, and $\Delta(t)$ is a crosscorrelation function that quantifies the deviations from the ideal Nernst–Einstein behavior.^{29,35}

The first term, $Z(t)$, describes the mobility of the ions due to their self-diffusion in solution. Mathematically, it is simply the sum of the self-diffusion coefficients of all ion types in solution weighted by their charges. The second term, $\Delta(t)$, describes the correlated motion of the ions in solution. Correlated motions of ion pairs of opposite charges in solution lower the electric conductivity ($\Delta(t) < 0$), and correlated motions of ion pairs with the same charge enlarge σ ($\Delta(t) > 0$). The magnitude of the electric conductivity is highly dependent on solution salinity, x , and increases with higher x for low and medium salinities.

In addition, the enthalpy of hydration of the ions, Δh_{hyd} , was investigated. It is defined as the difference between the enthalpy of the ions dissolved in the aqueous solution at infinite dilution and the enthalpy of the salt in an artificial ideal gas reference state. Using molecular simulation, Δh_{hyd} is derived from the enthalpy, H , of the aqueous electrolyte solution and the enthalpy, H_{O} , of the pure solvent divided by the amount of salt in solution, n_s ³⁶

$$\Delta h_{\text{hyd}} = \frac{H - H_{\text{O}}}{n_s} - k_B T \quad (14)$$

The enthalpy of hydration was determined for all alkaline-earth halide salts individually.

4. RESULTS AND DISCUSSION

Model Parameters. The LJ size parameter values of the alkaline-earth cations determined in the present work are presented in Table 1. The order of the LJ size parameter for the cations is consistent with their order in the periodic table of

Table 1. Lennard-Jones Size Parameter σ for Alkaline-Earth Cations Determined in the Present Work and for Halide Anions Taken from Preceding Work²² That Were Used Here^a

ion	$\sigma/\text{\AA}$	q/e
Be ²⁺	1.69	+2
Mg ²⁺	1.77	+2
Ca ²⁺	2.58	+2
Sr ²⁺	2.69	+2
Ba ²⁺	3.12	+2
F ⁻	3.66	-1
Cl ⁻	4.41	-1
Br ⁻	4.54	-1
I ⁻	4.78	-1

^aThe LJ energy parameter was $\epsilon/k_B = 200$ K for all ions.

elements (i.e. Be²⁺ < Mg²⁺ < Ca²⁺ < Sr²⁺ < Ba²⁺). Note that the ionic radii of the ions differ slightly from experimentally determined ionic radii reported in the literature.³⁷ Similar observations were already reported for alkali halide ions, as well.

Reduced Liquid Solution Density. The present ion models were parametrized to reduced liquid solution density data of five alkaline-earth halide salts (BeCl₂, MgBr₂, CaBr₂, SrBr₂, and BaBr₂) at low salinity. These data were thus matched within the experimental accuracy (cf. Figure 1). At higher salinity as well as for all remaining eight electrolyte solutions, the present simulation results for $\bar{\rho}$ are predictive. Note that neither the alkaline-earth fluoride salts nor the beryllium halide salts are soluble in water, except for BeCl₂. For reference, Table 1 also contains the halide anion parameters.²²

For the alkaline-earth chloride salts in aqueous solution, the reduced liquid solution density is well predicted at low salinity. The deviations to experimental reduced solution density data are <1%. For higher salinity, the present force fields underestimate the experimental data.

For the alkaline-earth bromide salts in aqueous solution, the agreement with experimental data³⁸ is excellent throughout the entire salinity range (cf. Figure 1). This is not surprising for low salinity, since most of the ion parameters were adjusted to this property. However, also at high salinity, where the experimental data show a significantly nonlinear behavior, the agreement between simulation and experiment is very good.

With respect to the alkaline-earth iodide salts in aqueous solution, similar results were obtained for the reduced liquid solution density. The deviations between the simulation data and experimental values are below 1% over the entire salinity range (cf. Figure 1). Again, this has to be seen in the light of the fact that the alkaline-earth iodide salts show a nonlinear increase of the solution density with increasing salinity, which the present force fields are able to predict. Note that the good agreement for the aqueous alkaline-earth bromide and iodide solutions are due to the parametrization strategy of using only alkaline-earth bromide salts for the parameter adjustment. A global fit of the model parameters to all alkaline-earth halide salts was possible and would have yielded better results for alkaline-earth chloride salts; however, this improvement for these salts results in significantly higher deviations for the remaining salts. Since the deviations of the alkaline-earth chloride salts could not be mapped solely to the cation model parameters, that global parametrization strategy was not followed.

Table 2. Properties of Aqueous Electrolyte Solutions at $T = 293.15$ K and $p = 1$ bar Determined by Present Molecular Simulations: Distances of the First $r_{\max,1}$ and Second Maximum $r_{\max,2}$ As Well As First $r_{\min,1}$ and Second Minimum $r_{\min,2}$ of the Ion–Water RDF^a

salt	$r_{\max,1}$, Å	$r_{\min,1}$, Å	$r_{\max,2}$, Å	$r_{\min,2}$, Å	n_{i-O} (1 M)	n_{i-O} (3 M)	$-\Delta h_{\text{hyd}}$, kJ mol ⁻¹	$-\Delta h_{\text{hyd}}^{\text{exp}}$, kJ mol ⁻¹
BeCl ₂	2.0	2.3	4.2	4.9	6.5	5.4	2461(1)	3256
MgCl ₂	2.0	2.3	4.2	4.9	5.9	5.3	2462(1)	2683
MgBr ₂	2.0	2.3	4.2	4.9	5.8	5.4	2430(1)	2615
MgI ₂	2.0	2.3	4.2	4.9	5.9	5.3	2378(1)	2531
CaCl ₂	2.4	3.0	4.6	5.4	7.8	6.9	2147(1)	2339
CaBr ₂	2.4	3.0	4.6	5.4	7.9	7.4	2117(1)	2271
CaI ₂	2.4	3.0	4.6	5.4	7.8	7.5	2066(1)	2187
SrCl ₂	2.5	3.1	4.7	5.5	7.9	7.6	2111(1)	2205
SrBr ₂	2.5	3.1	4.7	5.5	8.0	7.3	2084(1)	2137
SrI ₂	2.5	3.1	4.7	5.5	8.0	7.9	2031(1)	2053
BaCl ₂	2.6	3.2	4.8	5.7	8.4	7.8	1972(1)	2067
BaBr ₂	2.6	3.2	4.8	5.7	8.3	7.7	1940(1)	1999
BaI ₂	2.6	3.2	4.8	5.7	8.4	8.2	1891(1)	1915

^aThe hydration numbers, n_{i-O} , are given for varying salinity in terms of the molality $x^{(M)}$. The enthalpy of hydration Δh_{hyd} is given at infinite dilution and compared with experimental data.³⁷ The number in parentheses indicates the statistical uncertainty in the last digit. The experimental mean distances between the ions and the oxygen atom of water in the first hydration shell are $r_{\max,1}^{\text{Be}^{2+}} = 1.75$ Å, $r_{\max,1}^{\text{Mg}^{2+}} = 2.1$ Å, $r_{\max,1}^{\text{Ca}^{2+}} = 2.4$ Å, $r_{\max,1}^{\text{Sr}^{2+}} = 2.6$ Å, and $r_{\max,1}^{\text{Ba}^{2+}} = 2.9$ Å.³⁹

Hydration Properties. After parametrization, all aqueous alkaline-earth solutions were analyzed regarding structural and dynamic solution properties. The investigated structural data are the RDF, $g_{i-O}(r)$,²⁸ of water around the ion i and the hydration number, n_{i-O} .²⁹ In addition, the potential of mean force, $w_{i-O}(r)$,³¹ between cation i and water was determined. Furthermore, an analysis with respect to the net charge, Q_i , around the cations was performed. However, these results contain little information, since for all cations, the net charge had not decayed to a constant value within the cubic simulation volume with an edge length of ≈ 13 Å that was used in the present study. Although charge compensation within the boundaries of the simulation volume is desirable, the simulation error induced by this mismatch should not be important, given that periodic boundary conditions were employed.

The analysis of the dynamic properties covered the hydration dynamics of the first hydration shell, that is, the residence time, τ_O , during which a water molecule remains within the first hydration shell as well as the rate and transmission coefficients k , k^T , and κ , respectively, which characterize the dynamics of water molecules leaving the first hydration shell. Throughout, the water molecules were represented by their oxygen atom, O.

The general trends are individually discussed for each alkaline-earth ion in the following, and the results are summarized in Tables 2 and 3. For all investigated alkaline-earth cations, the studied properties hardly change with the type of counterion in solution and salinity. For example, for the cation–water RDF, the positions of the first four extrema (i.e. two maxima and minima) were found to be constant, which is in good agreement with experimental data.^{39,40} A typical RDF of water around the cation Mg^{2+} in an aqueous MgCl_2 solution is shown in Figure 2 for two salinities. The first maximum of the RDF is located close to the ion. The peak is very high, reaching up to 20, which is roughly a factor of 2.5 higher than the maximum values observed for alkali cations of approximately the same size.²² The width of the first peak of the alkaline-earth RDF is small, on the order of 0.3 Å for small alkaline-earth ions and 0.6 Å for larger ones starting with Ca^{2+} . This is roughly half as wide as in the case of monovalent

Table 3. Properties of Aqueous Electrolyte Solutions at $T = 298.15$ K and $p = 1$ bar Determined by Present Molecular Simulations^a

ion, i	k/ps^{-1}	k^T/ps^{-1}	κ	$D_i/10^{-10} \text{ m}^2 \text{ s}^{-1}$
Be^{2+}	<0.0003	0.000		
Mg^{2+}	<0.0003	0.000		6.5(6)
Ca^{2+}	0.0076	0.059	0.13	7.7(3)
Sr^{2+}	0.0095	0.015	0.63	7.2(2)
Ba^{2+}	0.0249	0.026	0.95	7.9(2)

^aRate coefficient, k ; maximum rate coefficient determined by transition state theory k^T , transmission coefficient κ ; and self-diffusion coefficient D_i . The number in parentheses indicates the statistical uncertainty in the last digit.

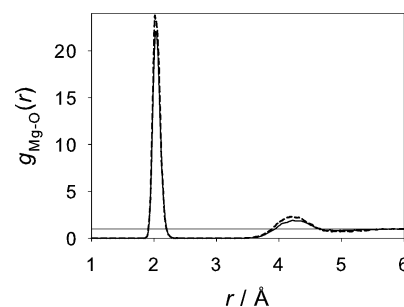


Figure 2. Radial distribution function around the magnesium cation Mg^{2+} in an aqueous MgCl_2 solution at $T = 293.15$ K and $p = 1$ bar for two salinities. Dashed line, $x_{\text{MgCl}_2} = 0.06$ g/g; solid line, $x_{\text{MgCl}_2} = 0.17$ g/g.

cations.²² This indicates a highly ordered structure around the cation that is caused by the electrostatic interactions between the cation and the solvent.

Because of the cation charge attraction, all water molecules in the first hydration shell are located in the closest vicinity around the cation that is sterically possible. As expected, the solvent molecules in the first hydration shell are oriented such that the negatively charged oxygen atom is directed toward the cation. This causes the very high peak of the RDF. The small width of

the first peak of the RDF can be explained by hindered solvent molecule motions. The electrostatic attraction not only inhibits translational motions of water molecules in form of leaving the first hydration shell but also constrains the rotational motions of the solvent molecules. The first peak of the RDF is followed by a broad minimum, where $g_{i-O}(r)$ is almost zero. The width of the minimum corresponds to the width of the first hydration shell, where the water molecules are constrained in their motions and solvent molecules from the bulk can hardly penetrate.

For all alkaline-earth cations, a second hydration shell was observed that is also quite pronounced (Figure 2). The peak of the second shell in the RDF reaches a value of 2 for MgCl_2 and is slightly lower for larger cations. After the second peak, the RDF decays rapidly to unity, showing almost no indication for the formation of a third hydration shell. The anion–water RDFs were found to be the same as reported for alkali halide solutions in preceding work.²²

Beryllium. The RDF of beryllium in aqueous BeCl_2 solutions exhibits the first maximum at a distance of 2.0 Å and the first minimum at 2.3 Å. Both values are larger by 0.3 Å than experimental data for the first maximum from X-ray diffraction⁴⁰ and ab initio calculations performed without counterions,⁴¹ indicating that the molecular model's attractive forces between ion and solvent are too weak. The second maximum of the RDF was found at a distance of 4.2 Å; the second minimum, at 4.9 Å. These results differ again from ab initio calculations by 0.4 Å.⁴¹ The hydration number for beryllium in the first shell was determined to be 5–6, which is higher than the experimental number of 4 water molecules around Be^{2+} .⁴⁰ The residence time exceeds the total simulation time of 3 ns that was used in the present work, which is in agreement with earlier MD studies.⁴² This high residence time in the proximity of the Be^{2+} ion is due to the very strong electrostatic attraction between this cation and the solvent. The energy barrier that a water molecule needs to overcome for leaving the first hydration shell could not be determined explicitly due to the lack of trajectories that show leaving water molecules. These results indicate that the structure around the beryllium cation is very static. Structural disorder occurs only in the second hydration shell and in the bulk solvent.

Magnesium. For magnesium cations, the first maximum of the RDF was determined at a distance of 2.0 Å, the first minimum at 2.3 Å. This is in agreement with experimental data from X-ray diffraction, which indicate an average ion–water distance of 2.1 Å,^{40,43} as well as in agreement with ab initio calculations performed without counterions, which determined the distance to be 2.1 Å, as well.⁴⁴ The maximum of the second shell was found to be at a distance of 4.2 Å from the ion; the second minimum, at 4.9 Å. The first shell hydration number was almost constant at a value of 5.3–5.9 water molecules around the cation, independent of counterion type and salinity. Experimentally, a hydration number of 6 was observed.^{39,45} Regarding the dynamics of the system, the behavior is similar to the Be^{2+} cation. The water residence time could not be determined for Mg^{2+} within the total simulation time of 3 ns, which is again caused by the strong electrostatic attraction between the cation and water molecules. Therefore, the results for the maximum rate constant for a water molecule leaving the first hydration shell from transition state theory, k^T , could not be determined. The energy barrier associated with a water molecule leaving the first hydration shell was found to be $>8 k_B T$.

Calcium. For the calcium cation, the first maximum and the first minimum of the RDF are shifted to larger distances due to the larger size of Ca^{2+} , being 2.4 and 3.0 Å, respectively. This is in agreement with experimental data, which locate the first maximum at 2.4 Å,⁴⁰ and ab initio calculations performed without counterions, which determined the distance to be 2.5 Å.⁴⁶ The second extrema of the RDF are located at distances of 4.6 and 5.4 Å, respectively, which match the ab initio distance of 4.6 Å for the second maximum excellently.⁴⁶ The increase in the RDF peak width, especially for the first one, indicates that the water structure around Ca^{2+} is less ordered than in the case of smaller alkaline-earth ions. The hydration number for calcium in solution with small anions showed a dependence on salinity, ranging between 6 and 7.5 water molecules in the first hydration shell. For large counterions, such as bromide and iodide, the hydration number remained almost constant between 7.5 and 8. This large hydration number is in very good agreement with experimental work that determined the number of water molecules in the first hydration shell to be 8.³⁹ On average, a water molecule remained within the first hydration shell around the cation for 131 ps. To leave the shell, an energy barrier of roughly $6 k_B T$ had to be overcome, which leads to a minimum rate coefficient of $k_T = 0.059 \text{ ps}^{-1}$. For the present model, the transmission coefficient was determined to be $\kappa \approx 0.13$.

Strontium. The RDF of water around strontium exhibits the first maximum at a distance of 2.5 Å from the ion, which is close to the experimentally observed value of 2.6 Å^{39,47} and is in excellent agreement with ab initio calculations performed without counterions.⁴⁸ The first minimum was observed at 3.1 Å. The locations of the second extrema of the RDF were determined to be 4.7 and 5.4 Å, respectively. The peak is slightly smaller than observed by ab initio calculations.⁴⁸ The hydration number in the first shell of Sr^{2+} was calculated to be $n_{i-O} \approx 8$, which is in excellent agreement with the experimental data at high salinity, being 7.9–8.⁴⁰ The hydration number showed no dependence on counterion type and salinity. On average, a water molecule remained in the first hydration shell of strontium for 105 ps. For an exchange of a water molecule in the first shell, an energy barrier of roughly $6 k_B T$ had to be overcome. The maximum rate of water molecule replacements in the first shell was determined to be 0.015 ps^{-1} , resulting in a transmission coefficient of $\kappa = 0.63$.

Barium. For barium, the first maximum of the RDF was found at 2.6 Å, and the first minimum, at 3.2 Å. These values differ from experimental data by 0.2–0.33 Å.^{39,49} Ab initio calculations performed without counterions suggest a maximum of 2.8 Å.⁵⁰ The following extrema in the RDF were determined to be at 4.8 and 5.7 Å. The hydration number was 8, independent of counterion type and salinity. The residence time of water molecules within the first shell was 40 ps. Removing a water molecule from the first shell is associated with an energy barrier of roughly $5.5 k_B T$, and the rate constant was 0.026 ps^{-1} , resulting in a transmission coefficient close to unity.

Self-Diffusion Coefficient. For all alkaline-earth cations in aqueous chloride solutions, the self-diffusion coefficient, D_i , was determined at $T = 298.15 \text{ K}$ and $p = 1 \text{ bar}$. Here, the different electrolyte solutions contain a constant number of cations ($x_{\text{MgCl}_2} = 0.03 \text{ g/g}$, $x_{\text{CaCl}_2} = 0.04 \text{ g/g}$, $x_{\text{SrCl}_2} = 0.05 \text{ g/g}$ and $x_{\text{BaCl}_2} = 0.07 \text{ g/g}$). The self-diffusivity is a measure for the ion mobility in solution and is therefore highly influenced by the

ion–solvent interactions and hence, the water force field, which was SPC/E²³ in this study. Due to the strong ion–solvent attraction, ions do not diffuse in solution as single particles, but together with the water molecules in their first shell. The ion–water complex can be described by a sphere with an effective radius that increases with stronger attractive forces between ion and water molecules. Within the complex, ion motion is short-ranged and fast, but does not contribute significantly to the ion self-diffusion coefficient.³⁰ A typical velocity autocorrelation function observed for an aqueous CaCl_2 solution is shown in Figure 3. Here, the motion of the water molecules in the first

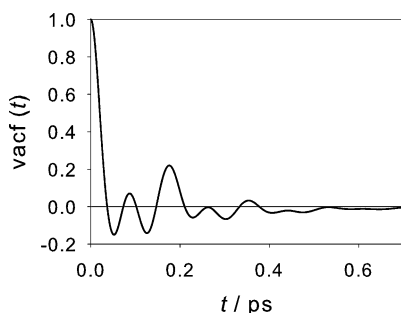


Figure 3. Normalized velocity autocorrelation function (vacf) of calcium Ca^{2+} in an aqueous CaCl_2 solution ($x_{\text{CaCl}_2} = 0.04$ g/g) at $T = 298.15$ K and $p = 1$ bar.

hydration shell with respect to the bulk water and the motion of the ion relative to its hydration shell contribute to the total motion of the Ca^{2+} cation. According to Impey et al.,³⁰ the oscillations of the velocity autocorrelation function indicate a faster motion of the ion within its first hydration shell.

Overall, the self-diffusion coefficient of the cations agrees well with experimental data⁵¹ (Figure 4 and Table 3). The

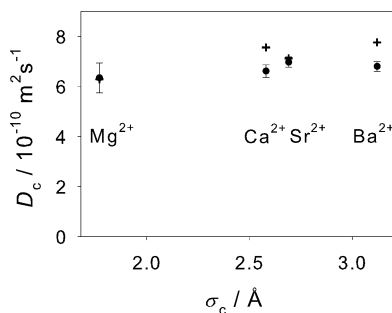


Figure 4. Self-diffusion coefficient of alkaline-earth cations in aqueous solutions containing a constant number of cations ($x_{\text{MgCl}_2} = 0.03$ g/g, $x_{\text{CaCl}_2} = 0.04$ g/g, $x_{\text{SrCl}_2} = 0.05$ g/g, and $x_{\text{BaCl}_2} = 0.07$ g/g) at $T = 298.15$ K and $p = 1$ bar: present simulation results (●) are compared with experimental data (+).⁵¹

diffusion coefficient shows only little dependence on the cation size, which is in agreement with experimental data. This independence is due to the hydration dynamics around the ions. Smaller cations are supposed to diffuse faster in solution; however, the attractive forces that these ions exert on the water molecules are larger. Thus, solvent molecules are more attached to the ion, forming a stable ion–water complex with a large effective radius. For large cations, the electrostatic attraction between ion and water is less dominant. However, because of their large diameter, the effective radius of the hydration sphere

is very similar to the one of small cations so that D_i does not significantly depend on the alkaline-earth cation species in aqueous solutions.

Electric Conductivity. The electric conductivity, σ , was determined for aqueous MgCl_2 and BaCl_2 solutions for varying salinity at ambient conditions to study the cation size dependence of σ . These two salts were chosen because sufficient experimental data are available. The agreement with experimental data^{29,52} is excellent (Figure 5). For salinities of

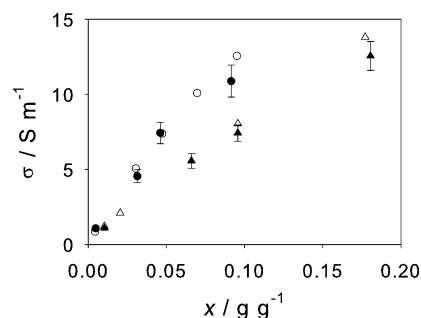


Figure 5. Electric conductivity σ as a function of salinity in aqueous MgCl_2 (●) and BaCl_2 (▲) solutions at $T = 298.15$ K and $p = 1$ bar. Simulation results (solid symbols) are compared with experimental data (open symbols).^{29,52}

up to 0.09 g/g for MgCl_2 and 0.18 g/g for BaCl_2 , the deviations are below 13%. The calculation of σ by molecular simulation gives further insight into the dynamics of the ions in solution. By separating the electric conductivity into the two terms according to eq 13, the contribution of the correlated ion motions was determined. This analysis was performed for aqueous MgCl_2 and BaCl_2 solutions containing a constant number of cations ($x_{\text{MgCl}_2} = 0.09$ g/g and $x_{\text{BaCl}_2} = 0.18$ g/g). The results of this analysis are discussed below and are shown in Figures 6 and 7.

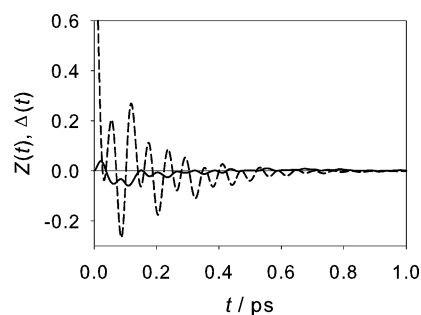


Figure 6. Electric current time autocorrelation function of MgCl_2 in aqueous solution ($x_{\text{MgCl}_2} = 0.09$ g/g) at $T = 298.15$ K and $p = 1$ bar separated into its contributions: velocity autocorrelation function $Z(t)$ (dashed line), velocity crosscorrelation function $\Delta(t)$ (solid line).

Magnesium. For very short times ($t < 0.01$ ps), the crosscorrelation, $\Delta(t)$, is positive. This is due to the random motions of the cation within its first hydration shell, which are dominated by the interactions of the cation with its nearest water molecules only. These motions are superimposed by the correlated motions of the cation with the anion due to their electrostatic attraction. For the chloride anion, the correlated motions are fully developed and show a characteristic behavior that is dominated by electrostatic repulsion. Hence, $\Delta(t)$ is

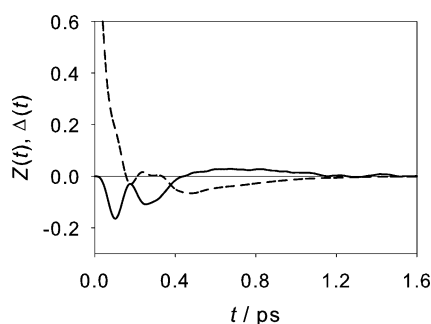


Figure 7. Electric current time autocorrelation function for BaCl_2 in aqueous solution ($x_{\text{BaCl}_2} = 0.18$ g/g) at $T = 298.15$ K and $p = 1$ bar separated into its contributions: velocity autocorrelation function, $Z(t)$ (dashed line), and velocity crosscorrelation function, $\Delta(t)$ (solid line). Note that the vertical scale is the same as in Figure 6.

positive. For longer times, the cage motions of Mg^{2+} are superimposed by the characteristic long time motion of the ion grouped with its hydration shell. $\Delta(t)$ is negative in this case, indicating the expected correlated motions of anion and cation. The rapid motions of Mg^{2+} within its hydration shell lead to oscillations of $\Delta(t)$ over time that are depicted in Figure 6 and that can also be seen for $Z(t)$. Within 0.8 ps, Mg^{2+} shows eight changes in direction due to the interactions with its hydration shell.

Barium. In aqueous BaCl_2 solutions, the oscillations of $Z(t)$ and $\Delta(t)$ are less pronounced (Figure 7), since the motions of larger cations within their first hydration shell are less rapid. Looking at the motions of the anions and the cations in detail, correlated motions of oppositely charged ions ($\Delta(t) < 0$) were observed only for short times ($t < 0.44$ ps). At longer times, $\Delta(t)$ is positive, which indicates correlated motions of ions of the same charge. The strong attractive forces between oppositely charged ions lead to a frequent exchange of the interaction partners in terms of correlated motions. Hence, $\Delta(t)$ is dominated for longer times by correlated motions of ions of the same charge, which is attributed to electrostatic repulsion.

Comparing the behavior of the ions, correlated motions of oppositely charged ions ($\Delta(t) < 0$) were observed in both of the studied aqueous alkaline-earth chloride solutions. For MgCl_2 , the absolute value of $\Delta(t)$ is significantly smaller than in the case of BaCl_2 . Correlated motions of ions highly depend on the ability of the anions to replace water molecules in the hydration shell of the alkaline-earth cations. For both cations, no chloride ions were observed in the first hydration shell. In this case, the correlated motions of the ions were caused by interactions between ions that are separated by one or more water molecules. For Mg^{2+} , the strong attraction between cation and water molecules in the second hydration shell inhibits a continuous exchange of water molecules. Hence, the chloride anion is not able to replace water molecules in the second hydration shell, and therefore, correlated motions are unlikely to occur. In contrast, there is more exchange of water molecules around the Ba^{2+} cation, and thus, correlated motions are more pronounced.

Enthalpy of Hydration. The enthalpy of hydration of alkaline-earth salts in aqueous solutions was determined. The results were obtained from molecular simulation at low salinity (10 cations, 20 anions, and 970 water molecules) at $T = 298.15$ K and $p = 1$ bar and are summarized in Table 2. The agreement

between data from simulation and experiment³⁷ is good for all salts, except for BeCl_2 , in which also some deviations for the structural properties were found. For the remaining salts, the deviations are below 10%, which is roughly the accuracy of the experimental data.³⁷ The deviations decrease with increasing ion size, which is not surprising, because for these solutions also, a better agreement with respect to the reduced solution density and other thermodynamic and structural data was achieved. The ion force fields also correctly predict the qualitative trend that the enthalpy of hydration decreases with increasing ion size.

5. CONCLUSIONS

Molecular models for the alkaline-earth ions based on the LJ approach with a superimposed point charge were developed. The force fields were parametrized using experimental data on the reduced liquid solution density of five electrolyte solutions, mainly containing the bromide anion at low salinity. These density data were reproduced exactly.

The present force fields can be applied in any mutual combination for the alkaline-earth halide salts. This was shown by predictive calculations using the reduced liquid solution density as a reference. The present simulations showed excellent agreement with experimental data for all studied aqueous electrolyte solutions at low salinity. At high salinity, the present force fields were also found to be very accurate for alkaline-earth bromides and iodides, whereas for alkaline-earth chloride solutions, the deviations from experimental density data were more significant.

The force fields were also investigated with respect to structural and dynamic properties. For the RDF and the hydration number, very good agreement was found for all electrolyte solutions, except for BeCl_2 . In this case, the attractive forces between the solvent and the ion model seem to be too strong, and hence, the ordering around the cation was overpredicted. For all cations, the RDF clearly indicated two hydration shells that are strongly developed. In the first shell, a very stable structure around the cations was observed. The oxygen atoms of the surrounding water molecules are oriented toward the cation, and their rotational motions are hindered by strong electrostatic attraction with the cation. The second shell is located 4–5 Å from the cation. There, the influence of the cation onto the solution is weaker; however, it is still significant.

Calculations of the potential of mean force suggest that the exchange of water molecules from the first to the second shell is hindered by a large energy barrier. This barrier decreases with increasing cation size and ranges between $\approx 6 k_B T$ and $> 8 k_B T$. The height of the energy barrier correlates with the hydration dynamics, that is, the residence time of water molecules in the first hydration shell increases with a higher energy barrier, and the rate coefficient decreases.

The cation mobility in solution was studied by means of the self-diffusion coefficient. For all alkaline-earth cations in aqueous halide solutions, the self-diffusion coefficient is in good agreement with the experimental data. The deviations from experimental data are $< 15\%$. The self-diffusion coefficient of the cations showed hardly any dependence on the ion size, which is in agreement with experimental observations.

The electric conductivity was determined for aqueous MgCl_2 and BaCl_2 solutions over a wide range of salinity. The agreement with experimental data is excellent. For both solutions, the influence of the cation size on the auto- and the crosscorrelation contribution to the electric conductivity

was investigated. This analysis showed the ion size dependence of the electric conductivity. For small cations, the ion motions tend to be highly correlated with the counterion. This behavior, however, is superimposed by short-range ion motions within their first hydration shell, especially at short times. For large cations, the correlated motions are similar for short times but are different for long times. This is attributed to the short lifetime of correlated motions of oppositely charged ions and the long-term electrostatic repulsion of evenly charged ions.

The solution was further studied with respect to the enthalpy of hydration. This quantity was predicted for all alkaline-earth halide solutions and also shows a very good agreement with experimental data, being mostly within the combined error bars.

■ APPENDIX

The present simulation study was performed with an extended version of ms2.⁵³ For the static properties, the classical Monte Carlo (MC) method was employed. In MC, all simulations were performed in the isothermal–isobaric (NpT) ensemble at 293.15 K and 1 bar. Electrostatic long-range contributions were considered by Ewald summation⁵⁴ with a real space convergence parameter $\kappa = 5.6$. The ions and the solvent molecules were initially placed onto a face-centered cubic lattice in random order. A physically reasonable configuration was obtained by 5000 equilibration loops in the canonical ensemble, followed by 80 000 relaxation loops in the NpT ensemble. Thermodynamic averages were obtained over 500 000 loops. Each loop consisted of $N_{\text{NDF}}/3$ steps, where N_{NDF} indicates the total number of mechanical degrees of freedom of the system. Configurations of the system were saved every 500 loops, which were used for the calculation of the RDF via postprocessing. For the calculation of dynamic properties of the aqueous electrolyte solutions, MD simulations were performed. The self-diffusion coefficient of the ions and the electric conductivity of the solution were calculated with the Green-Kubo formalism.^{33,34} First, the density of the electrolyte solution was determined by a NpT simulation at the desired temperature and pressure. Subsequently, the self-diffusion coefficient was sampled in the canonic (NVT) ensemble at the temperature and the density resulting from the first step. The sampling length of the velocity, and the electric current correlation functions was set to 11 ps and the separation between the origin of two autocorrelation functions was 0.06 ps. Within this time span, all autocorrelation functions decayed to less than $1/e$ of their normalized value.

For all simulations in the NpT ensemble, a physically reasonable configuration was attained by 10 000 steps in the NVT ensemble and 100 000 steps in the NpT ensemble, followed by a production run over 500 000 time steps. For simulations in the NVT ensemble, the equilibration was performed over 100 000 steps, followed by a production run of 1 800 000 and 2 400 000 time steps for the determination of the self-diffusion coefficient and the electric conductivity, respectively. Newton's equations of motion were solved with a Gear predictor-corrector scheme of fifth order with a time step of 1.2 ps. The MD unit cell with periodic boundary conditions contained 4500 molecules. For the calculation of the self-diffusion coefficient, the simulation volume contained 4419 water molecules, 27 alkaline-earth ions, and 54 chloride ions. The electric conductivity was determined for different salinities. Hence, the number of alkaline-earth ions in the simulation volume varied from 4 to 81. The electrostatic long-range

contributions were considered in the same way as in the case of the MC simulations.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hans.hasse@mv.uni-kl.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support for the project by BMBF “01H08013A - Innovative HPC-Methoden und Einsatz für hochskalierbare Molekulare Simulation” and computational support by the Steinbuch Centre for Computing under the grant LAMO as well as the High Performance Computing Center Stuttgart (HLRS) under the grant MMHBF 2. The present research was conducted under the auspices of the Boltzmann-Zuse Society of Computational Molecular Engineering (BZS).

■ REFERENCES

- (1) Debye, P.; Huckel, E. *Phys. Z.* **1923**, *24*, 185–206.
- (2) Chen, C. C.; Britt, H. I.; Boston, J. F.; Evans, L. B. *AIChE J.* **1982**, *28*, 588–596.
- (3) Chen, C. C.; Evans, L. B. *AIChE J.* **1986**, *32*, 444–454.
- (4) Pitzer, K. S. *J. Phys. Chem.* **1973**, *77*, 268–277.
- (5) Pitzer, K. S.; Mayorga, G. J. *J. Phys. Chem.* **1973**, *77*, 2300–2308.
- (6) Pitzer, K. S.; Mayorga, G. J. *Solution Chem.* **1974**, *3*, 539–546.
- (7) Sambriski, E. J.; Schwartz, D. C.; de Pablo, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 18125–18130.
- (8) Shi, W.; Inamdar, M. V.; Sastry, A. M.; Lastoskie, C. M. *J. Phys. Chem. C* **2007**, *111*, 15642–15652.
- (9) Dietz, W.; Riede, W. O.; Heinzinger, K. *Z. Naturforsch., A: Phys. Sci.* **1982**, *37*, 1038–1048.
- (10) Probst, M. M.; Radnai, T.; Heinzinger, K.; Bopp, P.; Rode, B. M. *J. Phys. Chem.* **1985**, *89*, 753–759.
- (11) Guardia, E.; Robinson, A.; Padro, J. A. *J. Chem. Phys.* **1993**, *99*, 4229–4230.
- (12) Koneshan, S.; Rasaiah, J. C.; Lynden-Bell, R. M.; Lee, S. H. *J. Phys. Chem. B* **1998**, *102*, 4193–4204.
- (13) Aqvist, J. *J. Phys. Chem.* **1990**, *94*, 8021–8024.
- (14) Cornell, W. D.; Cieplak, P.; Bayly, C. I.; Gould, I. R.; Merz, K. M.; Ferguson, D. M.; Spellmeyer, D. C.; Fox, T.; Caldwell, J. W.; Kollman, P. A. *J. Am. Chem. Soc.* **1995**, *117*, 5179–5197.
- (15) Ponder, J. W.; Case, D. A. *Protein Simul.* **2003**, *66*, 27–85.
- (16) Spangberg, D.; Hermansson, K. *J. Chem. Phys.* **2004**, *120*, 4829–4843.
- (17) Jiao, D.; King, C.; Grossfield, A.; Darden, T. A.; Ren, P. Y. *J. Phys. Chem. B* **2006**, *110*, 18553–18559.
- (18) Megyes, T.; Bako, I.; Balint, S.; Grosz, T.; Radnai, T. *J. Mol. Liq.* **2006**, *129*, 63–74.
- (19) Gavryushov, S.; Linse, P. *J. Phys. Chem. B* **2006**, *110*, 10878–10887.
- (20) Towhee; <http://www.towhee.sourceforge.org>. 2008.
- (21) Hess, B.; Kutzner, C.; van der Spoel, D.; Lindahl, E. *J. Chem. Theory Comput.* **2008**, *4*, 435–447.
- (22) Deublein, S.; Vrabec, J.; Hasse, H. *J. Chem. Phys.* **2012**, *136*, 0884501.
- (23) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. *J. Phys. Chem.* **1987**, *91*, 6269–6271.
- (24) Lorentz, H. *Annal. Phys.* **1881**, *248*, 127–136.
- (25) Berthelot, D. C. *R. Acad. Sci.* **1898**, *126*, 1703–1706.
- (26) Christen, M.; Hunenberger, P. H.; Bakowies, D.; Baron, R.; Burgi, R.; Geerke, D. P.; Heinz, T. N.; Kastenholz, M. A.; Krautler, V.; Oostenbrink, C.; Peter, C.; Trzesniak, D.; Van Gunsteren, W. F. *J. Comput. Chem.* **2005**, *26*, 1719–1751.

- (27) Deublein, S.; Reiser, S.; Vrabec, J.; Hasse, H. in preparation, 2012.
- (28) Allen, M.; Tildesley, D. *Computer Simulation of Liquids*; Clarendon Press: Oxford, 1987.
- (29) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworth: London, 1955.
- (30) Impey, R. W.; Madden, P. A.; McDonald, I. R. *J. Phys. Chem.* **1983**, *87*, 5071–5083.
- (31) Ciccotti, G.; Ferrario, M.; Hynes, J. T.; Kapral, R. *J. Chem. Phys.* **1990**, *93*, 7137–7147.
- (32) Rey, R.; Hynes, J. T. *J. Phys. Chem.* **1996**, *100*, 5611–5615.
- (33) Gubbins, K. *Statistical Mechanics*; The Chemical Society Burlington House: London, 1972; Vol. 1.
- (34) Hansen, J. P.; McDonald, I. *Theory of Simple Liquids*; Academic Press: Amsterdam, 1986.
- (35) Del Popolo, M. G.; Voth, G. A. *J. Phys. Chem. B* **2004**, *108*, 1744–1752.
- (36) Chandrasekhar, J.; Jorgensen, W. L. *J. Chem. Phys.* **1982**, *77*, 5080–5089.
- (37) Riedel, E. *Allgemeine und Anorganische Chemie*, 10th ed.; Gruyter: Berlin, 2010.
- (38) Weast, R. *Handbook of Chemistry and Physics*, 68th ed.; CRC Press: Boca Raton, 1987.
- (39) Marcus, Y. *Chem. Rev.* **1988**, *88*, 1475–1498.
- (40) Ohtaki, H.; Radnai, T. *Chem. Rev.* **1993**, *93*, 1157–1204.
- (41) Azam, S. S.; Hofer, T. S.; Bhattacharjee, A.; Lim, L. H. V.; Pribil, A. B.; Randolph, B. R.; Rode, B. M. *J. Phys. Chem. B* **2009**, *113*, 9289–9295.
- (42) Masia, M.; Rey, R. *J. Chem. Phys.* **2005**, *122*, 094502.
- (43) Caminiti, R.; Licheri, G.; Piccaluga, G.; Pinna, G. *J. Appl. Crystallogr.* **1979**, *12*, 34–38.
- (44) Tongraar, A.; Rode, B. M. *Chem. Phys. Lett.* **2005**, *409*, 304–309.
- (45) Smirnov, P. R.; Trostin, V. N. *Russ. J. Gen. Chem.* **2008**, *78*, 1643–1649.
- (46) Schwenk, C. F.; Rode, B. M. *Pure Appl. Chem.* **2004**, *76*, 37–47.
- (47) Caminiti, R.; Musinu, A.; Paschina, G.; Pinna, G. *J. Appl. Crystallogr.* **1982**, *15*, 482–487.
- (48) Hofer, T. S.; Randolph, B. R.; Rode, B. M. *J. Phys. Chem. B* **2006**, *110*, 20409–20417.
- (49) Persson, I.; Sandstroem, M.; Yokoyama, H.; Chaudhry, M. Z. *Naturforsch., A: Phys. Sci.* **1995**, *50*, 21–37.
- (50) Hofer, T. S.; Rode, B. M.; Randolph, B. R. *Chem. Phys.* **2005**, *312*, 81–88.
- (51) Mills, R.; Lobo, V. *Self-Diffusion in Electrolyte Solutions*; Elsevier: New York, 1989.
- (52) Than, A.; Amis, E. J. *Inorg. Nucl. Chem.* **1969**, *31*, 1685–1695.
- (53) Deublein, S.; Eckl, B.; Stoll, J.; Lishchuk, S. V.; Guevara-Carrion, G.; Glass, C. W.; Merker, T.; Bernreuther, M.; Hasse, H.; Vrabec, J. *Comput. Phys. Commun.* **2011**, *182*, 2350–2367.
- (54) Ewald, P. P. *Annal. Phys.* **1921**, *64*, 253–287.