Molecular dynamics simulations of concentrated aqueous electrolyte solutions

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(Received 18 May 2010; final version received 17 September 2010)

Transport properties of concentrated electrolytes have been analysed using classical molecular dynamics simulations with the algorithms and parameters typical of simulations describing complex electrokinetic phenomena. The electrical conductivity and transport numbers of electrolytes containing monovalent (KCl), divalent (MgCl2), a mixture of both (KCl + MgCl2) and trivalent (LaCl3) cations have been obtained from simulations of the electrolytes in electric fields of different magnitude. The results obtained for different simulation parameters have been discussed and compared with experimental measurements of our own and from the literature. The electroosmotic flow of water molecules induced by the ionic current in different cases has been calculated and interpreted with the help of the hydration properties extracted from the simulations.

Keywords: electrokinetic phenomena; ionic transport; electroosmotic flow; molecular dynamics

1. Introduction

Understanding the transport properties of electrolytes in aqueous solution is important in a wide range of electrokinetic phenomena such as streaming current experiments [1], ionic transport in biological and synthetic nanochannels [2,3] or colloidal electrophoresis [4,5].

Traditionally, electrokinetic and ionic transport phenomena have been described using primitive models in which the solvent is approximated as a continuum of dielectric constant \( \varepsilon \). Although such models provide an accurate description of a wide variety of phenomena, they fail for cases in which the discrete nature of the solvent plays a fundamental role, or to describe phenomena related to specific hydration of ions.

An alternative theoretical approach to understand electrokinetic phenomena which circumvents the limitations of primitive models is the use of molecular dynamics (MD) simulations of ions in explicit solvent. Due to recent improvements in algorithms and computer power, all-atom MD simulation studies of electrokinetic phenomena in some realistic systems are now possible [6,7]. From such atomistic descriptions, one can elucidate the microscopic mechanisms responsible for macroscopic measurable phenomena. For example, Aksimentiev and Schulten studied at atomic detail the permeation of individual ions through the transmembrane channel \( \alpha \)-Haemolysin with the help of MD simulations [6]. This approach has also been employed to understand from a microscopic perspective the electrophoresis of DNA immersed in multivalent ionic solutions when an external electric field is applied [8], the transport of monovalent and divalent ions through polymeric and silica nanopores [9,10] and the ionic selectivity of the OmpF porin biological nanochannel [11].

The realistic atomic description of such electrokinetic phenomena involves complex systems containing large number of particles. To be able to cope with such systems using MD simulations, we require the use of algorithms which enhance the computer performance. A MD simulation package which has been proven to be very successful in the description of biological molecules and electrokinetic phenomena is NAMD2 [12]. To accelerate the calculations of such large systems, we controlled in NAMD2 the temperature \( T \) of the system using the Langevin thermostat instead of the more rigorous but much more computationally demanding Nose–Hoover thermostat. Also to speed up the simulations, we usually employed the NAMD2 with a multiple timestep: a basic timestep for short-range interactions and a longer one for the evaluation of \( k \)-space contribution to the long-range electrostatic forces in the particle-mesh Ewald (PME) technique.

In this paper, we study, under different conditions, the transport properties obtained from MD simulations of electrolyte solutions using the same algorithms and conditions employed in simulations of complex systems. In particular, we focus our analysis on the transport properties of a monovalent electrolyte (KCl), a divalent electrolyte (MgCl2), the mixture of both (KCl + MgCl2) and a trivalent electrolyte (LaCl3) when an external electric field is applied. While the use of the KCl electrolyte is standard in MD studies and its transport
properties have been briefly analysed from this perspective before [6], the reliability of such simulation methods in dealing with transport properties of multivalent electrolytes has not been tested in detail in spite of the rich phenomenology that they originate [1,2,13,14] and their use in the simulation of electrokinetic phenomena involving divalent and trivalent ions [8,15–18].

2. Method

2.1 Simulation method

We have studied the transport properties of different electrolytes by performing MD simulations under external electric fields of different magnitudes. The systems considered were ionic solutions of KCl, MgCl₂, a mixture of KCl and MgCl₂, and LaCl₃, see Table 1. To study the effect of the system size on the ionic transport properties of bulk electrolytes extracted from MD simulations, we used two cubic simulation boxes of different size, \( L = 4 \) and 8 nm.

All simulations were carried out with the MD simulation package NAMD2 [12], because it is widely employed in the simulation of biological macromolecules. Water was described using a rigid TIP3P water model, as implemented by the CHARMM force field. The ions were modelled as charged Lennard-Jones particles with parameters given by the CHARMM force field for K⁺, Mg²⁺ and for Cl⁻, whereas the Lennard-Jones parameters for La³⁺ were taken from Ref. [19].

The initial configuration of the simulation was constructed as follows. The ions (K⁺, Mg²⁺ and Cl⁻) were inserted at random positions by employing the AutoIonize plugin of the visual molecular dynamics (VMD) software package [20] inside a cube of pre-equilibrated TIP3P water molecules, obtained with the help of the Solvate plugin of VMD (see Figure 1 for a diagram of the system). The faces of the cube are parallel to the \( XY \), \( XZ \) and \( YZ \) planes. In all simulations, we employed periodic boundary conditions in all directions. Lennard-Jones interactions were computed using a smooth (10–12 Å) cut-off, as it is customary done in NAMD2 simulations [6,8]. The electrostatic interactions were calculated using the PME method with a precision of \( 10^{-6} \) using a 128×128×128 grid and a 12 Å cut-off for the real space calculation. These are common parameters used to simulate complex and large biological macromolecules [6].

For each case, the equilibration procedure consisted of 50,000 steps of energy minimisation, a 1 ns run in the NPT ensemble (with \( p = 1 \) atm and \( T = 296 \) K) followed by a 1 ns run in the NVT ensemble (\( T = 296 \) K). Production runs in the NVT ensemble were performed in the presence of different electric fields to induce electromigration of the ions in solution. The NPT simulation runs were performed employing a combination of the Nosé–Hoover constant pressure method with the piston fluctuation control implemented using Langevin dynamics as implemented in NAMD2 (\( p = 1 \) atm, period of the oscillations of 0.1 ps and relaxation constant of 0.05 ps). As mentioned above, to speedup calculations, we carried out the NVT runs by applying Langevin dynamics, with parameters (also in the NPT run) \( T = 296 \) K and a damping coefficient of 1 ps⁻¹ (using 0.2 ps⁻¹ to test its effect in the dynamics for some cases specified later). Langevin forces were applied to all atoms except for hydrogen, which thermalise through interactions with the rest of the system.

In all cases, the equations of motion were solved using a multiple time step in order to speedup the simulations. A basic time step of 2 fs was used for the evaluation of short-range interactions and a longer time step of 4 fs for the calculations of the \( k \)-space contribution to the long-range electrostatic forces in the PME technique.

In the production runs, the instantaneous current induced by the external electric field applied along the \( Z \)-direction is calculated with the help of [6]

\[
I(t) = \frac{1}{A} \sum_{i=1}^{N} q_i [z_i(t + \Delta t) - z_i(t)], 
\]

where \( z_i \) and \( q_i \) are the \( Z \)-coordinate and the charge of atom \( i \), respectively, \( L \) is the size of the simulation box and \( \Delta t \) is the time interval employed to record data, which was chosen to be \( \Delta t = 10 \) ps. The average current is computed by linearly fitting the cumulative current that is obtained by integration of the instantaneous current. To ensure consistency of the results, we also computed the current by counting the flux of ions crossing a plane perpendicular to the direction of the electric field and located in the centre of the simulation box. The conductivity \( \kappa \) of the solution is defined by

\[
\frac{I}{A} = \kappa E, 
\]

where \( A = L^2 \) is the cross-sectional area perpendicular to the electric field \( E \). In order to obtain the conductivity of the electrolyte, we have performed simulations at different electric fields \( E \) and calculated the current \( I \) induced by them. In all cases, an ohmic behaviour was observed (i.e. consistent with a linear relation between \( I \) and \( E \)), and a linear fit of the data to Equation (2) gives the value of conductivity \( \kappa \).

The electromigration of ions in aqueous solutions as a result of the application of an external electric field is often accompanied by a net flow of water, the so-called electroosmotic flow. The electroosmotic flow was evaluated by keeping track, every \( \Delta t = 10 \) ps, of the accumulated number of water molecules crossing a plane perpendicular to the electric field. Crossings of such plane in the direction
Table 1. Simulation parameters for the simulations performed for the different electrolytes: cubic box edge length ($L$), damping constant of the Langevin thermostat ($\tau_{\text{Lan}}$), number of $K^+$ ions, number of $Mg^{2+}$ ions, number of $La^{3+}$ ions, number of $Cl^-$ ions, number of water molecules, simulation time, external electric field applied and potential difference between the edges of the cubic box along the direction of the electric field.

| Electrolyte | $L$ (nm) | $\tau_{\text{Lan}}$ (ps$^{-1}$) | No. $K^+$ | No. $Mg^{2+}$ | No. $La^{3+}$ | No. $Cl^-$ | No. $H_2O$ | Sim. time (ns) | Ext. field (mV/nm) | $\Delta V$ (mV) |
|-------------|---------|-------------------------------|----------|---------------|---------------|-----------|-----------|---------------|------------------|-----------------|
| 1 M KCl     | 3.88    | 1.0                           | 37       | 0             | 0             | 37        | 1907      | 210           | 14.2             | 55              |
|             | 3.88    | 1.0                           | 37       | 0             | 0             | 37        | 1907      | 90            | 26.0             | 109             |
|             | 3.88    | 1.0                           | 37       | 0             | 0             | 37        | 1907      | 90            | 43.3             | 168             |
|             | 7.82    | 1.0                           | 306      | 0             | 0             | 306       | 15,774    | 90            | 14.2             | 111             |
|             | 7.82    | 1.0                           | 306      | 0             | 0             | 306       | 15,774    | 90            | 26.0             | 203             |
|             | 7.82    | 1.0                           | 306      | 0             | 0             | 306       | 15,774    | 90            | 43.3             | 339             |
|             | 7.82    | 1.0                           | 306      | 0             | 0             | 306       | 15,774    | 90            | 86.6             | 677             |
| 1 M MgCl$_2$| 3.82    | 1.0                           | 0        | 37            | 0             | 74        | 1870      | 90            | 14.2             | 54              |
|             | 3.82    | 1.0                           | 0        | 37            | 0             | 74        | 1870      | 90            | 26.0             | 99              |
|             | 3.82    | 1.0                           | 0        | 37            | 0             | 74        | 1870      | 90            | 43.3             | 165             |
|             | 3.82    | 1.0                           | 0        | 37            | 0             | 74        | 1870      | 90            | 86.6             | 331             |
|             | 7.73    | 1.0                           | 0        | 306           | 0             | 612       | 15,468    | 90            | 14.2             | 110             |
|             | 7.73    | 1.0                           | 0        | 306           | 0             | 612       | 15,468    | 90            | 26.0             | 201             |
|             | 7.73    | 1.0                           | 0        | 306           | 0             | 612       | 15,468    | 90            | 43.3             | 335             |
|             | 7.73    | 0.2                           | 0        | 306           | 0             | 612       | 15,468    | 90            | 86.6             | 669             |
|             | 7.73    | 0.2                           | 0        | 306           | 0             | 612       | 15,468    | 90            | 14.2             | 110             |
|             | 7.73    | 0.2                           | 0        | 306           | 0             | 612       | 15,468    | 90            | 26.0             | 201             |
|             | 7.73    | 0.2                           | 0        | 306           | 0             | 612       | 15,468    | 90            | 43.3             | 335             |
|             | 7.73    | 0.2                           | 0        | 306           | 0             | 612       | 15,468    | 90            | 86.6             | 669             |
| 0.11 M MgCl$_2$| 7.83  | 1.0                           | 0        | 31            | 0             | 62        | 16,293    | 90            | 43.3             | 339             |
| 0.33 M MgCl$_2$| 7.80 | 1.0                           | 0        | 93            | 0             | 186       | 16,107    | 90            | 43.3             | 338             |
| 0.54 M MgCl$_2$| 7.79 | 1.0                           | 0        | 155           | 0             | 310       | 15,921    | 90            | 43.3             | 337             |
| 1 M MgCl$_2$| 7.72    | 1.0                           | 306      | 306           | 0             | 918       | 14,856    | 90            | 14.2             | 110             |
| + 1 M KCl | 7.72    | 1.0                           | 306      | 306           | 0             | 918       | 14,856    | 90            | 26.0             | 201             |
|             | 7.72    | 1.0                           | 306      | 306           | 0             | 918       | 14,856    | 90            | 43.3             | 334             |
|             | 7.72    | 1.0                           | 306      | 306           | 0             | 918       | 14,856    | 90            | 86.6             | 668             |
| 1 M LaCl$_3$| 7.71    | 1.0                           | 0        | 0             | 308           | 924       | 15,154    | 13.19         | 14.2             | 110             |
|             | 7.71    | 1.0                           | 0        | 0             | 308           | 924       | 15,154    | 10.87         | 26.0             | 201             |
|             | 7.71    | 1.0                           | 0        | 0             | 308           | 924       | 15,154    | 10.12         | 43.3             | 334             |
|             | 7.71    | 1.0                           | 0        | 0             | 308           | 924       | 15,154    | 10.52         | 86.6             | 668             |
of the electric field are counted as positive, whereas crossings in the opposite direction are counted as negative. Hence, the sign of the overall flow gives the direction of the electroosmotic flow with respect to the electric field direction. As reported before [6], the simulations might give a drift of the whole system which is unphysical since no net force is applied to the system (the electrolyte is globally electrically neutral). To avoid such spurious effects, the computation of the electroosmotic flow was done in the frame of reference of the centre of mass of the whole system.

The electric current flowing in an electrolyte solution is caused by the motion of anions and cations moving in opposite directions under the applied field. The fraction of the total current induced by each ion type defines its transport number, which is in general a function of the electrolyte concentration. The fraction of electrical current carried by cations defines the cationic transport number, $t_\text{c}$, and the fraction of the electrical current carried by anions the anionic transport number, $t_\text{a}$. A completely equivalent quantity to transport numbers is the ratio of the current induced by anions (anionic current) over the current induced by cations (cationic current), which will be referred to as the ratio of currents throughout the paper. Due to the global electroneutrality of the system, the total electric current flowing through an electrolyte as a result of the application of an external electric field is independent of the frame of reference in which it is measured. The ratios of currents and transport numbers, however, are frame dependent, and their computation must be done carefully. A proper account of the contribution to the total current from every ion in electrolyte solutions is important to describe phenomena in other more complex systems in which not only the total electric current but also the flow of each type of ion is relevant (e.g. in the study of the selectivity of ionic channels). Experimentally, the relevant frame of reference in which data of transport numbers and ratio of currents are provided is the frame of reference of the moving fluid. Therefore, to facilitate the comparison with experimental values, transport numbers and ratio of currents will be given in the frame of reference comoving with the fluid.

2.2 Conductivity measurements

The electrolyte conductivity measurements were performed using a MeterLab CDM210 (R) conductivity meter, Radiometer Analytical SAS (Lyon, France). The solutions were prepared using water from a Water Purification System Millipore Simplicity 185. Magnesium chloride 6-hydrated (MgCl$_2$) and potassium chloride (KCl) were from Panreac (Castellar del Vallés, Barcelona, Spain) in all cases following ACS specifications. Weighting of the compounds were done with a Mettler Toledo AB104-S, in the quantities necessary to achieve a 1 M concentration. The conductivity measurement included a stirring of the solution with a magnetic stirrer and heater JPSelecta Agimatic-E, with temperature monitoring using a laboratory thermometer at 296.0 K.

3. Results

3.1 A test case: transport properties of 1 M KCl

The results obtained from MD simulations for the electrical properties of the 1 M KCl electrolyte are given in Figure 2 and Table 2. We have used two different sizes for the simulation box, $L = 3.88$ and $7.82$ nm, to test the dependence of the results on the simulation’s box size. As can be seen, the values for the ionic conductivity for the two different box sizes do not differ significantly, $\kappa = 13.4$ S/m for the small box and $\kappa = 12.6$ S/m for the big one. Both results are in good agreement with our measured experimental value $\kappa_{\text{exp}} = 11.24 \pm 0.01$ S/m, being the value of the larger system closer to the experimental result as should be expected. Such values were obtained using a Langevin thermostat with a damping constant of 1 ps$^{-1}$, which is the typical choice for simulations of complex systems in contact with electrolyte (such as protein channels or silica nanochannels [6,11,12]). Our results show that with the standard simulation parameters employed in complex systems, the conductivity of the electrolyte KCl is correctly reproduced.

We have also calculated the ratio of the different contributions to the total current from anions and cations
As explained in Section 2.1, it is defined as the ratio of the anionic and cationic currents in the frame of reference of the moving fluid. The results for such ratio of currents are given in Table 2. As shown in the table, the values calculated from MD simulations are in good agreement with the experimental value of $I_{\text{Cl}}/I_K = 1.048$ (equivalent to a value of the cation transport number $t_+ = 0.488$ [21]) for both sizes of the cubic simulation box.

### 3.1.1 Electroosmotic flow

In addition to ionic currents, we also observe a net flow of water molecules. In Figure 3, the accumulated number of water molecules per unit area crossing a plane perpendicular to the electric field is represented as a function of simulation time. A linear fit of these magnitudes provides the flux of water molecules for every value of the electric field, as shown in Table 3. As shown in Figure 3 and Table 3, the electroosmotic flow for the 1 M KCl electrolyte is in the direction opposite to the external field, i.e. in the direction of the flow of chloride ions.

### 3.2 Transport properties of concentrated MgCl$_2$ solutions

A similar procedure was followed to obtain the transport properties of a 1 M MgCl$_2$ electrolyte. The electric current induced by the electromigration of ions was obtained for different values of the electric field using two different sizes of a cubic simulation box, $L = 3.88$ and 7.8 nm. The results of the simulations are given in Figure 4 and Table 4. The values for the ionic conductivity of the two different box sizes do not differ significantly, being $\kappa = 14.2$ S/m for the small box and $\kappa = 11.9$ S/m for the big one. Both results agree well with experimental values, the result from the larger simulation box being much more accurate.

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**Table 2. Ionic contributions to the total current, ratio of the anionic current over the cationic current and cationic transport numbers for different values of the applied electric field in the case of a 1 M KCl electrolyte.**

| System size | Electric field (mV/nm) | $I_{\text{Cl}}$ (nA) | $I_K$ (nA) | $I_{\text{Cl}}/I_K$ | $t_+$ |
|-------------|------------------------|---------------------|-----------|------------------|-------|
| $L = 3.88$ nm | 14.2 | 1.43 | 1.39 | 1.03 | 0.49 |
|             | 25.98 | 2.80 | 2.59 | 1.08 | 0.48 |
|             | 43.3 | 4.28 | 3.83 | 1.12 | 0.47 |
|             | 86.6 | 8.42 | 8.22 | 1.02 | 0.49 |
| $L = 7.82$ nm | 14.2 | 5.49 | 5.14 | 1.07 | 0.48 |
|             | 25.98 | 10.35 | 10.11 | 1.02 | 0.49 |
|             | 43.3 | 17.02 | 17.16 | 1.00 | 0.50 |
|             | 86.6 | 33.57 | 33.17 | 1.01 | 0.49 |

**Note:** All these quantities are calculated in the frame of reference of the moving fluid.
1 M LaCl$_3$ 14.2 $-0.64 \pm 0.07$

1 M KCl 14.2 $0.76 \pm 0.04$

1 M MgCl$_2$ 14.2 $0.43 \pm 0.15$

1 M KCl + 1 M MgCl$_2$ 14.2 $0.88 \pm 0.06$

1 M LaCl$_3$ 14.2 $-0.89 \pm 0.24$

Table 3. Flux of water molecules for different electrolytes and different values of the external electric field.

| Electrolyte         | Electric field (mV/nm) | Water flux (nm$^{-2}$ ns$^{-1}$) |
|---------------------|-------------------------|----------------------------------|
| 1 M KCl             | 14.2                    | $0.12 \pm 0.13$                 |
|                     | 26.0                    | $-0.13 \pm 0.04$                |
|                     | 43.3                    | $-0.43 \pm 0.14$                |
|                     | 86.6                    | $-0.64 \pm 0.07$                |
| 1 M MgCl$_2$        | 14.2                    | $0.76 \pm 0.04$                 |
|                     | 26.0                    | $1.47 \pm 0.05$                 |
|                     | 43.3                    | $2.30 \pm 0.14$                 |
|                     | 86.6                    | $5.11 \pm 0.09$                 |
| 1 M KCl + 1 M MgCl$_2$ | 14.2                    | $0.43 \pm 0.15$                 |
|                     | 26.0                    | $0.88 \pm 0.06$                 |
|                     | 43.3                    | $1.31 \pm 0.07$                 |
|                     | 86.6                    | $2.82 \pm 0.23$                 |
| 1 M LaCl$_3$        | 14.2                    | $-0.25 \pm 0.11$                |
|                     | 26.0                    | $-0.28 \pm 0.25$                |
|                     | 43.3                    | $-0.33 \pm 0.08$                |
|                     | 86.6                    | $-0.89 \pm 0.24$                |

According to Phang and Stokes [22], $\kappa_{\text{exp}} = 11.4$ S/m at [MgCl$_2$] = 0.9674 M and $T = 298.15$ K. A recent critical review [23] provides a slightly larger value of $\kappa_{\text{exp}} = 11.6$ S/m at [MgCl$_2$] = 1 M and $T = 25^\circ$C. Our own measurements give a value of $\kappa_{\text{exp}} = 11.92$ S/m.

The ratio between the different contributions of anions and cations to the total current was evaluated. The results for such a ratio of currents are given in Table 4. These results emphasise the need for using a large enough simulation box. The values for the ratio of currents and transport numbers obtained for the cubic simulation box of size $L = 3.82$ nm exhibit a spurious dependence on the applied electric field. For the large simulation box, the results are not field dependent, as should be expected. Such results show that the anionic contribution to the current is significantly larger than the cationic contribution (being a factor of 1.4 between them). In our simulations, these differences in the anionic and cationic contributions to the current can be attributed, to a large extent, to differences in diffusion coefficients between the two ions. In order to disentangle the diffusional and correlational contributions to the transport number, we have evaluated the translational diffusion coefficient of each ion by computing the mean square displacement of each ion in a 2 ns long NVE simulation run with no external field applied. The results of $D_{\text{Mg}} = 0.95 \times 10^{-5}$ cm$^2$/s and $D_{\text{Cl}} = 1.69 \times 10^{-5}$ cm$^2$/s for the diffusion coefficients of Mg$^{2+}$ and Cl$^-$ (Figure 5), respectively, lead to a ratio between the diffusion coefficients of $D_{\text{Cl}}/D_{\text{Mg}} = 1.8$.

Experimentally, both diffusion coefficients and transport numbers can be obtained, so we can compare both simulation results with experimental data. Using NMR, Struis et al. [24] obtained $D_{\text{Mg}} = 0.93 \times 10^{-5}$ cm$^2$/s and $D_{\text{Cl}} = 2.94 \times 10^{-5}$ cm$^2$/s (at $25^\circ$C and 0.985 mol/kg concentration), so the experimental ratio is

![Figure 4](image-url)
measurements [22,23] give a transport number for cations around 0.3, so the experimental ratio between anionic and cationic currents is $\approx 2.3$. The difference between the ratio of transport numbers obtained by electrochemical methods and the ratio between diffusion coefficients obtained by NMR can be interpreted in several ways. First of all, thermodynamic arguments [25] show that some experimental procedures mixed up different reference frames, so the electrochemical results have to be interpreted with caution. If the difference between both ratios is indeed physical, the difference can be attributed to electrokinetic processes (not accounted by diffusion coefficients) which are supposed to affect the transport numbers of each ion [21]. In any case, these electrokinetic processes were predicted in the framework of classical, continuum theory of electrolytes and are not clearly observed in our simulations, so its molecular origin remains unclear.

The effect of the damping constant of the Langevin thermostat was investigated by performing MD simulations on the same system of size $L = 7.73$ nm and the same conditions but using a Langevin thermostat with a damping constant of $\tau_{\text{Lan}} = 0.2 \text{ ps}^{-1}$ (instead of the damping constant of 1 ps$^{-1}$ employed in all other simulations). The electrolyte exhibits an ohmic behaviour, with conductivity $\kappa = 13.5 \text{ S/m}$, which slightly differs from the value obtained before and from the experimental value. Nevertheless, the major effect of the damping constant is in the different ionic contributions to the total current, as can be seen in Table 5. In comparison to the results of the simulations with $\tau_{\text{Lan}} = \text{ps}^{-1}$, it is evident that there is a spurious dependence of the ratio of the anionic current over the cationic current on the magnitude of the applied electric field.

### 3.2.1 Electroosmotic flow

The electroosmotic flow induced by the ionic current was also computed. In Figure 6, the accumulated number of water molecules per unit area crossing a plane perpendicular to the electric field is represented as a function of simulation time. The flux of water molecules for each electric field is given in Table 3. It is interesting to note the different direction and magnitude of the water flow obtained for 1 M KCl and for 1 M MgCl$_2$ electrolytes. Indeed, while in the presence of 1 M KCl, the direction of the net flow of water is opposite to the direction of the electric field, in the presence of 1 M MgCl$_2$ the net flow of water goes in the direction of the applied field. The magnitude of the net flow of water also differs significantly in both cases, being much larger (almost an order of magnitude) for the 1 M MgCl$_2$ electrolyte. These differences can be qualitatively understood from the hydration properties of the ions involved. For each ion, we have computed its hydration number, i.e. the average number of water molecules in its first coordination shell (as defined by the first minimum of the radial distribution function). We have also computed the average number of

![Figure 5. Diffusion of Mg$^{2+}$ and Cl$^{-}$ ions in 1 M aqueous solution as obtained from 2 ns NVE simulations with a cubic simulation box of $L = 7.73$ nm.](image)

![Figure 6. Accumulated number of water molecules per unit area crossing a plane perpendicular to the applied electric field vs. simulation time for the 1 M MgCl$_2$ electrolyte. Different lines represent the flow of water for different values of the electric field.](image)

| Electric field (V/nm) | $I_{\text{Cl}}$ (nA) | $I_{\text{Mg}}$ (nA) | $I_{\text{Cl}}/I_{\text{Mg}}$ | $t_+$ |
|----------------------|----------------------|----------------------|-----------------------------|------|
| 14.2                 | 5.88                 | 5.25                 | 1.12                        | 0.47 |
| 25.98                | 11.49                | 9.56                 | 1.20                        | 0.45 |
| 43.3                 | 19.82                | 15.03                | 1.32                        | 0.43 |
| 86.6                 | 38.59                | 31.15                | 1.24                        | 0.45 |

Note: All these quantities are calculated in the frame of reference of the moving fluid.
3.2.2 Concentration dependence of transport properties of MgCl₂

For the MgCl₂ electrolyte, we have also tested the dependency of the conduction properties of the electrolyte on its concentration, \( c \). We have performed simulations at different concentrations of MgCl₂ for a fixed value of the applied electric field \( E = 0.0433 \text{ V} / \text{nm} \) in a cubic simulation box of side \( L = 8 \text{ nm} \) (see Table 1 for precise values). The summary of the results is given in Table 7 and Figures 7 and 8. Here for each value of the electrolyte concentration, we obtained the conductivity from a single point \((I, E)\), under the assumption that the electrolyte exhibits an ohmic behaviour (suggested by the studies at 1 M concentration, see Figure 4). As expected, the electrical conductivity, \( \kappa \), of the MgCl₂ solution increases with increasing concentration, as can be seen in Table 7 and Figure 7. In Figure 7, the conductivity of the electrolyte obtained from MD simulations for each concentration is compared with experimental results [22] and Kohlrausch’s limiting law. The results obtained from MD simulations reproduce well the dependency of the electrolyte conductivity on the concentration, as compared with the experimental tendency. Besides, the absolute values of the experimental and simulated conductivities agree well with each other, especially for high and low salt conditions. In Figure 8, we represent the ratio of the anionic current over the cationic current as a function of the MgCl₂ concentration. The results from MD simulations indicate that the contribution of the anions becomes more prominent with increasing concentration of electrolyte. This tendency agrees with the experimental behaviour for 2:1 electrolytes [21].

| \( c \) (M) | \( I_{\text{tot}} \) (nA) | \( \kappa \) (S/m) | \( I_{Mg} \) (nA) | \( I_{Cl} \) (nA) | \( I_{\text{ad}}/I_{\text{cat}} \) | \( t_+ \) |
|---|---|---|---|---|---|---|
| 0.1 | 8.0 | 3.0 | 4.0 | 4.0 | 1.00 | 0.5 |
| 0.3 | 19.97 | 7.55 | 9.42 | 10.54 | 1.12 | 0.47 |
| 0.5 | 28.79 | 10.97 | 12.90 | 15.88 | 1.23 | 0.45 |
| 1.0 | 31.70 | 12.25 | 13.66 | 18.05 | 1.32 | 0.43 |

Table 7. Total current, electrical conductivity, ionic contributions to the total current, ratio of the anionic current over the cationic current and cationic transport numbers for different values of the concentration of the MgCl₂ electrolyte.
3.3 Transport properties of mixture composed of 1 M KCl and 1 M MgCl₂

We have also studied the transport properties of an electrolyte composed of 1 M KCl and 1 M MgCl₂. The addition of monovalent ions to a system immersed in a multivalent electrolyte is sometimes used experimentally to screen the electric charge of the multivalent ions [1]. This effect is also used in experiments and simulations to determine whether electrostatic correlations are responsible for a certain macroscopic effect [33,34].

The analysis is similar to the analysis done for the previous electrolytes. The electric currents caused by the drift of ions were obtained for four different values of the applied electric field. In this case, a single cubic box of size $L = 7.72\,\text{nm}$ was employed. The results for the conductivity are summarised in Figure 9, which results in a value for the conductivity $\kappa = 14.8\,\text{S/m}$. Our own experimental measurements give $\kappa = 16.83 \pm 0.01\,\text{S/m}$. The different contribution to the total current of the different ions as well as the cationic transport number is given in Table 8 for every value of the applied electric field.

3.3.1 Electroosmotic flow

The results for the net flow of water induced by the ionic current are given in Figure 10, in which the accumulated number of water molecules per unit area crossing a plane perpendicular to the electric field is represented as a function of simulation time. The flux of water molecules for each electric field is given in Table 3. Similarly, for the case of the 1 M MgCl₂ electrolyte, the net electroosmotic flow is in the direction of the flow of cations, in spite of being smaller than the net flow of anions (see Table 8). We interpret this result along the same lines as with the case of 1 M MgCl₂ electrolyte. As it is shown in Table 6, the hydration layer of Mg$^{2+}$ is much more robust than the hydration of Cl$^{-}$ and K$^{+}$, so the electroosmotic flow induced by the flow of Mg$^{2+}$ dominates.

3.4 Transport properties of 1 M LaCl₃

The lanthanum cation La$^{3+}$ is a highly charged and polarisable ion which, for most problems, requires the use of ab initio calculations or polarisable force fields to properly describe its interaction with water and ions [35]. However, there are systems for which only its electric charge and size are relevant to describe certain electrokinetic phenomena [34]. For such cases, La$^{3+}$ can be modelled as a charged Lennard-Jones particle and one can obtain the transport properties of a LaCl₃ ionic solution using classical MD calculations. The Lennard-Jones parameters used here to describe the lanthanum cation La$^{3+}$ were taken from Ref. [19].

The electrical transport properties of the 1 M LaCl₃ electrolyte in the presence of an external electric field are obtained using MD simulations which employ a non-polarisable force field (described above). The summary of the results is given in Figure 11 and Table 9. The electrolyte shows an ohmic behaviour (see Figure 11), with an electrical conductivity of $\kappa = 12.8\,\text{S/m}$. Considering the limitations of the description, this value is quite satisfactory compared with the experimental value of $\kappa_{\text{exp}} = 15.3\,\text{S/m}$ [36]. The ionic contribution, the ratio of currents and the cationic transport number are given in Table 9 for each value of the external electric field.
3.4.1 Electroosmotic flow

The results for the net flow of water induced by the ionic current are given in Figure 12, in which the accumulated number of water molecules per unit area crossing a plane perpendicular to the electric field is represented as a function of simulation time. The flux of water molecules for each electric field is given in Table 3.

The hydration properties of the 1 M LaCl₃ electrolyte are summarised in Table 6. In spite of the limitations of the non-polarisable model used to describe La³⁺, the values obtained for the hydration of La³⁺ are close to the values given in the literature (hydration ~8–9 and a residence time of hydrated water in the first coordination shell of ~1 ns [35]). As showed in Figure 12, the electroosmotic flow obtained for the 1 M LaCl₃ electrolyte is in the direction of the flow of chloride ions, opposite to the direction of the applied electric field. In this case, the higher hydration of La³⁺ is not enough to compensate the higher flow of chloride ions vs. the flow of lanthanum cation La³⁺.

Table 8. Ionic contributions to the total current, ratio of the anionic current over the cationic current and cationic transport numbers for different values of the applied electric field in the case of an electrolyte composed by 1 M MgCl₂ and 1 M KCl.

| Electric field (V/nm) | I_Cl (nA) | I_K (nA) | I_Mg (nA) | I_an/I_cat | t⁺ |
|----------------------|-----------|----------|-----------|------------|----|
| 14.2                 | 7.6       | 3.27     | 2.04      | 1.43       | 0.41 |
| 25.98                | 18.14     | 5.12     | 4.98      | 1.30       | 0.43 |
| 43.3                 | 21.69     | 9.29     | 7.89      | 1.26       | 0.44 |
| 86.6                 | 43.36     | 17.11    | 15.59     | 1.32       | 0.43 |

Note: All these quantities are calculated in the frame of reference of the moving fluid.
The electroosmotic flow of water induced by the ionic flow was also computed from the MD trajectories. It is shown that the direction and magnitude of the water flux depends on the electrolyte: although the flux is in the direction of the cation flow for electrolytes containing Mg$^{2+}$, it is in the opposite direction and weaker for all the other cases. These results are interpreted with the help of the hydration properties of the ions, which are calculated and successfully compared with previous studies on the subject.

4. Conclusions

Classical MD simulations of various electrolytes (KCl, MgCl$_2$, KCl + MgCl$_2$ and LaCl$_3$) in external electric fields were performed to study their transport properties. We have employed algorithms and parameters typically used in simulations of complex electrokinetic phenomena to test against experimental data their validity in the description of transport properties of electrolytes. The electrical conductivity and transport numbers (ionic contributions to the total current) of electrolytes containing monovalent (1 M KCl) divalent (1 M MgCl$_2$, 1 M MgCl$_2$ + 1 M KCl) and trivalent (1 M LaCl$_3$) cations were computed from the simulated ion trajectories. It is shown that in all cases, the electrical conductivities obtained from the simulations are in good agreement with our own experimental measurements and values from the literature. Also, for the MgCl$_2$ electrolyte, the dependence of the electrical conductivity on the electrolyte concentration was investigated and found that the MD results follow the experimental trend and give accurate results for the lowest (0.1 M) and the highest (1 M) concentrations studied. Transport numbers obtained for the 1 M KCl electrolyte agree well with the experimental values found in the literature. For the divalent electrolyte 1 M MgCl$_2$, there is a significant discrepancy between the transport numbers obtained from MD simulations and the experimental values, probably due to the poor result for the self-diffusion coefficient for anions provided by the Lennard-Jones parameters used in the simulations. The effect of the simulation box size on the electrical transport properties was also explored. It is found that a big enough simulation box is needed to avoid spurious effects of the simulation.

Acknowledgements

This work is supported by the Spanish Government (grants FIS2009-13370-C02-02, FIS2007-60205 and CONSOLIDER-NANOSELECT-CSD2007-00041), Generalitat de Catalunya (2009SGR164) and Fundació Caixa Castelló-Bancaixa (PI-1A2009-13). C.C. is supported by the JAE doc programme of the Spanish National Research Council (CSIC). The Supercomputing resources employed in this work were provided by the CESGA Supercomputing Center, Spain.

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