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Thermodynamically consistent force field for coarse-grained modeling of aqueous electrolyte solution

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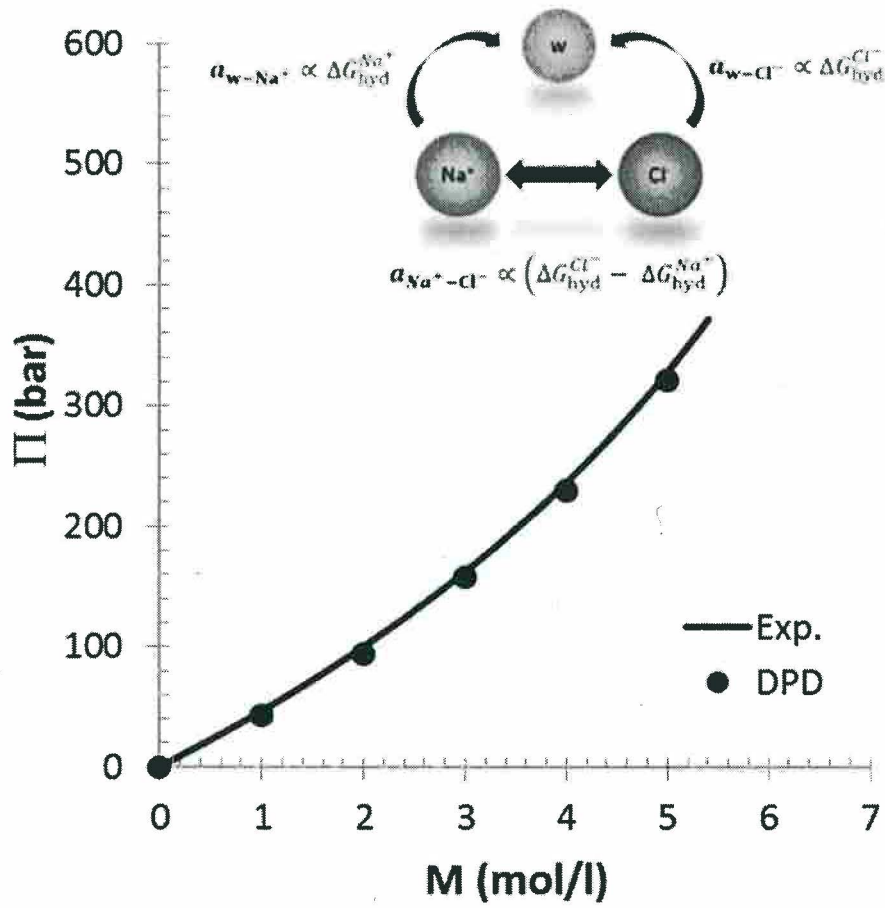
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ABSTRACT. We propose a thermodynamically consistent methodology to parameterize interactions between charged particles inside the dissipative particle dynamics (DPD) formalism. We have used experimental data of osmotic pressure as a function of the salinity in order to optimize the required interaction parameters. Our results for NaCl aqueous solution show that the use of mean osmotic coefficient, as well as the activity coefficient of individual ions, allow to unambiguously determine the Na^+ -water, Cl^- -water and Na^+ - Cl^- DPD repulsion parameters. We propose a simple linear relationship between the hydration free energies of ions and the ion-water repulsion parameters that allows the parameterization of the complete series of halide and alkaline ions. Two different strategies have been used to derive the anion-cation interaction parameters for halide and alkaline but NaCl. In the first one, parameters are obtained for all pairs of ions based on the numerical optimization of the anion-cation repulsion parameter with respect to experimental osmotic pressure data. The mean absolute relative deviation between simulated and experimental data is then smaller than 4%. Second, we propose a simple, purely predictive approach to obtain the anion-cation interaction parameters based on the free energy difference of hydration energies of anions and cations in the spirit of the law of matching water affinities (LMWA). This approach predict salt properties with a mean absolute relative deviation of the order of 13 %, and with an accuracy better than 6% if small ions (Li^+ and F^-) are removed.

TOC GRAPHICS



KEYWORDS Electrolytes, dissipative particle dynamics, interaction parameters, osmotic pressure, density, molecular simulation, thermodynamics.

Physical chemistry of aqueous electrolyte is a complex topic. Electrostatic interactions between ions and water molecules give rise to specific changes in the water structure with consequences on thermodynamics and transport properties of the solution.¹ Numerous fundamental processes in chemistry and biology are caused by the specific interactions of small alkali and halide ions with water molecules. A typical example is given by the salt effect on protein stability, also known as Hofmeister effect.^{2,3} Important effects can also be observed at water-oil interfaces⁴ or between electrolytes and air (bubble coalescence) or metals (corrosion processes).⁵

In order to predict the behavior of electrolytes, some models based on thermodynamic theories can be applied in numerous applications of industrial importance.⁶ Thermodynamics modeling is mostly based on the Specific Ion Interaction theory (SIT),^{7,8} or Pitzer framework.⁹ Pitzer equations work well for numerous binary and multicomponent mixtures, as long as there are sufficient experimental data of high quality for parameterization. This is a strong limitation as the required number of available experimental data is often too low for new applications.

Molecular simulations can be an alternative to thermodynamic modeling for the study of electrolytes. It is a commonplace to emphasize that accurate and predictive molecular simulations require i) a *good* description of interactions (embedded in a force field expression and parameters) and ii) a *correct* sampling (given by long trajectory time or building of a large ensemble of configurations). The accuracy of electrolyte force fields can be severely tested when trying to reproduce mixture thermodynamic properties such as ion-water activity coefficient or dielectric constant in function of ionic concentration.¹⁰ Results are strongly dependent on the complexity of the model as well as to the appropriate treatment of the calculations (algorithms, sampling, and convergence of the results, etc.).¹¹ The sampling can become quite complicated

when dealing with interfacial properties, due to the long time and length scales involved and also due to the different affinities of ions at the aqueous-hydrophobic interfaces.^{12,13,14}

There is a huge amount of work to derive accurate force field for molecular simulations at the atomistic level (all-atom force field). Joung and Cheatham have determined a set of parameters for alkali and halide monovalent ions for use in biological system simulations.¹⁵ The level of description does not include polarization effects and parameters are optimized from hydration free energies of ions and also lattice energies and lattice constants of salt crystals. Horinek et al.,¹⁶ suggest to use the solvation free energy in conjunction with the solvation entropy for the simulation of ion specific effects, again neglecting polarization effects. In more recent works, multi-body effects are considered by adding explicitly polarization terms in the interaction potential. Salanne et al. include dipole-quadrupole terms in the dispersion potential and many-body interactions through induced dipole interactions.^{17,18} Ab initio (DFT) calculations are used to derive and optimize interaction parameters for this force field. Roux et al. have proposed a polarizable force field for alkali and halide ions.^{19,20} The polarizable model is based on the classical Drude oscillator and a first set of parameters were derived from binding energies of gas-phase monohydrates and hydration free energies in the bulk liquid. More recently, the same group have developed methods to compute osmotic pressure using molecular dynamics simulations.²¹ To model accurately concentrated ionic solutions, the parameters of the potential functions are optimized to reproduce osmotic pressure data.^{22,23}

Thanks to the development of efficient codes, optimum atomistic polarizable force fields and the availability of large scale parallel computers and software, calculations of surface and interfacial tension of water air and water hydrocarbons can be realized.^{24,25} However, the computational

time required to compute interfacial phenomena in the presence of ions remains still prohibitive with such approaches and insufficient sampling may occur.^{4,12,13,26}

An alternative to atomistic simulations is the use of coarse grain or mesoscopic models. In this case the reduction of the degrees of freedom of the system (by grouping together several atoms or molecules in one particle) extends the boundaries of accessible time and length scales.^{27,28,29} The price to pay with coarse grain approaches is a lack of transferability of the force field.^{30,31} There are many types of coarse grain approaches in the literature,^{32,33} among which the MARTINI model and force field,^{34,35} and the dissipative particle dynamics (DPD)³⁶ are widely used. For electrolyte solutions, a standard procedure was applied to the parametrization of ions in the framework of MARTINI.³⁴

Mayoral et al. proposed a parameterization for the DPD repulsive parameters for the electrolyte using the dependence of the Flory-Huggins χ parameter on the concentration and the kind of electrolyte added, by means of the activity coefficients.³⁷ However, two facts make their approach difficult to use: i) ion-water repulsion parameters become concentration dependent, and ii) there is no specific differentiation between anions and cations (both species have the same repulsion parameter). In addition, methods available in the literature for the parameterization of repulsive parameters in DPD are no longer valid due to the combination of repulsive and electrostatic forces.²⁹ This fact prevents the use of DPD simulations of electrolyte solutions in agreement with standard ionic thermodynamic properties, such as activity or osmotic coefficients. As recently noted by several authors, up to date, no such approach exists in the DPD framework.^{38,39}

Our aim here is to check that standard thermodynamic properties of electrolytes can be reproduced using classical DPD simulations with charged particles. We focus on osmotic pressure and density data for different salts (with monovalent ions) in the range 0 to 3 M because it is a good measure of both ion-water and anion-cation interactions. Two different strategies will be used. In a first one, repulsion parameters between anion and cation will be obtained from brute force optimization versus experimental osmotic pressure data, thus providing a full set of parameters of *best parameters*. In a second one, anion-cation repulsion parameters will be predicted on the basis of free energy of hydration in the spirit of the law of matching water affinities (LMWA) proposed by Collins.⁴⁰

Two sets of experimental data were used to parameterize ion-ion and ion-water repulsion parameters including standard measurements of mean osmotic coefficient,⁴¹ as well as the activity coefficient of individual ions (which, in principle, give access to information of water-ion interactions for anions and cations separately).⁴² Most of the experimental osmotic/activity coefficients available in the literature correspond to the “practical” Lewis-Randall (LR) osmotic coefficient (ϕ), which can be defined from a thermodynamic point of view in terms of the activity of water ($a_{\text{H}_2\text{O}}$),

$$\phi = - \frac{\ln a_{\text{H}_2\text{O}}}{\nu_{\pm} m M_{\text{H}_2\text{O}}} \quad (1)$$

where m is the mean molality of the solution, $\nu_{\pm} = \nu_{+} + \nu_{-}$ is the number of completely dissociated ions of the salt in solution and $M_{\text{H}_2\text{O}}$ the molar mass of water. According to Bjerrum, the osmotic coefficient can be related to the mean activity coefficient (γ_{\pm}) of salts in a single solvent as,^{43,44}

$$\phi = 1 + \frac{2.302585}{m} \int_0^m m \, d\log \gamma_{\pm} \quad (2)$$

This equation is valid in the Lewis-Randall reference framework. Under the incompressibility approximation, the osmotic pressure (Π) can be estimated through,

$$\Pi = \phi \frac{\nu_{\pm} m M_{\text{H}_2\text{O}} RT}{\bar{v}_{\text{H}_2\text{O}}} . \quad (3)$$

The use of this equation requires the knowledge of the partial molar volume of water ($\bar{v}_{\text{H}_2\text{O}}$) at the same temperature, pressure and molarity and can be cumbersome if no experimental data are available. Alternatively, one can use the ‘‘McMillan-Mayer’’ (MM) scaling for thermodynamic properties.⁴⁵ LR and MM scales differ in the choice of independent variables. The LR framework is at constant pressure and mole numbers, whereas the MM framework is at constant volume, solute mole numbers and solvent chemical potential.⁴⁶ In this context, the MM osmotic coefficient ϕ^{MM} can be defined as the ratio Π/Π_0 (where Π_0 is the ideal osmotic pressure obtained by the van’t Hoff law). In order to compare our simulation results (in the MM framework) with the available experimental data (in the LR framework), one can use the following thermodynamic relation⁴⁷

$$\phi = \phi^{\text{MM}} (1 - M \cdot \bar{v}_s) \quad (4)$$

where M is the salt concentration in mol/l and \bar{v}_s is the partial molar volume of solute at temperature T , pressure P and molality m . We checked for NaCl in water that the term $(M \cdot \bar{v}_s)$ is negligible even close to the saturation concentration (see figure 2 in section 2 of SI) and that $\phi \approx \phi^{\text{MM}}$ is a good assumption. This may change with salt concentration and nature. Thus, it

should be a good practice to check that this approximation is satisfied before comparing data obtained in different frameworks (e.g. LR and MM).

Our methodology relies on different tools and a short description is given below. More information are available in sections 1, 2, 3 and 5 of SI. Numerical optimizations were realized using the ATOUT software (Advanced Tools for Optimization and Uncertainty Treatment) developed by IFP Energies nouvelles.⁴⁸ We use standard DPD simulations,⁴⁹ with electrostatic interactions treated using the Slater-type charge smearing method as presented in Gonzales-Melchor et al. paper.⁵⁰ In molecular simulation it is possible to compute the osmotic pressure in the LR framework using equation 5. The procedure is well described in the work of Smith et al.,¹¹ and was tested for NaCl aqueous systems. This approach requires the use of an Osmotic Ensemble Monte Carlo (OEMC) algorithm,^{51,52,53} and a precise knowledge of experimental partial molar volumes of the species in solution. This last property can in principle be computed directly from simulations when no experimental data is available, however, this requires a set of separate calculations and can be difficult to compute when flexible polyatomic ions are present (i.e. sulfonates, carbonates, etc.). In this work we use a different approach. We compute the osmotic pressure in our DPD simulations following the well-known method proposed by Luo and Roux.²¹ This method to obtain the osmotic pressure follows the MM framework, since all calculations are performed at a fixed “sample” volume with a known ionic concentration where solvent molecules are free to enter/leave the sample volume. This approach has been successfully used for the parameterization of ion-water interactions for atomistic as well as coarse grain models.^{23,54,55,56} Numerically, the osmotic pressure is computed by the force exerted by solute DPD particles over an hypothetical semi-permeable membrane represented by two planes located at $z_{\text{wall}} = z_0$ et $z_{\text{wall}} = z_1$ according to,

$$\langle F_{\text{wall}} \rangle_i = \frac{k_w}{N} \sum_N \sum_i (|z_i - z_{\text{wall}}|) \quad (5)$$

where $\langle F_{\text{wall}} \rangle_i$ is the force exerted by the i^{th} particle over the wall of area A placed at z_i inside the zone (i.e. $|z_i| > |z_{\text{wall}}|$), k_w is the force constant of $5 k_B T / r_c^2$ (in DPD units) applied to the ions in order to keep them inside the confinement zone and N is the number of simulation time steps. It is important to mention that the force is not applied to solvent molecules which are free to cross the membrane. Interestingly, this method gives access to osmotic pressure contribution of each ion, meaning that a better parameterization can be obtained if single ion activity/osmotic coefficients are available. The osmotic pressure of the system (Π) is the sum of the contribution of osmotic pressure of each solute (Π_i) present in the solution (N_{solute}) inside the control volume using the following expression,

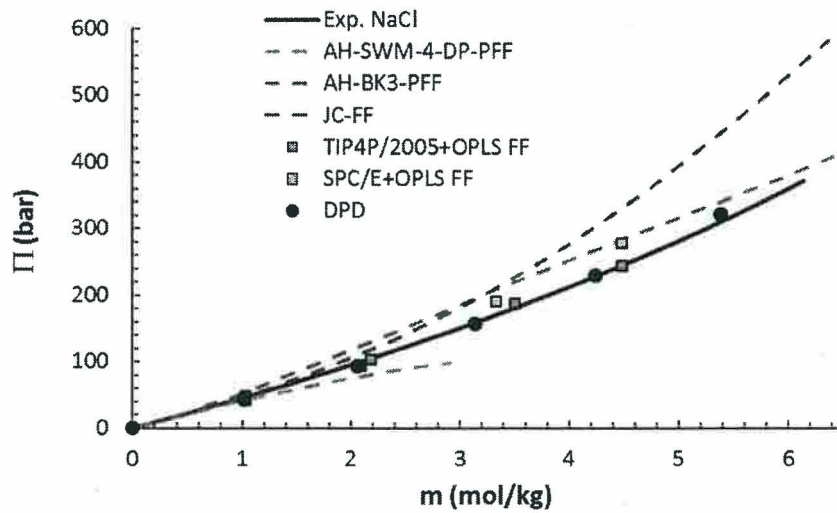
$$\Pi = \sum_{i=1}^{N_{\text{solute}}} \Pi_i = \frac{\sum_{i=1}^{N_{\text{solute}}} \langle F_{\text{wall}} \rangle_i}{A}. \quad (6)$$

All simulations are realized with periodical boundary conditions in x , y and z directions. The time step value is 0.01 in DPD units. The total momentum is cancelled out between the steps as required to compute the osmotic pressure. Density for every system was computed in a separate simulation using a cubic box $L_x = L_y = L_z$ with 6000 DPD particles with an initial density of $\rho = 3$. The density was obtained after an equilibration period of 100000 steps followed by a production run of 100000 steps using NPT at imposed pressure P_0 .

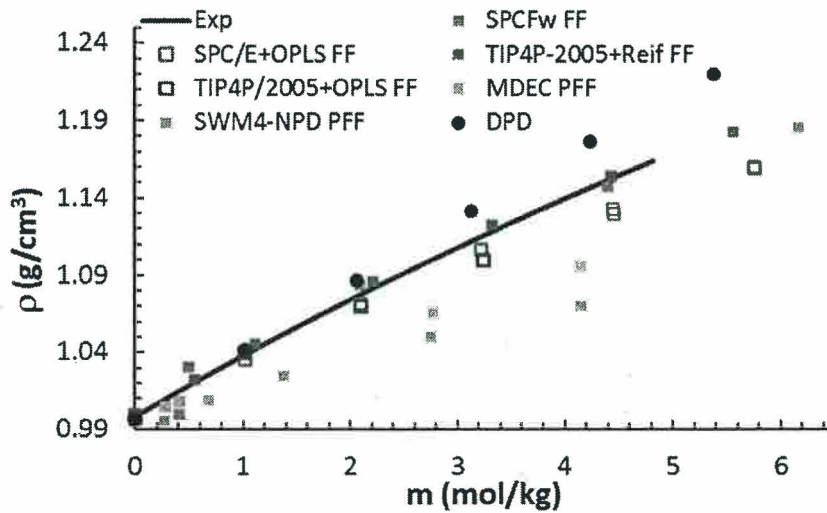
We now turn to the description of the construction of the DPD model. Every water bead contains three water molecules, i.e. the degree of coarse graining (N_m) is 3. As it is the case in standard DPD simulations, once N_m is chosen, the bead volume (v_m) and the characteristic length scale (r_c) are imposed. Ions are considered hydrated by a certain number of water molecules n_w , according to their ionic size, in order to satisfy constraint on v_m (3 for Na^+ and 2 Cl^-). Following the procedure proposed by Mayoral et al., where the degree of coarse grain and the isothermal compressibility of water at ambient conditions ($\kappa^{-1} = 16$ in DPD units) are used, the interaction parameter between water beads a_{ww} is 78 (in units of $k_B T$).⁵⁷ For simplicity, all pure component interactions are assumed to be identical to that of water-water interactions ($a_{cation-cation} = a_{anion-anion} = a_{ww}$).

Our parameterization process begins with the estimation of the full set of DPD repulsion parameters for NaCl in water (ion-water and anion-cation parameters) using the ATOUT platform.⁴⁸ The scan for optimum values was set by using 20 simulations, where the initial guess for the repulsion parameters were distributed in a grid using a Latin Hypercube Design (LHD).⁵⁸ In this case the values of $a_{\text{Na-w}}$, $a_{\text{Cl-w}}$ and a_{NaCl} have been taken from a uniform distribution centered at 78 within the range 56-100. Every simulation set (containing defined values of $a_{\text{Na-w}}$, $a_{\text{Cl-w}}$ and a_{NaCl}) consists of four independent simulations using the protocol described in detail in sections 2 and 5 of the SI. The values of the osmotic pressure are the result of the average of these four simulations, where we observe that the average deviation for the osmotic pressure is less than 1%. These values are compared with the experimental data of osmotic pressure for the NaCl electrolyte,⁴¹ plus single ion osmotic pressure values⁴² to evaluate a least square objective function (LSOFA). Contributions of single ion osmotic coefficient for Na^+ and Cl^- have identical weights inside the LSOFA. Finally, the LSOFA was numerically modelled by a 3D Kriging

response surface which was then used to perform a fine steepest descent gradient optimization (see section 5 in SI). The optimum values, obtained at the end of the process are 69.47, 80.25 and 75.00 for the repulsion parameters $a_{\text{Na-W}}$, $a_{\text{Cl-W}}$ and $a_{\text{Na-Cl}}$ respectively. The variation of the osmotic pressure and density of NaCl with the salinity obtained with our DPD electrolyte model can be observed in Figure 1 and compared with the experimental data.^{41,59} We also compare our results with literature data including atomistic simulations using polarizable (PFF),^{10,11,24,60} and non-polarizable (FF) force fields.⁶¹



a)



b)

Figure 1. Variation of the a) osmotic pressure (Π) and b) density (ρ) of the aqueous solution of NaCl with the molality. Comparison of the DPD results with the experimental data for osmotic pressure⁴¹ and density⁵⁹ and several simulation results from the literature, including polarizable (PFF),^{10,11,24,60} and non-polarizable (FF) force fields.⁶¹ The statistical error in the values of the osmotic pressure in DPD is less than 1%.

Results observed in Figure 1.a confirm that it is possible to accurately reproduce the experimental osmotic pressure over the entire range of NaCl solubility with a simple DPD model and using a robust parameterization procedure (i.e. mean absolute relative deviation –MARD– of 5% with respect to experimental results of ref. 41 and ref. 59 in the range of 0-3M). Atomistic models compared in Figure 1 were not optimized to reproduce the osmotic pressure; hence the results obtained from the literature are pure predictions. Non-polarizable force fields present deviations similar to our DPD simulations, whereas polarizable force fields show larger deviations.¹¹ Our DPD model presents a MARD of 1.0 % with respect to the experimental density when the concentration of NaCl is increased in the range of 0-3m (3% for the range between 3-5m) as can be seen in Figure 1.b. Usually, all other atomistic models (polarizable and non-polarizable models) tends to underestimate the experimental density, with the exception of the flexible SPCFw model for water (see supporting information for details) and the couple of TIP4P-2005 model for water and Reif model for ions.⁶¹ Overall, the present electrolyte DPD model is able to reproduce the variation of the osmotic pressure and density of aqueous solution of NaCl in the whole range of solubility with an accuracy which is equivalent to other more complex, time consuming atomistic simulations. It is important to remark that the obtained parameters, though valid exclusively at ambient conditions, do not depend on salinity.

It is interesting to notice that $a_{\text{Na-W}} < a_{\text{Cl-W}}$, in other words, there is a stronger interaction (smaller repulsion parameter, higher activity coefficient⁴²) between the hydrated Na^+ and water beads than the hydrated Cl^- and water beads. This is similar to the order observed for the free energy of hydration (ΔG_{Hyd}) of ions in water with -404.4 kJ/mol and -323.2 kJ/mol respectively for Na^+ and Cl^- .¹⁹ In a recent work, Andreev et al. propose a Lennard-Jones coarse grain model of electrolyte solutions where ion-water interactions were parameterized using the free energy of hydration of ions in water.^{62,63} In the spirit of the above mentioned papers, we have used a linear relationship between the ion-water repulsion parameter in DPD with the ΔG_{Hyd} . Thus, water-ion parameters can be obtained easily from the knowledge of free energy of hydrations, as presented in Figure 2.

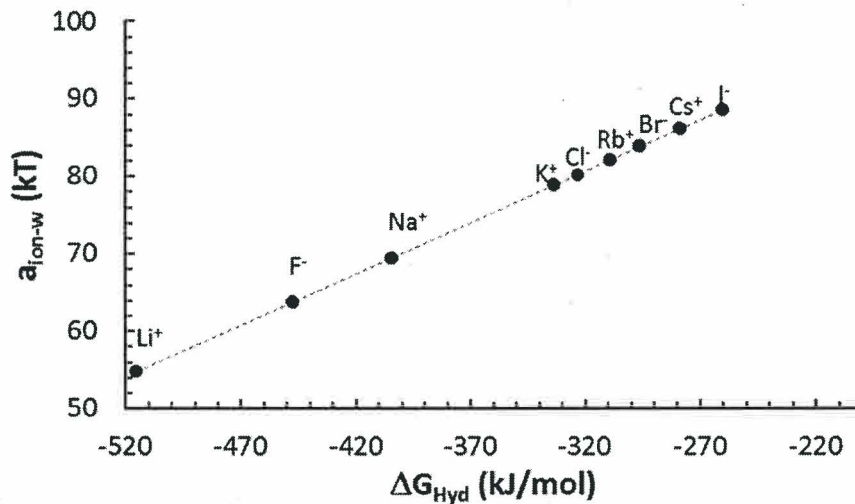


Figure 2. Assumed relationship between the DPD conservative repulsion parameter between ions and water with the free energy of hydration of ions.¹⁹ Proposed values (in red) are based on optimum values for Na^+ and Cl^- (black points, see text).

As mentioned earlier, we have used two different strategies to obtain anion-cation interaction parameters. The first one makes use again of the ATOUT software and of experimental osmotic pressure data of the concentration range 0 to 3M: for each salt, the optimization process samples the repulsion parameter $a_{anion-cation}$. The final values of the optimization process are presented in

Table 1. We present in figure 3, the MARD of DPD simulation results with the optimized set of parameters. We notice that a good agreement can be obtained between experimental and simulated osmotic pressures. The maximum deviation is smaller than 6% and the MARD is smaller than 4%. This result is not surprising in the sense that the target property of the optimization is the osmotic pressure. Meanwhile, it shows that this property can be reproduced using such a standard DPD model plus charges particles with very simple assumptions: repulsion parameters between like particles are obtained from the water compressibility, water-ion interactions are governed by free energy of hydration of corresponding ions, and finally, anion-cation interactions are optimized upon osmotic pressure.

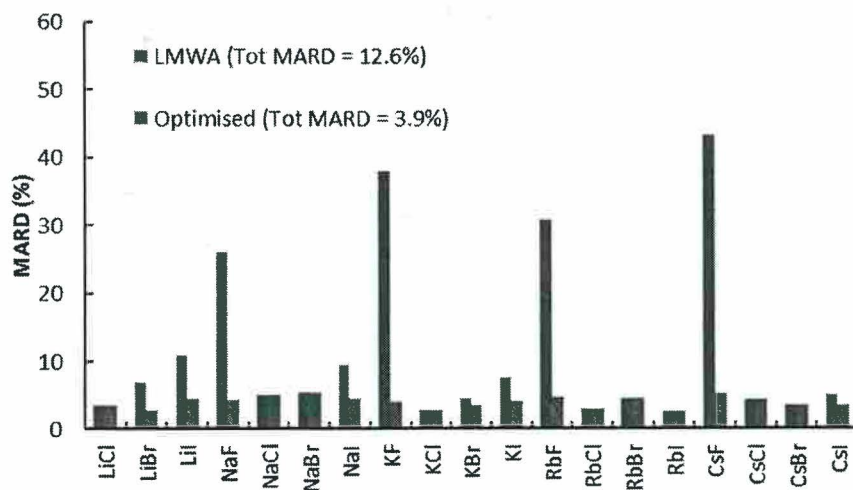


Figure 3. Mean average relative deviation (in %) between the osmotic pressure (Π) calculated from DPD simulations and the experimental values in the range of 0-3M concentration for the complete series of salts containing halide and alkaline ions. Comparison of the predicting method of parameters considering the difference between the free energy of hydration of anions and cations (LMWA), and the optimal ATOUT values with respect to experiments.

Table 1. Anion-cation repulsion parameters (in $k_B T$ units) obtained through (a) the ATOUT optimization procedure and, (b) from the free energy of hydration between anion and cation (values in parenthesis under individual ions are $\Delta G_{\text{hyd}}^{\text{ion}}$ in kJ/mol obtained from ref. 19, whereas those under the repulsion parameters are $\Delta\Delta G_{\text{anion-cation}}$).

	Li⁺ (-515.39)	Na⁺ (-404.44)	K⁺ (-333.27)	Rb⁺ (-308.99)	Cs⁺ (-278.42)
F⁻ (-447.15)	---*	(a) 60.0 (b) 42.2 (-42.71)	(a) 69.93 (b) 49.86 (-113.88)	(a) 72.01 (b) 58.33 (-138.16)	(a) 79.74 (b) 59.20 (-168.73)
Cl⁻ (-323.22)	67.43** (192.17)	75.0** (81.22)	83.206** (10.05)	91.17** (-14.23)	92.0** (-44.8)
Br⁻ (-296.01)	(a) 81.39 (b) 74.63 (219.38)	82.2** (108.43)	(a) 93.04 (b) 90.40 (37.26)	(a) 98.35 (b) 98.38 (12.98)	(a) 107.88 (b) 107.92 (-17.59)
I⁻	(a) 110.57	(a) 97.41	(a) 102.76	(a) 107.98	(a) 109.11

(-260.00)	(b) 84.16	(b) 91.73	(b) 99.9	(b) 107.92	(b) 108.73
	(255.39)	(144.44)	(73.27)	(48.99)	(18.42)

*Due to its low limiting solubility in water, we have not simulated LiF. **Optimized reference value for the predictive scaling procedure.

In addition, we would like to propose a rule to predict anion-cation repulsion parameter. We relate the variation of the anion-cation repulsion parameter with the rule of the law of matching water affinities (LMWA) proposed by Collins.⁶⁴ The LMWA suggests that inner sphere ion pairs are preferentially formed between oppositely charged ions with matching absolute hydration energies. Thus, anion-cation repulsion parameters should be related with the difference of free energy difference of hydration between anion and cation (i.e., $\Delta\Delta G_{\text{anion-cation}} = \Delta G_{\text{hyd}}^{\text{anion}} - \Delta G_{\text{hyd}}^{\text{cation}}$). In this context the anion-cation repulsion parameter can be obtained as follows,

$$(a_{\text{anion-cation}})_{\text{salt}} = c_1 \cdot \Delta\Delta G_{\text{anion-cation}} + c_0 \quad (7)$$

here c_1 and c_0 are constants. In this approximation we assume c_1 to be the same for all salts whereas c_0 is different for each series containing the same alkaline ion. In order to determine c_1 we need the repulsion parameter of a Na salt with different anion, we use for example the optimal ATOUT value of $a_{\text{Na-Br}}$. The $a_{\text{Na-Br}}$ parameter value is 82.2, higher than the one for NaCl, as expected from LMWA ($\Delta G_{\text{hyd}}^{\text{Br-}}$ larger than $\Delta G_{\text{hyd}}^{\text{Cl-}}$).¹⁹ In this case we obtain a value of $0.265 \text{ mol.kJ}^{-1}$ for c_1 . For c_0 we use the optimal ATOUT repulsion parameters for different salts with the same anion (Cl for instance) but different alkaline ions (LiCl, KCl, RbCl and CsCl with optimum anion-cation repulsion parameters of 67.43, 83.206, 91.17 and 92.00 -in units of $k_B T$ - for each salt respectively, see Table 1 for details). We obtain values of c_0 of 16.574, 53.502,

80.392, 94.942 and 103.855 (in $k_B T$ units) for Li, Na, K, Rb and Cs respectively. It is interesting to notice that c_0 scales linearly with the free energy of hydration of alkaline ions in water (see Figure 8 in section 8 of SI for details). The predicted values of the repulsion parameters obtained for the series of monovalent salts can be observed in Figure 4 and in Table 1.

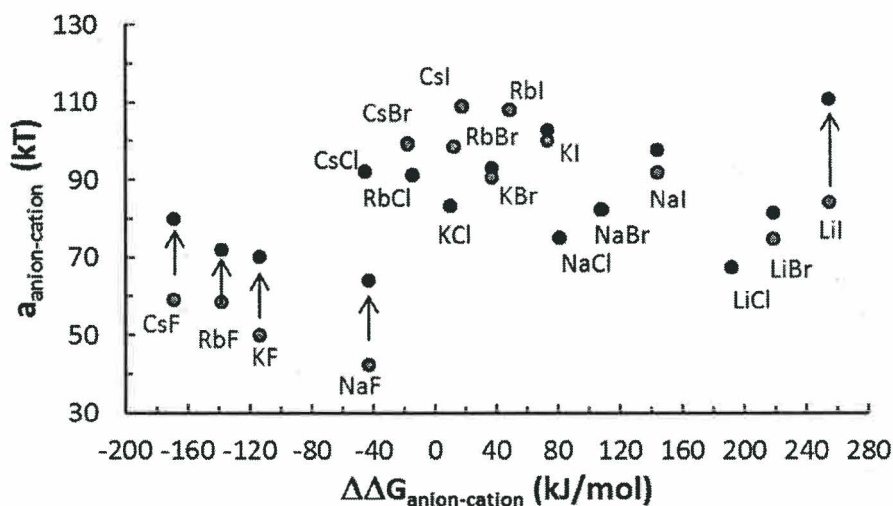


Figure 4. Relationship between the conservative repulsion parameter $a_{\text{anion-cation}}$ with the difference of free energy difference between anion and cation ($\Delta\Delta G_{\text{anion-cation}}$).¹⁹ ATOUT optimized repulsion parameters with respect to experimental values of the osmotic pressure are represented by full black symbols. Blue symbols represent repulsion parameters predicted using the LMWA. Arrows indicate the deviation between optimized and predicted parameters from salts containing Li^+ and F^- ions.

The variation of the MARD with respect to experimental data for our simulations for the osmotic pressure using the predictive strategy to estimate the anion-cation repulsion parameter can be observed in Figure 3. The predictive method based on the LMWA produces a MARD of 12.6%

when all ions are considered in the range of 0-3M concentrations. We observe larger deviations for all salts containing fluorine ions. In comparison, a total MARD of 9% and 5.9% are obtained if lithium and fluorine ions are not accounted for the estimation of the MARD, respectively.

We would like to emphasize that our approach can be easily extended to other coarse grained levels (i.e. N_m from 2 to 5), preserving the accuracy of the optimum model observed in Figure 1, by applying a lineal rescale of interactions based on the volume of water beads (which in turns is determined by N_m). In addition, even if a different choice for the parametrization of the water-water repulsion parameter is done (for instance, using the original approach proposed by de Groot & Warren,⁴⁹ leading to an a_{ww} of 25 $k_B T$), it is possible to apply a simple rescaling factor to unambiguously determine all the water-ion and ion-ion repulsion parameters (see section 6 of SI for details). This flexibility on the choice of the coarse graining level is, in our opinion, one of the strength of DPD simulations compared with other methods such as MARTINI, where a fixed volume of beads is imposed.³⁴

In conclusion, we have presented a simple and thermodynamically consistent methodology for the parameterization of the dissipative particle dynamics (DPD) repulsion parameters of electrolytes in aqueous solutions. Our methodology requires the computation of the osmotic pressure in order to obtain the required interactions by comparison with the available experimental data. Our results for NaCl show that the use of mean osmotic coefficient,⁴¹ as well as the activity coefficient of individual ions⁴² allows to unambiguously determine the Na-water, Cl-water and Na-Cl repulsion parameters. In this case we were able to obtain a mean relative average deviation of 5% and 0.9% for the osmotic pressure and liquid density in the concentration range of 0-3M. Moreover, we have seen that in concentrated NaCl solutions the

present model reproduces the expected trend of ion-pairing when compared with experimental data and atomistic simulations (see section 8 in SI).

We propose a simple linear relationship between the hydration free energies of ions and the ion-water repulsion parameters that allows the parameterization of the complete series of halide and alkaline ions. In addition, we propose a simple approach to estimate the anion-cation repulsion parameters based on the difference of free energy difference of hydration energies of anions and cations in the spirit of the law of matching water affinities (LMWA). This predictive approach reproduces the variation of the osmotic pressure with the salinity of the complete series of halide + alkaline salts with mean absolute relative deviations of the order of 13 %. The present methodology can be straightforwardly applied to other series of ions including bivalent ions as well as more complex polyatomic salts such as surfactants and charged polymers. Work is in progress to explore this kind of systems.

ASSOCIATED CONTENT

Supporting Information.

The supporting information is available free of charge on the ACS Publications website at DOI:10.1021/acs.jpct.XXXXXXX.

Details on the algorithms; treatment of inter-particle interactions; simulation set-up; workflow for the calculation of the osmotic pressure and additional simulation results are available in supporting information (PDF).

AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

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