

# Molecular Simulation of Aqueous Electrolyte Solutions New Models for Monovalent Cations and Anions

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## Introduction

Aqueous electrolyte solutions play an important role in industrial applications, especially as solvents in biochemistry and pharma. In the chemical industry, electrolytes are mainly introduced to permit and/or facilitate separation processes. Upon addition of electrolytes to solvents, their thermodynamic properties change drastically, being dominated by the strong electrostatic interactions between the ions and between the ions and the solvent molecules. One route to predict the thermodynamic properties is molecular modeling and simulation.

Molecular models for ions in aqueous solutions currently available in literature were mostly derived from solvation free energy calculations of one ion pair in solution. Applied to calculation of thermodynamic properties in solutions the models show significant deviation from experimental data. Therefore, "special care has to be taken in the application of ion models for molecular simulation of electrolyte systems" [1].

Here, a set of molecular models for all alkali and halide ions in aqueous solution is presented. The models were parameterized to reproduce experimental data on the reduced liquid solution density, independent of the ionic combination. The present study covers a wide range of salinity and shows no dependency on the molecular model for the solvent water. This is of particular interest for the application of the ion models for simulations of biomolecules, where specific biomolecular force fields are based on varying water models, mainly SPC[2], SPC/E [3] or TIP4P [4].

## Molecular models

For all molecular simulations performed, an extended version of *ms2* [5] was used.

### Molecular models for ions and water

Water model (fixed): SPC/E [3]



1 Center LJ sphere  
3 Point charges

### Ion models (parameterized)

Cation: 1 Center LJ sphere  
1 Point charge



Anion: 1 Center LJ sphere  
1 Point charge



### Dependency of ion models on water

Strong dependency on water model was resolved by investigating reduced properties, i.e. reduced density

$$\tilde{\rho} = \frac{\rho(T, p, x_{\text{Salt}}^{(m)})}{\rho_{\text{H}_2\text{O}}(T, p, x_{\text{Salt}}^{(m)} = 0)}$$

Advantages:

- High parameterization accuracy, since reference mainly depends on ion force fields
- Use of ion models in combination with a variety of different solvent force fields possible without much loss of accuracy

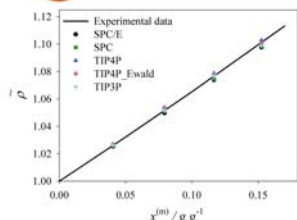


Fig. 1: Influence of the water model on  $\tilde{\rho}$  for an aqueous KCl solution. Five very common water models were investigated, the ion models were taken from this work.

## Reduced density for aqueous alkali halogen solutions

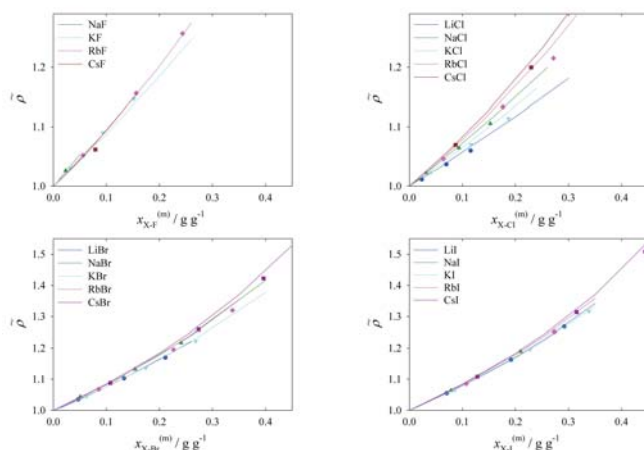


Fig. 5: Reduced density of aqueous alkali halogen solutions. Lines: Experimental data; Symbols: Simulation results with the new ion force field developed in this work

## Force field development

### Parameterization of LJ size parameter

- LJ size parameter  $\sigma_a$  and  $\sigma_c$  were adjusted to  $\tilde{\rho}$  over a wide range of salinity  $x_{\text{Salt}}^{(m)}$ .
- The ion LJ energy parameter was set to a constant value of  $\epsilon / k_B = 100\text{K}$  for all ions. Its influence on  $\tilde{\rho}$  is negligible.
- The influence of  $x_{\text{Salt}}^{(m)}$  on the reference was approximated by a first order Taylor expansion around state point pure water.

$$\tilde{\rho} = \tilde{\rho}_{\text{H}_2\text{O}}^{(m)} + \frac{d\tilde{\rho}}{dx_{\text{Salt}}^{(m)}} (x_{\text{Salt}}^{(m)} - x_{\text{H}_2\text{O}}^{(m)}) = 1 + \frac{d\tilde{\rho}}{dx_{\text{Salt}}^{(m)}} x_{\text{Salt}}^{(m)}$$

This approximation is accurate, since the experimental reference  $\tilde{\rho}^{\text{Exp}}$  shows an almost linear increase with increasing salinity.

### Parameterization strategy:

- Reduced density was determined for 42 combinations of ion size parameters systematically.
- Results regressed using polynomial functions  $f$

$$f: (\sigma_a, \sigma_c) \rightarrow \frac{d\tilde{\rho}}{dx_{\text{Salt}}^{(m)}}, \text{ determined in } \sigma_a \in [2.0; 4.5] \text{ \AA}$$

$$\sigma_c \in [1.5; 4.5] \text{ \AA}$$

Ion LJ parameters were result of optimization problem:

$$f(\sigma_a, \sigma_c) - \tilde{\rho}^{\text{Exp}} = \min$$

A global fit over 20 alkali halide salts was performed

### Parameterization of LJ energy parameter

LJ energy parameter  $\epsilon_a$  and  $\epsilon_c$  adjusted to osmotic coefficient  $\phi_{\text{H}_2\text{O}}$  of water in solution.

$$\phi_{\text{H}_2\text{O}} = \frac{\ln(a_{\text{H}_2\text{O}})}{\ln(x_{\text{H}_2\text{O}}^{(n)})}$$

The calculation of osmotic coefficients by molecular simulations is subject to high statistical uncertainties. Therefore, a parameterization of ion LJ energy parameters on basis of  $\phi_{\text{H}_2\text{O}}$  is only possible in orders of magnitude.

Reasonable fit:

$$\epsilon_a / k_B = \epsilon_c / k_B = 200 \text{ K}$$

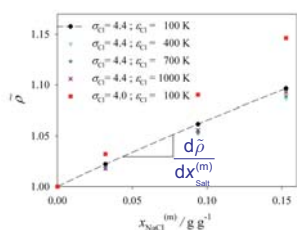


Fig. 2: Influence of the LJ parameters on the reduced density  $\tilde{\rho}$  for sodium chloride

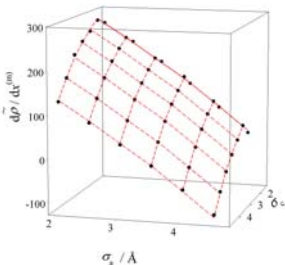


Fig. 3: Simulation results (black) and functional regression (red) of the reduced density as function of salinity

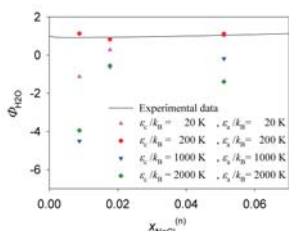


Fig. 4: Osmotic coefficient of water in aqueous sodium chloride solution for varying LJ energy parameters  $\epsilon$

## Structural properties and solubilities

### Radius of gyration (RDF) and hydration number, for NaCl in H<sub>2</sub>O as example

- Position of the first hydration shell in good agreement with experimental data
- Number of water molecules around the ions is well matched by experimental data

	$r_{\text{max}} / \text{\AA}$		$r_{\text{min}} / \text{\AA}$		$n$	
	Sim	Exp	Sim	Exp	Sim	Exp
Na <sup>+</sup>	2.2	2.3	3.0	3.0	5.2	5
Cl <sup>-</sup>	3.1	3.1	4.0	4.0	7.3	7

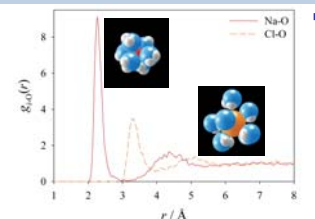


Fig. 6: RDF and sketch of water around Na<sup>+</sup> (red solid line) and Cl<sup>-</sup> (orange dashed line) in aqueous NaCl solution.

### Reduced Henry's coefficient of CO<sub>2</sub> in aqueous NaCl solution as example

Definition of the reduced Henry's coefficient

$$\tilde{H}_{\text{CO}_2, \text{ES}} = \frac{H_{\text{CO}_2, \text{ES}}}{H_{\text{CO}_2, \text{S}}}$$

Reduction necessary, since chemical reactions of CO<sub>2</sub> with the solvent are omitted in the calculation.

The reduced Henry's coefficient was calculated purely predictive at  $T = 313.15 \text{ K}$  and  $x_{\text{NaCl}}^{(m)} = 0.12 \text{ g/g}$ .

Prediction	Experiment
1.61	1.60

## Summary

Molecular models for alkali and halide ions in aqueous solution were developed, which are applicable for a wide range of salinity and for any mutual combination of ions. The models were determined by a global fit to experimental data of the reduced liquid solution density and the osmotic coefficient of the solvent.

The ions models are highly accurate with respect to structural data and, of course, the reduced liquid solution density. Other thermodynamic properties, i.e. Henry's coefficient, even at varying temperatures, can successfully be predicted.

A more detailed discussion of the parameterization procedure and the ion models is currently prepared for publication.

### Acknowledgement

The authors gratefully acknowledge financial support for the project by the 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.

### References

- [1] P. Auffinger, T. E. Cheatham, A. C. Vaiana, "Spontaneous formation of KCl aggregates in biomolecular simulations: A force field issue?", *Journal of Chemical Theory and Computation*, **2007**, 3, 1851 - 1859
- [2] H. J. C. Berendsen, J. P. M Postma, W. F. van Gunsteren, J. Hermans, "Intermolecular forces", *D. Reidel Publishing Company, Dordrecht*, **1981**
- [3] H. J. C. Berendsen, J. R. Grigera, T. P. Straatsma, "The missing term in effective pair potential", *Journal of Physical Chemistry*, **1987**, 91, 6269 - 6271
- [4] W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, M. L. Klein, "Comparison of simple potential functions for simulating liquid water", *Journal of Chemical Physics*, **1983**, 79, 926 - 935
- [5] S. Deublein, B. Eckl, J. Stoll, S. Lishchuk, G. Guevara-Carrion, C. Glass, T. Merker, M. Bernreuther, H. Hasse, J. Vrabcic, "ms2: A molecular simulation tool for thermodynamic properties", *Computer Physics Communication*, **2011**, 182, 2350 - 2367