Molecular simulation of aqueous and non-aqueous electrolyte solutions

M. T. Horsch,[1] S. Reiser,[1] M. Kohns,[1] J. Vrabec,[2] and H. Hasse[1]
TU Kaiserslautern[1] and University of Paderborn[2]

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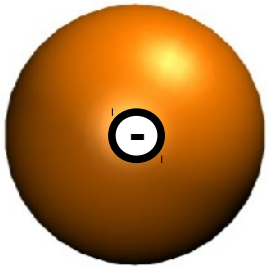
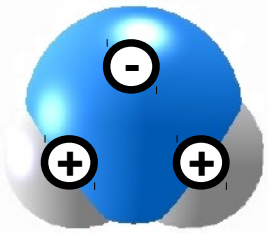
Computational Molecular Engineering

Modelling aqueous electrolyte solutions

Molecular models:



Ions
1 LJ site
1 point charge



Water
1 LJ site
3 partial charges

Literature models:

- Scattering of model parameters

Parameters for Na^+:

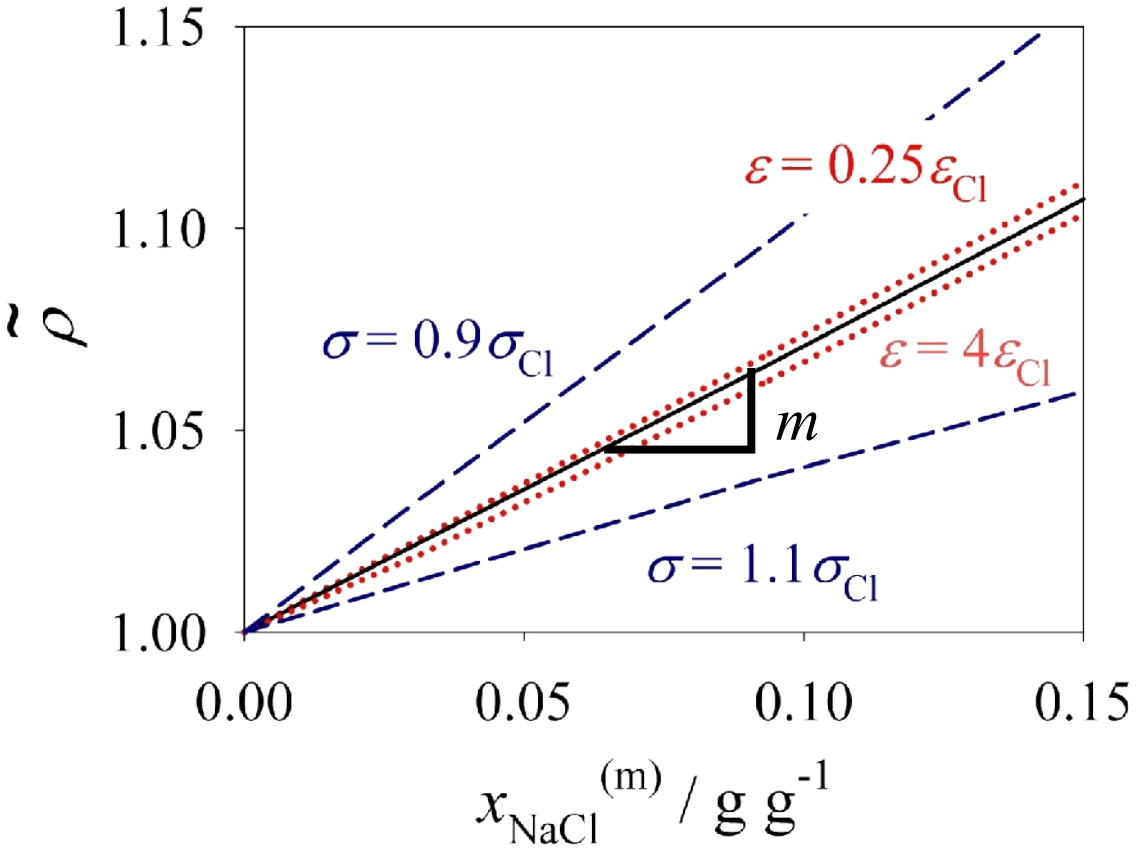
$1.9 < \sigma_{Na+} / Å < 4.1$

$0.06 < \varepsilon_{Na+} / K < 1068.8$

⇨ Large deviation from experimental data!

Reduced density over salt concentration

Reduced density of NaCl solutions (T = 298 K, p = 1 bar)

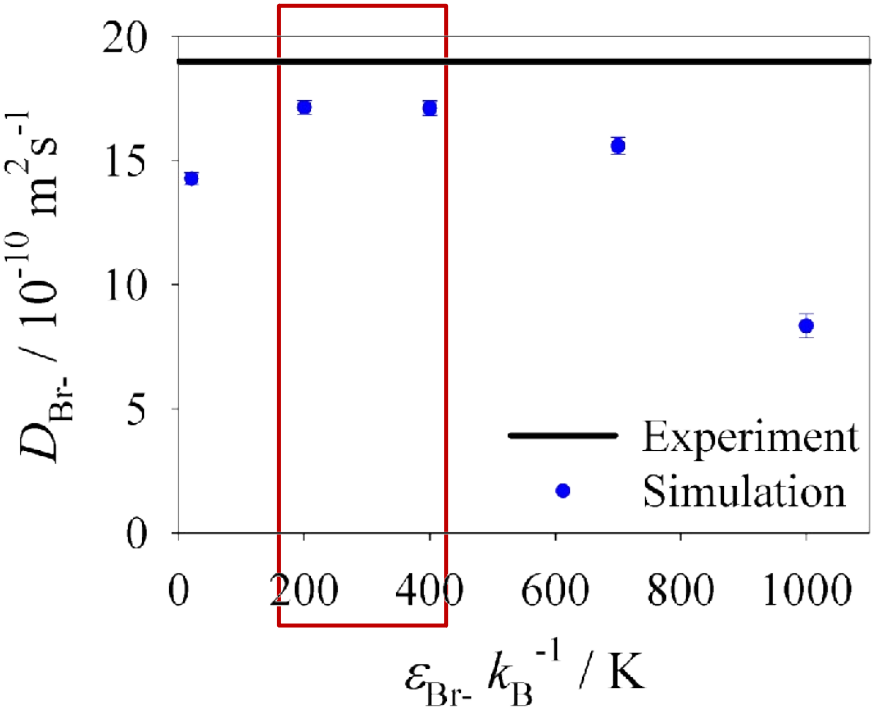


Sensitivity study:

- σ_{ion} dominant
- ε_{ion} negligible

Fine tuning of the molecular models

Adjustment of the LJ energy parameters ε_{ion} to the **self-diffusion coefficient** in solution (T = 298 K, p = 1 bar)

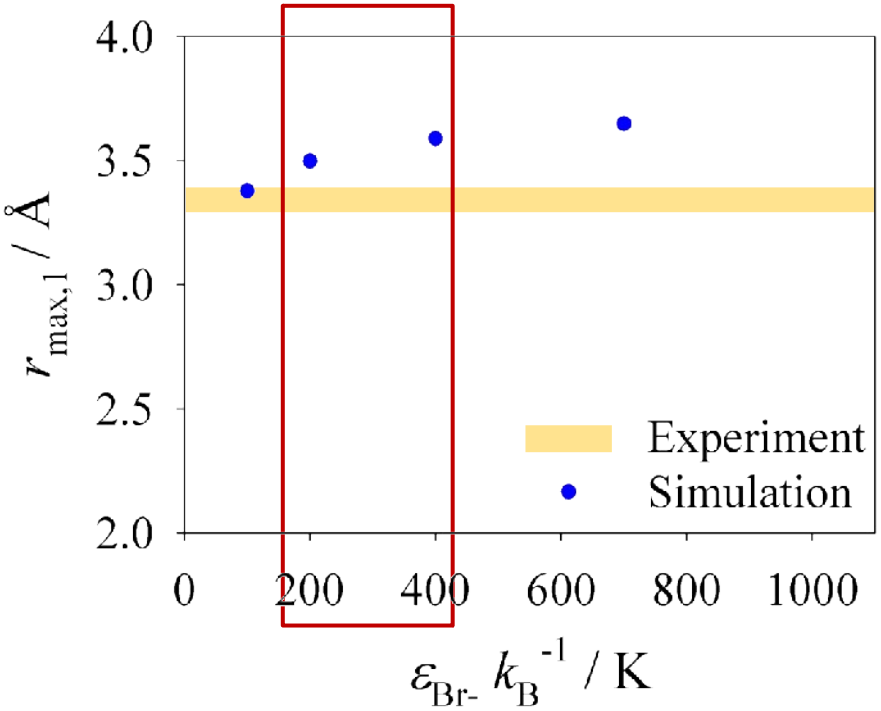


- Reasonable agreement: 200 K ≤ ε_{Br-} ≤ 400 K
- Similar dependence was found for all alkali and halide ions

(water model: SPC/E)

Fine tuning of the molecular models

Adjustment of the LJ energy parameters ε_{ion} to the first peak in the **radial distribution function** (T = 293 K, p = 1 bar)

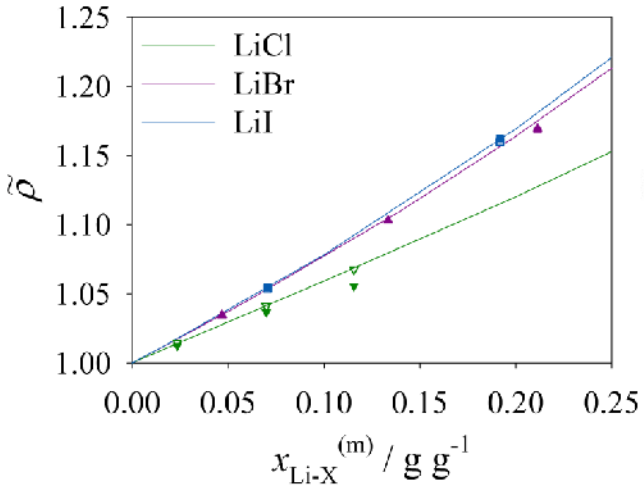


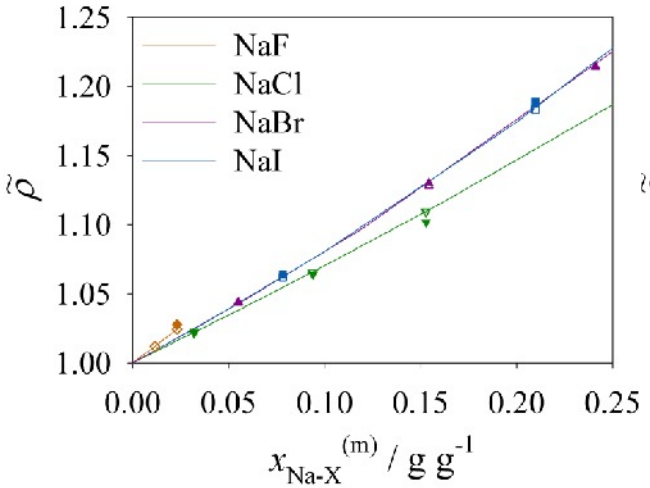
- Reasonable match: ε_{Br-} = 200 K
- Final compromise: $\varepsilon_{cat} = \varepsilon_{an}$ = 200 K

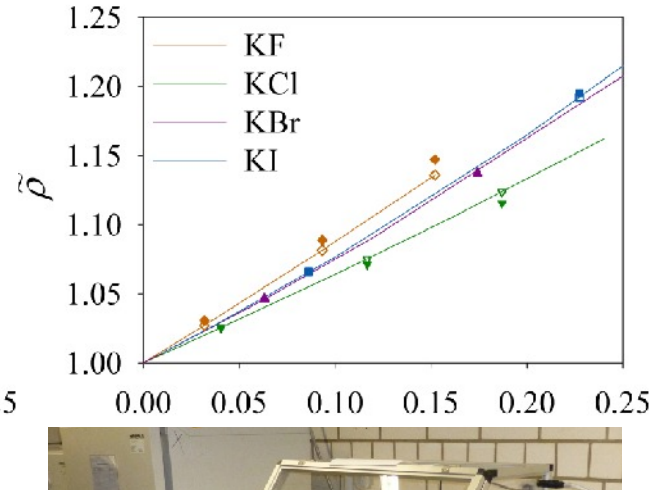
(water model: SPC/E)

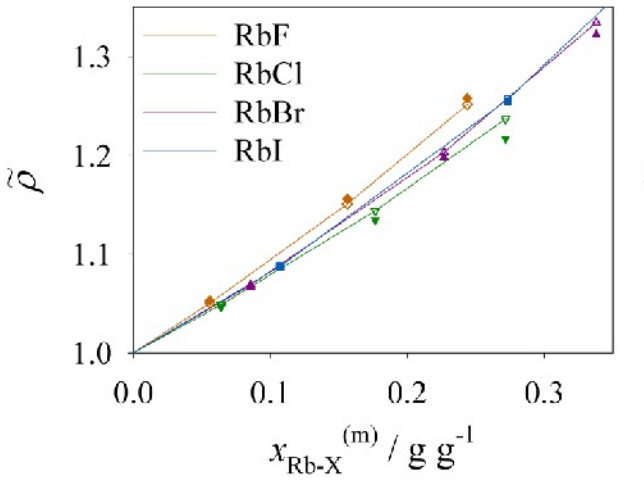
Temperature dependence of the density

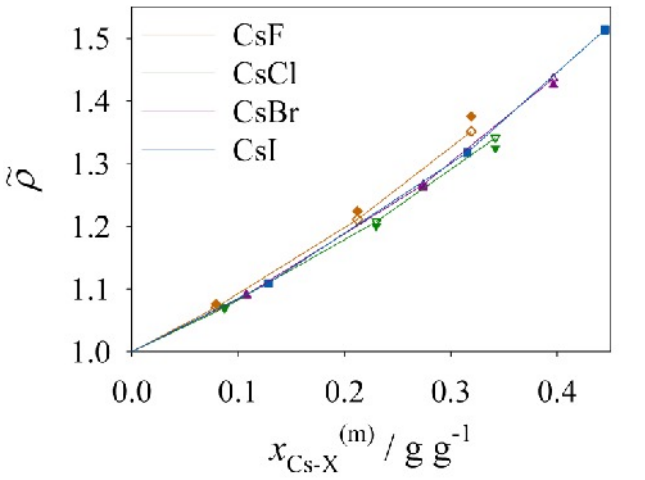
Predictions for aqueous solution (T = 333 K, p = 1 bar)





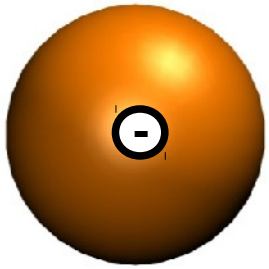




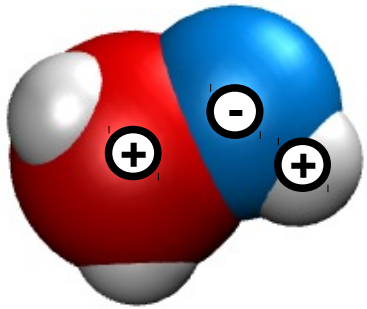


Methanolic electrolyte solutions

Molecular models:



Ions
1 LJ site
1 point charge



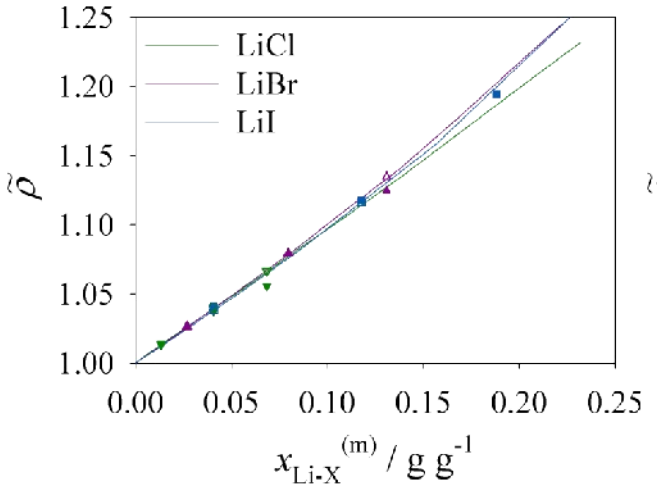
Methanol
2 LJ sites
3 partial charges

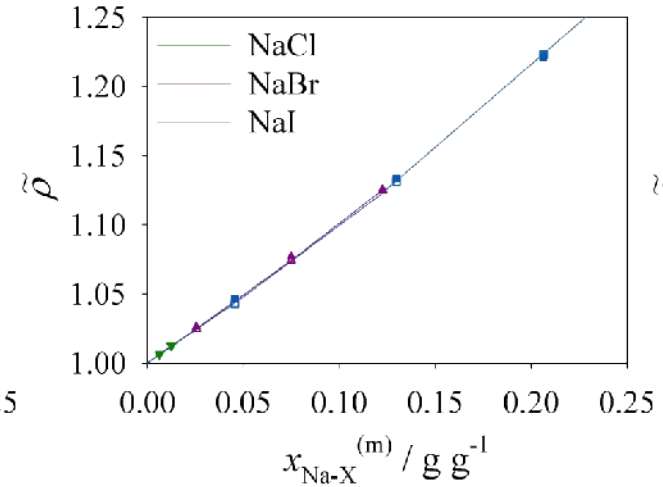
Reference property:

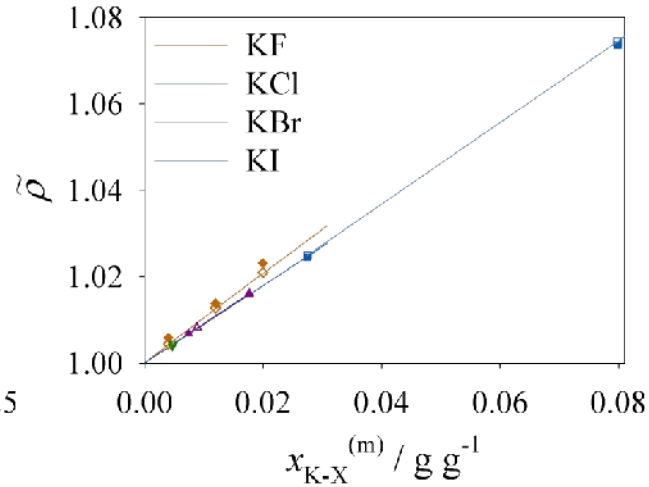
- Reduced density $\rho^{‰} = \frac{\rho_{solution}}{\rho_{pure\ solvent}}$

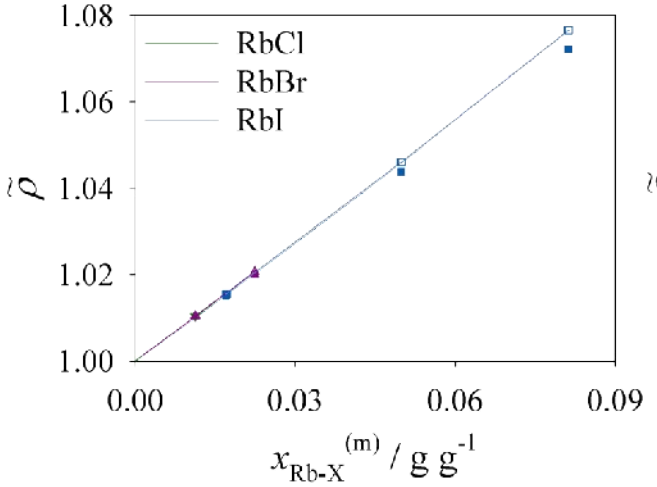
Methanolic electrolyte solutions

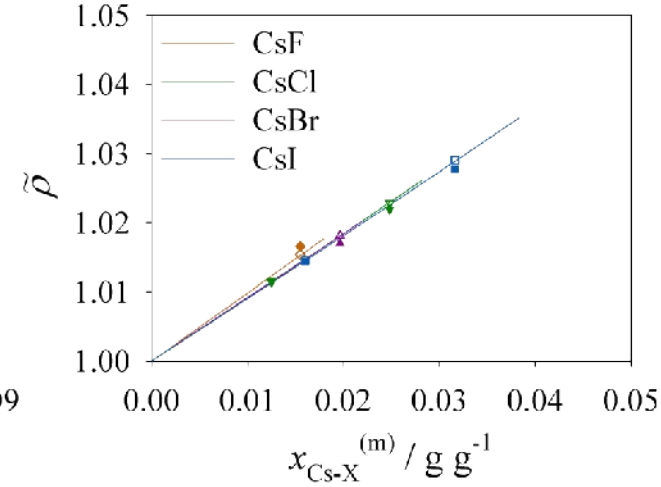
Predictions (T = 298 K, p = 1 bar)











- Experimental data (this work)
- Simulation