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Molecular simulation of aqueous and non-aqueous electrolyte solutions

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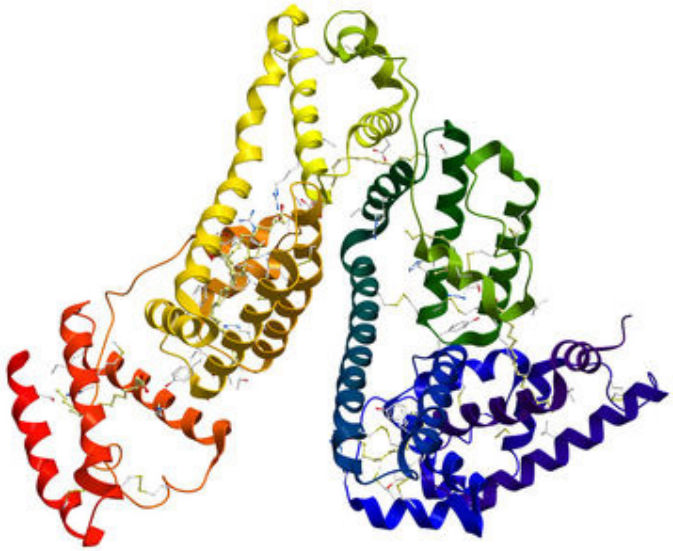
Computational Molecular Engineering

Electrolyte Solutions – Applications

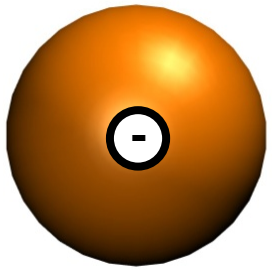


Buffer solutions in pharmaceutical and biochemical industry / purification of proteins

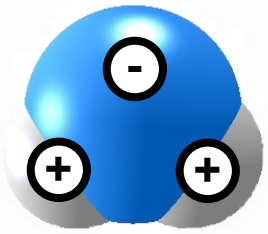
Electrochemistry / energy storages

Simulation of aqueous electrolyte solution

Molecular models:



Ions
1 CLJ
1 point charge



Water
1 CLJ
3 partial charges

Literature models:

- Scattering of model parameters

Parameters Na^+ :

$1.9 < \sigma_{Na+} / Å < 4.1$

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

Reference property:

- Density ρ

⇨ Large deviation from experiments

Parameter optimization for alkali halides

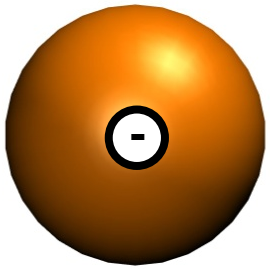
Adjustable parameters:

- Ions: 1 CLJ with 1 point charge (±1e) – 2 parameters

Target:

- Reduced density for varying salinity at T = 293 K, p = 1 bar

$$\tilde{\rho} = \frac{\rho_{\text{Electrolyte solution}}}{\rho_{\text{Solvent}}} = \tilde{\rho}(\sigma_+, \sigma_-, \varepsilon_+, \varepsilon_-, x_\pm)$$



σ_{Ion}, ε_{Ion}

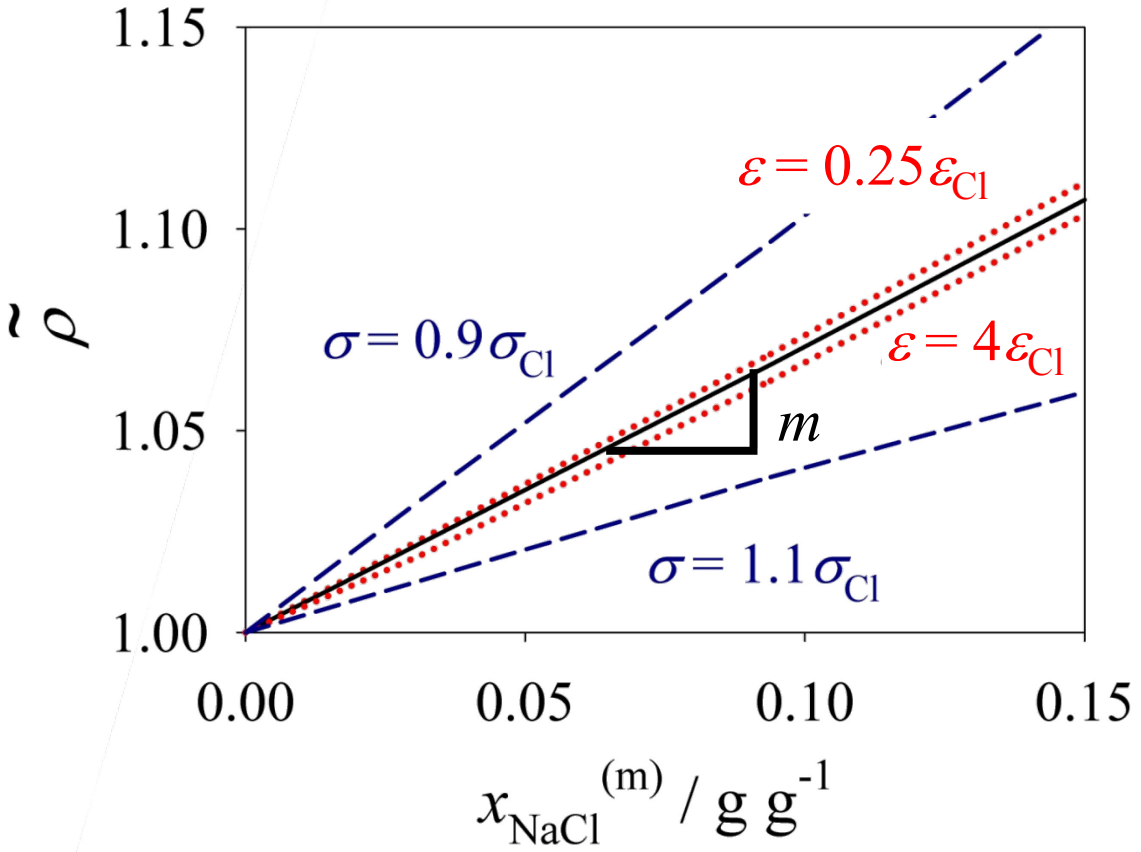
Simulation conditions:

- Monte Carlo simulation
- SPC/E water model
- Simulation code: extended version of *ms*2*

*Deublein et al., Computer Physics Communications (2011), 182, 2350 – 2367; http://www.ms-2.de

Target: Slope of the reduced density over the salt mass fraction

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



Sensitivity study of $\tilde{\rho}^{Sim}$:

- σ_{Ion} dominant
- ε_{Ion} negligible

$$\tilde{\rho}^{Sim} = \tilde{\rho}^{Sim}(\sigma_+, \sigma_-, x_\pm)$$

Adjustment:

$$m = \frac{d\tilde{\rho}^{Sim}}{dx^{(m)}} = \frac{d\tilde{\rho}^{Sim}}{dx^{(m)}}(\sigma_+, \sigma_-)$$

Parameter optimization for alkali halides

Electrolyte systems:

5 cations: Li^+, Na^+, K^+, Rb^+, Cs^+

4 anions: F^-, Cl^-, Br^-, I^-

} 20 salts modeled by 9 parameter

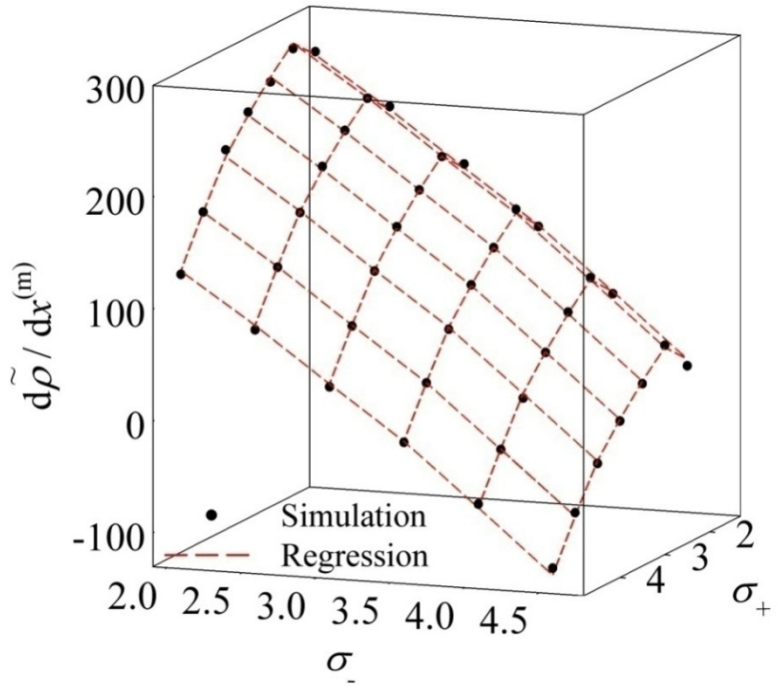
Size adjustment:

- Global fit

σ_+[1.5; 4.5] Å

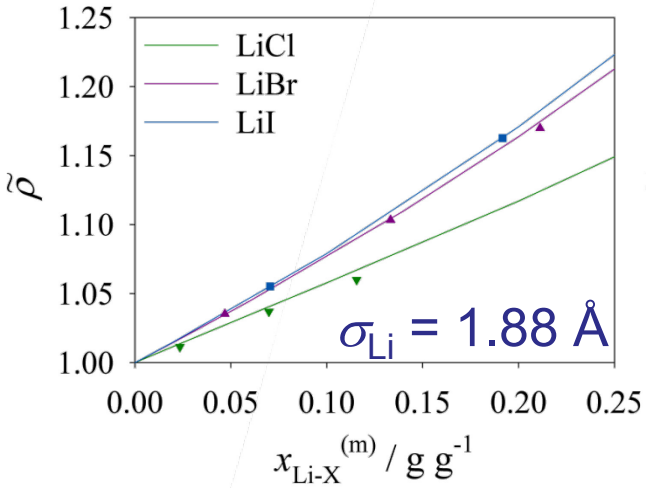
σ_- [2.0; 4.5] Å

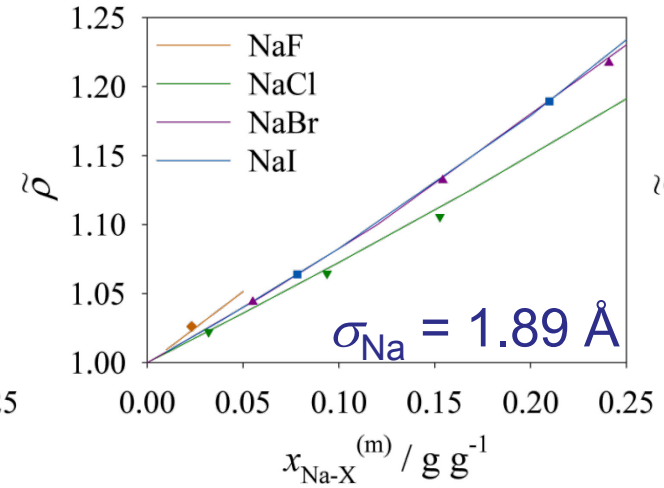
$$\frac{d\tilde{\rho}^{Exp}}{dx^{(m)}} \overset{!}{=} \frac{d\tilde{\rho}^{Sim}}{dx^{(m)}}(\sigma_+, \sigma_-)$$

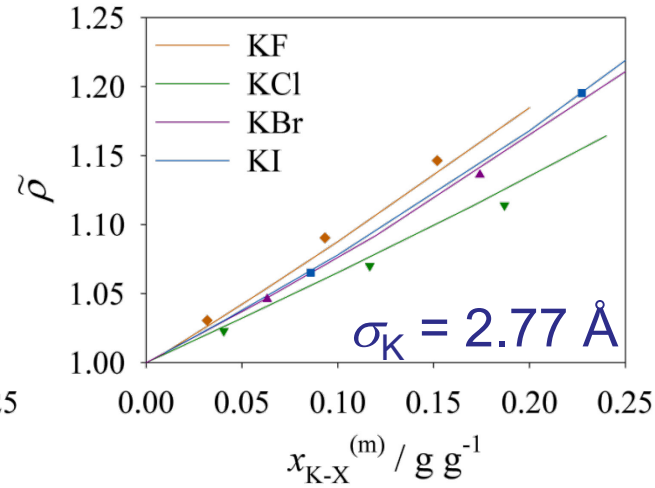


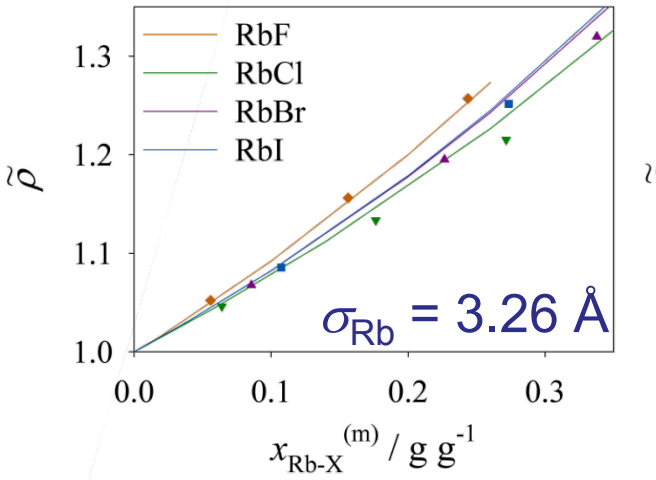
Aqueous electrolyte solutions

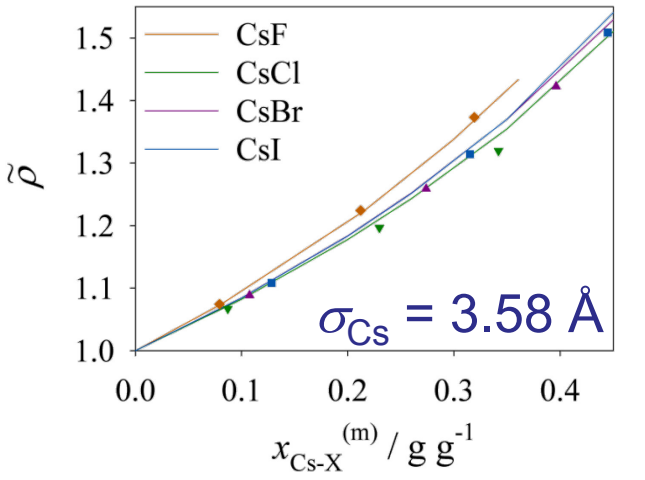
Reduced density (T = 293 K, p = 1 bar)











Anions

σ_{F} = 3.66 Å

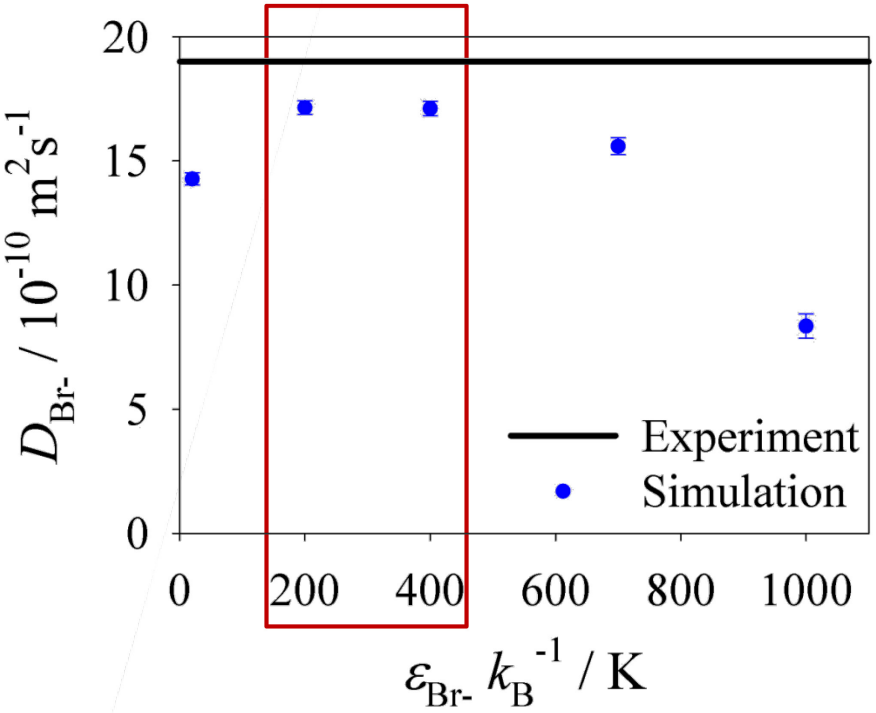
σ_{Cl} = 4.41 Å

σ_{Br} = 4.54 Å

σ_{I} = 4.78 Å

Self-diffusion coefficient of ions in aqueous solution (Example bromide)

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



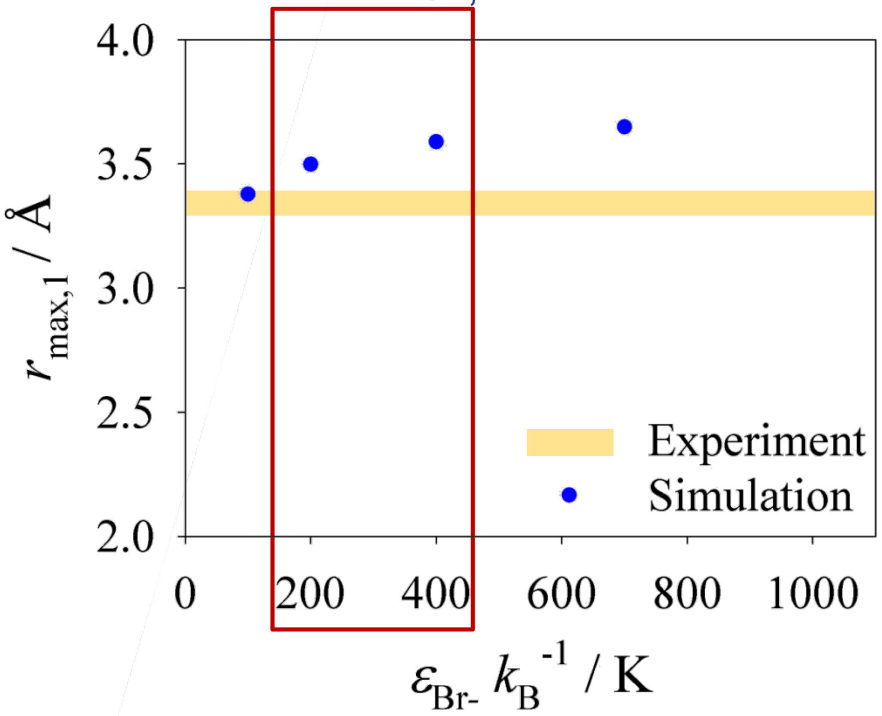
- Reasonable parameter range:

  200 K ≤ ε_{Br^-} ≤ 400 K
- Similar dependence of D_i on ε_i for all alkali and halide ions

Water model: SPC/E

Radial distribution function of water around the ions (Example bromide)

Adjustment of the LJ energy parameters ε_{Ion} to the first maximum $r_{max,1}$ in the RDF (T = 293 K, p = 1 bar)



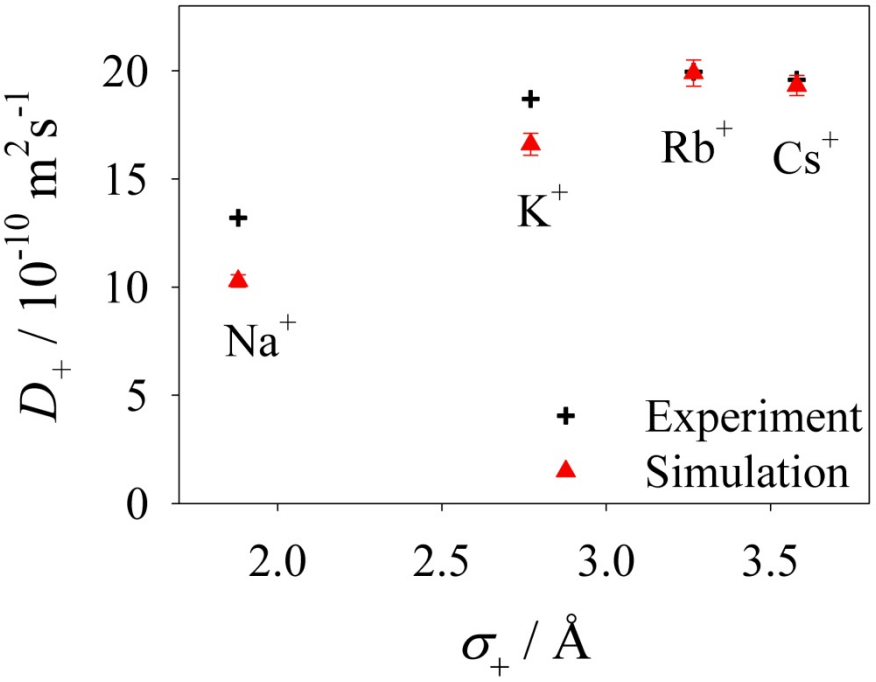
- Reasonable match: ε_{Br-} = 200 K
- Best choice: $\varepsilon_{+} = \varepsilon_{-}$ = 200 K

Water model: SPC/E

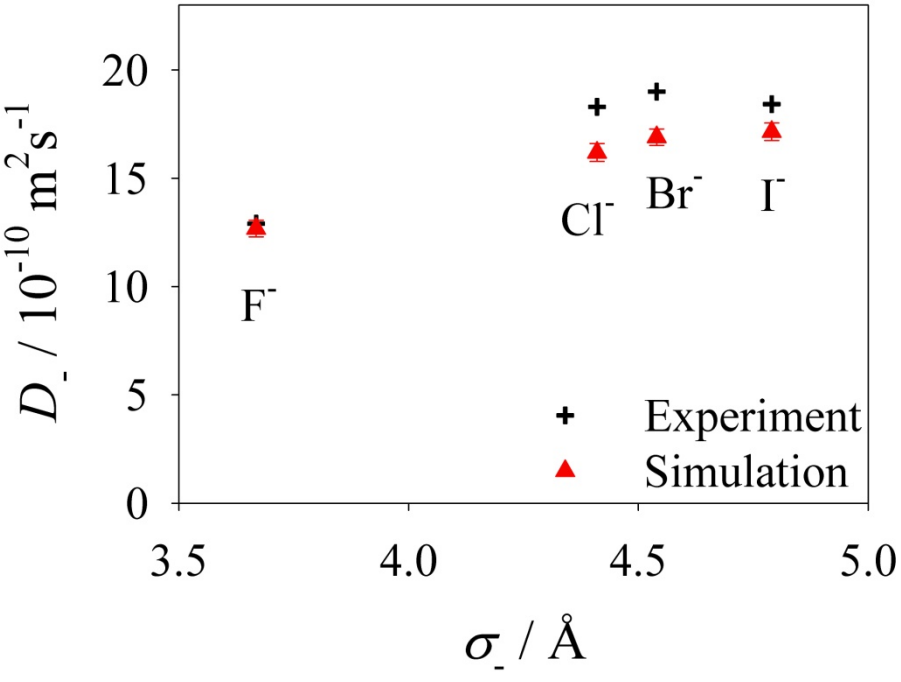
Self-diffusion coefficient of alkali cations and halide anions in aqueous solution

Comparison with experimental data (T = 298 K, p = 1 bar)

Cations



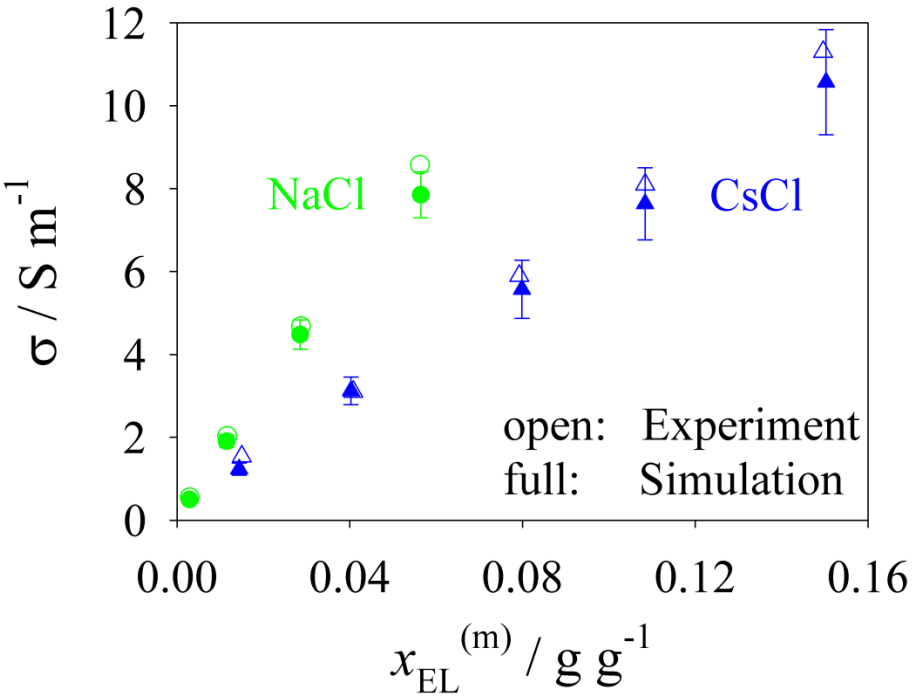
Anions



Water model: SPC/E

Electric conductivity of NaCl and CsCl in aqueous solutions at various salinities

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



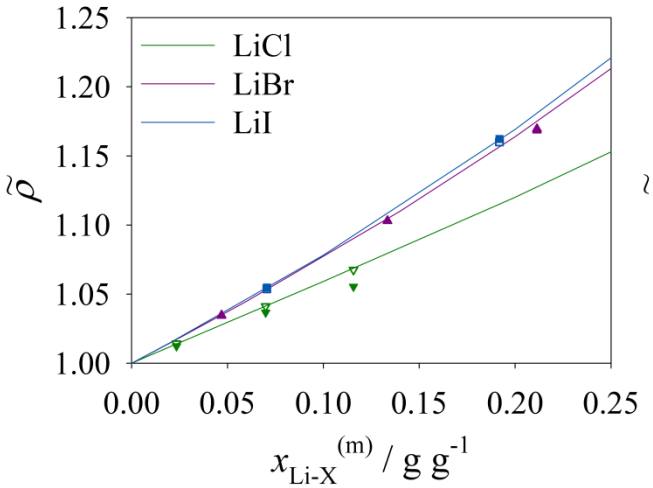
Electric conductivity:

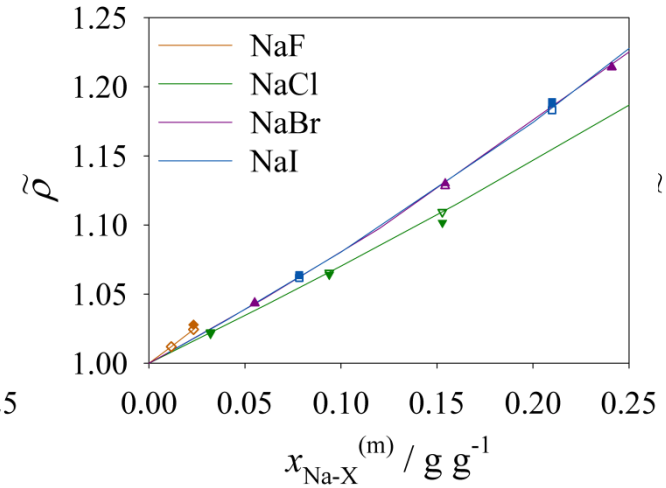
- Correlated motion of the ions in solution

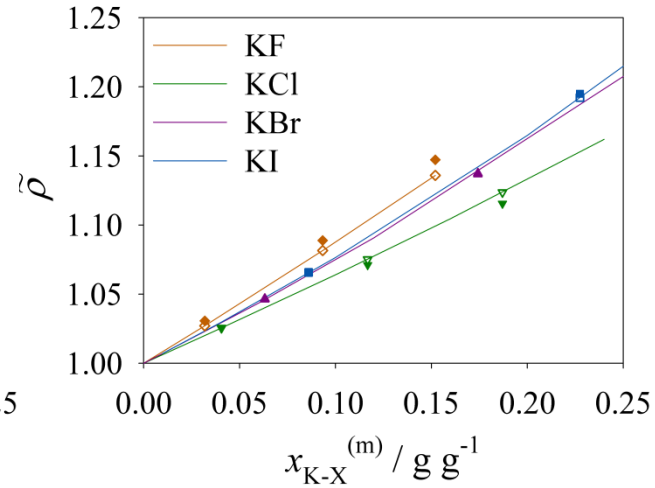
Water model: SPC/E

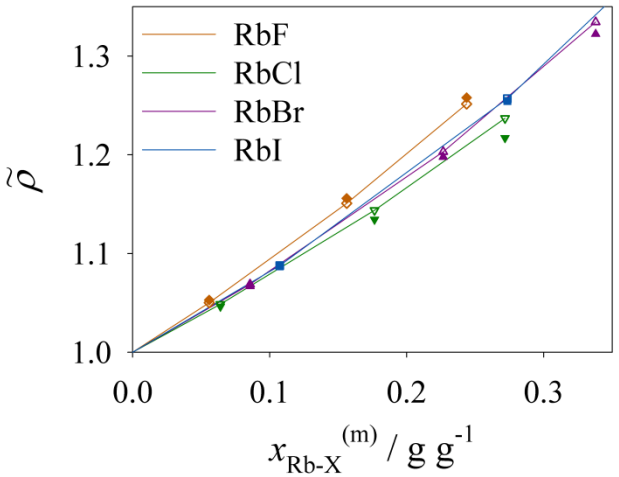
Temperature dependence of the density

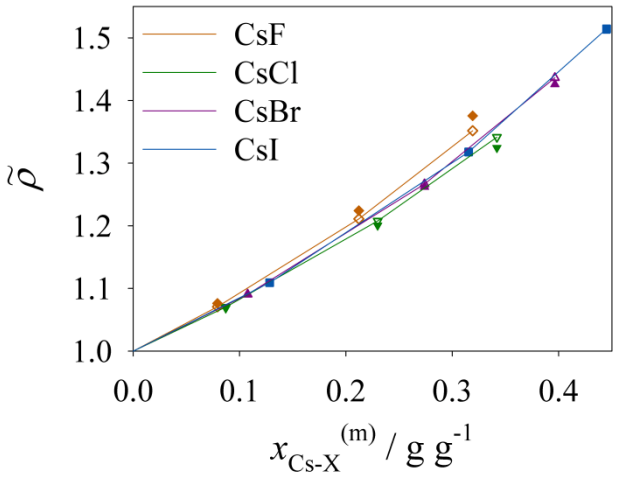
Predictions for aqueous solution (T = 333 K, p = 1 bar)







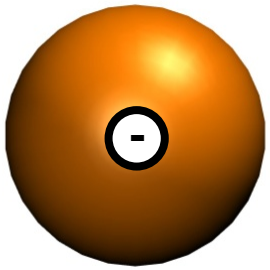




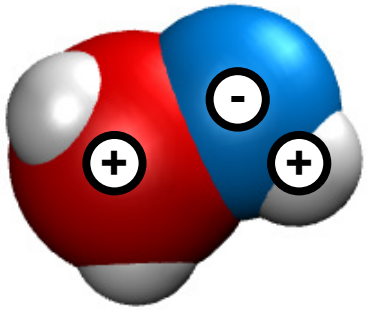
- Experimental data (this work)
- Simulation

Simulation of non-aqueous electrolyte solutions: solvent methanol

Molecular models:



Ions
1 CLJ
1 point charge



Methanol
2 CLJ
3 partial charges

Reference property:

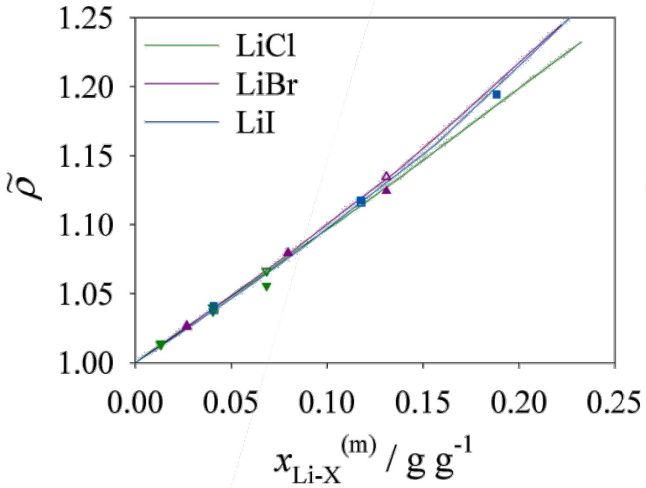
- Reduced density $\tilde{\rho} = \frac{\rho_{\text{Electrolyt solution}}}{\rho_{\text{Solvent}}}$

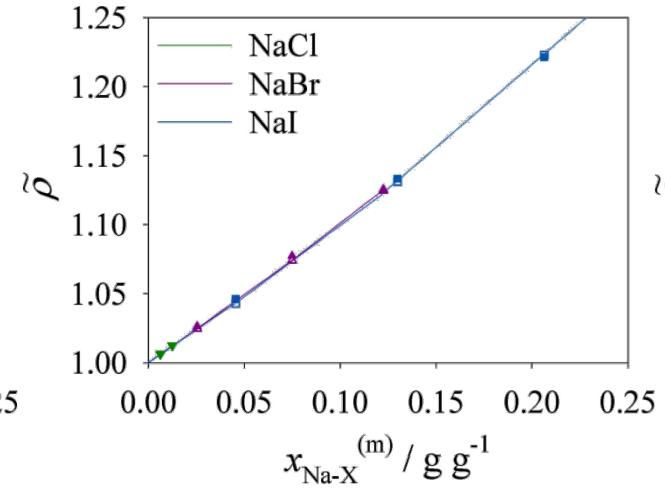
Simulation:

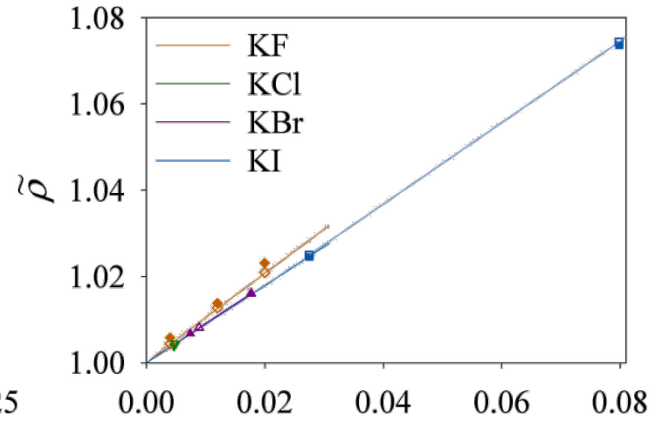
- MC simulations at T = 298 K, p = 1 bar

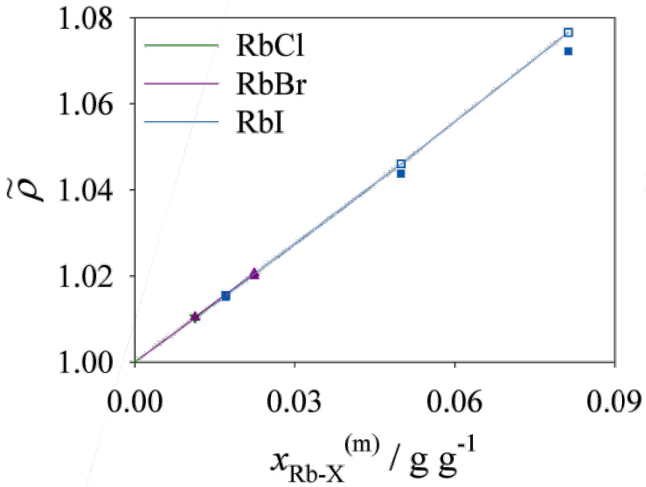
Methanolic electrolyte solutions

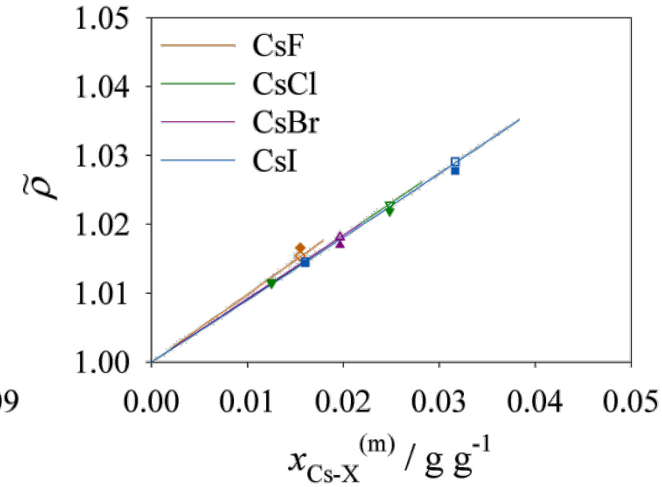
Predictions (T = 298 K, p = 1 bar)

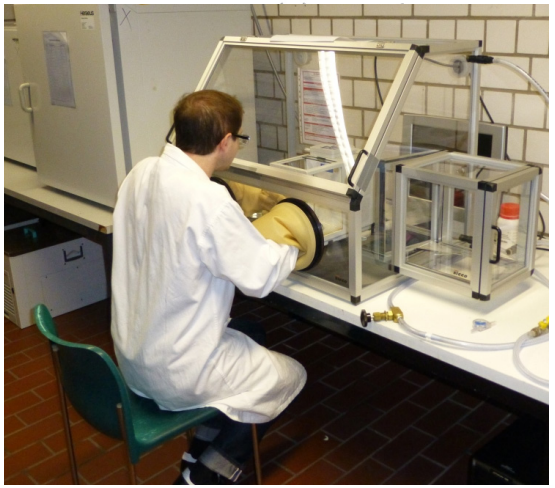






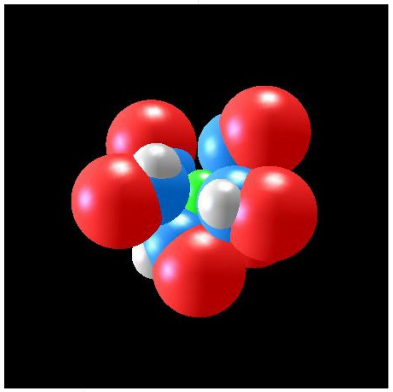




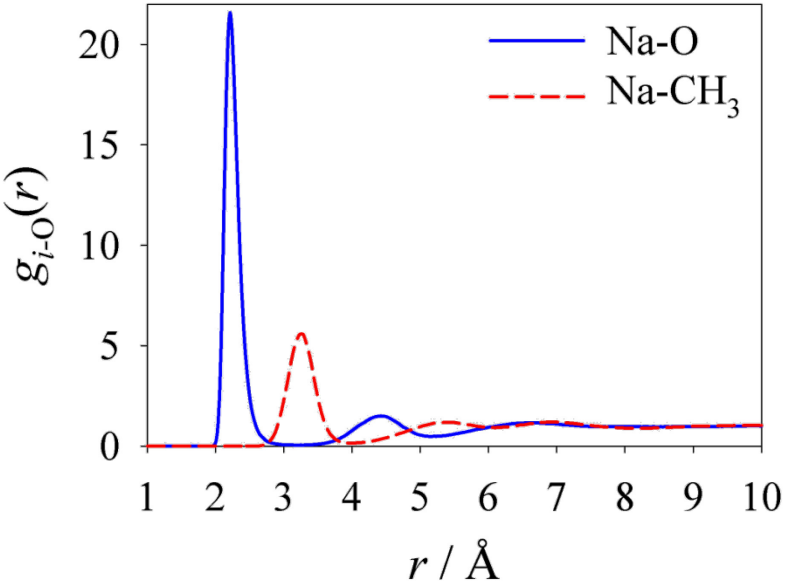


Radial distribution function of methanol

Diluted methanolic NaCl solution (T = 298 K, p = 1 bar)



Na^+



	$r_{1.\,Max}$ / Å		$r_{1.\,Min}$ / Å	
	Methanol	Water	Methanol	Water
Na – O	2.21	2.23	3.17	3.07

Summary

- ✓ New atomistic force fields for ions
  - ✓ Alkali-cations: Li^+, Na^+, K^+, Rb^+, Cs^+
  - ✓ Halide-anions: F^-, Cl^-, Br^-, I^-
- ✓ Model adjustment in aqueous systems
  - ✓ Reduced density
  - ✓ Self-diffusion coefficient and RDF
- ✓ Predictions
  - ✓ Electric conductivity
  - ✓ Temperature dependence of the reduced density
  - ✓ Reduced density of methanolic solutions