Activities in electrolyte solutions by molecular simulation of the osmotic pressure

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Osmotic pressure for activity of solvents

In a dense liquid, it is hard to compute the chemical potential (or activity) by inserting test particles.

**OPAS method:** Compute the osmotic pressure from the force acting on a virtual semipermeable membrane.

External harmonic potential constraining the solute inside.

No external potential for the solvent.

\[ \Pi = P^{\text{in}} - P^{\text{out}} \]
Osmotic pressure for activity of solvents

Step 1: Pseudo-$NPT$ run, where the barostat is adjusted to regulate $P_{\text{out}}$.

Step 2: $NVT$ simulation.

OPAS method: Compute the osmotic pressure from the force acting on a virtual semipermeable membrane.

Solvent activity (Raoult normalization) from osmotic pressure:

$$RT \ln a_{\text{solv}}^{\text{in}} = - \int_{P_{\text{out}}}^{P_{\text{in}}} dP \nu_{\text{solv}}^{\text{pure}} \approx -\Pi \nu_{\text{solv}}^{\text{pure}}$$

Density and compressibility of the pure solvent are easy to compute.

http://www.ms-2.de/
Validation of the OPAS method

Test case: Mixture of argon (LJ) and oxygen (2CLJQ).

Ar is treated as solvent and moves freely through the simulation volume. The solute $O_2$ is confined by the membranes to the inner compartment.
Validation of the OPAS method

Test case: Mixture of argon (LJ) and oxygen (2CLJQ).

Osmotic pressure from force acting on the membranes: $6.33 \pm 0.06$ MPa. Osmotic pressure from difference between compartments: $6.1 \pm 0.2$ MPa.
Aqueous alkali halide salt solutions: Model

Molecular models:

Ions
1 Lennard-Jones
1 point charge

Water (here: SPC/E)
1 Lennard-Jones
3 partial charges

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Adjusting the model to experimental data

Density ratio “solution : pure”

\[ T = 298 \text{ K} \]
\[ P = 100 \text{ kPa} \]

Self-diffusion coefficients

\[ \sigma = 0.9 \sigma_{\text{Cl}} \]
\[ \varepsilon = 0.25 \varepsilon_{\text{Cl}} \]
\[ \sigma = 1.1 \sigma_{\text{Cl}} \]

\[ \varepsilon = 4 \varepsilon_{\text{Cl}} \]

Lennard-Jones size parameter \( \sigma \)
Lennard-Jones energy parameter \( \varepsilon \)
Validation: Non-aqueous solutions

Density of methanolic electrolyte solutions at $T = 298$ K and $P = 1$ bar:

- Experimental data (this work)
- Simulation
Water activity in electrolyte solutions

Validation of OPAS simulation results against literature data for aqueous NaCl solution using

- the SPC/E water model,
- the Joung-Cheatham NaCl model.

\[ T = 298.2 \text{ K} \]
\[ P_{\text{out}} = 1 \text{ bar} \]
Salt activity coefficient in aqueous solution

Chemical potentials of the solute and the solvent are related by the Gibbs-Duhem equation.

Chemical potential of the salt expressed as activity coefficient (Henry normalization).
Salt activity coefficient in aqueous solution

Series of own models for

- alkali cations
- and halide anions,

collectively adjusted to

- reduced solution densities
- and self-diffusion coefficients.

Present simulation results

- Mester and Panagiotopoulos

Validation against:

- Correlation to experimental data by Hamer and Wu
Salt activity coefficient in aqueous solution

LiF

Not soluble in water

LiCl

LiBr

LiI

NaF

NaCl

NaBr

NaI

KF

KCl

KBr

KI
Revised $\sigma(K^+) = 2.06 \text{ Å} \text{ (before: 2.77 Å)}, \sigma(F^-) = 3.94 \text{ Å} \text{ (before: 3.66 Å)}$.

For a specific combination of ions, the accuracy for the chemical potential can be improved without a loss in accuracy for the density.
Conclusion

In previous work of our group, \textit{LJ + point charge} models of the alkali and halide ions were parameterized to the density of aqueous salt solutions.

The models were \textit{validated} against own experimental (density) data for non-aqueous solutions and for aqueous solutions at different conditions.

By \textit{OPAS simulation} with virtual semipermeable membranes, the influence of salts on the \textit{activity of the solvent} can be determined with a reduced effort, compared with methods based on particle insertion.

\textit{Activity coefficients of the solute} alkali halide salt can be obtained by Gibbs-Duhem integration.

In some cases, the models agree well with experimental activity data. In other cases, the \textit{agreement can be improved} substantially.