Molecular Simulation of Aqueous Electrolyte Solutions

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Electrolytes in Aqueous Solution – Applications

Buffer solutions in pharmaceutical and biochemical industry / purification of proteins

$\text{CO}_2$ -storage in saline aquifers
Simulation of aqueous electrolyte solution

Molecular models

Ions
1 CLJ
1 point charge

Water
1 CLJ
3 point charges

Reference property:
• Density $\rho$

Minimize the influence of uncertainties in water model:
• Reduced density: $\tilde{\rho} = \frac{\rho_{\text{Electrolyte solution}}}{\rho_{\text{Solvent}}}$
Literature models NaCl

Reduced density of NaCl solutions \( (T = 293\, \text{K}, \, p = 1\, \text{bar}) \)

- Parameters Na\(^+\) :
  - \( 1.9 < \sigma_{\text{Na}^+}/\text{Å} < 4.1 \)
  - \( 0.06 < \varepsilon_{\text{Na}^+}/\text{K} < 1068.8 \)

- Parameters Cl\(^-\) :
  - \( 3.5 < \sigma_{\text{Cl}^-}/\text{Å} < 4.8 \)
  - \( 38.0 < \varepsilon_{\text{Cl}^-}/\text{K} < 118.0 \)

- Scattering of model parameters also for other salts
- Large deviations 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

\[ \tilde{\rho} = \frac{\rho_{El}}{\rho_s} = \tilde{\rho}(\sigma_+, \sigma_-, \varepsilon_+, \varepsilon_-, x_\pm) \]

Simulation conditions

- MC simulations at \( T = 293 \) K, \( \rho = 1 \) bar
- SPC/E water model
- Simulation code: extended version of \( ms2^1 \)

1: Deublein et al.; CPC; 2011 ; http://www.ms-2.de
Sensitivity study

Reduced density of NaCl solutions ($T = 293$ K, $p = 1$ bar)

Sensitivity of simulation results of $\tilde{\rho}^{\text{Sim}}$:

- $\sigma_{\text{ion}}$ dominant
- $\varepsilon_{\text{ion}}$ negligible

$$\tilde{\rho}^{\text{Sim}} = \tilde{\rho}^{\text{Sim}}(\sigma_{\text{ions}}, x_{\pm})$$

Parameter adjustment:

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

Electrolyte systems:
5 cations:  Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺
4 anions:  F⁻, Cl⁻, Br⁻, I⁻

20 different salts
9 parameters

Global fitting approach:

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

with \( \sigma_+ \) [1.5;4.5]
\( \sigma_- \) [2.0;4.5]
Aqueous electrolyte solutions - Results

Reduced density \((T = 293 \text{ K}, \rho = 1 \text{ bar})\)

- \(\sigma_{\text{Li}} = 1.88 \text{ Å}\) for LiCl, LiBr, LiI
- \(\sigma_{\text{Na}} = 1.89 \text{ Å}\) for NaF, NaCl, NaBr, NaI
- \(\sigma_{\text{K}} = 2.77 \text{ Å}\) for KF, KCl, KBr, KI
- \(\sigma_{\text{Rb}} = 3.26 \text{ Å}\) for RbF, RbCl, RbBr, RbI
- \(\sigma_{\text{Cs}} = 3.58 \text{ Å}\) for CsF, CsCl, CsBr, CsI

Anions
- \(\sigma_{\text{F}} = 3.66 \text{ Å}\)
- \(\sigma_{\text{Cl}} = 4.41 \text{ Å}\)
- \(\sigma_{\text{Br}} = 4.54 \text{ Å}\)
- \(\sigma_{\text{I}} = 4.78 \text{ Å}\)
Osmotic coefficient of water

Adjustment of the LJ energy parameters $\varepsilon_{\text{ion}}$ to the osmotic coefficient $\phi_S$ of water in NaCl solutions ($T = 293$ K, $p = 1$ bar)

$$\phi_S = \frac{\ln(a_S)}{\ln(x_S^{(n)})}$$

- Large statistical uncertainties
- Reasonable match: $\varepsilon_{\text{Na}} = \varepsilon_{\text{Cl}} = 200$ K
- Reasonable choice: $\varepsilon_+ = \varepsilon_- = 200$ K
Radial distribution functions of water

Dilute aqueous NaCl solutions ($T = 298$ K, $p = 1$ bar)

\[ g_{i-o}(r) \]

\[ r_{1\text{. Max}} / \text{Å} \] | \[ r_{1\text{. Min}} / \text{Å} \]  
---|---|---|---
| Sim. | Exp. | Sim. | Exp. |
| Na – O | 2.2 | 2.3 | 3.0 | 3.0 |
| Cl – O | 3.4 | 3.3 | 3.9 | 4.0 |
Self-diffusion coefficient of alkali cations and halide anions in aqueous solution

Predictions ($T = 298\text{K, } p = 1 \text{ bar}$)

Water model: SPC/E

Concentration: $x_{EL}^{(n)} = 0.018 \text{ mol/mol}$
Electric conductivity of NaCl and CsCl in aqueous solution at various salinities

Predictions \((T = 298\text{K} \text{ and } p = 1 \text{ bar})\)

- Electric conductivity:
  - Correlated motion of ions in solution

Water model: SPC/E
Earth-alkali cations: Modeling

Molecular model

Counterion and solvent model

Adjustment of the cation model parameters:

- Reduced density $\rho$ of the aqueous earth-alkali halide solution ($T = 293$ K, $p = 1$ bar): 
  \[ \tilde{\rho} = \frac{\rho_{\text{El}}}{\rho_s} \]
Aqueous electrolyte solutions - Results

Reduced density \((T = 293 \text{ K}, \ p = 1 \text{ bar})\)

\[
\begin{align*}
\sigma_{\text{Be}} &= 1.69 \text{ Å} \\
\sigma_{\text{Mg}} &= 1.77 \text{ Å} \\
\sigma_{\text{Ca}} &= 2.58 \text{ Å} \\
\sigma_{\text{Sr}} &= 2.69 \text{ Å} \\
\sigma_{\text{Ba}} &= 3.12 \text{ Å}
\end{align*}
\]
Self-diffusion coefficient of earth-alkali cations in aqueous solution

Predictions ($T = 298\,\text{K}$, $\rho = 1\,\text{bar}$)

Water model: SPC/E

Concentration: $x_{\text{EL}}^{(n)} = 0.018\,\text{mol/mol}$
Electric conductivity of MgCl$_2$ and BaCl$_2$ in aqueous solution at various salinities

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

Water model: SPC/E
Summary

✓ New atomistic force field for ions
  ✓ Alkali cations: Li\(^+\), Na\(^+\), K\(^+\), Rb\(^+\), Cs\(^+\)
  ✓ Earth-alkali cations: Be\(^{2+}\), Mg\(^{2+}\), Ca\(^{2+}\), Sr\(^{2+}\), Ba\(^{2+}\)
  ✓ Halide anions: F\(^-\), Cl\(^-\), Br\(^-\), I\(^-\)

✓ Model adjustment
  ✓ Reduced density
  ✓ Osmotic coefficient

✓ Good agreement with experimental data
  ✓ Structural properties – radial distribution function
  ✓ Self-diffusion coefficients
  ✓ Electric conductivity
BACKUP
Alkali halides
Self-diffusion coefficients of Na\(^+\) / Cl\(^-\) in aqueous solutions

\(T = 298.15\ \text{K},\ \rho = 1\ \text{bar}\)

![Graph showing self-diffusion coefficients](image-url)
Activity of water in NaCl solution

$T = 298.15 \, \text{K}$, $p = 1 \, \text{bar}$
Hydration number of NaCl in solution

<table>
<thead>
<tr>
<th></th>
<th>$n (x_{NaCl}=0.09 \text{ g/g})$</th>
<th>$n (x_{NaCl}=0.15 \text{ g/g})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sim.</td>
<td>Exp.</td>
</tr>
<tr>
<td>Na – O</td>
<td>5.5</td>
<td>5 – 6</td>
</tr>
<tr>
<td>Cl – O</td>
<td>7.2</td>
<td>7</td>
</tr>
</tbody>
</table>
Electric conductivity

Time correlation function:

$$\sigma = \frac{1}{3V k_B T} \int_0^\infty \langle j(t) \cdot j(0) \rangle$$

Electric current flux:

$$j(t) = \sum_{k=1}^{N_{\text{ion}}} q_k \cdot v_k (t)$$

Split electric current flux:

$$\langle j(t) \cdot j(0) \rangle = \sum_{k=1}^{N_{\text{ion}}} \langle q_k^2 \cdot v_k (t) \cdot v_k (0) \rangle + \sum_{k=1}^{N_{\text{ion}}} \sum_{n=1, n\neq k}^{N_{\text{ion}}} \langle q_k q_n \cdot v_k (t) \cdot v_n (0) \rangle$$
Electric conductivity - split

Separation in diffusion (Z) and correlated motion of ions (Δ)

MgCl₂

BaCl₂
Dynamic properties – Residence time

- Definition: \[ \tau(t) = \frac{\sum \Theta(t) \Theta(0)}{N_{\text{Pairs}}} \]
- First hydration shell ends at the first minimum in the RDF
Temperature dependence

Lowering of vapor pressure: \( \Delta p = p_{EL} - p_S \)

<table>
<thead>
<tr>
<th>( T / \text{K} )</th>
<th>( \Delta p^{\text{Sim}} / \text{bar} )</th>
<th>( \Delta p^{\text{Exp}} / \text{bar} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>373</td>
<td>0.03</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Diagram showing the relationship between temperature and vapor pressure for pure solvent and electrolyte.
Earth-alkali halides
Enthalpy of solvation

<table>
<thead>
<tr>
<th></th>
<th>$-\Delta h_{\text{solv}}^{\text{Sim}}$ / kJ mol$^{-1}$</th>
<th>$-\Delta h_{\text{solv}}^{\text{Exp}}$ / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCl$_2$</td>
<td>2462</td>
<td>2683</td>
</tr>
<tr>
<td>MgBr$_2$</td>
<td>2430</td>
<td>2615</td>
</tr>
<tr>
<td>MgI$_2$</td>
<td>2378</td>
<td>2531</td>
</tr>
<tr>
<td>BaCl$_2$</td>
<td>1972</td>
<td>2067</td>
</tr>
<tr>
<td>BaBr$_2$</td>
<td>1940</td>
<td>1999</td>
</tr>
<tr>
<td>BaI$_2$</td>
<td>1891</td>
<td>1915</td>
</tr>
</tbody>
</table>
Complex salts
Multicenter Lennard-Jones models – Na$_2$SOH$_4$

Sulfate - model reproduces the reduced density in aqueous solution