

Activity Coefficients from Vapor-Liquid Interfaces: A Molecular Dynamics Approach for Separation Chemistry

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Activity Coefficients from Vapor-Liquid Interfaces: A Molecular Dynamics Approach for Separation Chemistry

Michael Bley[a], Magali Duvail[a], Philippe Guilbaud[b], and Jean-François Dufrêche[a]

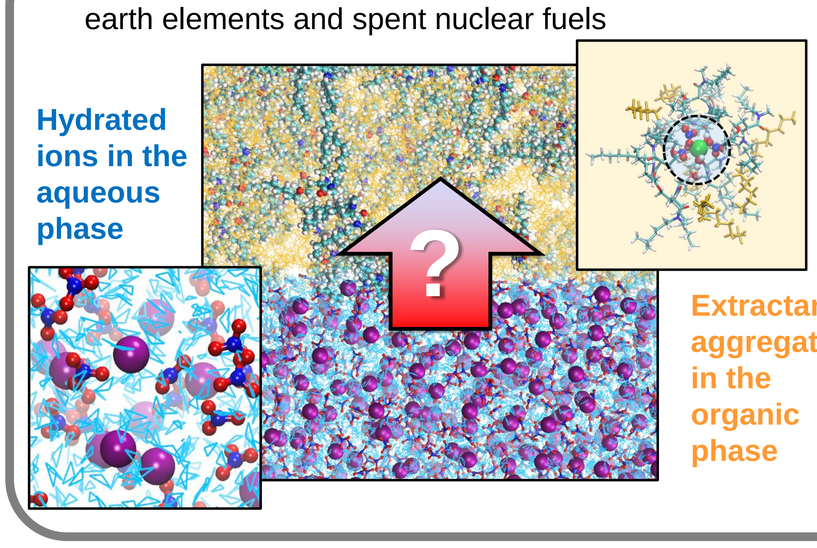
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Context

- Understanding **solvent extraction** – Recycling of rare earth elements and spent nuclear fuels

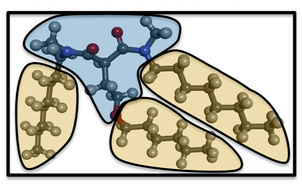


- The **equilibrium constant K°** describes the extraction process and is given by the Mass Action Law

$$Dy^{3+} + 3\,NO_3^- + m\,H_2O + \overline{n\,L} \rightleftharpoons \overline{Dy(NO_3)_3(H_2O)_m L_n}$$

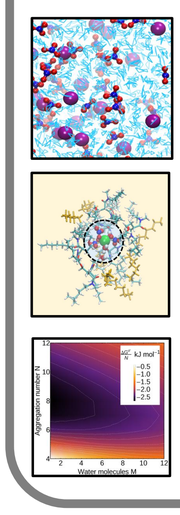
Aqueous electrolyte solution ⟷ **Organic solvent phase**

$$K^\circ = \underbrace{\frac{c_{Dy(NO_3)_3(H_2O)_m L_n}}{c_{Dy^{3+}}\, c_{NO_3^-}{}^3\, x_{H_2O}{}^m\, c_L{}^n}}_{\text{Concentrations}} \times \underbrace{\frac{\gamma_{Dy(NO_3)_3(H_2O)_m L_n}}{\gamma_{Dy^{3+}}\, \gamma_{NO_3^-}{}^3\, \gamma_{H_2O}{}^m\, \gamma_L{}^n}}_{\text{Activity coefficients}}$$



Ligand L: DMDOHEMA

- A **multiscale approach** provides mesoscopic thermodynamic properties



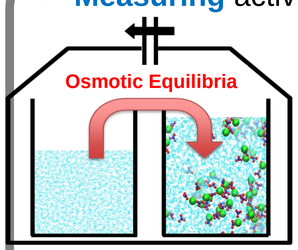
Classical Molecular Dynamics — 1 Å — **Ions and molecules in solution**

Thermodynamic models — 10 Å — **Aggregates**

10^2 Å — **Mesoscopic properties**

Methods and concepts

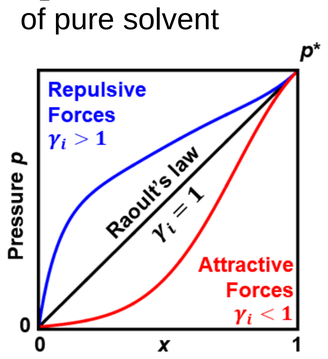
- **Measuring** activity and the vapor pressure



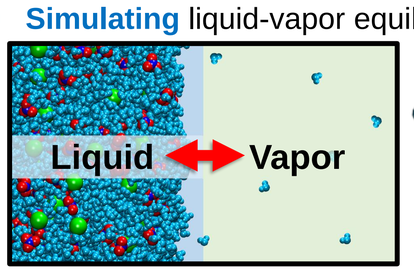
Isopiestic Measurements

- **Solvent flow**: Vapor pressure of the pure solvent always higher than of a mixtures
- Ideal case: Solvent vapor pressure by **Raoult's law**
- Otherwise: **Aggregation increases**, **dissociation decreases** solvent vapor pressure and thus activity

p_1^*: Vapor pressure of pure solvent



- **Simulating** liquid-vapor equilibria [1]



- Molecular Dynamics using **explicit polarization** [2,3] at 298.15 K for 15 ns

$$a_S = \frac{p}{p^*} = \frac{\rho}{\rho^*} = \frac{N \times V_{gas}^*}{N^* \times V_{gas}} = \frac{\lambda \times V_{gas}^*}{\lambda^* \times V_{gas}}$$

- **Controlling** the error of the method

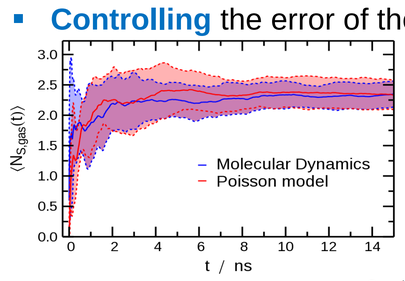


Fig. Mean amount of solvent molecules in the gas phase N and corresponding standard deviation ΔN(t).

$$N = \langle \tau_x \rangle \times \lambda \qquad \delta_N(t) = \frac{1}{\sqrt{\lambda \times t}}$$

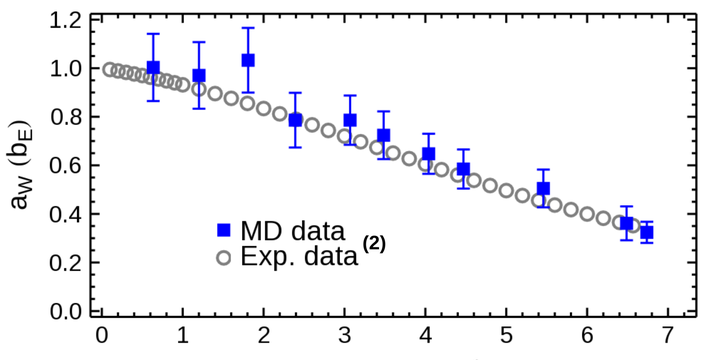
λ: Evaporation rate ‹τ_x›: Time of flight

$\delta_N(t)$: Relative error of the method

a_S: Solvent activity

Aqueous dysprosium nitrate $Dy(NO_3)_3$ solutions [2]

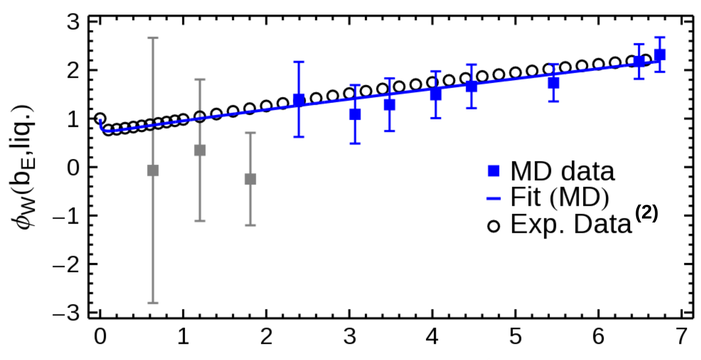
Water activity a_W



Salt molality:

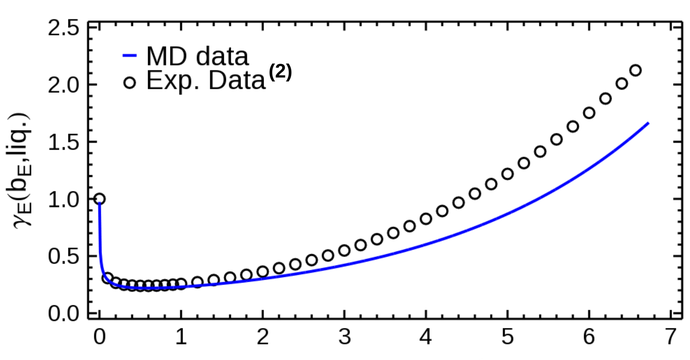
$$a_W(b_E) = \frac{p_{gas}(b_E)}{p^*_{gas}} = \frac{\rho_{gas}(b_E)}{\rho^*_{gas}}$$

Osmotic coefficient ϕ_W



$$\phi_W(b_E) = \frac{-\ln a_W(b_E)}{\nu M_W b_E}$$

Activity coefficient γ_E

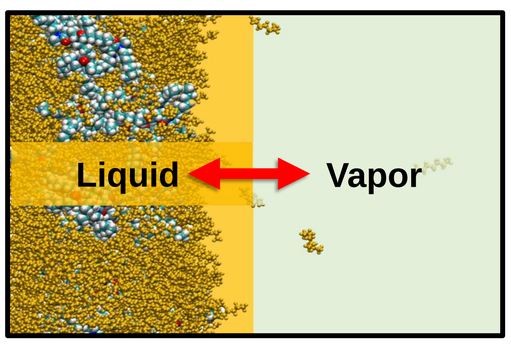


$$\ln \gamma_E(b_E) = \phi_W(b_E) - 1 + \int_{b=0}^{b=b_E} \frac{\phi_W(b) - 1}{b} \mathrm{d}\, b$$

Gibbs-Duhem relation

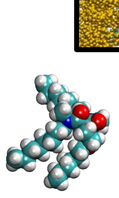
Organic phases – Binary Mixtures of DMDOHEMA and *n*-heptane

- Molecular dynamics simulation of liquid-vapor equilibria of organic solvent phases containing:

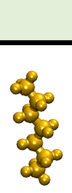


Pure solvent + **Extractant** + **Water** + **Ionic species**

Increasing computational cost

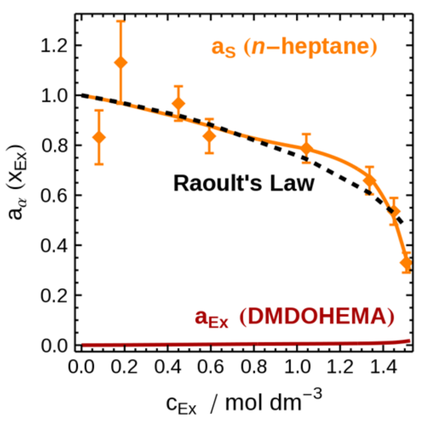


DMDOHEMA amphiphilic extractant

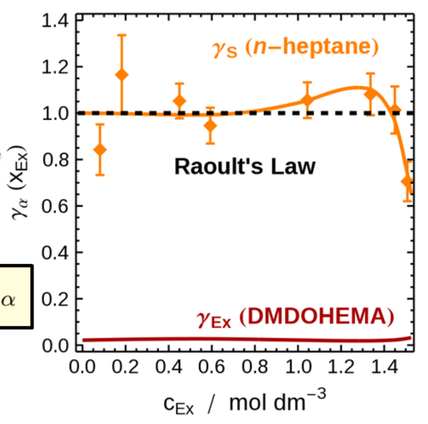


***n*-heptane** volatile solvent

➢ Aggregation of DMDOHEMA in the organic phase relies on the availability of water[3]



$$a_\alpha = \gamma_\alpha \cdot x_\alpha$$



- Solvent activities in binary mixtures of *n*-heptane and DMDOHEMA show ideal behavior and follow Raoult's law in good agreement up to a high extractant concentration
- Attractive and repulsive interactions in the mixtures cancel out

Outlook and conclusion

- **Aqueous salt solutions:** Results from molecular dynamics simulation are in good agreement with experimental data for different nitrate salts. This approach can be used for the validation of force fields for MD simulation with respect to thermodynamic properties.
- **Organic Phases:** Method has been successfully applied on binary mixtures (*n*-heptane and DMDOHEMA, but also ethanol and water[4]). Allows accessing more complex organic solvent phases containing water and ionic species.

➢ **Simulation of activity coefficients of complex solutions with volatile solvents for understanding solvent extraction**

References

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(4) Bley, M.; Duvail, M.; Guilbaud, P.; Penisson, C.; Theisen, J.; Gabriel, J.-C.; Dufrêche, J.-F.; *Mol. Phys.* **2018** (DOI: 10.1080/00268976.2018.1444209)

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