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To cite this version:

HAL Id: cea-02338585
https://hal-cea.archives-ouvertes.fr/cea-02338585
Submitted on 9 Dec 2019

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

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Context

- Understanding solvent extraction – Recalling of rare earth elements and spent nuclear fuels
- Hydrated ions in the aqueous phase
- Extractant aggregates in the organic phase

Methods and concepts

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

Aqueous dysprosium nitrate Dy(NO₃)₃ solutions

- Water activity $a_W$: Vapor pressure of pure solvent
- Osmotic coefficient $\phi_W$
- Activity coefficient $Y_e$

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
- Polymer aggregation of DMDOHEMA in the organic phase relies on the availability of water
- Solvent activities in binary mixtures of n-heptane and DMDOHEMA show ideal behavior and follow Raoult's law and high extractant concentration.

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). 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


Acknowledgements

This work was made possible thanks to the high performance computing facilities of TSGC/CCRT and the computing center of CEA Marcoule.