

Simulating osmotic equilibria: Introducing a new tool to calculate activity coefficients of concentrated solutions

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Introduction

For improving hydrometallurgical approaches such as solvent extraction, it is crucial to understand the physical chemistry behind separation chemistry. Solvent extraction of metal cations from an aqueous salt solution into an organic solvent phase with aggregate formation due to the presence of extractant molecules (e.g. DMDOHEMA) can be described by the mass action law and the corresponding equilibrium constant [1]. However, this equilibrium constant can only be calculated, if the activities of all involved compounds are known. In this work a new simulation method based on molecular dynamics is introduced, which allows the calculation of activities of concentrated solutions in good agreement with experimental findings. This method can be applied to any solvent, as long as the solvent is sufficiently volatile

Theory and Methods

Figure 1 is a schematic representation of a boxes for molecular dynamics. All simulations have been conducted with the AMBER14 package using polarizable force fields [2,3]. The activity of a liquid phase is given by the fraction of the vapor pressure of a mixture and the vapor pressure of the pure solvent. In the case that the solvent molecules in the gas phase show ideal behavior, the activity can be also expressed by the corresponding vapor phase densities. If the activity of the solvent is known, then the osmotic coefficient can be directly calculated. The osmotic coefficient of the solvent and the activity coefficient of the solutes are directly connected via the Gibbs-Duhem relation.

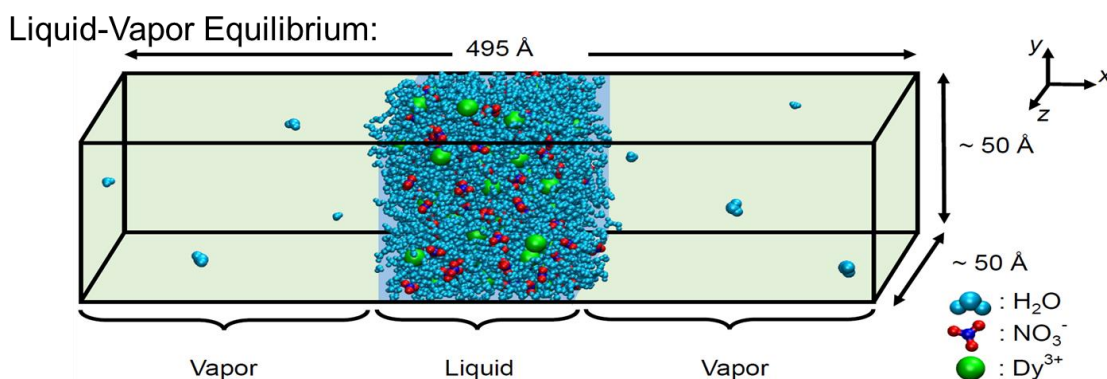


Fig. 1. Schematic representation of the structure of the molecular dynamics boxes for an aqueous solution of Dysprosium nitrate. The time-averaged amount of solvent molecules present in the vapor phase provides the vapor phase density at the current concentration.

For this method, it is also crucial to understand and to control the statistics of the method. The error of this approach is dependent on the evaporation rate of the solvent and duration of the

simulation. In the case that a higher precision is required, it is more favorable to increase the simulation time because of less computational cost.

Results and discussion

After a certain production time (15 ns, with 84 processor cores 3 days of calculation time) and a sufficient amount of individual runs per salt concentration (at least 3 different starting geometries) the resulting vapor phase densities are used to calculate directly osmotic and activity coefficients. Figure 2 shows the raw simulated results and their error in comparison with the experimental data [3]. The simulated data points are then used to derive the fitting parameters for the extended Debye-Hückel equation.

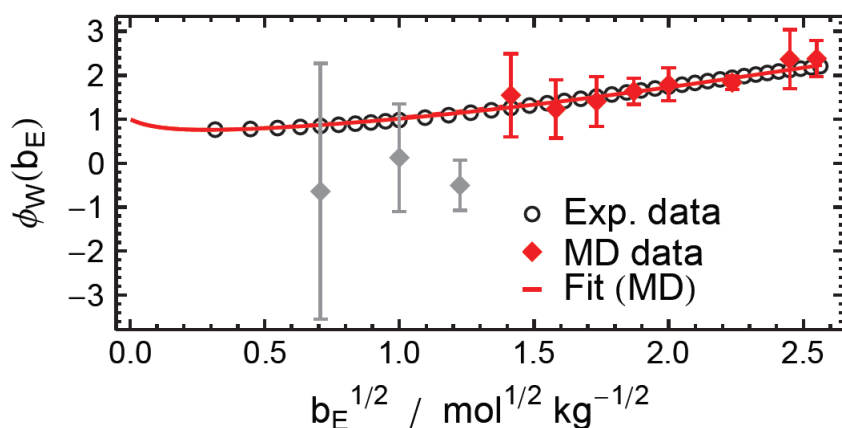


Fig. 2. Comparison of simulated and experimental [3] osmotic coefficients for an aqueous solution of Dysprosium nitrate at 298.15 K. Gray-colored simulated points are not taken into account for the Debye-Hückel fit.

A good agreement for the fitted simulated and experimental osmotic coefficients of water (and the corresponding activity coefficients of $\text{Dy}(\text{NO}_3)_3$) is obtained at Dysprosium nitrate concentrations higher than 1.5 mol kg^{-1} . The hydration properties of all involved species (molecules and ions) correlate with experimental observations. Time-averaged density profiles exhibit a structuration at medium salt concentration ($2.0 - 4.0 \text{ mol kg}^{-1}$) towards the liquid-vapor interface.

Conclusion and outlook

A new simulation method based on molecular dynamics for simulating activities of concentrated solutions in good agreement with experimental results has been developed [5]. For sufficiently volatile solvents, this method allows to access important thermodynamic data for models predicting solvent extraction even for complex mixtures. The next parts of this project cover the understanding of the sensitivity of the method for different cationic species, the activity of water-ethanol mixtures, and, to our knowledge for the first time, the simulation of activity coefficients of solutes in organic solvent phases taking into account extractant aggregation.

References

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