

Selecting Solvents for Intensification of Thermal Dissociation of Tri-n-octylamine Hydrochloride by Calculating Infrared Spectra from Ab Initio Molecular Dynamics

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Highlights

- Comparison of the stability of TOAHCl in different solvents by IR spectra (mainly from N-H stretching vibration).
- Calculation of the IR spectra with Ab Initio Molecular Dynamics applying explicit solvents model.
- Selection of most proper solvents with simulation method other than experiments.

1. Introduction

It is a promising way of carbon capture and storage (CCS) as well as treatment of metal chlorides containing waste liquors to use high molecular mass amine extractants. We call it the reactive extraction-crystallization coupled process. Direct thermal dissociation of amine hydrochlorides is a potential technique of zero-emission for resources utilization-amine extractants could be recycled while quite appealing gaseous HCl could be produced. The nature of the reaction is to break the N-H bond. It is known that solvents have crucial effects on the thermal dissociation of tri-n-octylamine hydrochloride (TOAHCl). While Nitrogen-hydrogen (N-H) stretch vibration modes serve as key probes in identification of the combination strength of amine and hydrogen chloride. Their assignments give us a theoretical viewpoint that could help us select the best suitable solvent used in the recycling extractant tri-n-octylamine (TOA) through the thermal dissociation of tri-n-octylamine hydrochloride (TOAHCl) methods, as well as other amine hydrochlorides. Through a combination of ab initio molecular dynamics (AIMD) and static normal mode analysis (NMA), as well as the experimental infrared spectra, we conclude that the AIMD simulations which include the explicit solvents could agree with the experimental results perfectly, whereas the NMA calculated with implicit solvents could not show the solvent effects on the $\nu(\text{N-H})$.

2. Methods

The AIMD simulations were carried out on the CP2K program package CP2K performs the Born Oppenheimer Molecular Dynamics, which calculates DFT forces “on the fly” with the Quickstep module using the GPW method. We used the BLYP exchange-correlation functional with the empirical dispersion correction D3 by Grimme. A time-step of 0.5 fs was applied and the simulations were run at 300 K using a Nosé-Hoover chain thermostat in an NVT ensemble. The systems were equilibrated for 2 to 3 ps then the simulation were run for at least 10 ps for the evaluation of infrared spectra. 15 solvents molecules with 1 solute model was built which agree with the density of real thermal dissociation experiments.

The static harmonic normal-mode analyses were performed using Gaussian 09 with the BLYP functional at the basis of 6-31++G(d, p). Here, we used the SMD model to calculate the infrared frequency in implicit solvents, where the specific interactions like e.g. hydrogen bonds between the solvent and the solutes are were unable to describe.

We use the trajectory analyzer TRAVIS developed by Martin Thomas, et al to calculate the the IR spectra from AIMD simulations. Their approach is thoroughly based on the maximally localized Wannier function scheme, which allows for direct calculation of individual molecular dipole moments also in bulk phase systems under periodic boundary conditions.

3. Results and discussion

Comparing the IR spectra obtained from AIMD simulations to the ones from static calculations, the overall shape of the solute (TOAHCl) agrees very well except for the position of NH bond. Moreover, the ones from AIMD simulations include the solvent effects explicitly not only from the IR spectra contribution but also from the influence on the NH stretching vibrations, which makes the prediction of solvents properties more precisely. The trend of frequencies of N-H for different solvents agree well with the experimental results.

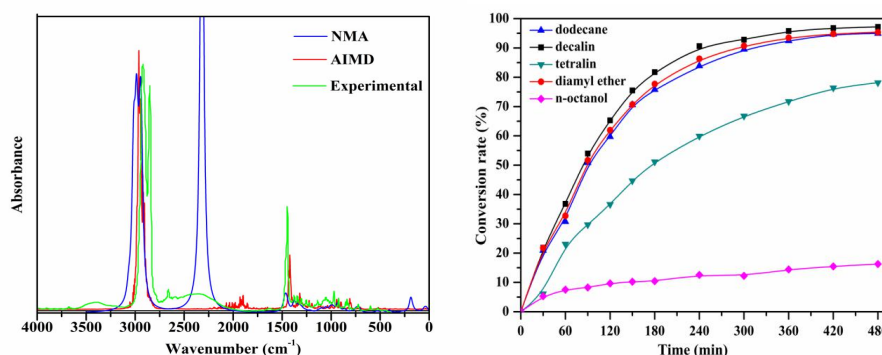


Figure 1. IR spectra of TOAHCl-decalin system got from NMA, AIMD and experimental methods

/Conversion rate of TOAHCl in various solvents

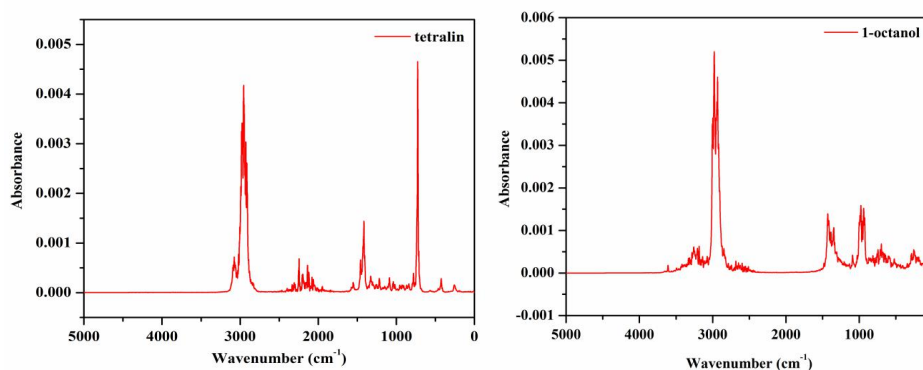


Figure 2. IR spectra of TOAHCl in tetralin and 1-octanol from AIMD

4. Conclusions

Not only the IR spectra from the solvent part were calculated very well, but also the order of the NH bonds were predicted good enough, which could be considered as the basis of realizing the goal of selection of solvents without experiments for certain systems, even extended to other systems after hundreds of testing.

References

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Keywords

Ab initio Molecular Dynamics; Infrared spectra; Solvent selection; Explicit solvent model

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