Molecular dynamics simulations of terpyridine, BTP, and their complexes with La^{3+}, Eu^{3+} and Lu^{3+}

P. Guilbaud, J.P. Dognon
Laboratoire de Chimie Théorique et Structurale, Commissariat à l'Energie Atomique, CEA/Valrhô, Centre de Marcoule, BP 171, 30200 Bagnols-sur-Cèze, France

Summary

This poster presents molecular dynamics simulations performed to study terpyridine and bis-triazinyl-pyridine with lanthanide cations for the gas phase and for water solution. Different counter-ions have been tested in order to assess their influence on complexes structures and stabilities in both phases. For stable complexes, Gibbs free energy calculations have been achieved to estimate the selectivity of these complexes towards the lanthanide cations. Finally, some tests have been done adding a polarization term in the potential energy in order to have a more precise description of interaction energies.

Introduction

The search for ligands which specifically separate actinides(III) from lanthanides(III) using liquid-liquid extraction has motivated lots of researches, especially for the nuclear fuel recycling. Ligands with soft donor atoms (N,S) that are likely to perform this separation have already been studied and researches are currently carried out to improve their performances for high acidic feeds. Theoretical chemistry researches are achieved in our laboratory in order to help the understanding of complexation and extraction of these cations with such ligands. Theoretical studies have been done first for the terpyridine (TPY) and the bis-triazinyl-pyridine (BTP) ligands that present quite good ability for separation and extraction of actinide(III) from lanthanide(III) ions.

Molecular dynamics simulations have been performed on terpyridine and bis-triazinyl-pyridine complexes with three lanthanide cations (La^{3+}, Eu^{3+} and Lu^{3+}) in vacuum or for water solutions. These calculations were carried out without counterions, with three nitrate ions, or, in the case of terpyridine, with three α-bromo-caprate anions that are likely to be used experimentally as synergistic agents for the separation and extraction of An(III) from Ln(III).

1. MD Simulations in the gas phase

First, molecular dynamics simulations have been performed in vacuum to evaluate distances between nitrogen and lanthanide atoms (Ln^{3+},N) and intrinsic interaction energies to the polynitrogenous ligands with or without NO_3^- ions, and for both ligands. The (Ln^{3+},N) distances decrease and the cation/ligand interaction energies increase along the La^{3+}, Eu^{3+}, Lu^{3+} series, according to the decreasing of Ln(III) ion radii. The introduction of nitrate counter-ions make the (Ln^{3+},N) distances slightly higher, and the TPY/Ln^{3+} and BTP/Ln^{3+} interaction energies lower, compared to complexes without NO_3^-. In contrast, with α-bromo-caprate anions, the TPY/Ln^{3+} interaction energy is the highest for Eu^{3+} (and not Lu^{3+}) owing to the strong interaction of the counter-ions with the smallest Ln^{3+} cation.

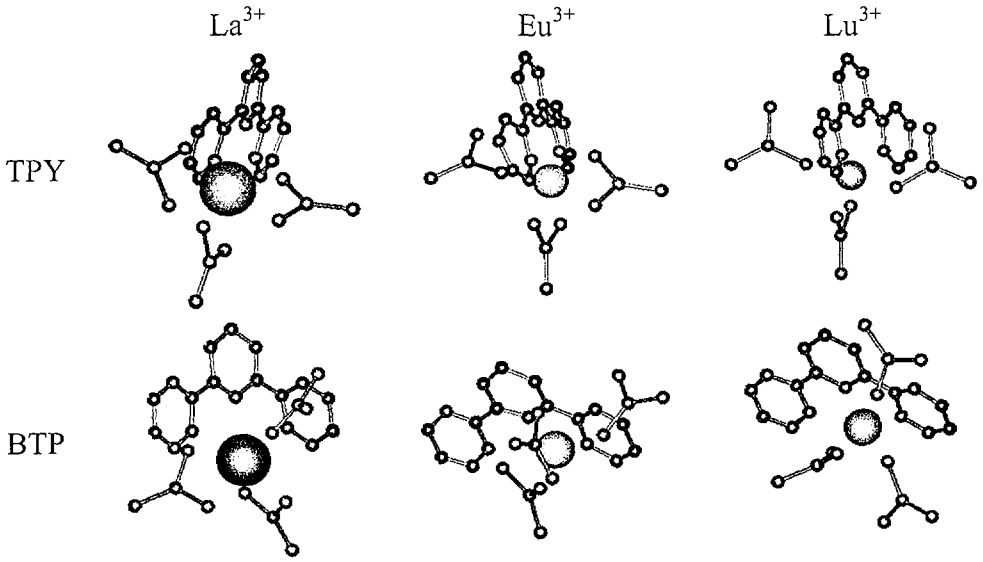

Figure 1: Snapshots of the complexes of Ln^{3+} cations with TPY (top) and BTP (bottom) and three nitrate ions after 300 ps of molecular dynamics simulation in the gas phase.

The calculation of Gibbs free energy differences ($\Delta\Delta G$) may be achieved within molecular dynamics simulations using the free energy perturbation theory. These calculations allow to take in account entropy and have been done for the vacuum phase first to assess the selectivity of TPY and BTP with respect to the lanthanide(III) cations, and then to assess the selectivity of each cation towards the two ligands. With or without nitrate counter-ions, both ligands are selective for the smaller Lu^{3+} cation. Without NO_3^- anions, every Ln^{3+} cation is selective towards BTP versus TPY, whereas with nitrate ions, the $\Delta\Delta G$ differences are closed to zero.

2. MD Simulations in the water phase

For the water phase, the Ln^{3+} complexes with TPY and with BTP including NO_3^- ions or without counter-ions, dissociate after few picoseconds of molecular dynamics simulations. The only complexes that do not dissociate are those with La^{3+} or Eu^{3+}, terpyridine, and three α-bromo-caprate anions. For these two complexes, one water molecule is bound to the cation, which is consistent with recent Time-Resolved Laser-Induced Fluorescence results. The Gibbs free energy difference between these two complexes in water solution displays a small preference for Eu^{3+}, emphasizing the future difficulty to calculate separation of lanthanide(III) from actinide(III) cations.

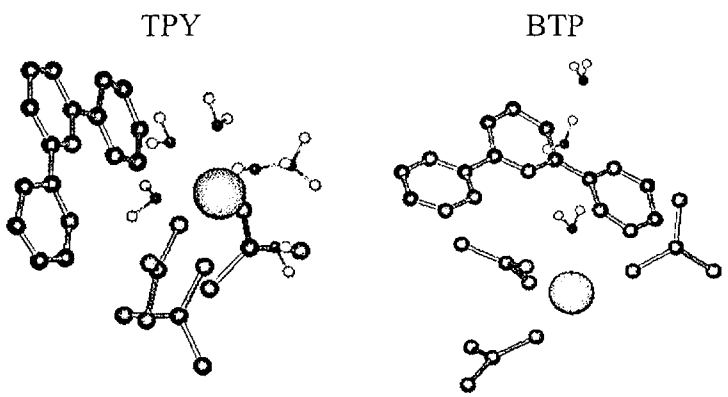

Figure 2: Snapshots of the TPY/Eu^{3+}/3NO_3^- (left) and BTP/Eu^{3+}/3NO_3^- (right) complexes after some picoseconds of molecular dynamics in a water box.

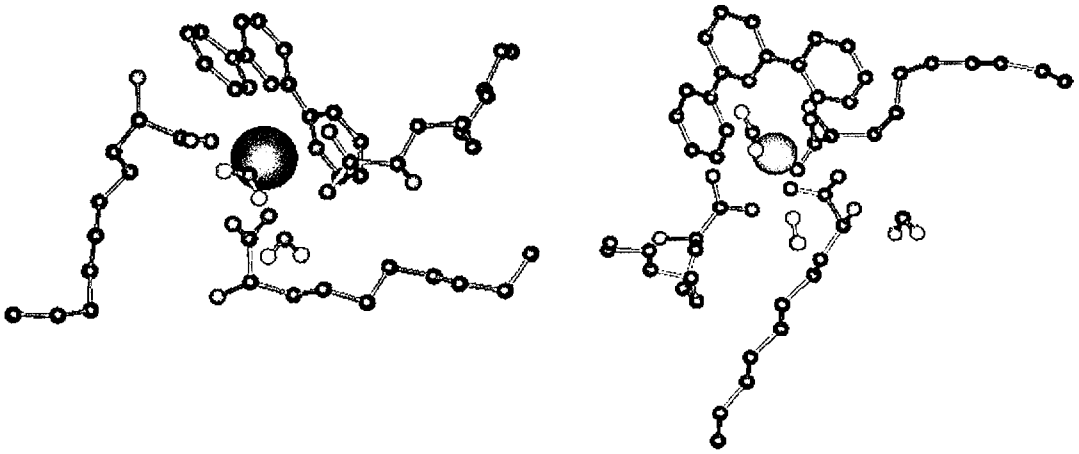

Figure 3: Snapshots of the TPY/La^{3+}/3αBrC^- (left) and TPY/Eu^{3+}/3αBrC^- (right) complexes after 300 picoseconds of molecular dynamics in a water box.

3. Polarization

At last, calculations have been performed in the gas phase adding a polarization energy term in the potential energy formula in order to assess the importance of polarization in such complexes, and to test the effect of this term on the geometry and interaction energies of these complexes. These calculations show the polarization of organic ligands such as TPY or BTP by lanthanide(III) cations is quite large, and that the use of such potential energy would require an adjustment of Lennard-Jones (van der Waals) parameters.

Conclusions

Molecular dynamics simulations have been performed on terpyridine and bis-triazinyl-pyridine complexes with lanthanide ions, with or without counter-ions, for the gas phase and for water. This study demonstrates that the solvent and the counter-ions may play a crucial role on the ligand conformation and the M^{3+} extraction mechanism(s). It is also emphasized that small enthalpy differences may be verified with Gibbs free energy calculations in order to take in account entropy.

The present work call for further investigations concerning for example, (i) the effect of an organic solvent on terpyridines free and complexed, (ii) the description of the interaction potential, especially concerning the inclusion of a polarization energy term or (iii) the competition between M^{3+} ions and the protons for polypyridine complexation sites.