MOLECULAR DYNAMICS SIMULATIONS OF POLYPYRIDINES WITH LANTHANIDES

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Polypyridines have been studied in our laboratories as selective extractants of actinides(III) versus lanthanides(III) using a synergistic mixture with aliphatic carboxylic acids. Our aim in this study was, using theoretical chemistry, to better understand the actinide and lanthanide trivalent cations complexation with polypyridines. We first decided : (i) to focus on small polypyridine units studying the terpyridine ligand (ii) to select three lanthanide ions (La^{3+}, Eu^{3+} and Lu^{3+}). Molecular dynamics (MD) simulations have been performed for timescales between 100 and 500 ps using the AMBER software. These calculations are related to : (i) the gas phase and (ii) water solutions, with an explicit representation of the solvent.

The free terpyridine ligands have been simulated in the water phase in order to investigate the influence of the water solvation on their conformation. The interaction between water molecules and the terpyridines stabilises the 111 conformers over the two others conformers. Using the Gibbs free energy perturbation theory, one is able to calculate the $\Delta\Delta G$ between two conformers. In the water phase, this calculation, that takes into account the entropy differences, reveal no energy differences between the three conformers. The water stabilises the 111 conformer over the two others, but there is no real preorganisation of the ligand. The (Ln^{3+}/terpyridine) complexes have been simulated in the gas phase and in water solution with different counter ions. 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 emphasised 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 (polarisation, charge transfer...), or (iii) the competition between M3+ ions and the protons for polypyridine complexation sites.