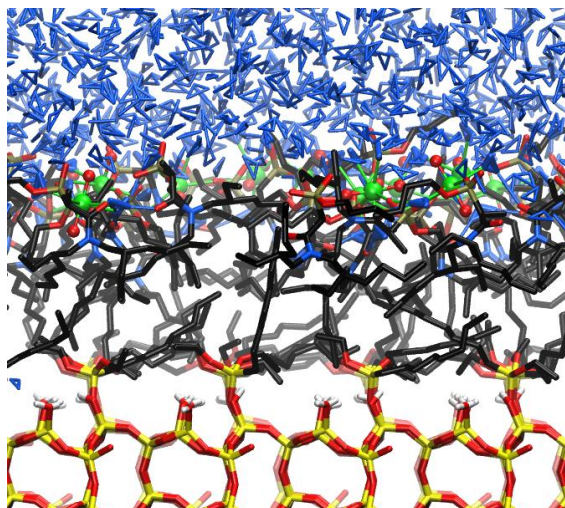


Molecular Dynamics Studies of the Separation of Uranium(VI) Using Organic Solvents or Solid Supports

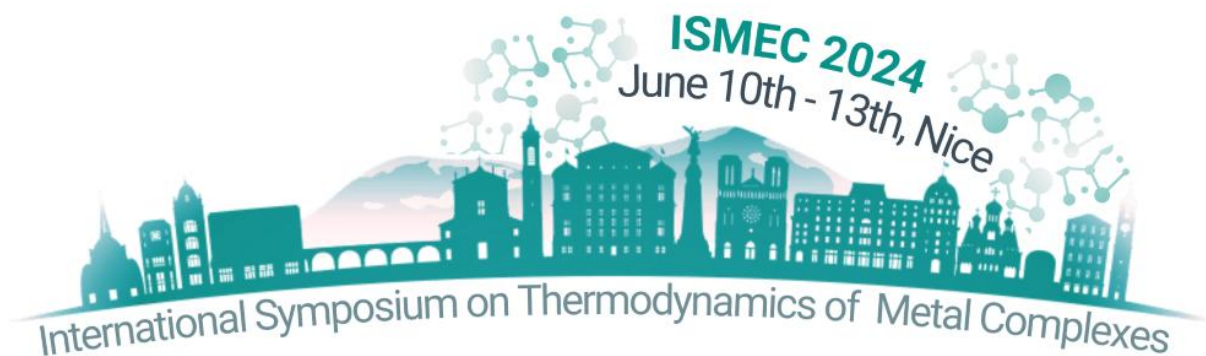
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In the front end of the nuclear fuel cycle, uranium is usually separated by solvent extraction processes. These processes are very efficient for the separation of uranium from concentrated effluents. For the recovery of the uranium in low-concentration solutions, separation using solid supports is much more promising. In both kinds of separation processes, bifunctional ligands of the amidophosphonate family can be used to recover selectively the uranium(VI) cation. However, despite several experimental studies, the mechanisms involved in its extraction are still not well understood at the molecular level in both kinds of processes. In this study, we used classical molecular dynamics to model organic phases and solid/liquid interfaces with amidophosphonate bifunctional ligands to better understand the separation process for both systems.



First, we developed new force fields parameters for the actinyl(VI) cations, using the 12-6-4 formalism [1], which is efficient to take into account polarization effects of the media by the cations.[2] This new force field parameters allowed us to perform molecular dynamic simulations ranging from a hundred to a thousand of nanoseconds, simulations times that were essential for the equilibration of the systems simulated here.



Organic phases containing an amidophosphonate extractant and uranyl(VI) cations were simulated at concentrations representative of the experimental conditions. The organization of these extractants and the speciation, with and without uranium, were then described, with a validation of the results using experimental data. The role of the organic functions of the amidophosphonate molecule has been highlighted: the molecule can extract uranium without fully dehydrating it thanks to a network of hydrogen interactions in the complexes.[3] Finally, representative molecular models of solid supports were designed. Essential information was obtained on two key points: i) the structuring of solid/liquid interfaces with and without uranium, and ii) the speciation of uranium at these surfaces.

References:

- [1] Moreno Martinez, D.; Guilbaud, P.; Guillaumont, D. Force Field Parameterization of Actinyl Molecular Cations Using the 12-6-4 Model. *Chem. Inf. Model.* 2022, 62 (10), 2432–2445
- [2] Li, P.; Roberts, B. P.; Chakravorty, D. K.; Merz, K. M. Rational Design of Particle Mesh Ewald Compatible Lennard-Jones Parameters for +2 Metal Cations in Explicit Solvent. *J. Chem. Theory Comput.* 2013, 9, 2733–2748.
- [3] Moreno Martinez, D.; Acher, E.; Vatin, M.; Dourdain, S.; Guillaumont, D.; Guilbaud, P.; *The Journal of Physical Chemistry B* 2021 125 (38), 10759-10771