Computer Modeling of liquid - liquid ion extraction

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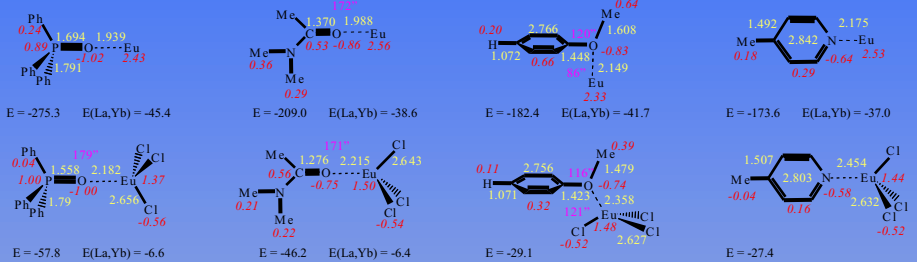
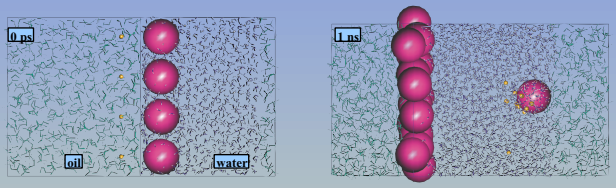
1) Assessment of intrinsic ligand / cation interactions : *Quantum Mechanical Calculations*

Fully optimized
Structures. See ref. [1,2]

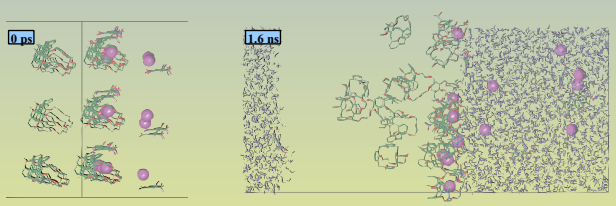
Distances (Å)
Angles ( )
Mulliken Charges
Interaction Energies (kcal.mol^{-1})



2) Molecular Dynamics Simulations of the water - "oil" interface :



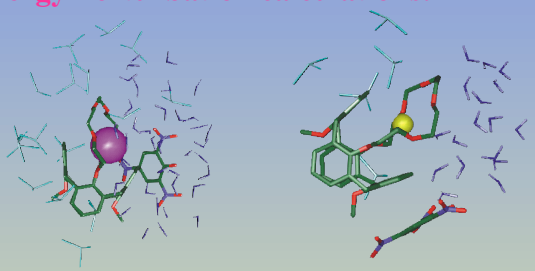
Interfacial behaviour of salts
Simulation of a 16Na $^{+}$S^{-} monolayer at a water - "oil" interface, where S^{-} mimics a hydrophobic anion (e.g. dicarbollides).
Notice the formation of an electrical double layer. See ref. [3].



(only water molecules are shown, the "oil" phase is omitted for clarity)

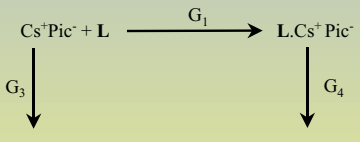
*Cs^{+} extraction by calix[4]arene-crown6 (**L**)*
Simulation of a 9(**L**.Cs^{+}Pic^{-}) layer + 8 **L** hosts in " oil" + 5 Cs^{+}Pic^{-} pairs initially in water. See ref. [4,5].

3) Prediction of Ion Recognition by Free Energy Perturbation calculations:



L.Cs^{+}Pic^{-} **L**.Na^{+}Pic^{-}

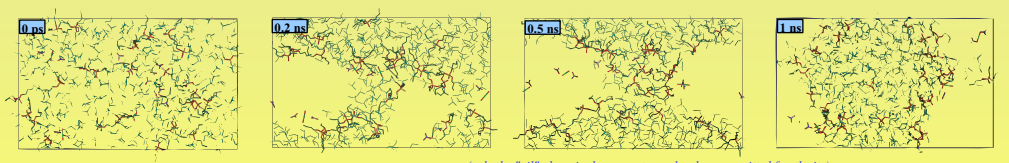
L = calix[4]arene-crown6



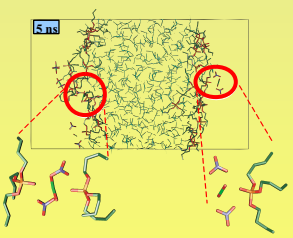
G = G_3 - G_4 = 14.9 kcal.mol^{-1} for Cs^{+}/Na^{+}.

Computations predict that Cs^{+} is better extracted than Na^{+}. See ref. [6,7].

4) Simulation of microscopic water - "oil" phase separation :



(only the "oil" phase is shown, water molecules are omitted for clarity)



1:2 and 1:1 complexes are formed

Uranyl extraction by TBP
The system containing 5 [$UO_2(NO_3)_2$] species and 30 tri-*n*-butylphosphate (TBP) molecules is completely mixed at the beginning of the simulation (0 ps, left). Very rapidly the phase separation takes places, and after 1 ns, the system has almost reached its final state (5 ns, right). Notice the interfacial adsorption of the $UO_2(NO_3)_2$ TBP complexes. See ref. [4,5].

References :

[1] F. Berny, N. Muzet, L. Troxler, A. Dedieu and G. Wipff, *Inorg. Chem.* **1999**, 38, 1244-1252. **[2]** M. Baaden, F. Berny, C. Boehme, N. Muzet, R. Schurhammer and G. Wipff, *J. Alloys Compounds*, in press. **[3]** R.Schurhammer and G. Wipff, *J. Mol. Struct. (THEOCHEM)*, in press. **[4]** M. Baaden, F. Berny, N. Muzet, L. Troxler and G. Wipff in *Calixarenes for Separations*, ACS: Washington, DC, **2000**, in press. **[5]** F. Berny, N. Muzet, L. Troxler and G. Wipff in *Supramolecular Science : where it is and where it is going, NATO ARW Lerici*; **1999**, R.Ungaro, E. Dalcanale Ed.; Kluwer Acad. Pub., Dordrecht, pp. 95-125. **[6]** N. Muzet, E. Engler and G. Wipff, *J. Phys. Chem. B*, **1998**, *102*, 10772-10788. **[7]** G. Wipff and M. Lauterbach, *Supramol. Chem.*, **1995**, *6*, 187-207

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