



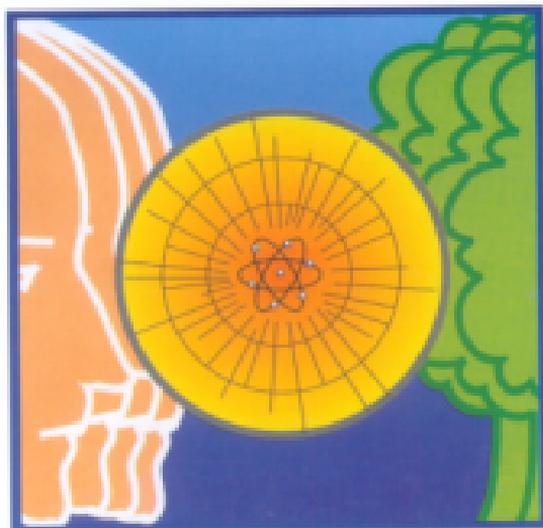
European Commission

# **Euradwaste 1999**

## **'Radioactive waste management strategies and issues'**

**Fifth European Commission Conference on Radioactive Waste  
Management and Disposal and Decommissioning**

**Luxembourg, 15 to 18 November 1999**



*Edited by*  
**C. Davies**

**EUR 19143 EN**

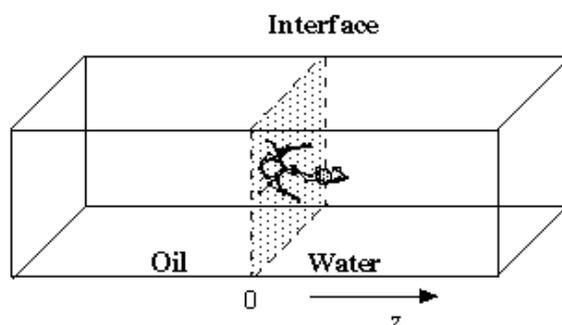
## SEPARATION OF $\text{Cs}^+$ AND $\text{UO}_2^{2+}$ CATIONS BY LIQUID-LIQUID EXTRACTION: COMPUTER SIMULATIONS OF THE DEMIXING OF WATER / OIL BINARY SOLUTIONS

M. Baaden, F. Berny, N. Muzet, R. Schurhammer, L. Troxler and G. Wipff\*  
Institut de Chimie, 4, rue Blaise Pascal, Strasbourg, 67100, France

### 1. INTRODUCTION.

Despite the importance of liquid-liquid extraction (LLE) separation techniques to separate ions from nuclear waste solutions, little is known about the detailed ion capture and selection mechanism and on the nature and solvation of the involved species. This led us to undertake related theoretical studies in two main directions. First, assess by QM (quantum mechanics) calculations the intrinsic characteristics of ion-ligand interactions (precise structures, interaction energies, electronic properties) in the gas phase [1]. This is achieved on small model ligands (phosphoryl derivatives, amides, pyridines) with different stoichiometries, including counterions. Second, simulate by molecular dynamics (MD) the solution behaviour of ions and of ligands in their free or complexed states. The  $\text{Cs}^+$  /  $\text{Na}^+$  extraction by calix[4]crown molecules represents a successful simulation study, where the cation selectivity was investigated as a function of the solvent, the nature of counterions and the conformation of the ligand [2].

What happens at the interface between water and oil is a key question in LLE. Simulations showed that extractant molecules like calixarenes, crown ethers, podants, CMPO and TBP are highly surface active, be they complexed with cations or not. Remarkable surface activity was found for anions like  $\text{Pic}^-$  (picrate),  $\text{ClO}_4^-$ ,  $\text{BPh}_4^-$  and dicarbollides, widely used in solvent extraction systems [3].



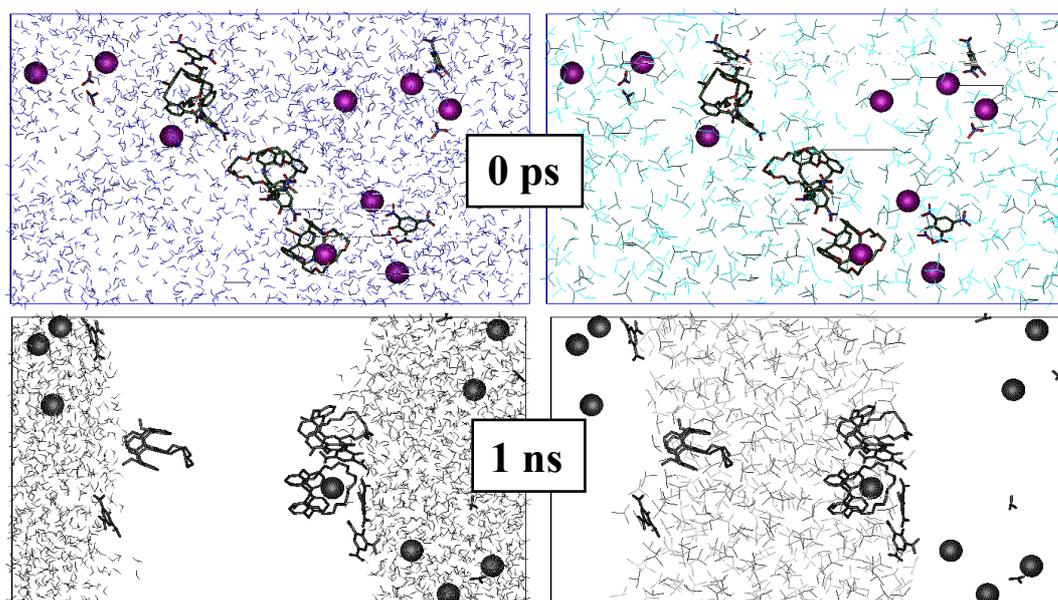
Here, we report MD simulations of the phase separation in two important systems, related to experiments performed in the EC project: (i) the  $\text{Cs}^+$  extraction by the calix[4]arene-crown6 ligand developed by R. Ungaro and (ii) the uranyl extraction by TBP. The latter relates to the PUREX process and represents a first step of modeling actinide and lanthanide extraction by calixarene-CMPO's developed by V. Böhmer. We follow the time evolution of perfectly mixed binary water-oil solutions containing cations, counterions and extractant molecules. How complete is the phase separation? Is there spontaneous formation and extraction of the complexes? What are the roles of counterions and of the medium? The results are reported in ref. [4,5].

## 2. METHODS.

A description of the MD method, force field representation of the systems and protocols used are given in ref. [4,5]. A typical simulation box is shown above, where the "oil" phase is chloroform. It is about  $50 \times 50 \times (40+40) \text{Å}^3$  and contains 1500 to 4000  $\text{H}_2\text{O}$  and 400 to 800  $\text{CHCl}_3$  molecules represented explicitly. The main results are presented below, showing typical situations at the beginning (completely mixed system at 0 ps) and at the end of the dynamics.

## 3 RESULTS

### 3.1- $\text{Cs}^+$ extraction by a calix[4]crown6 ligand (L): demixing of a binary water - chloroform solution of $\text{LCs}^+$ , L, $\text{NO}_3^-$ , $\text{Pic}^-$ and $\text{Cs}^+$ .



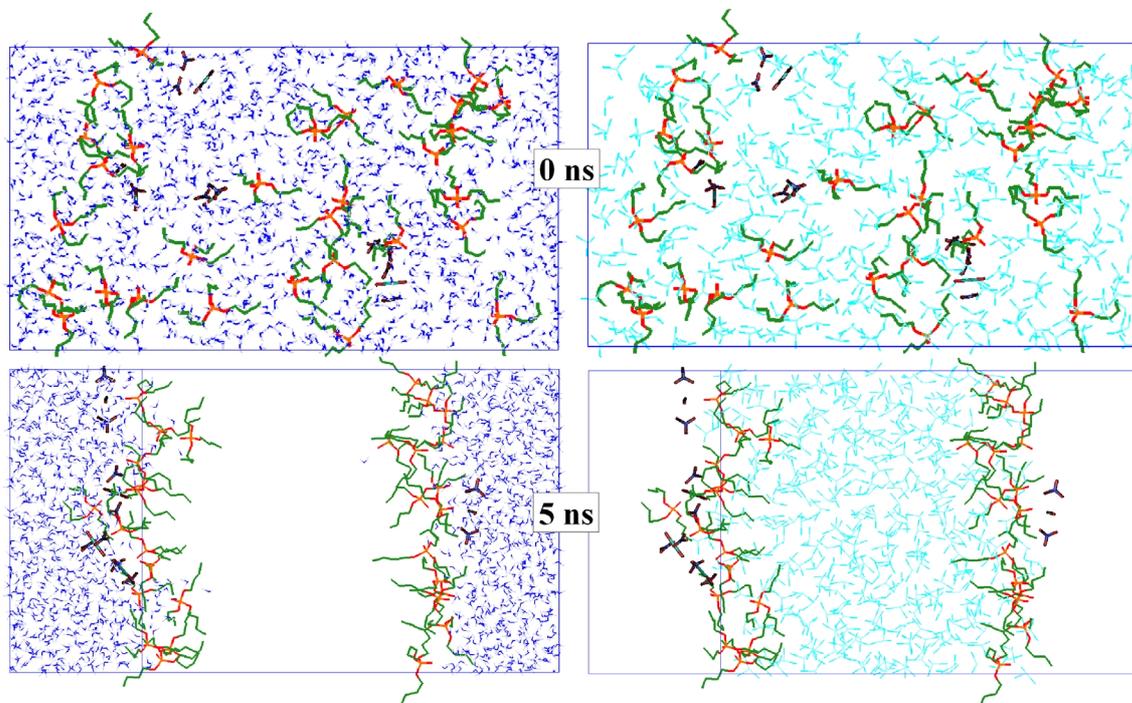
**Fig. 1.** The mixed system at 0 ps and 1 ns. The water (*left*) and chloroform (*right*) solvents are shown separately, instead of being superposed, for clarity.

At 0 ps, the two liquids are completely mixed, equally spread in the simulation box (Fig. 1). The solution contains a mixture of 9  $\text{Cs}^+$ , 4  $\text{Pic}^-$  and 4  $\text{NO}_3^-$  ions, plus two uncomplexed calixarenes L and one  $\text{LCs}^+\text{Pic}^-$  complex. Rapidly, in less than 0.2 ns, water aggregates around the hydrophilic species, while the  $\text{Pic}^-$  anions, L and the  $\text{LCs}^+$  complexes sit at the border between water and oil. At 1 ns, the phase separation is complete, leading to two flat interfaces. The water slabs contain the uncomplexed  $\text{Cs}^+$  cations and  $\text{NO}_3^-$  anions, while all  $\text{Pic}^-$ , L and  $\text{LCs}^+$  species are adsorbed at the interface between water and oil. The oil phase is dry, and contrary to expectations from macroscopic results, there is no extraction of the  $\text{LCs}^+$  complexes. We suggest that extraction requires saturation of the interface by extractant or synergistic species, which reduce the interfacial tension.

### 3.2- Demixing of a binary water - chloroform mixture of TBP and uranyl nitrate salts

Initially, the mixed water chloroform system contains 30 TBP molecules and 5  $\text{UO}_2(\text{NO}_3)_2$  salt species, randomly diluted (Fig. 2). In this system, TBP is both a cosolvent and a potential ligand for uranyl. Rapidly, in less than 0.5 ns, water separates from oil, first forming

"bubbles" where the salts are immersed, while all TBP's sit at the boundary between the two liquids. At 1 ns, the two liquids are separated, but the interface is still irregular. At 5 ns, it gets more flat and regular (Fig. 2). Two remarkable events take place during the demixing. (i) First, all uranyl species bind to TBP molecules, forming four 1:1  $\text{UO}_2(\text{NO}_3)_2\text{TBP}$  and one 1:2  $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$  complexes. (ii) Second, these complexes sit right at the interface, surrounded by other TBP's which form an irregular and unsaturated monolayer.



**Fig. 2.** The mixed system at 0 and 5 ns. Water (*left*) and chloroform (*right*) solvents are shown separately, instead of superposed, for clarity.

One key question is why the uranyl-TBP complexes should quit the interface. Compared to the real PUREX extraction system, the simulated one has been simplified. First, the aqueous phase is neutral, instead of 3-6M in nitric acid. Second, the TBP concentration is lower (about 5 times). It is stressed that these effects contribute markedly to the uranyl extraction. They are presently considered in ongoing simulations.

#### 4. CONCLUSIONS.

The simulations demonstrate the *importance of interfacial phenomena* in LLE. *At no time are water and oil mixed at the microscopic level.* They likely form droplets, microemulsions, micelles or aggregates. Based on our results, important conclusions were drawn: (i) Extractant molecules and their cation complexes, although more soluble in oil than in water, are highly *surface active*. *The peculiar properties of calixarene extractants are not solely determined by their ability to form inclusive host-guest complexes, but also by their amphipathic character and surface activity.* Similar features are expected at the water interface with polymeric membranes. (ii) Lipophilic anions like  $\text{Pic}^-$  are also surface active, although they do not possess, like classical amphiphiles, a polar head flanked by an apolar tail. Accumulation of such anions at the interface creates a negative potential, which attracts cations close to the interface. We suggest that *dicarbollide anions* play such a role in extraction systems. (iii) A consequence of (i) and (ii) is that *cation uptake and recognition take place at the interface.*

This is supported by computations we performed on the Na<sup>+</sup> / Cs<sup>+</sup> complexation by L at the interface [4] and by experiment.

Generally speaking, despite its importance, the liquid-liquid interfacial region is difficult to study by experiment. It represents a challenge for future computer simulations.

#### ACKNOWLEDGMENTS.

The authors are grateful to the European Commission for financial support of contract F14WCT96-0022 in the framework of its R&T specific programme « Nuclear Fission Safety 1994-1998 » and to CNRS IDRIS and Université Louis Pasteur for computer resources. MB, NM, RS are supported by grants from the French Ministry of research.

#### REFERENCES

1. F. Hutschka, L. Troxler, A. Dedieu, G. Wipff, *J. Phys. Chem. A* 102 (1998) 3773. L. Troxler, A. Dedieu, F. Hutschka and G. Wipff, *J. Mol. Struct (THEOCHEM)* 431 (1998) 151. F. Berny, N. Muzet, L. Troxler, A. Dedieu, G. Wipff, *Inorg. Chem.* 38 (1999) 1244. C. Boehme, G. Wipff, *J. Phys. Chem. A* 103 (1999), 6023. M. Baaden, F. Berny, C. Boehme, N. Muzet, R. Schurhammer, G. Wipff, *J. Alloys Compounds* (1999) in press.
2. G. Wipff, M. Lauterbach, *Supramol. Chem.* 6 (1995) 187. M. Lauterbach, A. Mark, W. van Gunsteren, G. Wipff, *Gazzetta Chim. Ital.* 127 (1997) 699. A. Varnek, G. Wipff, *J. Mol. Struct. (THEOCHEM)* 363 (1996) 67. M. Lauterbach, E. Engler, N. Muzet, L. Troxler, G. Wipff, *J. Phys. Chem. B* 102 (1998) 225.
3. F. Berny, N. Muzet, R. Schurhammer, L. Troxler, G. Wipff In *Current Challenges in Supramolecular Assemblies, NATO ARW Athens*; G. Tsoucaris Ed.; Kluwer Acad. Pub., 1998; p. 221. F. Berny, N. Muzet, L. Troxler, G. Wipff In *Supramolecular Science: where it is and where it is going*; R. Ungaro Ed.; Kluwer Acad. Pub., 1999; p. 95.
4. N. Muzet, E. Engler, G. Wipff, *J. Phys. Chem. B* 102 (1998) 10772-10788.
5. M. Baaden, F. Berny, G. Wipff, *J. Mol. Liquids* (1999) in press. M. Baaden, F. Berny, N. Muzet, L. Troxler, G. Wipff In *Calixarene Molecules for Separation*; G. Lumetta Ed.; ACS pub., New York, 1999; in press.