Russian Chemical Bulletin, International Edition, Vol. 53, No. 7, pp. 1459—1465, July, 2004 1459

Accumulation of host—guest ion complexes with different counterions at the water—supercritical CO_2 interface: a molecular dynamics study*

A. Chaumont, N. Galand, R. Schurhammer, P. Vayssière, and G. Wipff ★

Institute of Chemistry, Louis Pasteur University,
4, rue B. Pascal, 67 000 Strasbourg, France.
*wipff@chimie.u-strasbg.fr***

The behavior of ion complexes at the water—supercritical carbon dioxide interface was considered by molecular dynamics simulations. The following complexes were studied: $Cs^+\subset$calix[4]crown-6, $K^+\subset$**222** cryptate with chloride or dicarbollide (CCD^-) counterions, the $Sr^{2+}\subset$**18C6** complex with the picrate (Pic^-) or perfluorooctanoate (PFO^-) counterions, and the $Cl^-\subset$**Tet**$^{4+}$ complex with chloride counterions (**Tet**$^{4+}$ is a tetrahedral tetraammonium cation). The simulations demonstrate the analogy between aqueous interfaces with organic immiscible liquids and the CO_2 phase. Water and supercritical CO_2 are poorly miscible and form an interface. Most of the complexes are accumulated at the interface, instead of diffusing into the organic phase in which they should be more soluble. In addition, marked counterion effects are observed. The CCD^-, Pic^-, and PFO^- anions are surface active and are concentrated at the interface, but show different relationships with the complexes. The formation of ion pairs is precluded by the very hydrophobic CCD^- anions, which promote the extraction of cryptates as separated ion pairs to the CO_2 phase. Conversely, the extraction of the Sr^{2+} ions with **18C6** proceeds *via* a co-complexation mechanism, including the formation of the Sr$\subset$**18C6**$(PFO)_2$, complex having a CO_2 affinity. The mechanism of assisted ion transfer to the CO_2 phase is discussed.

Key words: supramolecular chemistry; complex formation; liquid—liquid extraction; interface; self-assembly.

Assisted ion extraction from the aqueous phase to an immiscible organic phase ("oil") is a fundamental issue in supramolecular chemistry[1—6] addressed in numerous theoretical investigations, focusing on elucidating the nature, the conformations, and the solvation properties of complexes in various liquid media, and the selectivity of binding.[7—9] Little is known, however, about the microscopic nature of aqueous interfaces and the detailed mechanisms for ion capture and transfer through the interface. Our knowledge is largely based on electrochemical[10] and thermodynamic (surface tension) measurements,[11] kinetic models,[12] and surface spectroscopy studies at water—air interfaces,[13] which display analogies with liquid—liquid interfaces. This prompted us to perform computer simulation of this peculiar solvent environment and different species involved in the extraction process, namely, electrolytes,[14] ligands, complexes, or mixtures of these components.[15—19] Most of the studies at interfaces dealt with chloroform as a computationally tractable organic solvent, while other studies used 1,2-dichloroethane or solvent models such as soft spheres. Recently, we developed the first simulations of supercritical carbon dioxide as the receiving phase in liquid—liquid extraction and found close analogies between classical organic solvents and CO_2.[20—22] The most important finding was the adsorption of hydrophobic species (ions, ligands, and complexes) at the interface, no matter whether they are amphiphilic (*e.g.*, calixarenes in the cone conformation) or not.[9,19,23—26] For instance, 18-crown-6 ether (**18C6**) and **222** cryptand, which lack an amphiphilic topology, are adsorbed at the interface rather than diffuse spontaneously into the phase in which they are better soluble, *i.e.*, oil or CO_2.[27,28]

This study deals with typical supramolecular systems based on host—guest complexes between ions and synthetic hosts, at the water—CO_2 interface. An important aspect is the self-assembly, *i.e.*, a local increase in the concentration at the interface induced by the solvent

---

* Materials were presented at the Russian—French Symposium "Supramolecular Systems in Chemistry and Biology" (Kazan, September 22—25, 2003).

** Laboratoire MSM, Institut de Chimie, UMR CNRS 7551, Université Louis Pasteur, 4, rue B. Pascal, 67 000 Strasbourg (France).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1404—1410, July, 2004.

asymmetry. Figure 1 shows the ligands in the simulated solutes, namely, nine Cs^+ complexes with 1,3-alternate calix[4]crown-6 (designated by $Cs^+\subset$**CalixC6**),* sixteen $K^+\subset$**222** cryptates with Cl^- or CCD^- counterions, 25 $Sr^{2+}\subset$**18C6** complexes with Pic^- or PFO^- counterions, and nine $Cl^-\subset$**Tet**$^{4+}$ complexes with Cl^- counterions, where **Tet**$^{4+}$ is a tetraammonium cation of tetrahedral shape. Note the diversity of the simulated counterions, which range from hydrophilic halides Cl^- to less hydrophilic picrate Pic^- (widely used in classical extraction experiments), the chlorinated cobalt dicarbollide CCD^- (used to extract actinides and lanthanides, cesium, and strontium from nuclear waste solutions in the UNEX process),[29] and the perfluorinated PFO^- anion used for Sr^{2+} extraction into supercritical CO_2.[30] Among these, only PFO^- has an amphiphilic topology, while CCD^- has an ellipsoid shape and Pic^- is a disk-shaped anion. It was important to determine how these anions behave at the interface, *i.e.*, whether they migrate to the phase in which they are most soluble and what is their relationship with the complexed cations.

Methods. The systems at the water—CO_2 interface were simulated by classical molecular dynamics (MD) using the modified AMBER software[31] and the following relation for the potential energy U:

$$U = \sum_{\text{bonds}} k_b(b-b_0)^2 + \sum_{\text{angles}} k_\theta(\theta-\theta_0)^2 + \\ + \sum_{\text{dihedrals}} \sum_n V_n[1+\cos(n\varphi-\gamma)] + \\ + \sum_{i<j} \frac{q_i q_j}{R_{ij}} - 2\varepsilon_{ij}\left(\frac{R^*_{ij}}{R_{ij}}\right)^6 + \varepsilon_{ij}\left(\frac{R^*_{ij}}{R_{ij}}\right)^{12}$$

The approach is based on a fixed ball-and-stick representation of the molecules and considers the deformation of angles, bonds, and dihedral angles, the nonbonded interactions being represented as additive pair contributions. The water and CO_2 solvents were represented explicitly at the molecular level using the TIP3P and Murthy three-point models, respectively.[32,33] The parameters of the K^+, Cs^+, and Sr^{2+} cations were fitted on the free energy of hydration,[34] while the charges of the ligands were derived from the electrostatic potentials calculated by *ab initio* quantum mechanical methods (detailed description for **18C6**,[35] **calixC6**,[20] **222**,[28] and **Tet**$^{4+}$ [36] ligands has been reported).

The interface was represented at the molecular level starting from adjacent ~40—50 Å long cubic boxes of water and of CO_2, containing ~3000 H_2O molecules and ~1000 CO_2 molecules (Fig. 2). The solutes were initially placed at the interface and it was checked that the final distribution of the solutes after equilibration does not actually depend crucially on the starting configuration. This was done by running mixing—demixing simulations and by other simulations starting with different positions of the solutes. The equilibration of the systems included the following steps: minimization, dynamics with frozen solutes, and simulation in the (N,V,T) and (N,P,T) thermodynamic ensembles at temperatures of 305 K or 350 K.

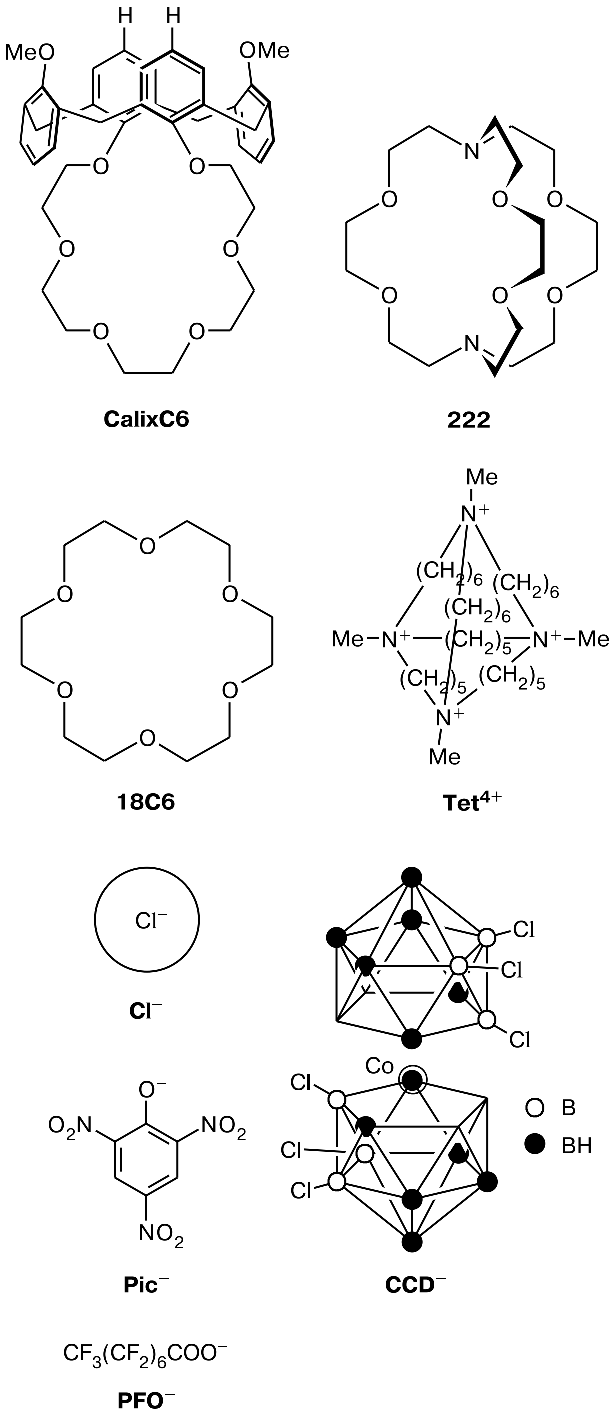

Fig. 1. Simulated complexes and anions.

---

* The character $\subset$ means that the ion is encapsulated in the ligand.

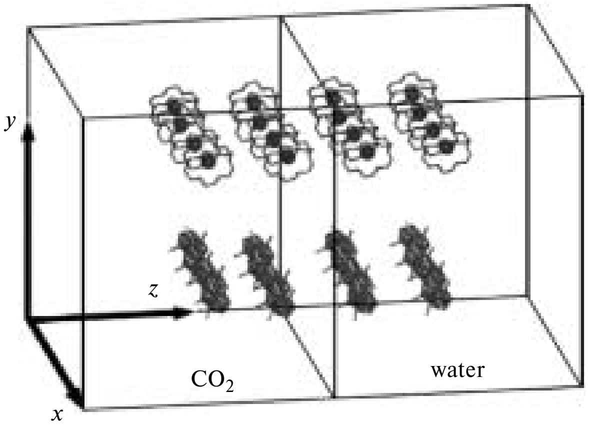

Fig. 2. Schematic representation of the CO_2—water interface (the solvent molecules are not shown) with 16 K^+⊂**222** cryptates with CCD^- counter-ions at the beginning of the MD simulation.

Technical aspects such as temperature monitoring, evaluation of the electrostatics (classical, Ewald, and reaction field methods) may also be important for the distribution and solvation properties of the charged solutes. Typical cut-off distances used for nonbonded interactions were 12 to 15 Å, while the simulated times were 1—2 ns, which is long enough to allow the diffusion and solvation of the solutes.

The simulated systems are complex, relatively big, and dynamic in nature. They were therefore analyzed by statistical averaging over the last steps of the dynamics (typically 0.3 ns, *i.e.*, 600 saved configurations) in terms of density curves, energy components, and radial distribution functions. In addition, we display typical snapshots which are representative for the statistics.

Results and Discussion

General features. At the end of dynamics, all simulated systems display a number of common features. First, there exists a limit in the mutual solubility of water and CO_2, which form two distinct phases. Only ~10—20 CO_2 molecules are dissolved in water, whereas the CO_2 phase does not contain water. The only exception is found when water molecules extracted by the solute through specific hydrogen bonds or ion—dipole interactions. The most important result is the fact that, in most cases, the complexes are concentrated near the interface rather than diffuse into CO_2 as could be expected in view of their hydrophobic nature. This is mainly due to specific interactions with water molecules at the interface. According to energy component analysis, all complexes are attracted more efficiently by water than by CO_2. They generally remain at the interface, however, because at the interface, they are still involved in attractive interactions with water, without having to pay for the high cavitation energy of water. Yet another factor, which will be addressed below, is the importance of the counterions. Different behaviors are observed, depending on the hydrophilic or hydrophobic character, the surface activity, and ion-binding properties of counterions.

The results are illustrated by typical snapshots at the end of the dynamics (Fig. 3).

Extraction of Cs^+ ions by calix[4]crown-6. The first example is concerned with the Cs^+⊂**CalixC6** complex simulated with the Pic^- counterions. During the simulation, the nine complexes and anions remain at the interface, which is therefore electrically neutral. The solute molecules oscillate along the z axis by a few Ångstroms and diffuse in the xy plane of the interface. The Cs^+ cations are not fully shielded by the crown moiety of the calixarene and are thus attracted by water. As a result, each cation is hydrated, on average, by one or two water molecules. The complexes form loose ion pairs with the Pic^- counterions. Some of the anions are close to the Cs^+ side of the complex, while others display π-stacking interactions with the phenolic groups of the calixarenes, thus acting as relays between two ligands. Several stacked Pic^-—Pic^- dimers are located between calixarenes at the interface. Clearly, such specific interactions could not be achieved by, *e.g.*, Cl^-, CCD^-, or PFO^- anions. The surface activity is observed in the computer experiments for individual Pic^- anions and also for the Cs^+⊂**CalixC6** complex alone (without counterions), but is clearly enhanced by their mutual interactions when they are simulated together.

Extraction of K^+ ions by cryptands. The role of counterions is further demonstrated for the case of K^+ extraction by the **222** cryptand, a system of major importance in supramolecular chemistry, which has not yet been investigated, to our knowledge, in supercritical CO_2. The simulation of sixteen K^+⊂**222** cryptates in the presence of hydrophilic Cl^- anions showed that most of the anions migrate to the aqueous phase within 1.5 ns, presumably, due to the high temperature (350 K). Free **222** cryptands remain in the CO_2 phase, whereas the cryptates are located at or near the interface. Thus, cryptates are more surface-active than cryptands. This was to be expected in view of their +1 charge and stronger attraction by water molecules at the interface. A completely different situation is observed when sixteen K^+⊂**222** cryptates are simulated with the CCD^- counterions under the same conditions and for the same duration (1.5 ns). These anions are hydrophobic and none of them finally remains in water. Six of the sixteen anions sit at the interface, which attests to their surface activity, while the other ten are found in the CO_2 phase, together with most of the cryptates, which can therefore be considered as extracted into CO_2. The CCD^- anions are heavier and diffuse more slowly than the Cl^- anions. Another feature is the neutralization of the CO_2 phase by the cryptates and the

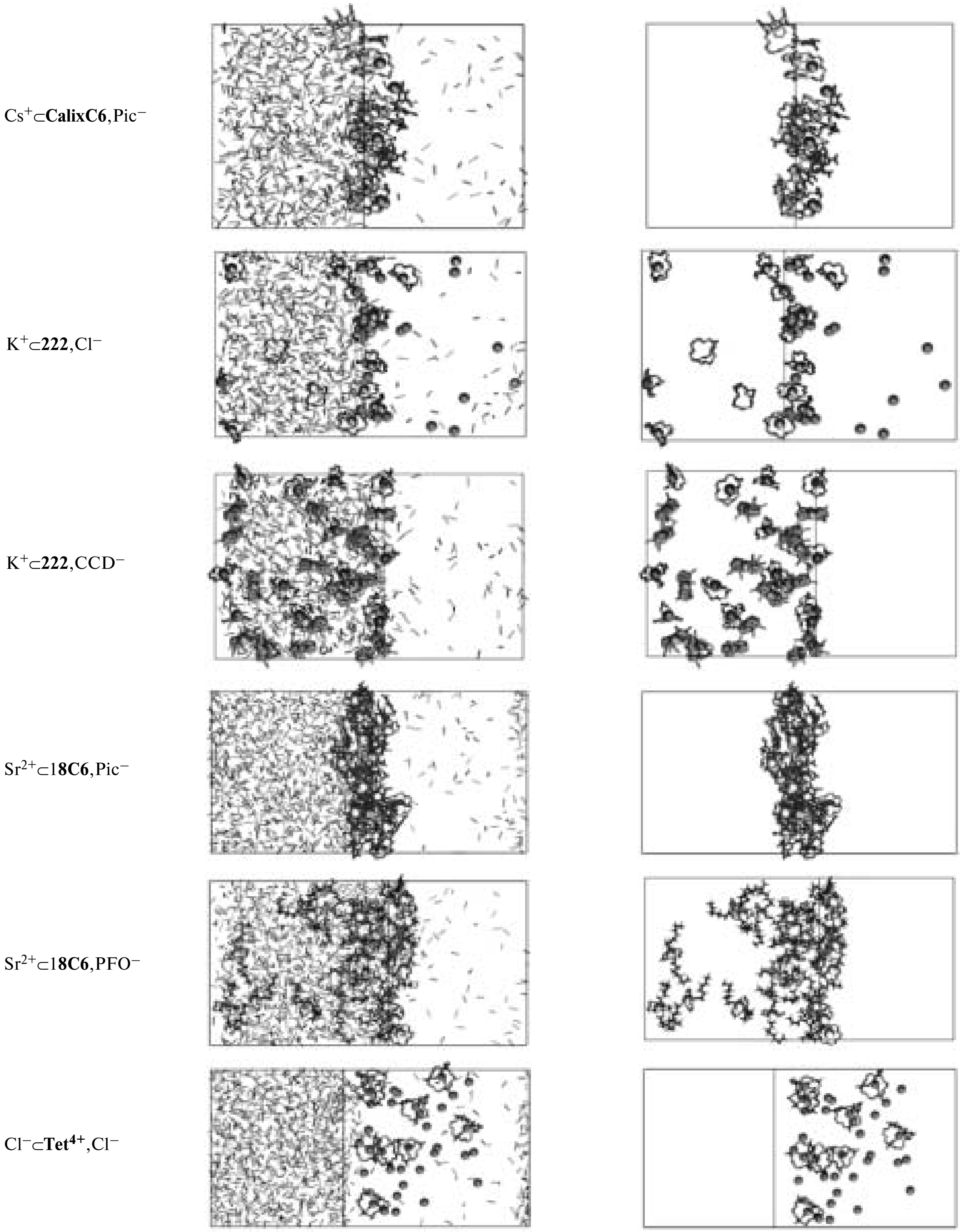

Fig. 3. Typical distribution of complexes at the interface. From top to bottom: nine $Cs^+\subset$**CalixC6**,Pic^- complexes; sixteen $K^+\subset$**222** cryptates with the Cl^- and CCD^- anions; twenty five $Sr^{2+}\subset$1**8C6** complexes with the Pic^- and PFO^- anions; nine $Cl^-\subset$**Tet^{4+}** complexes with the Cl^- counterions. Each system is shown only with the CO_2 solvent (water is omitted; left column) and without a solvent (right column).

cryptate...CCD$^-$ Coulombic attractions also prevent or, at least, restrict the diffusion of these species to the interface. In the case of CCD$^-$ M^{n+} salts (M^{n+} = Cs$^+$ or Eu^{3+}), which do not form complexes, the CCD$^-$ anions form an interfacial layer, neutralized by the M^{n+} cations, which reside on the aqueous side of the interface. This comparison illustrates once again the importance of the cation—anion relationship for the distribution of one ionic component with respect to the interface. These results provide better understanding of the fact that cryptate extraction into supercritical CO$_2$ should be facilitated by CCD$^-$ type counterions.

Extraction of Sr^{2+} ions by 18C6 crown ether. It is of interest to compare the extraction of Sr^{2+} by **18C6** with the extraction of K$^+$ by **222** cryptand. The Sr^{2+} extraction by **18C6** seems quite unfavorable for three main reasons: (*i*) first, the dehydration energy is much higher for the divalent Sr^{2+} cation than for the monovalent K$^+$ cation ($\Delta\Delta G_{\text{hyd}}$ = 259 kcal mol^{-1}), resulting in a much higher energy cost needed to remove Sr^{2+} from the aqueous phase; (*ii*) **18C6** crown ether is less hydrophobic than **222** cryptand, and (*iii*) ring shape of **18C6** prevents full shielding of the complexed cation from the solvent. According to our simulations, these problems can be circumvented by an adequate choice of the counterion, as demonstrated by comparison of the Pic$^-$ and PFO$^-$ counterions. First, 25 Sr^{2+}⊂**18C6** complexes were combined with 50 X$^-$ anions, which formed contact ion pairs with the Sr^{2+} cation. The resulting Sr⊂**18C6**(X)$_2$ complexes are formally neutral, which is a necessary condition for extraction into an organic or CO$_2$ phase. As shown in Fig. 3, the results are different, depending on the nature of X$^-$. In the case of Pic$^-$ counterions, all complexes are located at the interface. A closer look at the computer graphics system reveals two types of specific attraction between them. First, due to delocalization of the negative charge over the seven oxygen atoms, the picrate anions bind simultaneously two complexed Sr^{2+} cations through the nitro or phenoxide oxygen atoms and thus link complexes together. Second, stacked Pic$^-$ dimers act as relays, leading to the aggregation of Sr⊂**18C6**(Pic)$_2$ complexes at the interface. The formation of such supramolecular assemblies has a deleterious effect in the context of ion extraction, as the resulting film forms a kind of "crust" that prevents the transfer from one phase to the other. This resembles the formation of the interfacial "crust" formed by phosphate zirconium salts, as characterized by Raman spectroscopy.[37]

The strontium complexes with PFO$^-$ counterions behave quite differently. Some of the 25 simulated Sr⊂**18C6**(PFO)$_2$ complexes are adsorbed at the interface, while the majority are finally found in the CO$_2$ phase and can thus be considered as extracted. This feature is fully consistent with the experimental observation of Sr^{2+} extraction by perfluorinated octanoate or perfluorinated sulfonate counterions.[35] Comparison with the Pic$^-$ anions allows one to interpret this result. Unlike the Pic$^-$ anions, the monodentate PFO$^-$ anions cannot simultaneously bind two Sr^{2+} cations, thus preventing aggregation of the Sr^{2+} complexes. The second important feature concerns the "free moiety" of the PFO$^-$ anions, which is hydrophobic and CO$_2$-philic. This favors the solvation of the Sr⊂**18C6**(PFO)$_2$ complexes by CO$_2$ molecules. According to experimental data and our simulations,[38] fluorination of aliphatic or aromatic hydrocarbons enhances their solubility in CO$_2$, mainly due to enhanced van der Waals contacts with the solvent, which facilitates the extraction into supercritical CO$_2$. For the same reasons, the noncomplexed Sr(Pic)$_2$ and Sr(PFO)$_2$ salts also behave quite differently at the water—CO$_2$ interface.[35]

Extraction of Cl$^-$ ions by the Tet^{4+} cation. When the charge of host—guest complexes increases, they become more hydrophilic, which decreases their interfacial activity. This is indeed observed in the simulations we performed for nine Cl$^-$⊂**Tet**$^{4+}$ inclusion complexes in the presence of chloride counterions. The **Tet**$^{4+}$ host is a tetracharged quasi-spherical cation; hence, it is much more hydrophilic than the neutral calixarene or cryptand molecules. As a result, six of the nine simulated complexes finally (after 1.5 ns) sit in the aqueous phase. The other three complexes, which are located at the interface, sit on its aqueous side. We believe that this is indicative of their hydrophobic character. The complexes are quite bulky and their solvation by water requires a high cavitation energy. Attempts to migrate at the interface may thus be considered as being due to hydrophobic forces. It is of interest to compare these results with those obtained under the same conditions at the water—chloroform interface, where most of the Cl$^-$⊂**Tet**$^{4+}$complexes are accumulated, instead of diffusing into water.[36] This is consistent with a reduced surface tension at the water—CO$_2$ interface and larger diffusion coefficients under supercritical conditions.

* * *

We report a series of molecular dynamics simulation experiments dealing with ion complexation at the water—CO$_2$ interface, which manifest noncovalent interactions in two main domains of supramolecular chemistry: (*i*) host—guest interactions between the macrocyclic molecules and hydrophilic ions, which allow the transport of the latter from the aqueous to hydrophobic medium (supercritical CO$_2$); (*ii*) formation of supramolecular structures (two-dimensional layers) at the interface, as do classical amphiphiles. In fact, the nature of these layers markedly depends on the nature of the counterions. We have found an example of "crust" formation at the interface with the Sr⊂**18C6**(Pic)$_2$ complexes, which differs from the partitioning of the Sr⊂**18C6**(PFO)$_2$ complexes in CO_2. Halide anions like Cl^- are too hydrophilic to concentrate at the interface and, hence, to follow a complexed cation on passing to the organic or the supercritical CO_2 phase, following the well-known trends in classical extraction, where the efficiency decreases with the hydrophilicity of the counterion. For instance, the rates of K^+ transport through chloroform with crown ethers decrease in the following order: $Pic^- > PF_6^- > ClO_4^- > IO_4^- > BF_4^- > I^- > SCN^- > NO_3^- > Br^- > BrO_3^- > Cl^- > OH^- > F^- > acetate^- > SO_4^{2-}$, which is roughly the order of increasing hydration energies[39] (see also Refs. 40—43). In addition to lipophilicity, the nature of the extracted ion pair and the anion interactions with the complexed cation in the organic phase are important factors. This can be seen in the case of the $Sr\subset$**18C6**$(PFO)_2$ complexes, which are extracted as contact ion pairs. Thus, noncoordinating hydrophobic anions like CCD^- would be less efficient than PFO^- for extraction of Sr^{2+} with the **18C6** ligand. Conversely, in the case of K^+ extraction with **222** cryptand, the PFO^- ions would be less efficient than CCD^-, as confirmed by molecular dynamics simulations. The main reason is the shielding of the cation by the **222** ligand, which prevents the formation of contact ion pairs with PFO^-. In this case, extraction involving dissociated ion pairs would also be disfavored, as the polar carboxylate head of PFO^- would be poorly solvated in supercritical CO_2.

According to simulation results, anions play another important role in liquid—liquid extraction at the complexation stage. Since simulated ligands are also surface active in the noncomplexed state, one can speculate that ion binding by the ligands also takes place at the water—CO_2 interface. This is supported by theoretical studies at classical interfaces (*e.g.*, free energy calculations for Na^+ and Cs^+ complexation by **CalixC6** at the water—chloroform interface[17]) and by kinetic[12] and electrochemical[10] studies (see also Ref. 44). The key question is to understand how hydrophilic ions (*e.g.*, Cs^+ and more hydrophilic Sr^{2+} or trivalent cations) can approach the interface closely enough to be captured by the interfacial ligands. In our opinion, the answer is in the nature of counterions. Apparently, hydrophobic anions are generally surface active, even when they lack an amphiphilic topology. This is the case with Pic^- or CCD^- anions, which concentrate at the interface and, therefore, create a negative potential, which attracts the uncomplexed cations toward the interface. Surface activity also implies increased concentrations, which reduce the interfacial tension and enhance the local mixing of water with CO_2. Thus, synergistic effects of counterions are observed at the interface. This facilitates the capture of cations by the ligands and desorption of the complexes from the interface to the CO_2 phase. Another feature, recently pointed out for classical liquid—liquid extraction,[45] refers to the formation of microphases, microdroplets, micelles, or aggregates. Evidently, they may also form in the case of supercritical fluid extraction with marked counterion effects. This calls for further theoretical and experimental research. The field of assisted ion extraction, an important issue of supramolecular chemistry, develops as a topical field of research, in particular, in "green chemistry" in nonconventional liquids (*e.g.*, room temperature ionic liquids),[46—48] at interfaces, and in heterogeneous solutions.

This work was financially supported by the European Economic Community (EEC) and the PRACTIS foundation and by the Ministry of Education of France (grant for N. Galand and P. Vayssière). The authors are grateful to IDRIS, CINES, and Louis Pasteur University for allocation of computer resources.

References

1. D. J. Cram, *Science*, 1988, **240**, 760.
2. J. M. Lehn, *Struct. Bonding*, 1973, **161**, 1.
3. M. Kirch and J. M. Lehn, *Angew. Chem. Int. Ed.*, 1975, **14**, 555.
4. J. M. Lehn, *Angew. Chem.*, *Int. Ed. Engl.*, 1988, **27**, 89.
5. J.-M. Lehn, *Angew. Chem.*, *Int. Ed. Engl.*, 1990, **29**, 1304.
6. C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017.
7. G. Wipff, *J. Coord. Chem.*, 1992, **27**, 7.
8. G. Wipff and L. Troxler, in *Computational Approaches in Supramolecular Chemistry*, Ed. G. Wipff, Kluwer, Dordrecht, 1994, p. 319.
9. G. Wipff, in *Calixarenes-2001*, Ed. J. Vicens, Z. Asfari, J. Harrowfield, and V. Böhmer, Kluwer Acad. Publishers, Dordrecht, 2001, p. 312.
10. H. H. Girault and D. J. Schiffrin, in *Electroanalytical Chemistry*, Ed. A. J. Bard, Dekker, New York, 1989, p. 1.
11. J. Szymanowski, *Solv. Extract. Ion Exch.*, 2000, **18**, 729.
12. P. R. Danesi, in *Principles and Practices of Solvent Extraction*, Ed. J. Rydberg, C. Musikas, and G. R. Choppin, M. Dekker, Inc., New York, 1992, p. 157.
13. K. B. Eisenthal, *Ann. Rev. Phys. Chem.*, 1992, **43**, 627.
14. F. Berny, R. Schurhammer, and G. Wipff, *Inorg. Chim. Acta*, *Special Issue*, 2000, **300—302**, 384.
15. G. Wipff and M. Lauterbach, *Supramol. Chem.*, 1995, **6**, 187.
16. M. Lauterbach, E. Engler, N. Muzet, L. Troxler, and G. Wipff, *J. Phys. Chem. B*, 1998, **102**, 225.
17. N. Muzet, E. Engler, and G. Wipff, *J. Phys. Chem. B*, 1998, **102**, 10772.
18. F. Berny, N. Muzet, L. Troxler, and G. Wipff, in *Supramolecular Science: where it is and where it is going*, Eds. R. Ungaro and E. Dalcanale, Kluwer Acad. Publishers, Dordrecht, 1999, p. 95.
19. M. Baaden, F. Berny, N. Muzet, L. Troxler, and G. Wipff, in *Calixarenes for Separation. ACS Symposium Series 757*, Eds. G. Lumetta, R. Rogers, and A. Gopalan, ACS, Washington DC, 2000, p. 71.
20. R. Schurhammer, F. Berny, and G. Wipff, *Phys. Chem. Chem. Phys.*, 2001, **3**, 647.
21. R. Schurhammer and G. Wipff, in *Separations and Processes Using Supercritical Carbon Dioxide*, Eds. A. S. Gopalan, C. Wai, and H. Jacobs, ACS, 2003, p. 223.

22. P. Vayssière and G. Wipff, *Phys. Chem. Chem. Phys.*, 2003, **5**, 127.
23. G. Wipff, E. Engler, P. Guilbaud, M. Lauterbach, L. Troxler, and A. Varnek, *New J. Chem.*, 1996, **20**, 403.
24. M. Baaden, F. Berny, N. Muzet, R. Schurhammer, L. Troxler, and G. Wipff, in *Euradwaste 1999: Radioactive Waste Management Strategies and Issues*, Ed. C. Davies, European Commission, Brussels, 2000, p. 519.
25. M. Baaden, M. Burgard, and G. Wipff, *J. Phys. Chem. B*, 2001, **105**, 11131.
26. M. Baaden, R. Schurhammer, and G. Wipff, *J. Phys. Chem. B*, 2002, **106**, 434.
27. L. Troxler and G. Wipff, *Analytical Sciences*, 1998, **14**, 43.
28. P. Jost, N. Galand, R. Schurhammer, and G. Wipff, *Phys. Chem. Chem. Phys.*, 2002, **4**, 335.
29. R. S. Herbst, J. D. Law, T. A. Todd, V. N. Romanovskiy, I. V. Smirnov, and B. N. Zaitsev, *Solv. Extract. Ion Exch.*, 2002, **20**, 429.
30. C. M. Wai, Y. Kulyako, H.-K. Yak, X. Chen, and S.-J. Lee, *Chem. Commun.*, 1999, 2533.
31. D. A. Case, D. A. Pearlman, J. C. Caldwell, T. E. Cheatham III, W. S. Ross, C. L. Simmerling, T. A. Darden, K. M. Merz, R. V. Stanton, A. L. Cheng, J. J. Vincent, M. Crowley, D. M. Ferguson, R. J. Radmer, G. L. Seibel, U. C. Singh, P. K. Weiner, and P. A. Kollman, *AMBER5*, *University of California*, *San Francisco*, 1997.
32. W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, *J. Chem. Phys.*, 1983, **79**, 926.
33. C. S. Murthy, K. Singer, and I. R. McDonald, *Mol. Phys.*, 1981, **44**, 135.
34. J. Åqvist, *J. Phys. Chem.*, 1990, **94**, 8021.
35. P. Vayssière and G. Wipff, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2842 (and references cited therein).
36. A. Chaumont and G. Wipff, *J. Comput. Chem.*, 2002, **23**, 1532.
37. H. G. M. Edwards, M. A. Hughes, and D. N. Smith, *Vibrational Spectrocopy*, 1996, **10**, 281.
38. N. Galand and G. Wipff, *New J. Chem.*, 2003, **27**, 1319.
39. J. D. Lamb, J. J. Christensen, S. R. Izatt, K. Bedke, M. S. Astin, and R. M. Izatt, *J. Am. Chem. Soc.*, 1980, **102**, 3399.
40. U. Olsher, M. G. Hankins, Y. D. Kim, and R. A. Bartsch, *J. Am. Chem. Soc.*, 1993, **115**, 3370.
41. H. D. Willauer, J. G. Huddleston, S. T. Griffin, and R. D. Rogers, *Sep. Sci. Technol.*, 1999, **34**, 1069.
42. B. A. Moyer, in *Molecular Recognition: Receptors for Cationic Guests*, Ed. J. L. Atwood, J. E. D. Davies, D. D. McNicol, F. Vögtle, and J.-M. Lehn, Pergamon, New York, 1996, p. 325.
43. Y. Shibahara, K. Nishizawa, Y. Yasaka, and Y. Fujii, *Solv. Extract. Ion Exch.*, 2003, **21**, 435.
44. H. Watarai, *Trends in Analytical Chemistry*, 1993, **12**, 313.
45. B. Coupez, C. Boehme, and G. Wipff, *J. Phys. Chem. B*, 2003, **107**, 9484.
46. J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser, and R. D. Rogers, *Chem. Commun.*, 1998, 1765.
47. A. E. Visser, R. P. Swatlosli, W. M. Reichert, S. T. Griffin, and R. D. Rogers, *Ind. Eng. Chem. Res.*, 2000, **39**, 3596.
48. A. E. Visser, R. P. Swatloski, S. T. Griffin, D. H. Hartman, and R. D. Rogers, *Separ. Sci. Technol.*, 2001, **36**, 785.

Received January 16, 2004