

Molecular Dynamics Study of the Uranyl Extraction by Tri-*n*-butylphosphate (TBP): Demixing of Water/“Oil”/TBP Solutions with a Comparison of Supercritical CO₂ and Chloroform

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We report molecular dynamics simulations on the phase separation of “perfectly mixed” water/oil/tri-*n*-butylphosphate (TBP) solutions containing 30 or 60 TBP molecules and 5 UO₂(NO₃)₂ complexes. The oil phase is mimicked by one of two liquids, either chloroform or supercritical CO₂ (SC-CO₂). The simulations demonstrate the importance of TBP concentration. In the TBP₃₀ systems, the water and oil phases separate on the nanosecond time scale, leading to two interfaces onto which all TBPs adsorb. Some of them spontaneously form 1:1 and 1:2 complexes with UO₂(NO₃)₂ at the interface. With the more concentrated TBP₆₀ systems, water and oil do not separate but form microemulsions containing neat water “droplets” surrounded by oil in which TBP is solubilized, sitting at the oil–water boundaries delimiting the droplets. All UO₂(NO₃)₂ salts are complexed by TBP at the liquid boundaries, sitting somewhat more in oil than in water. Following the Le Chatelier rule, the proportion of 1:2 complexes is larger in the TBP₆₀ system than in the TBP₃₀ system. Thus, TBP acts not only as a complexant but also as an “interface modifier”. The simulations reveal strong analogies between chloroform and SC-CO₂ as organic phases. These novel results are crucial for our understanding of the state of heterogeneous solutions involved in uranyl extraction by TBP as well as assisted cation extraction by other extractants.

Introduction

Uranyl and plutonyl complexation and extraction by tri-*n*-butyl phosphate (TBP) are the key features of the PUREX process in which these ions are separated from radioactive wastes.^{1–4} In this process, the metals are dissolved in a highly acidic aqueous source phase (about 3 M), and uranyl is extracted as UO₂(NO₃)₂TBP₂ complexes using a mixture of organic solvents (total petroleum hydrocarbons (TPH) and kerosene with other organic diluents) and about 30% by volume of TBP. Generally speaking, what happens at the microscopic level in assisted ion extraction is unclear from experiment alone. This led our group to undertake molecular dynamics (MD) investigations on extractant molecules and ions at a water–oil interface, in which “oil” was modeled by chloroform,^{5–8} dichloroethane,⁹ or supercritical CO₂ (SC-CO₂).¹⁰ They revealed the importance of interfacial phenomena: all extractant molecules, be they of amphiphilic topology (like calixarenes, TBP, CMPO, podants) or not (like crown ethers, cryptands) were found to adsorb at the interface between water and oil. Their cation complexes were found to be also surface active. The distribution of ions and nitric acid was investigated in relation to their surface activity.^{11,12} Hard ions (like divalent or trivalent metallic cations)^{13,14} were found to be “repelled” by the interface, while hydrophobic ions (like picrate, tetraphenylborate, dicarbollide anions, or guanidinium cations) or neutral acid molecules adsorbed at the interface. A qualitative correlation was observed between self-association in water and surface activity for ions. Most simulations considered the time evolution of extractants

and ions immersed near a preformed water–oil interface. Additional valuable information was obtained from demixing simulations, starting from “perfectly mixed” water/oil solutions. In the absence of solutes or in diluted conditions (0.05 to 0.2 M solutions), complete phase separation was observed on the nanosecond time scale, leading to distinct water and oil phases connected by a relatively flat “interface”.^{8,15,16}

In this paper, we focus on the effect of TBP concentration and compare the demixing of oil/water/TBP/salt systems, with a TBP content of 30 or 60 molecules (concentrations of about 0.4 and 0.8 mol L^{−1}) and 5 UO₂(NO₃)₂ salts. Important questions concern the extent and rate of phase separation, the distribution of TBPs, and the possible complexation of uranyl by TBP: Will water and oil separate and form distinct phases or mixed systems or even more complex “microemulsions”? Do the TBPs concentrate at the water–oil interface? Is the latter saturated? Is water dragged to oil? Will uranyl be complexed and extracted by TBP to the oil phase? In a first series of experiments, oil will be modeled by chloroform for convenience and to remain consistent with our previous work. This reduces the computer time and sampling of the solvent configurations, compared to simulations with long-hydrocarbon-chain-containing solvents (e.g., dodecane). A second series will be carried out with SC-CO₂ as the organic liquid, because this technique is very promising for the purpose of lanthanide and actinide cation extraction by phosphoryl-containing ligands.^{17–19} Metal ions in solid or liquid matrixes can be extracted by SC-CO₂ upon chelation by appropriate ligands.²⁰ For instance, fluorinated β-diketones extract highly charged ions such as Ni²⁺ or Cr³⁺,²¹ as well as lanthanide and actinide cations,^{22,23} while organophosphorus ligands extract UO₂²⁺ and Th⁴⁺ ions from nitric

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acid solutions.^{24–27} We thus want to compare the demixing of the chloroform and SC-CO₂ mixtures. Note that the simulation on the 30TBP/water/chloroform solution has been reported¹⁶ and serves as a reference for simulations of the more concentrated TBP solutions and for comparison with the corresponding SC-CO₂ ones.

Methods

The MD simulations were performed with the modified AMBER5.0 software²⁸ in which the potential energy, U , is described by a sum of bond, angle, and dihedral deformation energies and pairwise additive 1-6-12 (electrostatic + van der Waals) interactions between nonbonded atoms.

$$U = \sum_{\text{bonds}} K_r (r - r_{\text{eq}})^2 + \sum_{\text{angles}} K_\theta (\theta - \theta_{\text{eq}})^2 + \sum_{\text{dihedrals}} \sum_n V_n (1 + \cos n\phi) + \sum_{i < j} [q_i q_j / R_{ij} - 2\epsilon_{ij} (R_{ij}^*/R_{ij})^6 + \epsilon_{ij} (R_{ij}^*/R_{ij})^{12}]$$

Parameters for the solutes were taken from the AMBER force field²⁹ and from previous studies in pure homogeneous solvents. The atomic charges of TBP are from ref 30. The parameters of UO₂²⁺ have been fitted on free energies of hydration by Guibaud and Wipff,³¹ while those of NO₃[−] are the same as in ref 6.

Water was represented with the TIP3P model,³² while chloroform was either modeled by the all-atom model of Chang et al. used without polarization,³³ or by the four-site OPLS model³⁴ in some of the initial simulations of 5UO₂(NO₃)₂/30TBP. CO₂ was depicted by the three-site model of Murthy et al.³⁵ charges $q_C = 0.596$, $q_O = -0.298$ e and van der Waals parameters $R_O^* = 1.692$, $R_C^* = 1.563$ Å and $\epsilon_O = 0.165$, $\epsilon_C = 0.058$ kcal/mol. For simplicity, the products of aqueous phase reactions of CO₂ (carbonic acid H₂CO₃ and the corresponding HCO₃[−] and CO₃^{2−} species) were neglected. All bonds were constrained with SHAKE, using a time step of 2 fs. The UO₂(NO₃)₂ salt was constrained to a pseudo-*D*_{2h} symmetrical structure in which the two nitrates are bidentately bound in the equatorial plane of UO₂²⁺. This is to model a situation close to experimental conditions in which NO₃[−] anions are in excess and the salt is mostly associated and to possibly facilitate its extraction as a neutral species to the oil phase. The nonbonded interactions were calculated with a residue-based cutoff of 13 Å for the CO₂-containing systems and with a twin 12/15 Å cutoff for the chloroform-containing systems.

The interface has been built as indicated in ref 36, starting with two adjacent boxes of pure water and “oil”, respectively (Figure 1). The simulation conditions and definitions of the different systems, named from A to D, are given in Table 1. The TBPs were initially placed at the interface with 15 TBPs per layer pointing their O_P phosphoryl oxygens to water, while the UO₂(NO₃)₂ complexes were immersed in the aqueous phase. The initial density of the CO₂ box was 0.802 g/cm³, which is above the critical density (0.468 g/cm³ at 304 K) and close to the density of 0.79 g/cm³ at 345 K and a pressure of 30 MPa.³⁷ Although it would be desirable to run the simulations at constant pressure, this procedure turned out to be difficult because of the high fluctuations and problems to correctly monitor the pressure of both phases in metastable conditions. This is why we decided to perform the CO₂ simulations at constant volume, starting with a density of 1.0 g/cm³ for water and 0.80 g/cm³ for CO₂. The chloroform-containing systems were simulated at

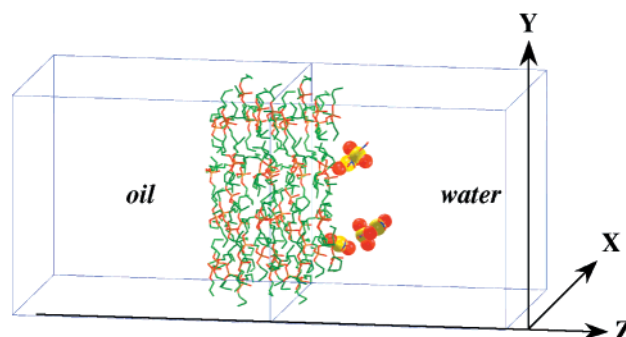


Figure 1. Schematic representation simulation box with the initial configuration of the 4 × 15 TBPs and 5 UO₂(NO₃)₂ salts, where “oil” is either chloroform or SC-CO₂.

TABLE 1: Simulation Conditions of the Solutions Containing 5 UO₂(NO₃)₂ + *n* TBPs and Chloroform vs SC-CO₂ as the “Oil”^a

	<i>n</i> TBP	“oil”	<i>N</i> _{oil} + <i>N</i> _{wat}	<i>X</i> × <i>Y</i> × (<i>Z</i> _{oil} + <i>Z</i> _{wat}) (Å)	time ^c (ns)
A	30	CO ₂	595 + 1832	40 × 40 × (43 + 35)	3
B ^b	30	chloroform	357 + 1469	40 × 40 × (35 + 32)	5
C	60	CO ₂	619 + 1992	42 × 39 × (43 + 45)	5.6
D	60	chloroform	357 + 1459	34 × 32 × (35 + 35)	5.2

^a Number of solvent molecules, size of the simulation box and simulated time of demixing are reported. The axes are defined in Figure 1. ^b From ref 16. ^c Time of demixing.

a constant volume, V , which was determined from the $V(t)$ curve obtained for preequilibration runs at a pressure of 1 atm for up to 700 ps. All systems were represented with 3D periodic boundary conditions applied along the X , Y , and Z directions (i.e., parallel to the plane of the interface). Thus, the water and oil liquids formed before mixing alternating slabs of about 30–40 Å thickness, separated by an interface.

After energy minimization and MD equilibration at a constant pressure of 1 atm, the dynamics was run at a constant volume and temperature which was coupled to a thermal bath with a relaxation time of 0.1 ps. For the CO₂-containing systems, CO₂, water, and the solutes were independently coupled to three thermal baths (at 350 K), while for the chloroform-containing systems, two baths of 300 K were used, one for water and another one for the remaining system. Mixing was obtained by heating the system to 700 K and scaling down the Coulombic interactions by a factor 100. From the solvent and solute density curves, we monitored the mixing. A homogeneous mixture was obtained after 1–2 ns. Demixing was performed for 3–5 ns (Table 1) by resetting the dielectric constant to 1.0 and the temperature to 300 K for the chloroform solutions and 350 K for the SC-CO₂ solutions.

The results were analyzed as described in ref 15. The position of the interface was recalculated every 0.2 ps as the intersection between the water and chloroform density curves. The distribution of different species was characterized by the corresponding density curves. The demixing index χ_{demix} has been defined as in ref 15 and ranges from 1.0 for a perfectly mixed water/oil system to 0.0 for nonoverlapping separated phases.

Results

I. Demixing of the TBP₃₀ + UO₂(NO₃)₂ Binary Oil/Water Solution: Phase Separation and Spontaneous Formation of TBP Complexes at the Interface. In this section, we mostly concentrate on system A with SC-CO₂ as the organic liquid. The results will be compared with those of system B with chloroform described in ref 16. Typical snapshots can be found

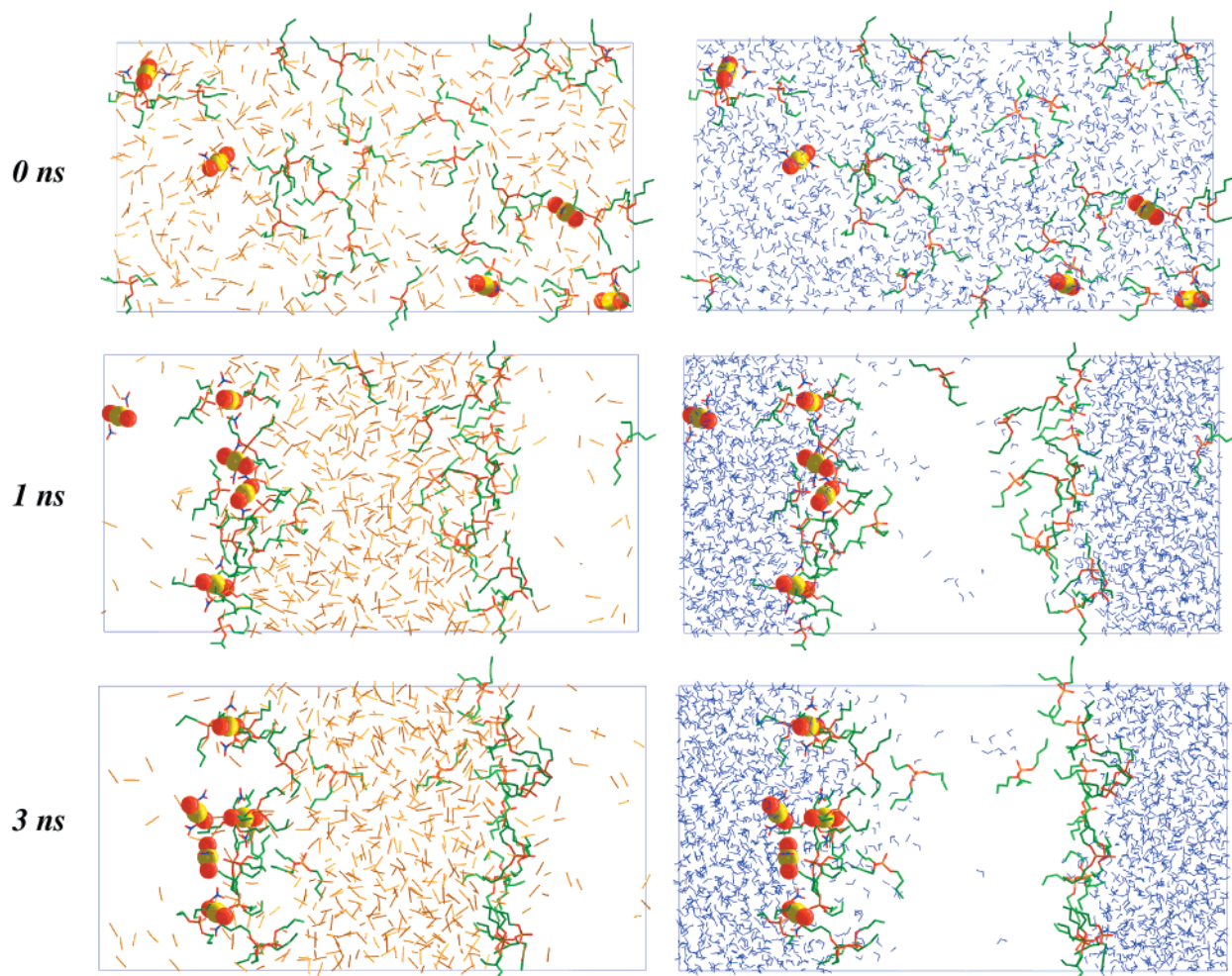


Figure 2. Phase separation of the “perfectly mixed” water/CO₂/TBP mixture A containing 30 TBP and 5 UO₂(NO₃)₂ salt molecules: snapshots at 0, 1, and 3 ns. For clarity, CO₂ (left) and water (right) are shown separately instead of superimposed.

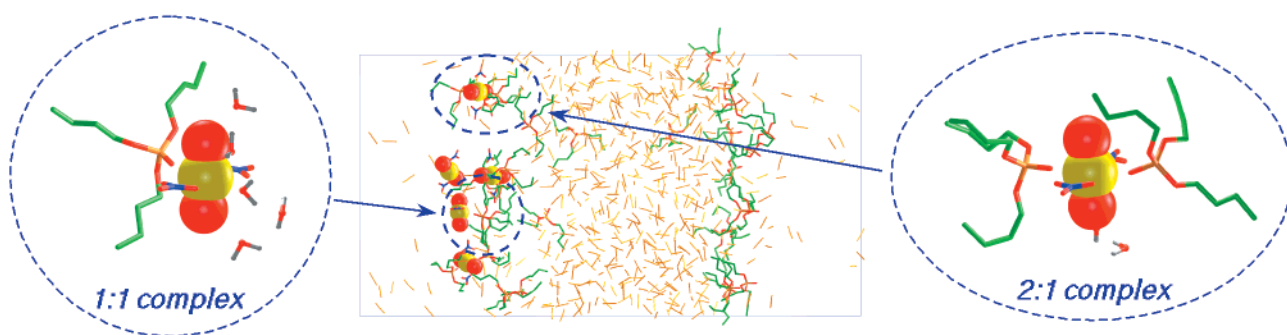


Figure 3. Enlargement of UO₂(NO₃)₂·TBP·H₂O and UO₂(NO₃)₂·TBP₂ complexes that formed at the interface between water and SC-CO₂ upon demixing of system A.

in Figure 2, which shows that water and CO₂ liquids are nearly separated after 1 ns of demixing and form two interfaces onto which most TBPs concentrate. One also observes the spontaneous formation of one 1:1 UO₂(NO₃)₂·TBP complex and of three 1:2 UO₂(NO₃)₂·TBP₂ complexes at the boundaries between the two liquids. Until the end of the simulation (3 ns), there is no marked evolution of the system. There is no TBP in water, in agreement with its low solubility.³⁸ Among the two interfaces, one contains TBP only (right-hand side in Figure 2) while the other interface (left in Figure 2) contains a mixture of uncomplexed TBP molecules and of 1:1 and 1:2 complexes (Figure 3). Interestingly, the interface with TBP only is rather flat and sharp, compared to the other interface where the complexes

adsorbed. Because the first coordination sphere of the uranium atom in the 1:1 complexes is completed by one equatorial H₂O molecule, these complexes are more hydrophilic and sit more on the water side of the interface than the 1:2 complexes to which no water is coordinated. The uncomplexed uranyl salt molecule, even more hydrophilic, is surrounded by water. Although none of the interfaces is fully covered by TBPs, some TBPs remain solubilized in the oil phase, without direct contact with the interfacial TBP layer. The corresponding phosphoryl groups are hydrogen-bonded to several water molecules. Another feature of interest concerns the solvent mixing. The “bulk liquids” are not pure. Even after 3 ns, one finds about 20 water molecules in the CO₂ phase, some of them forming hydrogen-

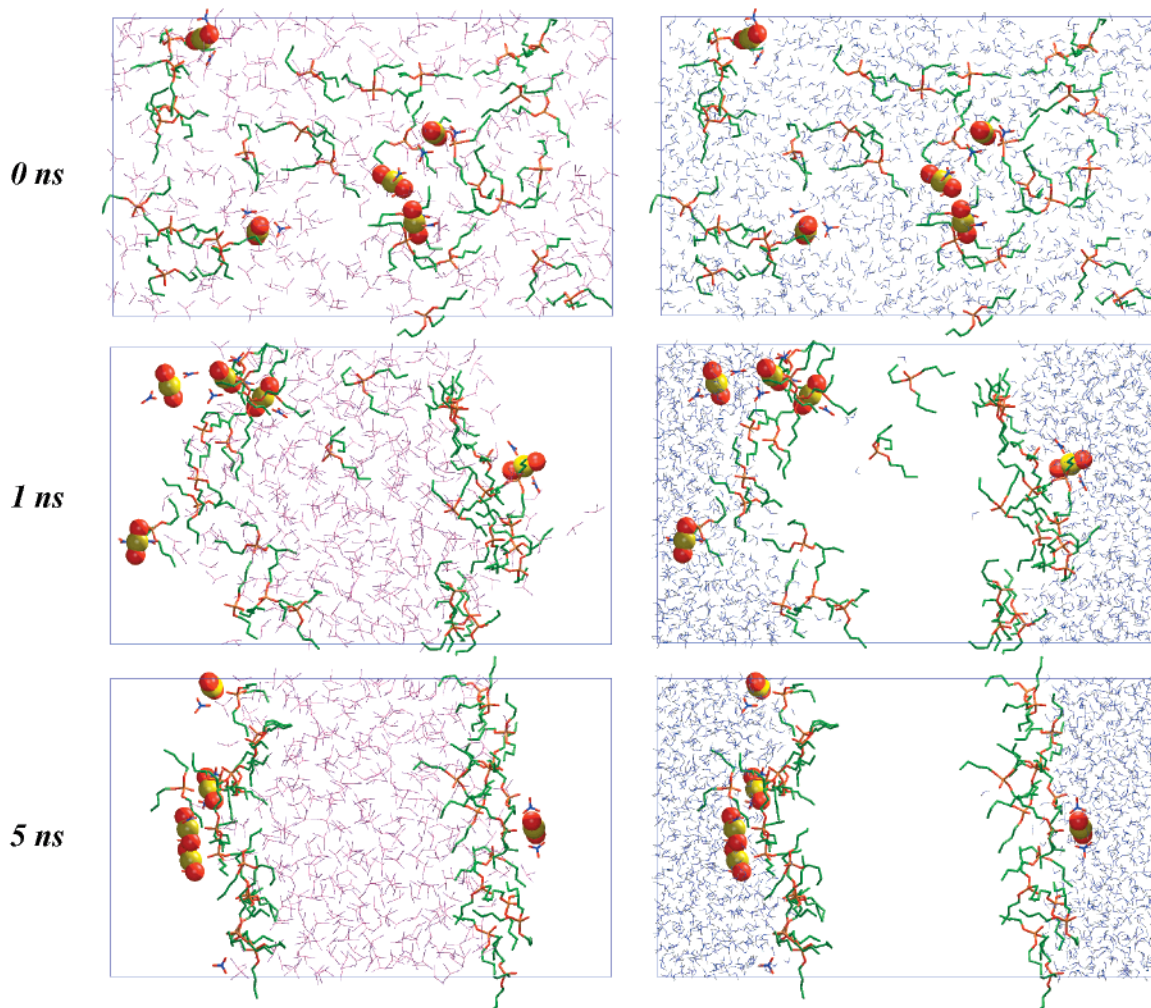


Figure 4. Phase separation of the “perfectly mixed” water/chloroform/TBP mixture B containing 30 TBP and 5 $\text{UO}_2(\text{NO}_3)_2$ salt molecules: snapshots at 0, 1, and 5 ns. For clarity, chloroform (left) and water (right) are shown separately instead of superimposed.

bonded chains connected to phosphoryl oxygens of TBPs, while others are isolated or exchange with small water oligomers. Conversely, one finds about 40 CO_2 molecules in the water phase, more or less randomly dispersed. Because CO_2 is a poor coordinating molecule,³⁹ no self-aggregation nor specific interaction with TBP is observed.

The chloroform-containing system B displays many similarities with the CO_2 -containing system A (see Figure 4), as far as uranyl complexation and solvent separation are concerned. With chloroform as the organic phase, one also observes the formation and interfacial adsorption of complexes: all uranyl salts are complexed with TBP, forming four 1:1 and one 1:2 adducts. The distribution of the $\text{UO}_2(\text{NO}_3)_2$ species in system B is very different from the one observed for the “pure” uranyl salt in the absence of TBP as described by Berny et al.¹⁶ Free uranyl salts of $\text{UO}_2(\text{NO}_3)_2$ type, be they dissociated or not, are “repelled” by the interface and migrate to the bulk aqueous phase. At the end of simulation B, the two liquids are completely separated, leading to a dry chloroform phase adjacent to a water phase without solvent mixing beyond the interface. One also notices that interfaces are more planar and better defined with chloroform than with CO_2 .

II. Demixing of the $\text{TBP}_{60} + \text{UO}_2(\text{NO}_3)_2$ Binary Oil/Water Solutions: Formation of Microemulsions with Spontaneous Uranyl Complexation and Extraction. When the TBP concentration is doubled (compare the TBP_{30} systems A and B with the TBP_{60} systems C and D), interesting new features appear.

One could simply have anticipated that the TBP layer observed with 30 TBP at the water/oil interfaces would be thicker. This is not the case. After even longer simulated demixing times (5.6 ns with CO_2 and 5.2 ns with chloroform as the organic liquids), there is no real phase separation or clear formation of “flat interfaces” at the surface of water. The resulting liquid mixtures are complex and difficult to describe in detail. Furthermore — as known from simulations and experiment — surfactants in SC- CO_2 systems and other supercritical fluids tend to form reverse micelles which span a wide range in size from 10 to well over 10^2 Å.^{40–45} Because of the limited size of our simulation box, we may thus only perceive a fraction of such entities. The simulated systems were carefully examined at the computer graphics system. Typical views are given in Figures 5 and 6. The demixing index, χ_{demix} calculated as a function of time (see Figure 7), which ranges from about 0.8 to 0.3 (SC- CO_2 liquid) or to 0.2 (chloroform liquid) in the A and B systems with 30 TBPs, reaches a plateau of 0.4 and 0.5, respectively, in the more concentrated TBP systems C and D, indicating that the phase separation is not achieved in the latter systems. The plateaus also suggest that the systems are equilibrated and will not separate further if the simulation times are increased.

Let us first consider the CO_2 -containing system C with 60 TBPs (Figure 5). The most rapid events concern the self-aggregation of water molecules, which at 1 ns already form a “homogeneous slab” free of TBP, with only some diluted CO_2 molecules and one uncomplexed uranyl $\text{UO}_2(\text{NO}_3)_2$ species. At

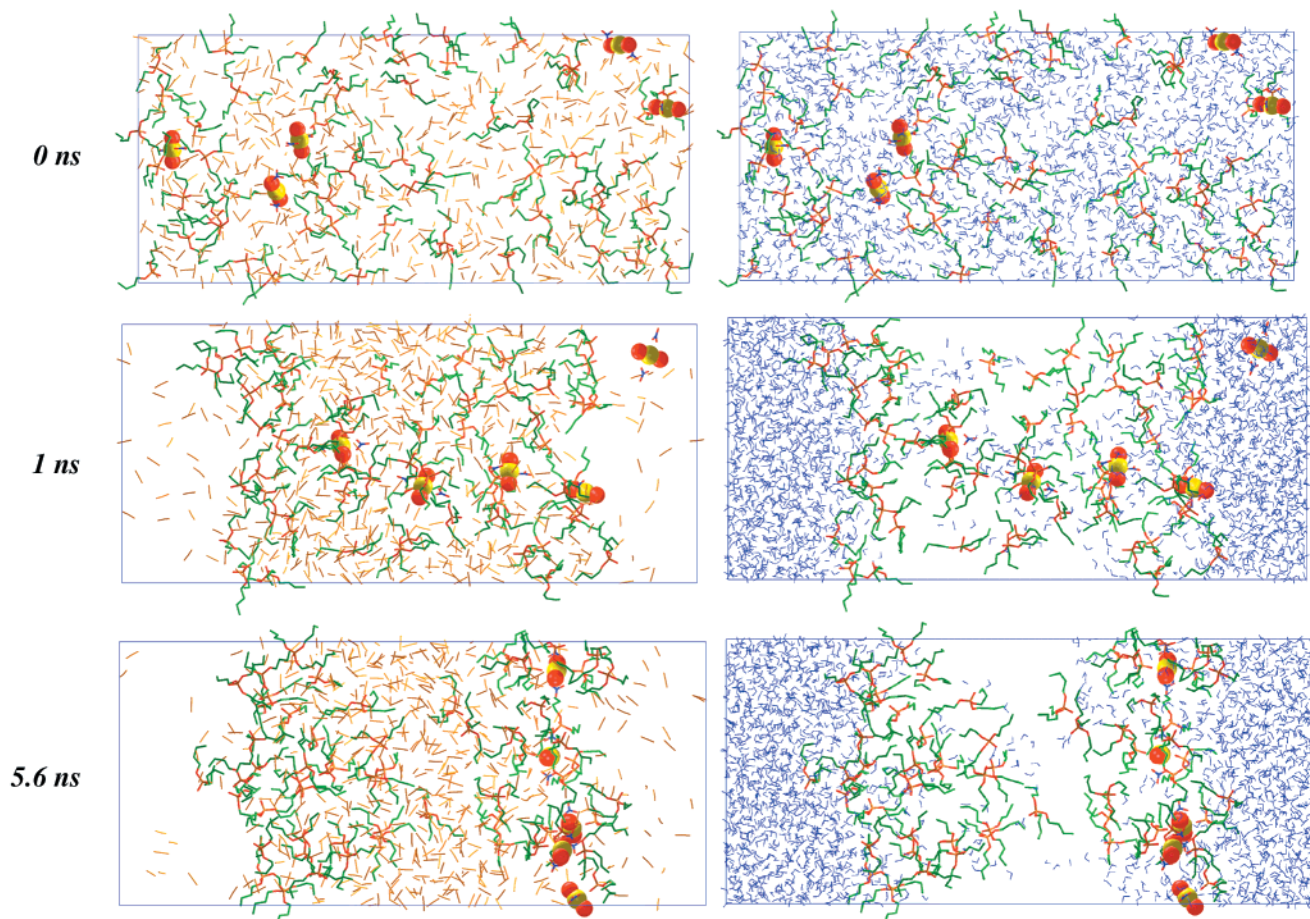


Figure 5. Demixing of the “perfectly mixed” water/ CO_2 /TBP mixture C containing 60 TBP and 5 $\text{UO}_2(\text{NO}_3)_2$ salt molecules: snapshots at 0, 1, and 5.6 ns. For clarity, CO_2 (left) and water (right) are shown separately instead of superimposed.

that stage, two 1:1 and two 1:2 complexes with TBP are formed, but they do not sit at the surface of water. Only one 1:1 complex is near the solvent boundaries, while the other complexes are found in the mixed phase containing CO_2 , water, and TBPs. There is little evolution or “simplification” of the system between the first nanosecond and the end of the dynamics (5.6 ns), except further complexation of uranyl salts. At 2 ns, one finds one 1:1 and four 1:2 complexes, while at 4 ns, all five complexes are of 1:2 stoichiometry, which is the stoichiometry suitable for uranyl extraction by TBP and confirmed by experiment.¹ Because there is no clear interface, the complexes remain in a mixed solvent environment, also containing TBP molecules. Between 1 and 4 ns, one observes water aggregates and dynamically exchanging water “pools” surrounded by CO_2 and TBP molecules. There is no marked tendency for this water to diffuse and condense with the “bulk water” phase. Interestingly also, the TBP molecules near the water surface rarely adopt the expected classical amphiphilic orientations with O_P pointing to water and the O-alkyl chains in oil, as observed under more diluted conditions.³⁰ The local water concentration seems to remain always high enough to form hydrogen bonds with the phosphoryl oxygens. Some TBP molecules are even fully hydrated, without clear connections with oil. After 4 ns, the dynamics has been restarted for 1.6 ns using a larger cutoff of 12/15 Å to test whether this could lead to different phase behavior. This was not the case, as seen from the time evolution of the χ_demix index (see Figure 7), thus confirming that the system will not separate further.

Again, demixing of the chloroform-containing system D with 60 TBPs is very similar to demixing of system C with CO_2

(Figure 6). At the end of the dynamics (5.2 ns), there is no water/oil separation or formation of a well-defined “flat interface”. One observes instead a kind of microemulsion with neat water “bubbles”, containing neither TBP nor chloroform molecules. These are surrounded by a mixed chloroform/TBP phase, also containing the uranyl complexes which progressively formed. At the end of the simulation (5.2 ns), there are two 1:1 and three 1:2 complexes between uranyl nitrate and TBP. Thus, we can confirm that increasing the TBP concentration leads to enhanced uranyl complexation. This situation is also more favorable, as far as uranyl extraction is concerned, because the concentration of extractable hydrophobic species has increased. The 1:1 complexes sit at the periphery between water and chloroform, while two 1:2 complexes are immersed in an oil environment, without direct contact with water. This can thus be viewed as the premise of uranyl extraction by TBP to an oil phase. Compared to the CO_2 -containing system C, one notices that the mixed oil phase is drier, likely because of the lower miscibility of water with chloroform. The only exceptions concern a few hydrogen-bonded water “fingers”, which interconnect water “bubbles”. Thus, as known from experiment,⁴⁶ the nature of the organic phase is important for liquid–liquid extraction purposes.

Discussion and Conclusions

We report a series of molecular dynamics simulations of the phase separation of “perfectly mixed” solutions of water, “oil”, TBP, and uranyl nitrate salts. These are the key components of the industrial PUREX process used to separate uranyl from

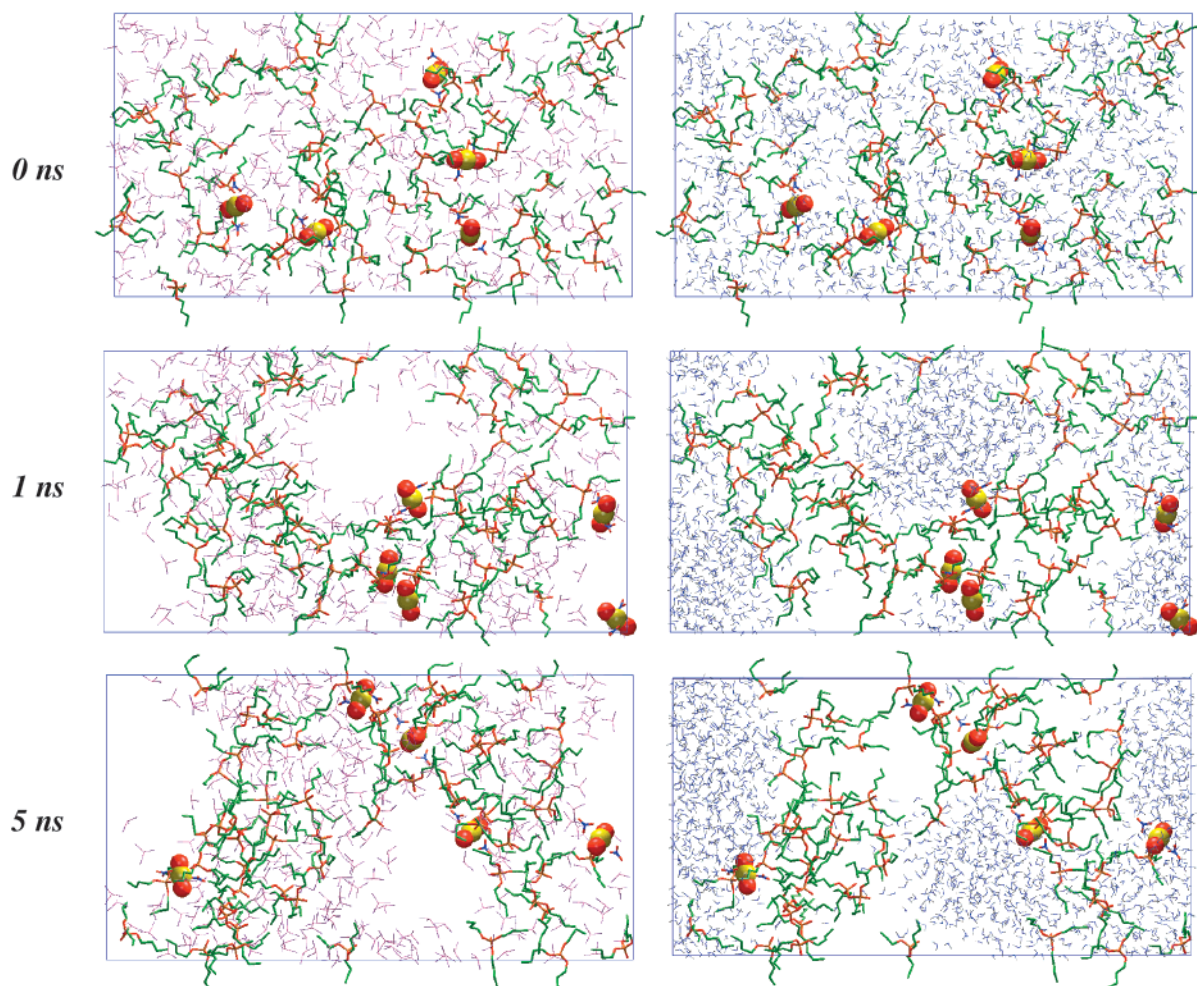


Figure 6. Demixing of the “perfectly mixed” water/chloroform/TBP mixture D containing 60 TBP and 5 $\text{UO}_2(\text{NO}_3)_2$ salt molecules: snapshots at 0, 1, and 5 ns. For clarity, chloroform (left) and water (right) are shown separately instead of superimposed.

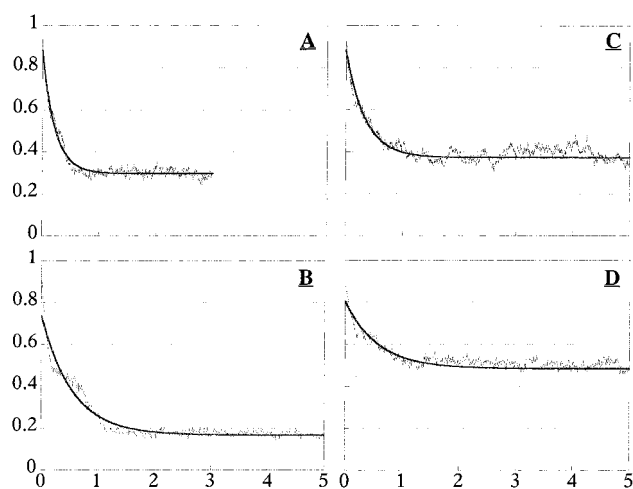


Figure 7. Demixing index, χ , for systems A–D as a function of time.

nuclear waste solutions. One important difference between simulated and experimental systems relates to acidity and salinity, because our study has been conducted at neutral pH, whereas nuclear waste solutions are very acidic (3–6 M in nitric acid) and contain other metallic salts in high concentrations. Uranyl extraction to SC- CO_2 also often starts with acidic aqueous solutions.^{25,47} The high acidity leads to a reduction of the water activity in the interfacial region and presumably increases the TBP concentration at the interface because of

enhanced hydrogen-bonding interactions. Some H_2CO_3 acid should also form and likely concentrate in the interfacial region.¹² The high salinity causes the salt to be mostly associated and thus present as a neutral (and therefore less hydrophilic) species. Both factors facilitate the capture and extraction of the uranyl salt. Studying these effects raises a number of methodological questions related to the state of the proton¹² and to the treatment of long-range electrostatic effects. They will be investigated in further studies.

Key questions that motivated our investigations concerned the nature of the interface between water and oil and how the complexed ion crosses this interface. Our simulations confirm that at relatively low TBP concentration (TBP₃₀ systems), water and oil fully separate, leading to an interface covered by the extractant molecules. Because the phase separation occurs on a nanosecond time scale, one can consider that, in a real experiment, water and oil are never mixed at the microscopic level but form droplets separated by an “abrupt” interface where the extractant molecules and their complexes adsorb. The collapse of droplets reduces the interfacial area, thus leading to the expulsion (extraction) of the complexes to the “oil phase”.

When the TBP concentration is doubled, however, there is no more formation of a well-defined interface between water and oil. Instead, water self-aggregates and forms “pools” or “bubbles”, surrounded by a mixed TBP/oil phase. Thus, at high concentrations, TBP does not act as a surface active molecule but as a hydrophobic cosolvent, more soluble in “oil” than in water. There is no more “flat interface” between water and oil

but formation of a water-in-oil microemulsion. TBP also acts as a complexant molecule, spontaneously forming complexes with uranyl nitrate in all simulated systems. Following the Le Chatelier principle, increasing the TBP concentration leads to an increased concentration of uranyl-TBP complexes and of 1:2 compared to 1:1 adducts. All of the features described above are observed with two different oil phases, modeled by chloroform and SC-CO₂, which points out their generality. Also, specifically relating to system D, this is the first system in which spontaneous complex formation combined with spontaneous extraction to an oil environment was observed. It can thus be seen as a major step toward realistic simulations of liquid-liquid extraction systems. To observe a complete extraction process, it would presumably be necessary to increase the amount of chloroform to allow a pure organic bulk phase to form.

Phosphoryl-containing molecules such as TBP are used as synergistic agents for lanthanide and actinide cation extraction, together with other extractant molecules. For instance, the recently developed "CYANEX-301" dithiophosphinic acid derivatives have been shown to display enhanced extraction properties when an excess of about 30% of phosphoryl-containing agents are added to the system.⁴⁸ This roughly corresponds to the concentration of our TBP₆₀ systems. Similarly, addition of voluminous soft anions such as chlorinated cobalt dicarbollides markedly enhances the extraction of trivalent ions.^{49,50} According to our simulations, such hydrophobic ions are surface active^{9,11} and bear therefore strong analogies with classical amphiphiles such as TBP. Our simulations on the TBP₆₀ systems demonstrate that at sufficiently high TBP concentrations, there is no more well-defined water/oil interface at the microscopic level but formation of microemulsions. This is a favorable feature as far as the mechanism of ion capture is concerned. Indeed, without synergistic agents, the concentration of hard ions such as actinides or lanthanides near an abrupt interface would be very small. They would be "repelled by the interface", preventing therefore their capture by interfacial extractant species. When the concentration of synergistic agents such as TBP is increased, the interfacial tension is first reduced, facilitating therefore the approach of the ion to the interface where it is complexed and the crossing of the phase boundary by the ion embedded in an overall hydrophobic complex forming a neutral ion pair with its counterion(s). Further increase of TBP or acid⁵¹ concentration leads to a progressive mixing with the oil phase and to formation of water-in-oil/TBP microemulsions where extractant molecules and the metallic ions to be extracted can meet. We believe that "solution modifiers", like the perfluorinated agents used to enhance ion extraction,⁵² deeply change the properties of the interface between water and oil, and facilitate the formation of supramolecular assemblies, which may span the range from microemulsions to micelles. It has been recently noted that lanthanide extraction by CMPO at the surface of water-in-oil anionic micelles is spectacularly enhanced.⁵³ This is consistent with the trends observed in our simulations. Also, note the strong analogies between diamide and TBP solutions involved in ion extraction processes.⁵⁴⁻⁵⁸ Finally, as far as the nature of the oil phase is concerned, our simulations point to a strong analogy between chloroform and SC-CO₂. The most noticeable differences relate to the lower solubility of water in chloroform, compared to that in CO₂ and to the higher mobility of the molecules in the supercritical conditions.

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