

Molecular dynamics study of dicarbollide anions in nitrobenzene solution and at its aqueous interface. Synergistic effect in the Eu(III) assisted extraction†

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Received 24th July 2007, Accepted 11th September 2007

First published as an Advance Article on the web 28th September 2007

DOI: 10.1039/b711284j

We report a molecular dynamics study of chlorinated cobalt bis(dicarbollide) anions $[(B_9C_2H_8Cl_3)_2Co]^-$ “CCD⁻” in nitrobenzene and at the nitrobenzene–water interface, with the main aim to understand the solution state of these hydrophobic species and why they act as strong synergists in assisted liquid–liquid extraction of metallic cations. Neat nitrobenzene is found to well solubilize CCD⁻, Cs⁺ salts in the form of diluted pairs or oligomers, without displaying aggregation. In biphasic nitrobenzene–water systems, CCD⁻ anions mainly partition to the organic phase, thus attracting Cs⁺ or even more hydrophilic counterions like Eu³⁺ into that phase. The remaining CCD⁻ anions adsorb at the interface, but are less surface active than at the chloroform interface. Finally, we compare the interfacial behavior of the Eu(BTP)₃³⁺ complex in the absence and in the presence of CCD⁻ anions and extractant molecules. It is found that in the absence of CCDs, the complex is trapped at the interface, while when the CCDs are concentrated enough, the complex is extracted to the nitrobenzene phase. These results are compared to those obtained with chloroform or octanol as organic phase and discussed in the context of synergistic effect of CCDs in liquid–liquid extraction, pointing to the importance of dual solvation properties of nitrobenzene or octanol to solubilize the CCD⁻ salts as well as the extracted complex.

Introduction

Cobalt bis-dicarbollides $[(B_9C_2H_{11})_2Co]^-$ belong to a class of bulky sandwich metallocarborane anions of ellipsoidal shape that are highly hydrophobic, chemically, thermally and radiolytically stable, allowing for important applications in the field of radionuclide M^{n+} cations separation by solvent extraction.^{1,2} Typically, the hexachloro-derivative $[(B_9C_2H_8Cl_3)_2Co]^-$, hereafter noted CCD⁻ (see Fig. 1) has been used as extraction reagent in polar aromatic solvents and, depending on the nature of complexant additives, can extract M^+ cations (mainly alkali like Cs⁺), divalent cations (e.g. Sr²⁺ with polyethylene glycol derivatives), or trivalent M^{3+} actinides or lanthanides cations (e.g. with phosphoryl containing ligands).^{3,4} The dicarbollide anions can be used as synergistic additives to a classical extraction system (e.g. in the “UNEX” solvent extraction process)⁵ or covalently grafted onto extractant molecules like crown-ethers, calixarenes, or phosphoryl-containing ligands, leading to increased cation extraction efficiency, compared to the ungrafted analogues.^{6–9} They have also been found recently to display specific interactions with biological systems, opening interesting perspectives, e.g. in the boron neutron capture therapy of tumors,¹⁰ or in the inhibition of HIV-1 protease.¹¹ Besides these important technological applications, this class of anions is interesting from a more fundamental point of view, especially concerning

the solution state of their salts and, more generally of electrolytes based on hydrophobic anions, in aqueous and non-aqueous solvents. For instance, although the sodium dicarbollide salt is as strong an electrolyte as is sodium chloride,¹² mild shaking of a 0.5 M water solution with an equal volume of diethyl ether transfers the salt completely to the organic layer.¹⁰ The partitioning of the salts results from the antagonistic contributions of the hydrophobic dicarbollide anion and of the hydrophilic metallic cation.

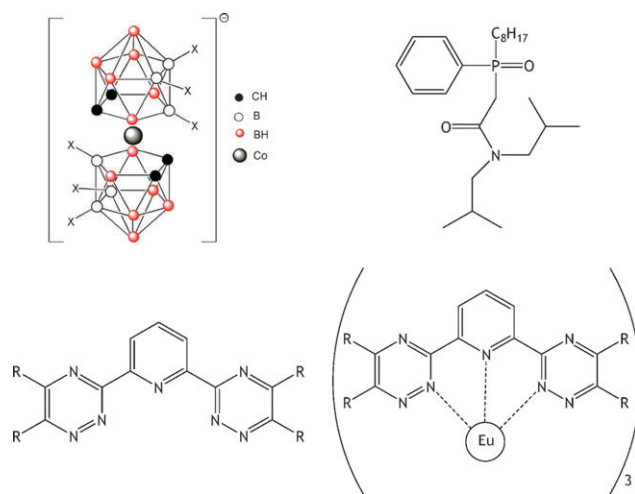


Fig. 1 CCD⁻ (X = Cl), CMPO ((N,N-diisobutylcarbamoylmethyl)octylphenylphosphine oxide), BTP (2,6-bis(5,6-isopropyl-1,2,4-triazin-3-yl)pyridine; R = *i*-Pr) and the Eu(BTP)₃³⁺ complex.

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† Electronic supplementary information (ESI) available: Table S1 and Fig. S1–S7. See DOI: 10.1039/b711284j

Following our investigations on interfacial phenomena in solvent extraction,^{13–16} we have been particularly interested with the behavior of $\text{CCD}^- \text{M}^{n+}$ salts in water–oil biphasic systems, and simulated by molecular dynamics the salts in monophasic water and oil solutions, as well as at their interfaces, where the oil phase was either chloroform (as simple model of water–immiscible organic solvents),^{17,18} or octanol,¹⁹ a more complex solvent. The simulations revealed interesting features. First, in spite of their “spherical” shape, CCD^- anions are surface active.^{17–20} Like charged amphiphiles, they accumulate at the water–oil interface, and their surface activity is modulated by the counterion (*e.g.* Na^+ to Cs^+ series of monovalent ions, divalent UO_2^{2+} or trivalent Eu^{3+} counterions). They are also more surface active at the aqueous interface with chloroform than with octanol.¹⁹ Another important finding was the solvent dependent supramolecular organization of concentrated solutions of CCD^- salts. For instance the $\text{CCD}^- \text{Cs}^+$ ions dilute in the octanol solution,¹⁹ but not in chloroform which is not polar enough to well solvate the cation or the anion and, as result, the $\text{CCD}^- \text{Cs}^+$ ions condense in that solvent into a neutral droplet with a “molten salt” structure.¹⁸ A still different behavior was observed in water where the CCDs tends to condense into a “superanionic aggregate” surrounded by Cs^+ or H_3O^+ counterions, and the tendency for aggregation was found to be greater with Cs^+ than with H_3O^+ as counterions.¹⁸ The computational findings were supported by experiments confirming the surface activity of dicarbollides,²⁰ and their aggregation in water.²¹

The present paper extends our MD studies to the case of aromatic solvents, selecting nitrobenzene (noted NBZ) as a prototype, for the following reasons. First, due to its high dielectric constant,²² nitrobenzene is a good medium to dissolve ions and, in particular, dicarbollide salts. It has a low miscibility with water, however, and has been used as a receiving phase in ion extraction.^{23–25} Basically it differs in nature from chloroform or octanol and lacks the amphiphilic topology of fatty alcohols where dicarbollides can also be dissolved, and it will thus be interesting to compare these solvents. Furthermore, on the theoretical side, there have been Monte Carlo and MD reports on the structure of the NBZ liquid dry^{26–28} or humid,²⁹ on the neat NBZ–water interface,³⁰ and on the corresponding migration and distribution of ions like NMe_4^+ ,³¹ Ca^{2+} ³² or $\text{TBA}^+ \text{Br}^-$ (tetrabutylammonium bromide).³³ The transfer of ions from water to NBZ has also been extensively studied experimentally.^{34–37} It is thus interesting to compare concentrated solutions of the $\text{CCD}^- \text{M}^{n+}$ salts in NBZ and at the NBZ–water interface, to those with chloroform or octanol as organic phase. For consistency with our previous studies, the simulated electrolyte solutions contain 30 CCD^- anions (corresponding to *ca.* 0.2 M solutions), with either Cs^+ or Eu^{3+} as neutralizing counterions. Unless otherwise specified, the NBZ/water volume ratio in the binary mixtures is *ca.* 50 : 50. In the case of the $\text{CCD}^- \text{Cs}^+$ salt, a 90 : 10 mixture will also be modeled, to mimic the case where the oil component is in excess, as in the course of phase separation in an extraction experiment. Beyond the case of dicarbollide salts, we also want to gain insights into the interfacial landscape in assisted ion extraction, selecting as in ref. 19 the case of the Eu^{3+} extraction by

2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine ligands (noted BTP), *via* the formation of the $\text{Eu}(\text{BTP})_3^{3+}$ complex where the cation is shielded from solvent by the three BTP ligands (Fig. 1). This complex has been characterized experimentally in extraction experiments,^{38,39} by X-ray studies in the solid state,³⁹ by QM calculations⁴⁰ and by EXAFS and TRFLS spectroscopies in solution.⁴¹ Because BTP-like ligands display a very interesting actinide/lanthanide extraction selectivity,^{38,39} the simulation results are also important in the context of nuclear waste partitioning.

Methods

Molecular dynamics simulations were performed with the AMBER 7.0⁴² software with the following representation of the potential energy U :

$$U = \sum_{\text{liaisons}} k_l(l - l_0)^2 + \sum_{\text{angles}} k_\theta(\theta - \theta_0)^2 + \sum_{\text{dièdres}} \sum_n V_n(1 + \cos(n\varphi - \gamma)) + \sum_{i < j} \left[\frac{q_i q_j}{R_{ij}} - 2\epsilon_{ij} \left(\frac{R_{ij}^*}{R_{ij}} \right)^6 + \epsilon_{ij} \left(\frac{R_{ij}^*}{R_{ij}} \right)^{12} \right]$$

It accounts for the deformation of bonds, angles, dihedral angles, electrostatic and van der Waals interactions. For the dicarbollide anions, the l_0 and θ_0 values were taken from experiment.⁴³ The CCD^- charges come from ref. 17 and have been derived from quantum mechanical calculations. The parameters for CMPO, BTP, NO_3^- , the $\text{Eu}(\text{BTP})_3^{3+}$ complex can be found in ref. 19.

The Lennard-Jones parameters for the Cs^+ ⁴⁴ and Eu^{3+} ⁴⁵ cations were fitted on their free energies of hydration. The solvents were represented explicitly at the molecular level, using the Jorgensen’s TIP3P model⁴⁶ for water and the flexible Michael’s model⁴⁷ derived from the AMBER for field for NBZ. The latter model has been found to yield similar properties of the NBZ–water interface as a polarizable model.⁴⁷ Non-bonded interactions were calculated with a 12 Å atom based cut-off, correcting for the long-range electrostatics by using the Ewald summation method (PME approximation). The solutions were simulated with 3D-periodic boundary conditions, thus as alternating slabs of water and “oil” in the case of juxtaposed liquids.

The interface was built from adjacent boxes of water and nitrobenzene. The electrolyte solutions contain 30 CCD^- anions neutralized by 30 Cs^+ , or 10 Eu^{3+} cations. The biphasic solution with the $\text{Eu}(\text{BTP})_3^{3+}$ complex contains three neutralizing NO_3^- counterions, 12 CMPO and 12 BTP free ligands, to which 12 $\text{CCD}^- \text{H}_3\text{O}^+$ ions have been added to study the role of CCDs. The characteristics of the different systems are given in Table 1. After 1000 steps of energy minimization (100 steps by the steepest descent + 900 steps by conjugate gradients), we performed 50 ps of MD with fixed solutes (“BELLY” option of AMBER) and 50 ps without constraints, followed by 50 ps at a constant pressure of 1 atm (monitored with a weak coupling method⁴⁸). The production stage was performed at 300 K in the (N, V, T) ensemble for at

Table 1 Characteristics of the simulated solutions: number of solvent molecules, simulated time and box size

System	$N_{\text{NBZ}}/N_{\text{water}}$	Time/ns	Box size/ \AA^3
Neat nitrobenzene	1286/0	2	$61 \times 61 \times 61$
Neat nitrobenzene–water interface			
Juxtaposed 50 : 50	604/3361	4	$45 \times 45 \times 100$
Demixing 50 : 50	604/3361	5	$45 \times 45 \times 100$
Demixing 90 : 10 (cubic box)	1152/723	7	$60 \times 60 \times 60$
Demixing 10 : 90 (cubic box)	66/6402	2	$59 \times 59 \times 59$
30 $\text{CCD}^- \text{Cs}^+$ in nitrobenzene	1073/0	5	$59 \times 59 \times 59$
30 $\text{CCD}^- \text{Cs}^+$ at the nitrobenzene–water interface (50 : 50)			
Starting at the interface	638/3869	5	$50 \times 50 \times 100$
Starting in oil	519/4083	10	$49 \times 49 \times 98$
Starting in water	740/3558	14	$51 \times 51 \times 101$
30 $\text{CCD}^- \text{Cs}^+$ in the 90 : 10 mixture	965/702	3	$59 \times 59 \times 59$
30 CCD^- 10 Eu^{3+} in the 50 : 50 binary mixture	747/3497	20	$50 \times 50 \times 101$
Eu(BTP) $_3^{3+}$ complex at the nitrobenzene–water interface (50 : 50)			
Eu(BTP) $_3(\text{NO}_3)_3$ + 12 BTP + 12 CMPO	563/3709	15	$49 \times 49 \times 97$
Eu(BTP) $_3(\text{NO}_3)_3$ + 12 BTP + 12 CMPO + 12 CCD^- , H_3O^+	539/3586	15	$49 \times 49 \times 98$

least 2 ns. The temperature was maintained constant by coupling the solution to a thermal bath using the Berendsen algorithm⁴⁸ with a relaxation time of 0.2 ps.

The coordinates were saved every 1 ps, and analysed using the MDS and DRAW software.⁴⁹ Some snapshots were redrawn with the VMD software.⁵⁰ The position of the interface was dynamically defined as the intersection between the water and NBZ density curves.⁵¹ The percentage of ions “at the interface” was calculated during the last 0.75 ns, selecting the species that are within 10 \AA from the interface. We defined the density of solvents and solutes (g cm^{-3}) at a z -position by their mass per volume unit ($dv = xy dz$). Insights into energy components were obtained from the average interactions between selected groups during the last 0.4 ns, calculated with a 17 \AA cutoff distance and a shift cutoff correction. The ion–ion and ion–solvent environments were characterized by the radial distribution functions (RDFs) during the last 0.25 ns. The average coordination numbers (noted CN) were obtained by integration of the first peak of the RDFs. The diffusion coefficient D was calculated from the Einstein equation:⁵² $D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle |r_i(t) - r_i(0)|^2 \rangle$ over the last nanosecond of dynamics, where $r_i(t)$ is the position of atom i at the time t .

Results

I. Phase separation of a water–nitrobenzene mixture and the resulting interface

According to our simulations, nitrobenzene forms a biphasic system with water, delineating a well defined interface when the liquids are in a 50 : 50 ratio. This is observed in a 4 ns MD simulation that started from juxtaposed liquids, as well as from a subsequent mixing–demixing simulation (Fig. 2, Fig. S1 and Fig. S2, see ESI[†]).⁵³ In both cases, the final water slab contains no NBZ molecule, while the NBZ phase contains *ca.* 17 H_2O molecules (juxtaposed liquids) or 23 H_2O molecules

(demixing simulation), in qualitative agreement with the lower solubility of NBZ in water (mole fraction of 2.7×10^{-4}), compared to the water solubility in NBZ (1.62×10^{-2}).²² Water dissolves in the NBZ phase as a mixture of monomers, dimers or even trimers, hydrogen-bonded to the O_{NO_2} groups of NBZ (see Fig. 2). The water–NBZ interface is quite narrow (*ca.* 6.5 \AA) and locally sharp on the molecular scale, as found in previous MD studies,⁴⁷ as well from synchrotron X-ray reflectivity studies.⁵⁴ As seen in Fig. 2, it is far from being instantaneously “flat”, however. Interestingly, some ordering is found for the NBZ molecules at the interface, as indicated by the ordering parameter $\langle S \rangle = \langle 3 \cos^2 \theta - 1 \rangle$, where θ is the angle between the C_2 symmetry axis of the NBZ molecule and the z -direction (perpendicular to the interface; see Fig. 2). In the bulk NBZ phase, $\langle S \rangle$ is nearly zero, corresponding to an isotropic orientation of the molecules, but as one moves towards interface, $\langle S \rangle$ becomes slightly positive on the NBZ side of the interface, and negative on the water side, indicating that the NBZ dipoles tend to align somewhat parallel to the water surface, in qualitative agreement with previous results.^{47,54}

When one liquid is in excess over the other (90 : 10 or 10 : 90 ratio; see Fig. 3), the separation is less clear-cut, as each liquid forms several micro-domains instead of a single one. Even after 7 ns of dynamics of the 90 : 10 NBZ–water mixture, water mainly condenses into a big and very irregular droplet, in equilibrium with a smaller one and other aggregates, thus differing from, *e.g.* the case of the analogous mixture with the less polar chloroform liquid where water rapidly condenses into a single droplet.¹⁸ Likewise, in the 10 : 90 mixture where water is in excess, NBZ is dispersed in the form of monomers and oligomers involving hydrophobic π -stacking interactions (Fig. 3).

II. Dicarbolide Cs^+ salts in nitrobenzene solution

In dry NBZ solution, the simulated $\text{CCD}^- \text{Cs}^+$ ions tend to dilute, generally in the form of chains of loosely interacting

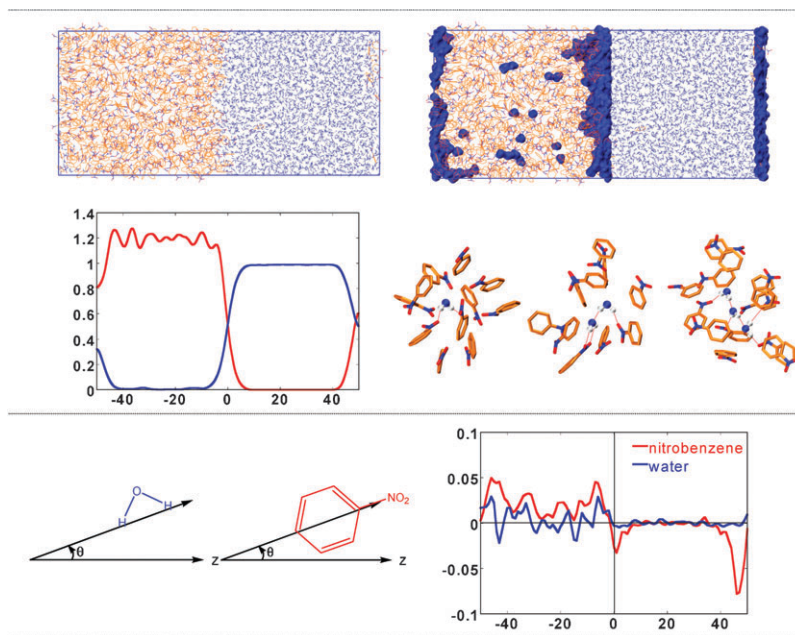


Fig. 2 NBZ–water 50 : 50 mixture simulated from juxtaposed liquids. Top: final solvent boxes (at 4 ns), with H₂O molecules in NBZ and at the interface highlighted in dark blue color (right). Second line: average density curves of the liquids, and snapshots of an H₂O monomer, dimer and trimer in the NBZ phase. Bottom: average order parameter $\langle S \rangle$ for H₂O and NBZ molecules as a function of their z -position. The results of the demixing simulation are shown in Fig. S1 and Fig. S2.†

pairs, as seen on a snapshot and cumulated positions over the last ns (Fig. 4). Each Cs⁺ cation tends to be coordinated by the most polar moieties of the system, *i.e.* by the nitro oxygens of the solvent and Cl atoms of the CCD[−] anion. The RDF's of O_{NO₂} oxygens and of Cl_{CCD} around Cs⁺ peak at *ca.* 3.2 and 3.7 Å, respectively, and integrate to *ca.* 12.7 oxygen atoms and 2.5 Cl atoms, within 5.9 Å. The coordinated NBZ molecules are rather perpendicular to the Cs⁺ ions, but more tangential arrangements are also observed, combining π -aromatic and NO₂ interactions with Cs⁺. Between 6.8 and 10.1 Å from Cs⁺, one finds 1.7 C_{OCCD} atom, on the average, and each anion is coordinated to *ca.* one cation at each trichlorinated cap. The

environment of the CCD[−] anions is less polar, as expected, with the exception of the Cs⁺ counterion(s), and mainly involves “ π -interactions” with the aromatic moiety of the NBZ molecules. There are thus interesting analogies between octanol and NBZ solutions. The ions disperse in both liquids, which contrasts with the condensation observed in chloroform and aqueous solution.¹⁹ Also note that the CCD[−] and Cs⁺ ions diffuse somewhat faster in NBZ than in octanol: their diffusion constants are (in 10^{−7} cm² s^{−1}), respectively 10 and 19 in NBZ, and 6 and 8 in octanol.

III. Dicarbolide Cs⁺ or Eu³⁺ salts at the nitrobenzene–water interface

In this section, we first consider binary NBZ–water systems of 50 : 50 volume ratio, where the 30 CCD[−] anions are neutralized by either Cs⁺ or Eu³⁺ counterions. This will be followed by the case of the CCD[−] Cs⁺ salt in a 90 : 10 solvent mixture, *i.e.* in a NBZ solution oversaturated with water.

The CCD[−] Cs⁺ salt in a 50 : 50 binary mixture. Because of the slow diffusion of the CCD[−] anions and related sampling issues, we performed three MD simulations of the NBZ–water binary system, testing different initial positions of the 30 CCD[−] Cs⁺ ions, *i.e.* either in the NBZ phase (*i.e.* where they are generally introduced experimentally), in the water phase, or shared between both phases at the interface (see Fig. 5). The final distributions obtained after quite long simulations (14 ns, 10 ns and 5 ns, respectively) are not identical, but reveal consistent trends. First, the highly hydrophobic CCD[−] anions are found in no case in water. In particular, those that were initially in water diffused to the interface and sometimes further into the NBZ phase. Second, they are surface active, as at least half of

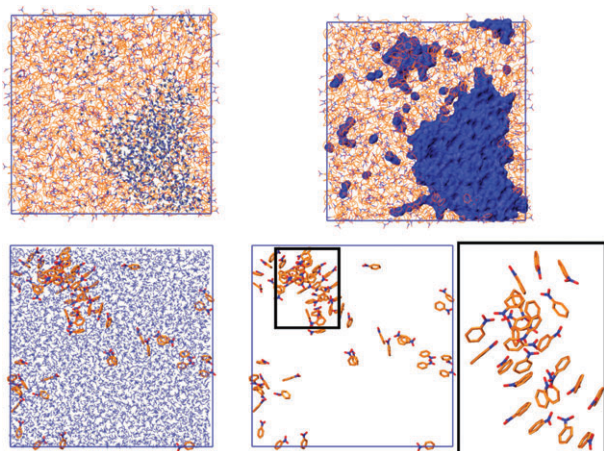


Fig. 3 NBZ–water mixtures at 90 : 10 (top) and 10 : 90 ratio (bottom). Final configurations (after 7 and 2 ns). Top right: H₂O molecules are highlighted in dark blue color. Bottom right: zoom on NBZ molecules in water.

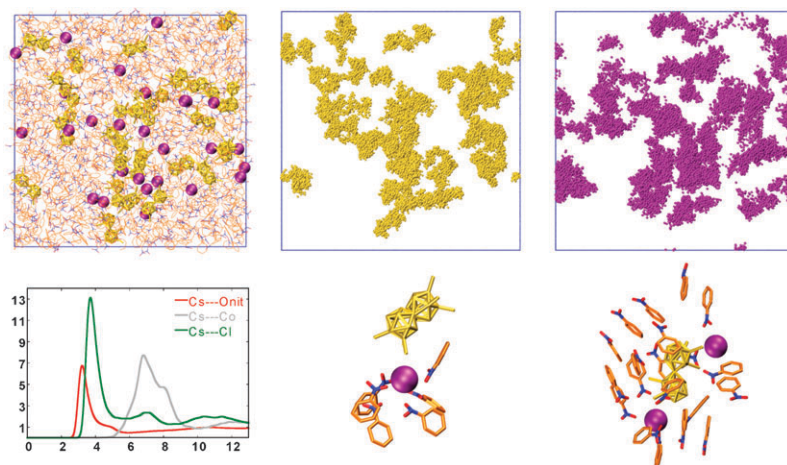


Fig. 4 NBZ solution of 30 $\text{CCD}^- \text{Cs}^+$ ions. From top left to bottom right: final snapshot (at 5 ns), cumulated positions of Co(CCD) (colored yellow) and Cs atoms (colored purple) during the last ns, RDF's around the Cs atom, and typical solvation of Cs^+ and CCD^- ions.

them concentrate at the interface(s), while the remaining ones dilute in the NBZ slab. Their proportion at the interface ranges from 50% (ions initially in NBZ) to 63% (ions initially at the interface) and 66% (ions initially in water). This is less than observed at the chloroform–water interface (*ca.* 100%),¹⁸ and comparable to what was found at the octanol–water interface.¹⁹ The NBZ interface is thus not saturated by the CCDs, but is negatively charged, thereby attracting an important proportion of the Cs^+ cations (from 32% to 55%, depending on the starting configuration). Some of the remaining Cs^+ cations are partitioned between the water phase and the NBZ phase. As a result, none of the microphases is neutral: the water slab is always positively charged, while the NBZ slab is negatively charged (by a lesser magnitude, due to the adsorption of the remaining CCDs at the interface). The

NBZ phase is not dry, but contains *ca.* 45 to 90 H_2O molecules, depending on the simulation. This is more than at the neat interface, because most of these water molecules have been dragged by the Cs^+ ions.

It is interesting to follow the migration of selected Cs^+ and CCD^- ions from water to the NBZ phase, *i.e.* from the simulation that started with all ions in water (see Fig. 6 for snapshots and Fig. 7 for the number of ions in the NBZ phase and the average number of $\text{O}_{\text{H}_2\text{O}}$, N_{NBZ} and Cl_{CCD} atoms coordinated to Cs^+ as a function of the z -position). At the beginning, Cs^+ is fully hydrated (by *ca.* 9 H_2O molecules) in bulk water without contact with CCD^- anions and, at 7.70 ns, has approached close enough from the interface to be significantly attracted by CCD^- anions. At 7.73 ns, it sits at the interface ($z \approx 0 \text{ \AA}$), solvated by a mixture of H_2O and

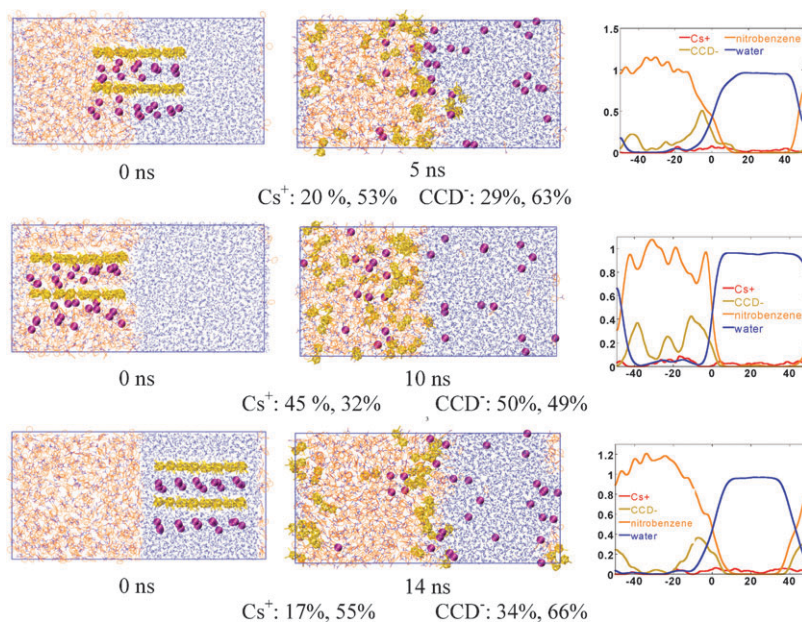


Fig. 5 30 $\text{CCD}^- \text{Cs}^+$ ions at the NBZ–water interface, simulated with the ions initially at the interface (top), in NBZ (middle), or in water (bottom). Initial and final views, and average densities as a function of the z -position. Percentage of Cs^+ and CCD^- ions in “bulk” NBZ and within 10 \AA from the interface.

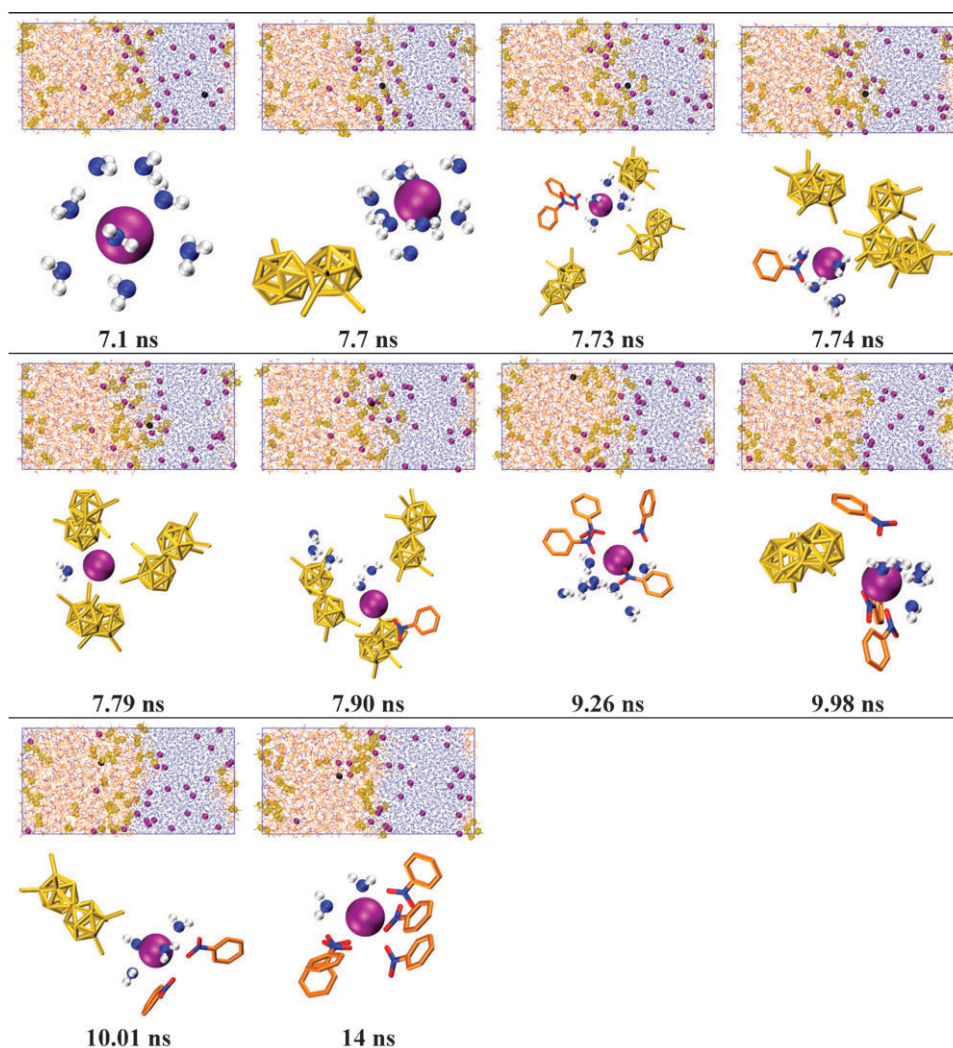


Fig. 6 30 $\text{CCD}^- \text{Cs}^+$ ions at the NBZ–water interface, simulated with the ions initially in water. Typical snapshots of the solvent box and of a selected Cs^+ ion (colored in black in the solvent box) that migrates from water to NBZ.

NBZ molecules, and surrounded within 10 Å by *ca.* 3 CCD^- anions that clearly “catalyze” its transfer. From there until the end of the dynamics, Cs^+ progressively diffuses to the NBZ phase, surrounded by a mixture of *ca.* 2 H_2O , 5 NBZ molecules and 1 loosely coordinated CCD^- . The number of CCD^- neighbours thus decreases from the interface to the bulk NBZ (see Fig. 7), which clearly illustrates the critical role

of interfacial CCD^- anions to assist the Cs^+ transfer from the aqueous to the NBZ phase.

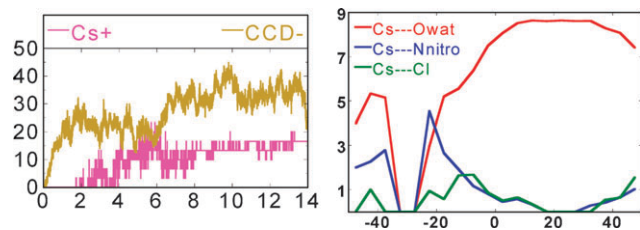


Fig. 7 30 $\text{CCD}^- \text{Cs}^+$ ions at the NBZ–water interface, simulated with the ions initially in water. Left: percentage of Cs^+ and CCD^- ions found in “bulk nitrobenzene” as a function of time. Right: average coordination number of $\text{O}_{\text{H}_2\text{O}}$ (red), N_{NBZ} (blue) and Cl_{CCD} atoms around Cs^+ ions as a function of their z -position.

The $\text{CCD}^- \text{Eu}^{3+}$ salt in a 50:50 binary mixture. In order to investigate the role of the CCD^- counterions on their distribution in the biphasic system, we considered the case of the highly hydrophilic Eu^{3+} cation (10 Eu^{3+} for 30 CCD^-) initially all positioned where could be expected to be, *i.e.* in the water phase. The main results are shown in Fig. 8. The final view (20 ns) clearly shows that the CCDs prefer the NBZ phase (65%) and, to a lesser extent than in the case of the Cs^+ salt, the interface (35%). There is thus no CCD^- in water, in keeping with its high hydrophobicity. The Eu^{3+} distribution is more surprising: the majority of these cations sit at the interface (53%) and in the NBZ phase (40%) instead of the water phase (7%). This is clearly due to the attraction by the CCD^- anions, stronger than in the case of the Cs^+ cations. We note that the Eu^{3+} cations are always fully hydrated, whatever their position, by a first shell of *ca.* 9 H_2O molecules and have thus never direct contacts with the CCDs. There is still also

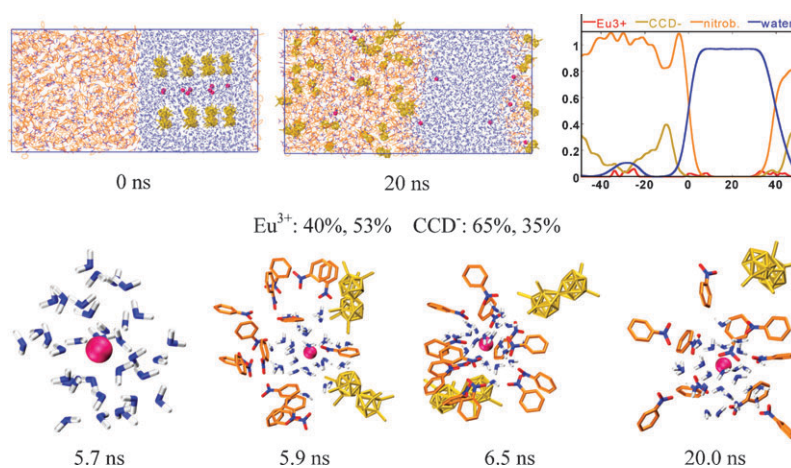


Fig. 8 30 CCD^- and 10 Eu^{3+} ions at the NBZ–water interface, simulated with the ions initially in water. First line: initial and final views, and density curves. Second line: zoom on the hydrated $\text{Eu}(\text{H}_2\text{O})_n^{3+}$ complex extracted to octanol at 5.7, 5.9, 6.4 and 20 ns. A full version is given in Fig. S3.†

water in the second shell and beyond, even for the Eu^{3+} cations that transferred to the organic phase (*vide infra*).

As for Cs^+ , it is instructive to follow the migration of a selected Eu^{3+} cation from the bulk water to the bulk NBZ phase (see Fig. 8 and Fig. S3.†). At 5.7 ns, the cation is fully hydrated and sits at *ca.* 10 Å on the water side of the interface, *i.e.* close enough to be attracted by the CCD^- anions that concentrate in that region. About 0.2 ns later, this cation has diffused “at the interface”, surrounded by *ca.* 25 H_2O molecules and, further away, by *ca.* 12 NBZ molecules on the “oil side” plus 2 to 3 CCD^- anions. From that time until the end on the dynamics, the Eu^{3+} cation further diffused up to 15 Å away from the interface into the NBZ phase, retaining most of its first water shells (*ca.* 20 H_2O molecules), surrounded by NBZ molecules and a “cage” of CCD^- anions. Generally, the deeper the cation migrates into the NBZ phase, the more distant are the surrounding CCDs. Conversely, the CCDs make tighter contacts with the hydrated cation in the interfacial region, again emphasizing the role of interfacial electrostatic assistance by CCDs for the cation transfer process.

The $\text{CCD}^- \text{Cs}^+$ salt in a 90:10 binary NBZ–water mixture.

What happens in a water-oversaturated NBZ solution reflects the main trends observed above for the neat solvents and for the dicarbolide salts at the interface (see Fig. 9). First, most of the water molecules are concentrated after 4 ns into irregular big domain, where about 1/3 of the Cs^+ cations are solubilized. One also finds a smaller water “droplet”, as well as a few

dispersed H_2O monomers and oligomers interacting with Cs^+ cations. Most of the CCD^- anions are dispersed in the NBZ phase, neither interacting with water nor with Cs^+ counterions. Some of the anions, however, also sit at the boundaries between the NBZ and water microdomains, in keeping with their surface activity observed above at the “flat” NBZ–water nano-interface.

IV. On the synergistic effect of dicarbolide salts in the Eu^{3+} extraction by BTP ligands

In order to elucidate why the CCDs can promote the extraction of the complexed Eu^{3+} and related trivalent actinide cations (*e.g.* Am^{3+} or Cm^{3+}), we simulated the $\text{Eu}(\text{BTP})_3^{3+}$ complex with NO_3^- counterions at the NBZ–water interface, with and without CCD^- synergistic agents. Because extraction experiments of Eu^{3+} by BTP and parent ligands can be conducted in the presence of other extractant molecules (malonamide derivatives, or phosphoryl containing ligands), we added to the solution 12 CMPO ligands plus 12 uncomplexed BTP ligands, that are in excess over the metal. Dicarbolides were introduced as 12 $\text{CCD}^- \text{H}_3\text{O}^+$ ions, corresponding to the case where their organic solution has been pre-equilibrated with an acidic aqueous phase. No acid is however present in the simulated system, thus preventing the issues of ligand protonation and salting out effects in ion extraction.

The simulations start with the 12 CMPO and BTP ligands equally distributed between the two phases at the interface, as are the $\text{CCD}^- \text{H}_3\text{O}^+$ ions, when present. The $\text{Eu}(\text{BTP})_3(\text{NO}_3)_3$

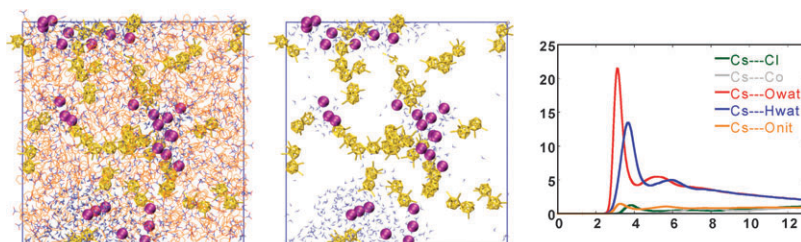


Fig. 9 30 $\text{CCD}^- \text{Cs}^+$ ions simulated in a 90:10 NBZ–water mixture. Final snapshots (at 5 ns) with the two liquids (left), with NBZ hidden for clarity (center), and RDFs around Cs^+ atoms (right).

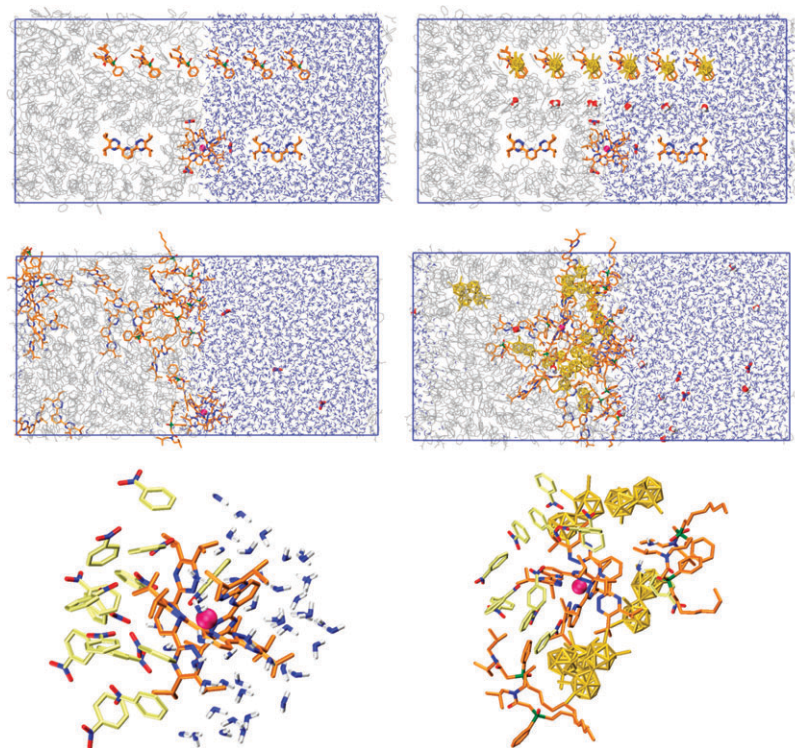


Fig. 10 The $\text{Eu}(\text{BTP})_3^{3+}$, 3NO_3^- complex in the presence of 12 CMPO and 12 BTP ligands at the NBZ–water interface, without CCD^- 's (first line) and with $12 \text{CCD}^- \text{H}_3\text{O}^+$ added ions (second line). Initial and final views, with typical snapshots of the $\text{Eu}(\text{BTP})_3^{3+}$ complex adsorbed at the interface (top) or extracted (bottom) after 15 ns of dynamics.

complex is initially positioned at the interface, and we want to see whether or not it will diffuse to the NBZ phase. The initial and final distributions of these species are shown in Fig. 10. Looking at the most important issue, *i.e.* the extraction of the europium complex, one observes a clear difference, depending on the presence, or not, of the dicarbolide salts, after 15 ns of dynamics: in the absence of dicarbolides, the $\text{Eu}(\text{BTP})_3^{3+}$ complex remains trapped at the interface, whereas in the presence of dicarbolides, it is extracted to the NBZ phase. In both cases, the hydrophilic NO_3^- anions have migrated to the aqueous phase where they are best solvated, while the hydrophobic species that were initially in water have been expelled out of the aqueous phase. There is thus finally neither BTP, CMPO, nor CCD^- molecule in the water phase. Interestingly, these species tend to accumulate near the interface instead of diluting into the organic phase, in keeping with their amphiphilic or surface active character. This has already been observed computationally⁵⁵ and experimentally for CMPO,⁵⁶ and also with BTP ligands (see Fig. S4–S7†)⁵⁷ that can enjoy some specific hydrogen bonding attractions with water near the interface.⁵⁸

In the absence of dicarbolides, the $\text{Eu}(\text{BTP})_3^{3+}$ complex is strongly attracted by water at the interface, and can thus hardly migrate into the organic phase. Although the complexed cation is well shielded from water, it still displays strong charge–dipole attractions with the water molecules at the interface. A zoom (Fig. 10) clearly shows a mixed solvation of the complex, by water on one side, and NBZ molecules on the other side. Note that the latter point their less polar aryl moiety, rather than their nitro groups, towards the aromatic

rings of the complexed BTP ligands. At the interface, the interaction of the complex with water amounts to $-177 \pm 20 \text{ kcal mol}^{-1}$, with a contribution of $-70 \text{ kcal mol}^{-1}$ for the $\text{Eu}(\text{III})$ cation itself, due to charge–dipole interactions.⁵⁹ This is much less than the corresponding interaction energies with the NBZ phase (-90 and $-15 \pm 10 \text{ kcal mol}^{-1}$, respectively).

In the presence of an excess of $\text{CCD}^- \text{H}_3\text{O}^+$ ions, the $\text{Eu}(\text{BTP})_3^{3+}$ complex spontaneously diffused during the dynamics from the interface to the NBZ phase, at *ca.* 10 \AA from the interface. We notice that at the end of the dynamics, it has not any direct contact with water molecules nor *a fortiori* with the water phase, and can thus be considered as extracted. The key feature is the presence of *ca.* 4 CCD^- anions within 12 \AA that attract the complex, making it quasi-neutral and more hydrophobic (see Fig. 10). The extracted complex is additionally surrounded by a mixture of solvent NBZ molecules, uncomplexed BTP and CMPO ligands that are hydrophobic, thus without dragging water. As a result, its interaction energy with water is small, but repulsive ($+6 \pm 5 \text{ kcal mol}^{-1}$), with a null contribution of the $\text{Eu}(\text{III})$ ion itself ($0 \pm 3 \text{ kcal mol}^{-1}$), which markedly contrasts with the high attraction energies with water in the absence of CCD^- anions (*vide supra*).

Discussion and conclusions

We report a MD simulation study on dicarbolide salts in pure NBZ solution and at its aqueous interface, with the main aim to understand how these hydrophobic anions promote the extraction of complexed trivalent lanthanide or actinide cations from an aqueous phase. The results, compared to

those obtained with the same methodology in pure water, chloroform and octanol liquids and their interfaces allows us also to assess the role of the organic phase in solvent extraction. Overall, the results obtained with NBZ are qualitatively similar to those obtained with octanol. First, the $\text{CCD}^- \text{Cs}^+$ ions dilute in both solvents, in contrast to chloroform where they remain condensed in the form of a “molten salt” amorphous droplet.¹⁸ This follows experimental observations concerning the solubility of dicarbollides, that are quasi insoluble in aliphatic solvents or their halo-derivatives, but dissolve better, *e.g.* in polar aromatic solvents, or in alcohols.¹⁰ As mentioned in the introduction, NBZ is more polar, with a dielectric constant ϵ of 34.8, compared, *e.g.* to chloroform ($\epsilon = 4.9$) but the dielectric constant is not sufficient to explain the solubility of dicarbollide salts because the latter do not dissolve in water ($\epsilon = 78.4$). On the computational side, we simulated the $\text{CCD}^- \text{Cs}^+$ salts in model “polar chloroform” solutions where the dipole moment of CHCl_3 was scaled up by a factor of 2.0 or 3.0, and found that the ions also condense in a single droplet, instead of diluting.¹⁸ In that case, the increased interactions with the solvent are not sufficient to overcome the increased intra-solvent cohesive forces. Arguably, the salts dissolve better in NBZ because NBZ is more polarizable than chloroform (their polarizabilities are $\alpha_{\text{NBZ}} = 13$ and $\alpha_{\text{chloroform}} = 8.5 \text{ \AA}^3$, respectively),²² but this effect should not be crucial as our simulations have been conducted without explicit representation of polarization effects. The analogy between NBZ and octanol points towards the importance of dual solvation properties and heterogeneity of these liquids, that are beneficial for the dissolution of such salts. The analogy is apparent in Fig. 11 where the polar groups of both liquids ($\text{OH}_{\text{octanol}}$ and NO_2_{NBZ}) are colored differently from the less polar ones (aryl or alkyl groups). Basically, the hard ion of the salt (Cs^+) is mainly solvated by the polar nitro groups of NBZ (or polar OH groups of octanol), while the soft CCD^- anion prefers the soft aryl groups of NBZ (or the alkyl chain of octanol). Similar solvent heterogeneities and dual solvation properties have been recently observed in room temperature ionic liquids,^{60–62} as illustrated in Fig. 11 in the case of the $[\text{BMI}][\text{PF}_6]$ liquid (butylmethylimidazolium hexafluorophosphate) with polar (imidazolium⁺ ring and PF_6^-) and apolar (butyl chains) microdomains. It should thus be interesting to study experimentally the dicarbollide salts in such liquids and at their aqueous interfaces.

Concerning the synergistic effect of dicarbollide anions in solvent extraction of hard cations like $\text{Eu}(\text{III})$, our results point to the importance of interfacial phenomena. The CCD^- anions are surface active as are, *e.g.* hydrophobic ions, even of “spherical shape” (AsPh_4^+ or BPh_4^- ,⁶³ K^+ cryptates,⁶⁴ or spherical models of them⁶⁵).⁶⁶ The main reason is the high cavitation of water: the CCD^- ions tend to be expelled out of water in order to avoid paying the price for the cavitation energy.⁶⁷ On the other hand, when they sit on the “oil side” of the interface, they still enjoy attractive charge–dipole interactions with water. Surface activity increases the local concentration of the anions, and therefore their mutual repulsions at the interface. Their concentration

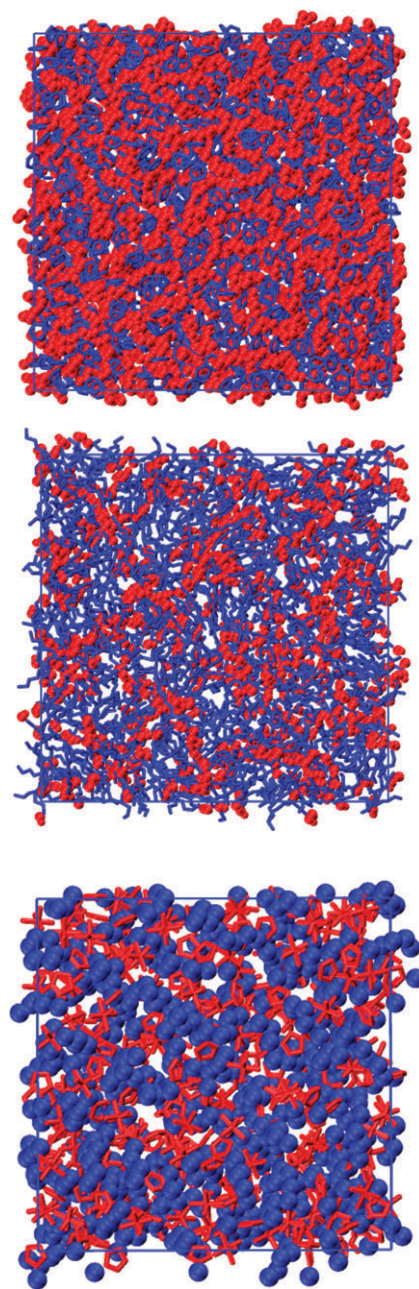


Fig. 11 Neat NBZ (top), octanol (middle) and $[\text{OMI}][\text{PF}_6]$ (bottom) liquids, coloring in red their polar (NO_2_{NBZ} , $\text{OH}_{\text{octanol}}$, imidazolium ring of BMI^+ , PF_6^-) and in blue the apolar groups (aryl_{NBZ}, octyl_{octanol}, butyl_{BMI}).

at the interface thus depends on the nature of their counterions, and on their solubility in the organic phase. They are more soluble in NBZ than in chloroform, and thus less surface active at the NBZ aqueous interface.

An important synergistic contribution stems from the exchange of one $\text{M}(\text{III})$ cation from water for three Cs^+ of H_3O^+ cations of the CCD^- salt introduced in the organic phase, also avoiding the co-extraction of the hydrophilic NO_3^- anion to the oil phase to retain the neutrality of the source and receiving phases. We have seen in the case of octanol as organic phase that this is not sufficient to promote

the extraction, because the $\text{Eu}(\text{BTP})_3(\text{CCD})_3$ complex alone is not extracted, but remains trapped at the interface.¹⁹ The CCDs must be sufficiently concentrated to partition between the interface and the organic phase, and this is clearly observed in our simulation where the extracted complex is locally neutralized by an “anionic cage” of CCDs, while other CCDs remain near the interface together with other surface active species (e.g. free ligands and additives like other extractant molecules).⁵⁸ Adsorption at the interface lowers the interfacial pressure, thereby facilitating the ion transfer. In the case of CCDs, another very important feature is to attract the $\text{Eu}(\text{III})$ ions close enough to the interface to be captured by the ligands “right at the interface”. According to our results, in the presence of CCD’s, the local concentration of the extraction partners (the cations, the ligands, the counterions) is higher at the interface than in the bulk phases, thereby facilitating the complexation process. Without suitable anions like CCD’s, the hydrophilic cations would be “repelled” by the interface, preventing their complexation.^{68,69} Furthermore, ligands like BTP are quasi insoluble in water, ruling out a dominant shuttle mechanism where the complex would form in water, and later on transferred to the oil phase.⁵⁸ All these features support an interfacial complexation mechanism, consistent with previous theoretical studies (see e.g. ref. 70 and 71) and with experimental observations on related systems.⁷² We hope that the present study will stimulate further investigations on “what happens at the interface” in the extraction of highly hydrophilic cations by suitable ligands,⁷³ including the effect of aqueous phase acidity on the interfacial landscape. Beyond the choice of the ligands, it is important to consider the nature of “nano-scale” water–“oil” mixtures and their interfaces as a function of the complexity of the oil phase (involving synergistic ions, additives, or solvent modifiers), as well as of the source phase (e.g. salting out reagents, acids).⁷⁴

Acknowledgements

The authors are grateful to IDRIS, CINES, Louis Pasteur University, and the GDR-PARIS for computer resources, to the European Union EUROPART project (FI6W-CT-2003-508854) for financial support, and to Etienne Engler for assistance. GC thanks the Louis Pasteur University for a PhD grant.

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