

Comparing an Ionic Liquid to a Molecular Solvent in the Cesium Cation Extraction by a Calixarene: A Molecular Dynamics Study of the Aqueous Interfaces

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We report a molecular dynamics (MD) study of the interfacial behavior of key partners involved in the Cs^+ cation extraction by a calix[4]arene-crown-6 host (**L**), comparing an ionic liquid (IL) to a classical molecular solvent (chloroform) as receiving “oil” phase. The IL is composed of hydrophobic 1-butyl-3-methylimidazolium cations (BMI^+) and bis(trifluoromethylsulfonyl)imide anions (Tf_2N^-) and forms a biphasic system with water. The simulations reveal similarities but also interesting differences between the two types of interfaces. Much longer times are needed to “equilibrate” IL systems, compared to classical liquid mixtures, and there is more intersolvent mixing with the IL than with chloroform, especially concerning the water-in-oil content. There is also some excess of the BMI^+ cations over the Tf_2N^- anions in the aqueous phase. Simulations on the Na^+NO_3^- and Cs^+NO_3^- ions show that they sometimes interact at the interface with the IL ions, forming hydrated intimate ion pairs, whereas they are “repelled” by the classical interface. The LCs^+ complex and **L** ligand also behave differently, depending on the “oil phase”. They are better solvated by the IL than by chloroform and thus poorly attracted at the IL interface, whereas they adsorb at the chloroform interface, adopting well-defined amphiphilic orientations. The results are discussed in the context of assisted ion transfer and provide a number of arguments explaining the specificity and efficiency of IL based, compared to classical extraction systems.

Introduction

Room-temperature ionic liquids (ILs) have recently emerged as a new class of “green” alternative (nonvolatile, nonflammable, and thermally stable) to conventional solvents.^{1–3} They display versatile solvation properties, and depending on the nature of their constitutive ions, they can solubilize solutes of different polarities and hydrophilic/hydrophobic balance, allowing for important applications in organic synthesis, catalysis, and analytical chemistry. Imidazolium-based ILs incorporating hydrophobic anions, such as hexafluorophosphate (PF_6^-) or bis(trifluoromethylsulfonyl)imide (Tf_2N^- ; see Figure 1), form biphasic systems with water and can be used for liquid–liquid extraction processes.^{4–9} Interestingly, extractant molecules that are generally used in classical liquid–liquid extraction (e.g., crown ethers,^{6–8,10} diketonates,¹¹ or organophosphorus derivatives)^{4,5} also extract metallic cations to ILs, but with higher efficiency compared to organic solvents. As an example, Luo et al. found that BOBCalixC6 (calix[4]arene-bis(*tert*-octylbenzo-crown-6)) calixarene (Figure 2) dissolved in imidazolium-based ILs efficiently extracts Cs^+ from aqueous solutions, under conditions where extraction to 1,2-dichloroethane or chloroform is negligible.⁹ Interestingly, even in the absence of extractant molecules, some partitioning of the “free” Cs^+ cation to the IL phase was observed, which contrasts with classical hydrophobic liquids to which no cation transfer was detected.^{7,12} Moreover, the extraction mechanism may also differ, sometimes involving a cation exchange with the IL (e.g., Cs^+ with an IL cation to ensure the neutrality of source and receiving phases), without coextraction of the accompanying counterions as generally required with classical organic liquids.^{4,9,13}

Interfacial phenomena play a crucial role in such processes, as the interface is believed to be the place where the ions (initially in water) and the extractants (initially in the oil phase) meet and form an extractable complex. In the case of classical organic liquids, insights into “what happens at the interface”¹⁴ can be experimentally obtained from spectroscopy,¹⁵ electrochemistry,¹⁶ kinetic studies,¹⁷ surface tension measurements,¹⁸ and, theoretically, by computer simulations, mainly of the molecular dynamics (MD) type.^{19–22} It has been found that classical aqueous interfaces are quite narrow and molecularly sharp and that the key partners involved in the liquid–liquid extraction^{23,24} or phase transfer catalysis²⁵ processes are surface-active and thus accumulate at the interface. Similar studies at the aqueous interface with hydrophobic ILs are still scarce. A few of them deal with the IL–water^{26–28} or IL–gas interface.^{29–32} This led us to investigate the interfacial behavior of the different partners involved in the Cs^+ extraction by a calixarene derivative to the $[\text{BMI}][\text{Tf}_2\text{N}]$ IL, choosing the 1,3-alternate-dimethoxycalix[4]arene-crown-6 (**L**) as ligand. The latter is a good mimic of BOBCalixC6 as far as the complexation of Cs^+ is concerned (Figure 2). The solvation and complexation properties of **L** have been studied by MD in the pure $[\text{BMI}][\text{Tf}_2\text{N}]$ IL,³³ as well as at classical water–oil interfaces.³⁴ In this paper, we present an “apples to apples” comparison¹¹ of the aqueous interface with the ionic liquid versus chloroform as “oil” phases, i.e., starting with identical positions of the solutes. Chloroform is a typical organic solvent used in liquid–liquid extraction of Cs^+ by the **L** ligand itself³⁵ or by BOBCalixC6⁹ and is easily amenable to computational investigations.^{21,34,36} As solutes, we first consider the uncomplexed Cs^+ and Na^+ cations in the form of their nitrate salts and compare their solvation and distribution at the two interfaces. We next focus on the LCs^+ complexes and **L** ligands.

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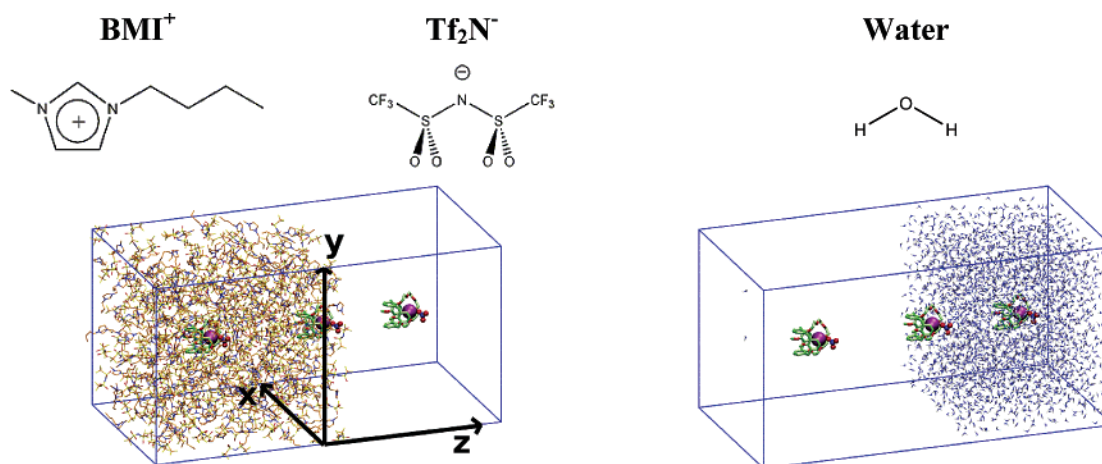
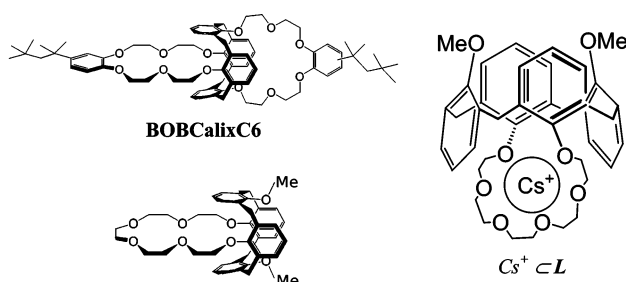


Figure 1. BMI⁺ and Tf₂N[−] ions and schematic representation of the IL–water binary systems containing three LCs⁺NO₃[−] complexes (system C_{IL}). The IL molecules and water molecules are represented separately side by side for clarity.



1,3-alternate-dimethoxycalix[4]arene-crown-6 (L)

Figure 2. BOBCalixC6, L, and the LCs⁺ complex.

Simulations on the chloroform–water binary systems showed that these species, initially in the receiving phase (i.e., where they are macroscopically partitioned) or in the aqueous phase (in the case where the complex would form in water), diffused to the interface, attracted by interfacial water.³⁴ ILs are more polar than classical oil phases and should better solvate the polar ligands and their complexes, possibly reducing their interfacial activity. It will thus be interesting to compare the LCs⁺ complexes and L ligands at the interfaces with the [BMI][Tf₂N] versus chloroform phases. One important difference between both liquids concerns the cohesive forces which are much stronger with the IL, leading to relaxation times and diffusion of solvent and solute molecules which are several orders of magnitude larger with the IL than with the organic solvent. These manifest also in the MD simulations. For the chloroform-containing mixtures, the simulations typically converge in 1–2 ns, whereas the IL solutions are hardly “equilibrated” after more than 10 ns.²⁸ Due to computer time limitations, the IL/ water systems will be simulated for 20 ns in most cases (sometimes up to 60 ns), revealing analogies but also interesting differences compared to the chloroform/water systems, as far as the distribution of the different solutes is concerned. The resulting microscopic views should allow us to better understand why extraction to hydrophobic ILs can be more efficient than to organic solvents.

Methods

Molecular Dynamics. The MD simulations were performed with the modified AMBER7.0 software³⁷ where the potential energy 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.

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

Cross terms in van der Waals interactions were constructed using the Lorentz-Berthelot rules ($R_{ij}^* = R_i^* + R_j^*$ and $\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}$). For the solvents, we used the TIP3P model for water of Jorgensen et al.³⁸ and the OPLS model for chloroform³⁹ where CH is represented in the united atom approximation. The parameters of the IL stem from literature and were developed to reproduce the bulk solvent properties: those of BMI⁺ were taken from Andrade et al.,⁴⁰ while those from Tf₂N[−] were from Canongia-Lopes et al.⁴¹ This model was used in conjunction with the TIP3P model of water to simulate neat IL–water interfaces, effectively reproducing experimental properties of such systems.²⁸ Atomic charges and van der Waals parameters of the calixarene (L) and of the nitrate were, respectively, from refs 21 and 42. Parameters of the Na⁺ and Cs⁺ cations were fitted on the hydration free energies by Åqvist⁴³ with an atomic charge of +1. Quantum mechanics calculations showed that these parameters give satisfactory interaction energies with ILs.³³ 1–4 van der Waals interactions were scaled down by a factor of 2, and the corresponding Coulombic interactions were scaled down by 1.2, as recommended by Cornell et al.⁴⁴ The liquid systems were represented with 3D periodic boundary conditions, thus corresponding to alternating slabs of water and of the IL when they form a “flat” interface. The nonbonded interactions were calculated using a 12 Å atom-based cutoff correcting for the long-range electrostatics using the Ewald summation method (PME approximation).^{45,46} The MD simulations were performed at 300 K, starting with random velocities. The temperature was monitored by coupling the system to a thermal bath using the Berendsen algorithm⁴⁷ with a relaxation time of 0.2 ps. All C–H and O–H bonds were constrained with SHAKE, using the Verlet leapfrog algorithm with a time step of 2 fs to integrate the equations of motion.

The liquid–liquid “preformed” interface was built from two adjacent cubic boxes of bulk solvents. The IL–water binary systems contained 219 BMI⁺Tf₂N[−] ion pairs and 2657 H₂O molecules (Figure 1), whereas the chloroform–water ones contained 722 chloroform molecules and 2657 H₂O. After 1000 steps of energy minimization, the IL–water systems were

TABLE 1: Simulated Systems

	solutes	starting position	box size (Å ³)	time ^a (ns)
A _{IL}	12 (Cs ⁺ ; NO ₃ ⁻)	in water	45.0 × 45.0 × 90.5	20
A _{CLF}	12 (Cs ⁺ ; NO ₃ ⁻)	in water	44.6 × 44.6 × 91.1	2
B _{IL}	12 (Na ⁺ ; NO ₃ ⁻)	in water	45.0 × 45.0 × 90.5	20 ^b
B _{CLF}	12 (Na ⁺ ; NO ₃ ⁻)	in water	44.6 × 44.6 × 91.1	2
C _{IL}	3 (LCs ⁺ ; NO ₃ ⁻)	1–1–1 ^c	45.6 × 45.6 × 89.5	20
C _{CLF}	3 (LCs ⁺ ; NO ₃ ⁻)	1–1–1 ^c	44.8 × 44.8 × 91.4	2
D _{IL}	3 (LCs ⁺ ; NO ₃ ⁻)	random system	45.6 × 45.6 × 89.5	60
D _{CLF}	3 (LCs ⁺ ; NO ₃ ⁻)	random system	44.8 × 44.8 × 91.4	2
E _{IL} ^c	3 (L; Cs ⁺ ; NO ₃ ⁻)	random system	45.6 × 45.6 × 89.5	60
E _{CLF} ^c	3 (L; Cs ⁺ ; NO ₃ ⁻)	random system	44.8 × 44.8 × 91.4	2
F _{IL}	2 (LCs ⁺ ; NO ₃ ⁻) + 2 L	at the interface	45.5 × 45.5 × 90.4	20
F _{CLF}	2 (LCs ⁺ ; NO ₃ ⁻) + 2 L	at the interface	45.0 × 45.0 × 90.3	0.4

^a Production time, after “equilibration” for systems starting from preformed interfaces and after mixing procedure for the others. ^b Restart from the A_{IL} simulation (at $t = 15$ ns) for 5 ns. ^c One complex in water, one at the interface, and one in IL.

equilibrated by a sequence of (i) 50 ps of dynamics at constant volume with frozen solute and water (BELLV option of AMBER), (ii) 100 ps of dynamics with frozen solute and water at a constant pressure of 1 atm, (iii) 50 ps of dynamics at constant volume with frozen solute and water, and (iv) 400 ps of unconstrained dynamics at a constant pressure of 1 atm. The chloroform–water systems were similarly equilibrated by a sequence of steps (i) and (iv). “Randomly mixed” systems were obtained by 1–2 ns of MD at constant volume, using a higher temperature (500 K) with biased potentials (electrostatic interactions scaled down by a factor 100). The systems were then

simulated at constant volume for 20–60 ns in the case of the IL and for 0.4 to 2 ns in the case of the chloroform-containing mixtures. The MD trajectories were saved every 1 ps and analyzed using our *DRAW* and *MDS* software.⁴⁸ Typical snapshots have been redrawn with the *VMD* software.⁴⁹ The characteristics of the simulated systems are gathered in Table 1.

Analysis of the Trajectories. The solvent densities were calculated as a function of the z -coordinate in slices of $\Delta z = 0.5$ Å width (axes are defined in Figure 1), and the position of the interface ($z = 0$) was dynamically defined by the intersection of the water and IL density curves (Gibbs dividing surface). Three domains were then defined: the interfacial domain (within ± 12 Å from the interface) and the “bulk” IL and “bulk” water phases (beyond 12 Å from the interface). The amount of IL in a given domain was calculated as an average of BMI⁺ and Tf₂N⁻ contributions. The width of the interface was defined as the distance between the z -positions where the densities of the solvent components reach 90% of their bulk density.

In “demixing” simulations, the degree of phase separation was monitored as a function of time by the demixing index λ , which would range from 1 (fully mixed system) to 0 (perfectly separated phase): $1/\lambda = 1/N (1/d_w + 1/d_{IL})$, where d_w and d_{IL} correspond to the densities of water and IL in the mixture and N is a normalization factor. The simulation box was split in cubic boxes of 10 Å side in which the densities were calculated and averaged over the different boxes.

Insights into the energy components were obtained by group

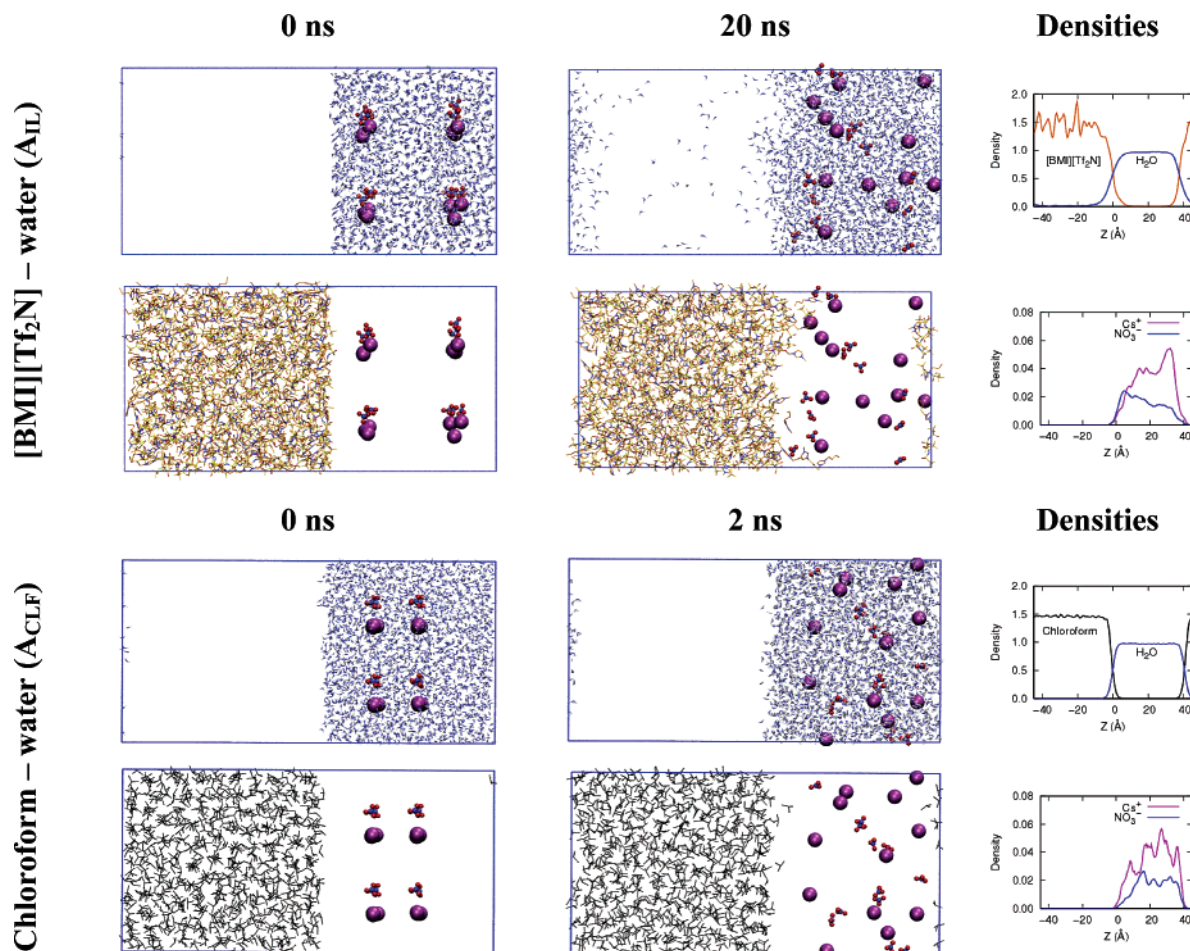


Figure 3. 12 Cs⁺NO₃⁻ ion pairs at the [BMI][Tf₂N]–water interface (system A_{IL}) and at the chloroform–water interface (system A_{CLF}). Initial and final snapshots are shown. For each system, the solvents are displayed separately on two lines for clarity. Right column: densities of solvents and of solutes as a function of the z -position (Å). Averages over the last 3 ns of MD for system A_{IL} and the last 0.5 ns for system A_{CLF}.

analysis using a 17 Å cutoff distance and a reaction field correction for electrostatics. The solute/IL interactions (E_{int}) were dissected into the contributions of the BMI⁺, Tf₂N[−], and H₂O molecules.

Results

We first describe the cesium and sodium nitrate-containing binary “oil”–water systems, where “oil” is represented either by the [BMI][Tf₂N] IL or by chloroform. This is followed by the study of LCs⁺ complexes and L ligands, consistently compared with the two types of oil phases.

1. Cesium And Sodium Nitrate Salts. *Nitrate Salts at the [BMI][Tf₂N]–Water Interface.* To investigate the distribution of uncomplexed cations, we first considered 12 Cs⁺NO₃[−] ion pairs (corresponding to an aqueous concentration of ~0.25 mol/L) initially placed in the aqueous phase (system A_{IL}; see Figure 3). During the dynamics, these ions remained immersed in the aqueous phase, displaying, however, important interactions with the IL phase. These can be seen first from the density curves of Cs⁺ and NO₃[−] ions, which display a broad peak near the interface, overlapping with the ion distribution in bulk water. During the dynamics, however, the ions oscillate from one interface to the other, spending short periods (~0.1 ns) in contact with the IL phase, linked with the bulk water via “water fingers”. Some ions even diffuse to the IL side of the interface, losing part of their hydration shell due to ion pairing with the IL ions of opposite charge (i.e., Cs⁺...Tf₂N[−] and NO₃[−]...BMI⁺; see Figure 4). Nevertheless, such “transfer” to the IL side is quite rare (only 2–3 ions are involved during the 20 ns of dynamics), and these ions always retain a connection with the bulk water via H-bonded H₂O molecules. A similar system (hereafter noted B_{IL}) containing the Na⁺NO₃[−] salt was investigated by restarting the A_{IL} simulation at $t = 15$ ns and replacing Cs⁺ by Na⁺ cations. The dynamics was then pursued for 5 ns, and the final snapshots and density curves (Figure 4 and Supporting Information Figure S1) show that the Na⁺ cations, although more hydrophilic than Cs⁺, also interact with the IL at the interface. The same feature is observed with the nitrate anions. Moreover, we note that some IL/water mixing occurs during the dynamics of both Na⁺NO₃[−] and Cs⁺NO₃[−] solutions (Figure 5). After 20 ns, there are ca. 30 H₂O molecules in the IL phase and 1–5 BMI⁺ cations plus 0–1 Tf₂N[−] anions in the aqueous phase.

The Cs⁺NO₃[−] and Na⁺NO₃[−] ion distributions are consistent with the results of an energy component analysis (see Table S1 in Supporting Information), showing that the NO₃[−] anions are attracted by the IL (by −18 and −15 kcal/mol, respectively, on the average per anion), due to interactions with BMI⁺ cations at the interface and in water. For the cations, the interaction is either weakly attractive (−2.4 kcal/mol in the case of Cs⁺) or repulsive (0.5 kcal/mol in the case of Na⁺), due to opposite contributions: At the interface, they are attracted by the IL Tf₂N[−] anions, but in water, they are repulsed by some BMI⁺ cations in excess.

Nitrates Salts at the Chloroform–Water Interface. When chloroform is used as the hydrophobic phase, nitrate anions and alkali cations are “repelled” by the interface.³⁴ This can be seen from the simulations of 12 Cs⁺NO₃[−] (system A_{CLF}; see Figure 3), whose average density is maximal in the middle of the bulk water. None of these ions directly interact with chloroform molecules at the interface, and this feature is also observed with the more hydrophilic Na⁺ cation (system B_{CLF}; Figure S1). Another distinguishing feature compared with the IL is the lack of intersolvent mixing during the dynamics. At the interface, each water molecule remains connected to its bulk phase,

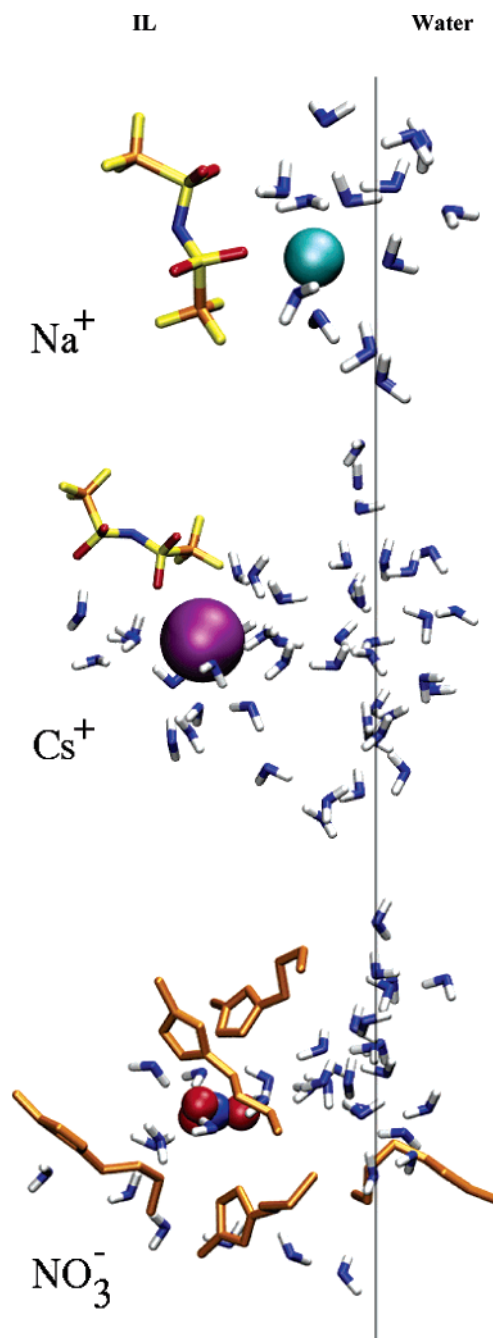


Figure 4. Typical solvation patterns of Na⁺, Cs⁺, and NO₃[−] ions at the IL side of the [BMI][Tf₂N]–water interface (systems A_{IL} and B_{IL}).

whereas a few chloroform molecules undergo short transient excursions to water, generally not exceeding 100 ps.

2. The Calix[4]crown-6 Ligand and Its Cs⁺ Complexes. In this section, we focus on the interfacial behavior of LCs⁺NO₃[−] complexes in “oil”–water binary systems, comparing the [BMI][Tf₂N] ionic liquid with chloroform as the oil phase. Different initial configurations were considered, e.g., by starting either with adjacent phases (systems C_{IL} and C_{CLF}) or with mixed solvents (systems D_{IL}, D_{CLF} and E_{IL}, E_{CLF}). Selected snapshots taken along the dynamics are depicted in Figures 6, 8, and 9 and Figures S2–S7 in the Supporting Information.

The LCs⁺ Complexes in [BMI][Tf₂N]–Water Binary Systems. We first simulated three LCs⁺ complexes with NO₃[−] counterions at the preformed [BMI][Tf₂N]–water interface (system C_{IL}; see Figure 6). One complex was initially immersed in water, one at the interface, and one in the bulk IL, and nitrates formed

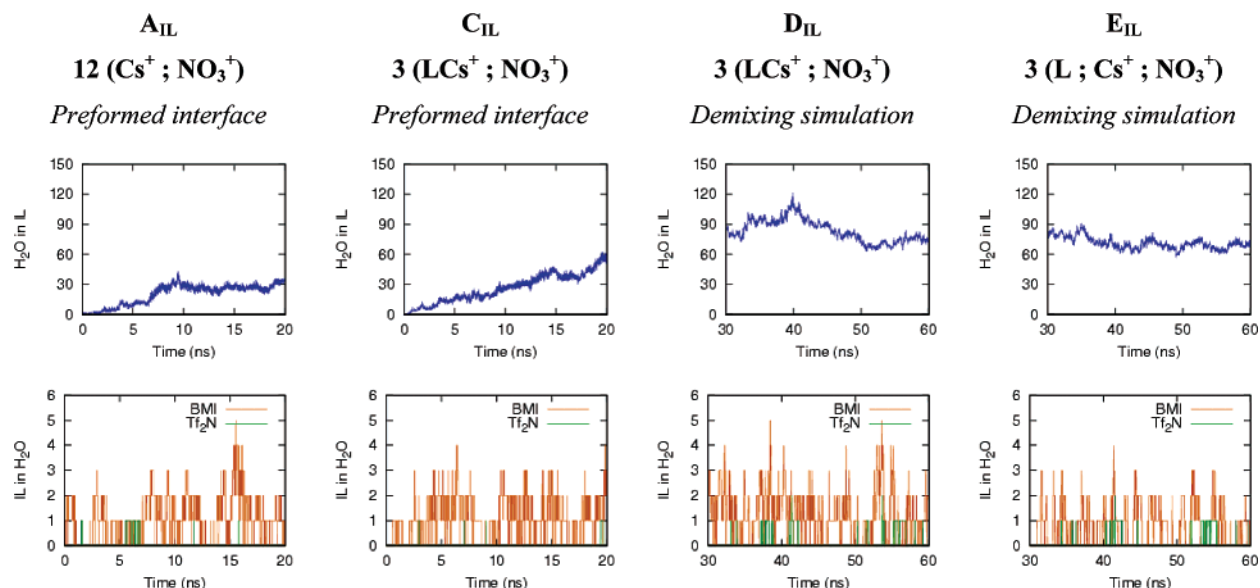


Figure 5. Number of H₂O molecules in bulk IL (top) and of IL ions in bulk water (bottom; BMI⁺—orange and Tf₂N[−]—green) as a function of time (ns).

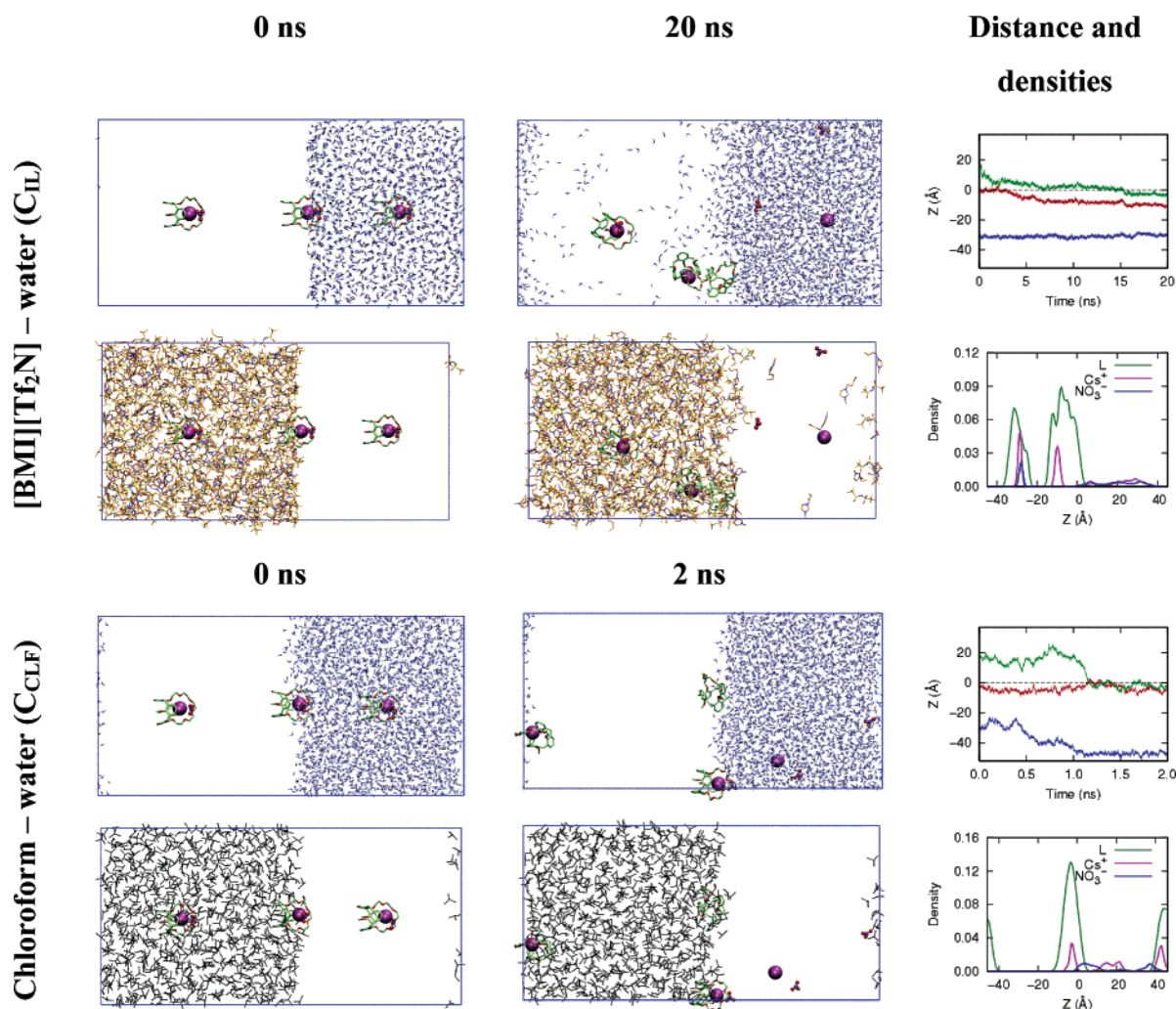


Figure 6. Simulation of 3 LCs⁺ complexes in [BMI][Tf₂N]—water (C_{IL}) and chloroform—water (C_{CLF}) binary systems. Initial and final snapshots are shown. For each system, the solvents are displayed separately on two lines for clarity. Right column: distance (Å) between the center of mass of L and the interface as a function of time (ns) and densities of solutes averaged over the last 3 ns (C_{IL}) or the last 0.5 ns (C_{CLF}) of MD.

intimate pairs with the complexed Cs⁺ cations. During the dynamics, the complexes behaved differently, depending on their location. The first one first diffused from the bulk water to slowly reach the IL side of the interface at the end of the

dynamics. However, its Cs⁺ cation decomplexed after 14 ns (i.e., as the complex reached the water side of the interface), and it migrated to the bulk aqueous phase, while the uncomplexed calixarene reached the IL side interface and stayed there

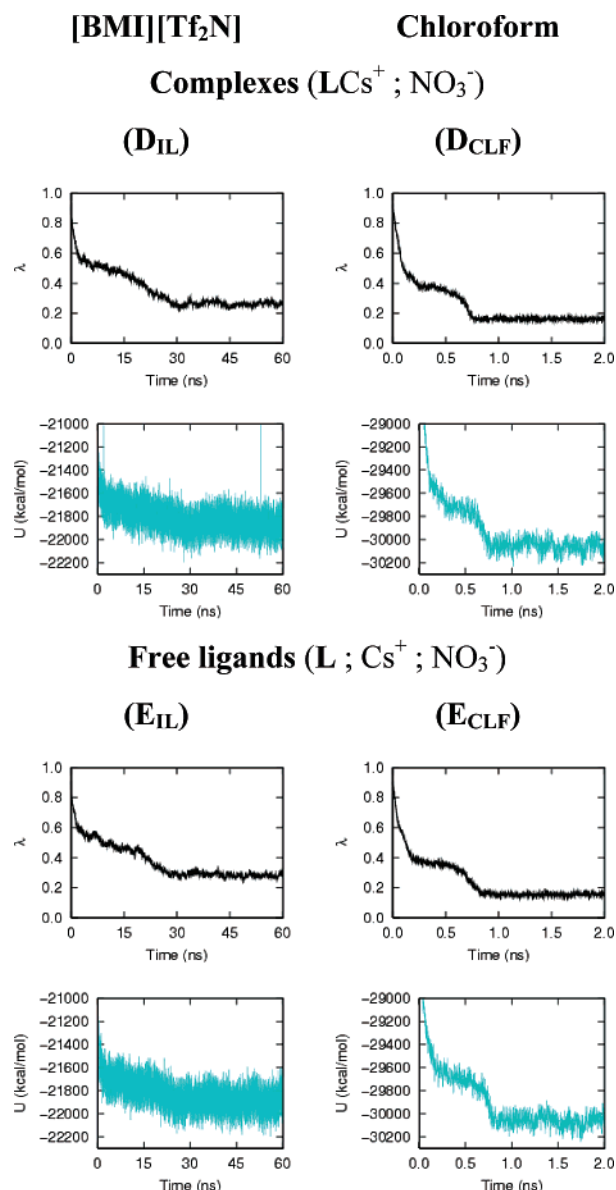


Figure 7. Evolution of the demixing index (λ) and of the potential energy (U , in kcal/mol) of the **D_{IL/CLF}** and **E_{IL/CLF}** systems as a function of time (ns).

until the end of the dynamics. The complex that was initially at the interface slowly moved toward the IL, up to ~ 10 Å from the interface after 20 ns. Its Cs⁺ cation coordinated one H₂O molecule on the average, hydrogen-bonded to a “second shell” of Tf₂N⁻ anions.³³ The third complex initially in the bulk IL remained there, without diffusion, and retained its nitrate coordinated counterion. This **C_{IL}** simulation clearly shows that the complex is hydrophobic and expelled out of the aqueous phase, but whether it prefers the interface or the bulk IL phase is unclear and further investigated below.

To avoid being initially trapped in a given interfacial domain, we decided to start from randomly mixed liquids and perform a “mixing–demixing” simulation on the system **C_{IL}** (hereafter noted **D_{IL}**). To prevent decomplexation of Cs⁺, the Cs⁺...O_{crown} distances were constrained by harmonic potentials. The phase separation, monitored as a function of time by the demixing index (λ) and the potential energy (U) (see Figure 7), occurred in three main sequences: First, λ “quickly” decreases from ~ 1 to 0.5 (in ca. 3 ns), followed by a linear decrease to 0.25 at $t = 30$ ns, when it reaches a plateau until the end of the dynamics. At the beginning of the dynamics, the IL/water phases separate

faster in the presence of solutes than without solute,²⁸ suggesting that the latter induces some organization of the solvents, “catalyzing” the separation. By visual inspection at the trajectories (Figures 8 and S3) one sees that, very early, the complexes are immersed in IL-rich domains surrounded by water, without displaying any specific “amphiphilic” orientation with respect to the forming interface. This suggests that complexes prefer the IL over the water environment. This dynamics has been pursued up to 60 ns, after which the two liquids are separated and two complexes sit on the IL side of the interface (at ~ 10 Å from the interface), whereas the third one sits in the bulk IL (at ~ 20 Å from the interface; see Supporting Information Figure S8). Nitrate counterions sit in water, together with some BMI⁺ cations but no Tf₂N⁻ anion. Interestingly, the extracted Cs⁺ cations are hydrated by one H₂O molecule, H-bonded to Tf₂N⁻ anions or to 1–3 other H₂O molecules (Supporting Information Figure S9). Such solvation patterns are reminiscent of those observed in the humid [BMI][PF₆] ionic liquid^{33,50} or in a chloroform solution oversaturated with water.⁵¹ We also note that all complexes are shielded from the aqueous phase by the IL. Even the LCs⁺ complex z -positioned near the interface is in fact fully surrounded by IL ions, delineating a micro-IL groove at the interface which is thereby more rough than the neat interface (see “Complex 3” in Figure S9).

The stability of the system was further tested by running the dynamics at higher temperature, to enhance the sampling. For this purpose, we started from the demixing **D_{IL}** configuration at 30 ns and ran 10 ns of dynamics at 400 K (system **D'_{IL}** in Supporting Information Figure S10). This indeed led to enhanced intersolvent mixing, making the interface broader and less well-defined. However, the location of the LCs⁺ complexes did not change significantly during the dynamics: one remained on the IL side of the interface, and two others in the bulk IL, indicating that there is no strong driving force to exchange from one of these regions to the other, as supported by the energy component analysis (vide infra). All three complexes clearly prefer, however, the IL side over the water side of the interface.

The LCs⁺ Complexes in Chloroform–Water Binary Systems. At the classical interface with chloroform, the complexes are clearly surface-active and, regardless of their initial position, adsorb with the Cs⁺/crown moiety pointing toward water and the calixarene skeleton pointing toward the organic phase, i.e., in an amphiphilic manner.^{34,52} This is first observed in the simulation of system **C_{CLF}** with three LCs⁺ complexes (Figures 6 and S4). The complex initially in chloroform reached the interface in 1 ns of MD only, keeping its nitrate counterion as an intimate pair as long as it had no contact with water, while the complex initially at the interface remained adsorbed during the whole dynamics. The third complex initially positioned in water decomplexed in less than 0.5 ns, and the freed ligand diffused to the interface where it adsorbed, as in the case of the IL. This suggests that the complex is less stable in water than at the interface or in the receiving phases (IL or chloroform) and is thus unlikely to form in water.

The interfacial activity of LCs⁺ is confirmed by the demixing simulation of randomly mixed chloroform and water liquids (**D_{CLF}** system with three LCs⁺NO₃⁻ complexes; see Figures 7, 8, and S5). The phases separated in less than 0.8 ns (ca. 40 times faster than IL–water mixture), and the three complexes finally adsorbed at the interfaces.

The Free Calixarenes in [BMI][Tf₂N]–Water Binary Systems. The simulation **C_{IL}** hints at the surface activity of the calix[4]-crown-6 **L** itself, and to further explore this feature, we simulated a system **E_{IL}** with three **L** calixarenes and three

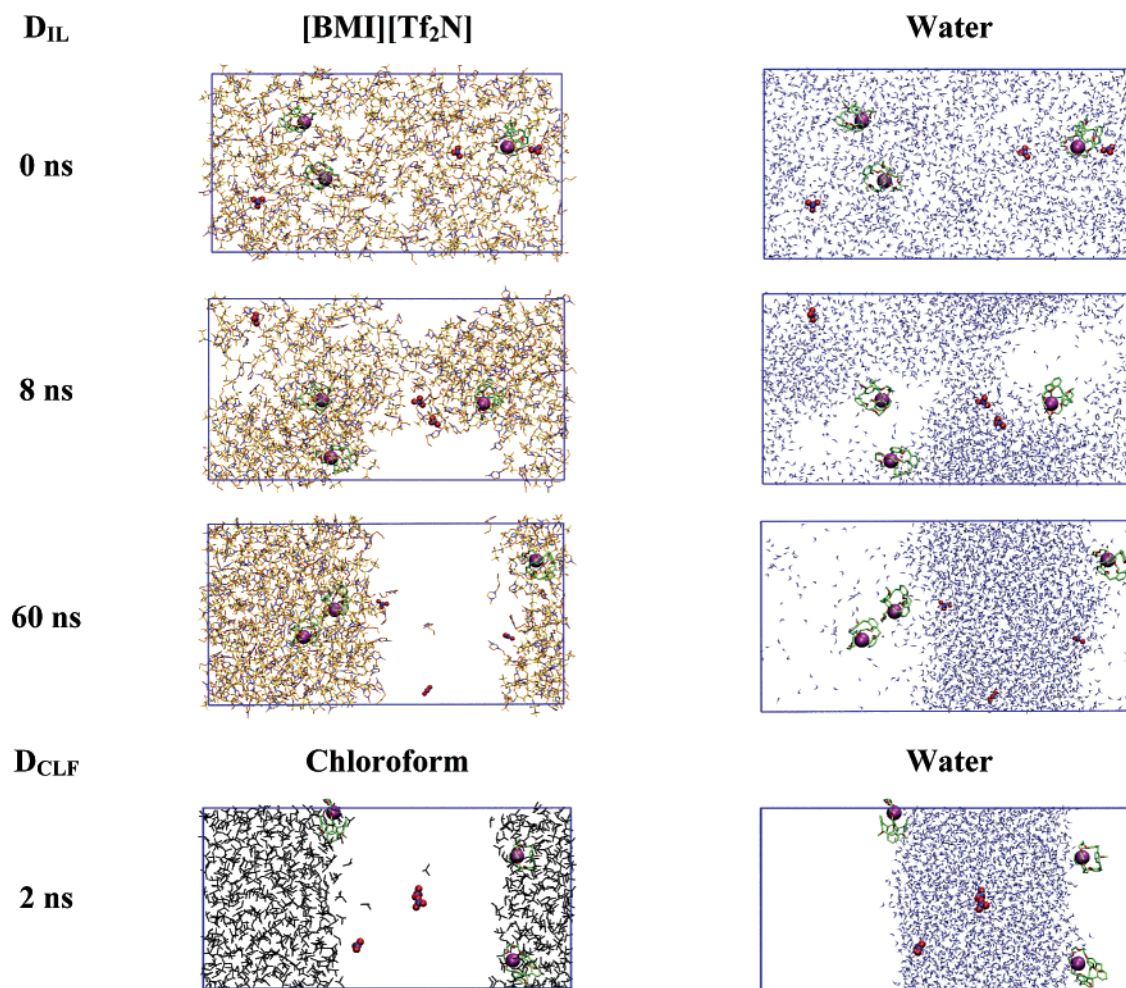


Figure 8. Simulations of 3 $\text{LCs}^+\text{NO}_3^-$ complexes starting from completely mixed liquids (systems \mathbf{D}_{IL} and \mathbf{D}_{CLF}). Typical snapshots with solvents represented side by side for clarity. A full version of this figure is given in the Supporting Information (Figures S4 and S5).

Cs^+NO_3^- ions. The latter was prepared by restarting the simulation of system \mathbf{D}_{IL} (at $t = 0$ ns; i.e., after mixing), first forcing the Cs^+ cations to decomplex (via 2 ps of biased dynamics, fixing its charge to -1 and the NO_3^- charge to $+1$). The subsequent dynamics with reset charges on Cs^+ and NO_3^- was pursued for 60 ns (see Figures 9 and S6). During the simulation, the free ligands **L** are immersed in IL domains, and the phases separate in ca. 30 ns. During the last 30 ns of MD, the system seems to have reached an equilibrium state, as the demixing index (λ), the potential energy (U), and the number of H_2O s in IL slightly oscillate around an average value (Figure 7), but the interface slowly “flattens” (see Figures 9 and S6). At the end of the dynamics, the **L** ligands are fully immersed in the IL at -11 to -17 Å from the nearest interface. Interestingly, no water solvates the crown ether moiety of the **L**, which instead complexes one BMI^+ cation, as found for 18-crown-6 itself.⁵⁰ The Cs^+ and NO_3^- ions attracted water at the early steps of the demixing simulation, to be finally immersed in the bulk water phase.

The Free Calixarenes in Chloroform–Water Binary Systems. The demixing simulation of the chloroform mixture with water containing three (**L**, Cs^+ , NO_3^-) species leads to rapid phase separation (in ca. 0.8 ns), after which the hydrophilic Cs^+ and NO_3^- ions are fully immersed in water, and the uncomplexed calixarenes adsorb at one interface or the other. The calixarenes are oriented with their aromatic skeleton pointing toward water, as a result of the complexation of one H_2O guest molecule in the cavity (H-bonded over the two opposite anisole oxygens),

which acts as a relay with the interfacial water. This is consistent with previous MD results,³⁴ according to which the calixarene adsorbs at the interface with two possible orientations: one with the crown in contact with water and the one observed here. The exchange between these two states is not observed during our dynamics, because this would disrupt the attractive interactions with water, while exposing the more hydrophobic aromatic groups to water at the intermediate stages.

Discussion and Conclusions

We report MD investigations on the interfacial behavior of key partners involved in the selective Cs^+/Na^+ extraction to the $[\text{BMI}][\text{Tf}_2\text{N}]$ ionic liquid, systematically comparing the results with those obtained in identical conditions with a classical molecular organic solvent (chloroform) as receiving phase. All systems have been simulated consistently in terms of size, initial configurations, and representation of the solutes and solvents. The force field is based on 1–6–12 representation of nonbonded interactions for convenience, as widely used for liquid–liquid interfaces^{53,54} and for IL solutions.^{26,40,41,55} As shown with classical liquids, more sophisticated force fields, using nonadditive terms and explicit polarization, should allow fine-tuning of the representation of the solvents at the interface,⁵⁶ as well as their solvation properties in this peculiar region.^{20,57} In the case of ILs, polarizable models have been reported for studying the bulk liquid⁵⁸ and the vacuum interface of the 1-ethyl-3-methylimidazolium nitrate liquid,³¹ but their consistency for modeling polyphasic systems needs to be assessed. Furthermore,

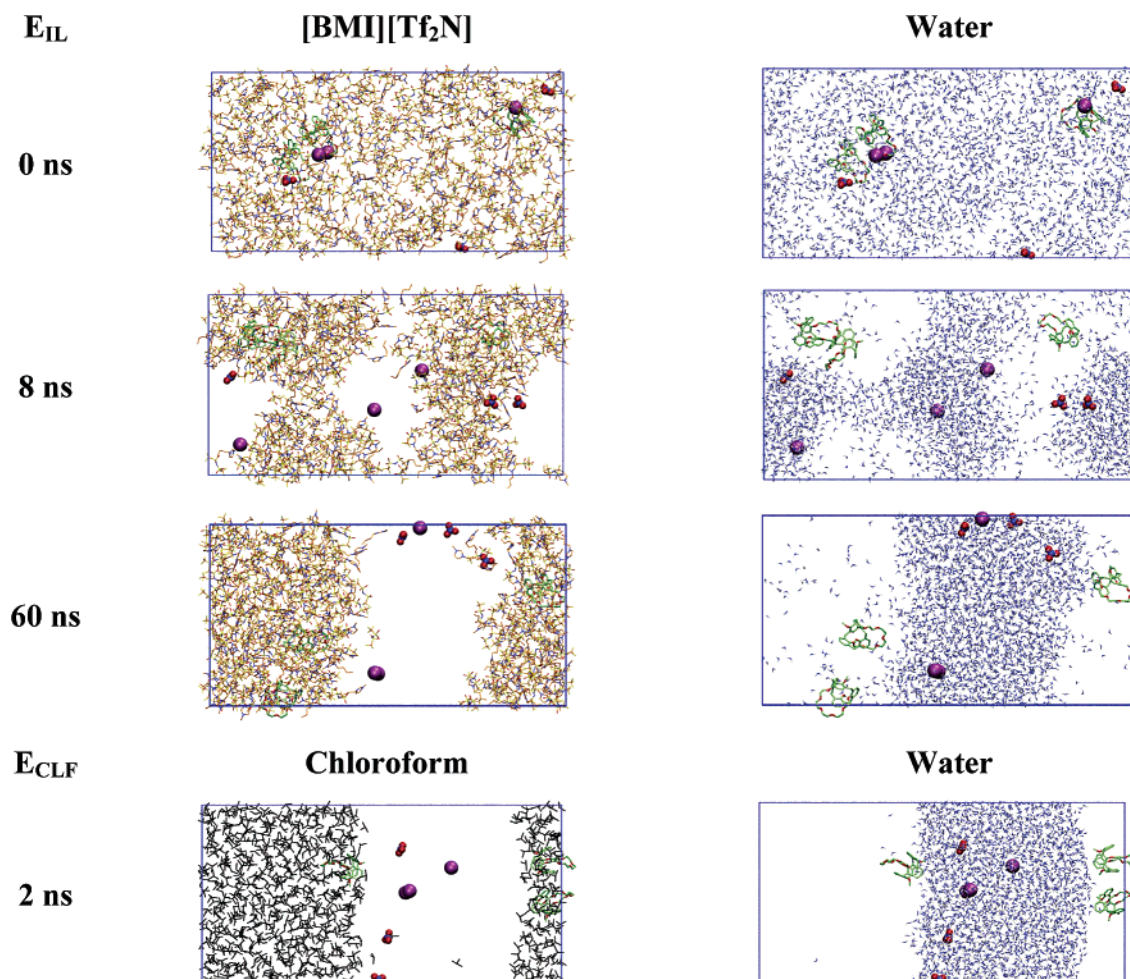


Figure 9. Simulations of 3 **L** ligands + 3 Cs^+NO_3^- ion pairs starting from completely mixed liquids (systems **E_{IL}** and **E_{CLF}**). Typical snapshots with solvents represented side by side for clarity. A full version of this figure is given in the Supporting Information (Figures S6 and S7).

such calculations would presently demand too much computer time for the studied IL systems. We note that the TIP3P water model used here implicitly accounts for water polarization in the bulk liquid and that this model should be more compatible with ILs than with weakly polar molecular solvents. We therefore believe that the present results, discussed below in the context of assisted ion extraction are, at least qualitatively, meaningful.

Our results confirm that, at a nanoscopic level, the IL forms a well-defined interface of ca. 10 Å width, which is somewhat larger than with classical hydrophobic solvents (~5 Å with chloroform in this study; see density curves in Supporting Information Figure S11). There are, however, a number of specific features of the interface with the IL compared to the classical solvents. First, there is some partitioning of the IL ions in water, with some excess of BMI^+ cations over Tf_2N^- anions. The macroscopic water phase should be neutral, and the MD results indicate that, at a few nanometers away from the interface, it is not. About 1 to 5 BMI^+ cations and 0–1 Tf_2N^- anions are solubilized in water, with the different simulated solutes (see Figure 5), as observed with the neat $[\text{BMI}][\text{Tf}_2\text{N}]$ –water mixtures.²⁸ We note that the higher solubility of BMI^+ over Tf_2N^- in water is fully consistent with a cation exchange mechanism in assisted cation extraction when the IL cation is not too hydrophobic.

Another distinguishing feature concerns the Na^+NO_3^- and Cs^+NO_3^- electrolytes whose cations and anions may be “attracted by the IL interface”, due to specific interactions with

IL counterions. The electrolyte ions are thus partially dehydrated, more than they are at classical interfaces whose organic solvent molecules are not polar enough to compete with water.⁵⁹ Although no real transfer to the IL is observed in our simulations (which correlates with the relatively small partitioning to $[\text{BMI}][\text{Tf}_2\text{N}]$),¹² the mixed solvation at the interface likely corresponds to a key step along the transfer that should be easier than toward traditional organic liquids.

Concerning the **L** calixarene and its LCs^+ complex, they adsorb at the classical interfaces in less than 1 ns, whereas there is no strong driving force to diffuse from the IL–water interface to the bulk IL or vice versa (during 20 ns of dynamics). This is observed in the **C_{IL}** simulation starting with 3 LCs^+ positioned at different regions of the solution, as well as in a separated simulation starting from 2 LCs^+ and 2 **L** species initially positioned at the interface (system **F_{IL}**; see Supporting Information Figure S12). It is therefore difficult to safely draw conclusions on their surface activity at the IL–water interface.

Demixing simulations, starting from “random” configurations, allow us to further investigate the preferred solvent surrounding of the solutes and to avoid being trapped close to an initial local-energy minimum. In the course of these simulations, the solvents gradually aggregate around the solutes, thereby forming IL-rich domains surrounded by water-rich domains, to finally converge to well-separated phases. The free NO_3^- or Cs^+ ions are hydrophilic and “capture” water molecules at the beginning of the dynamics, to be immersed in bulk water, whatever the nature of the organic phase. This contrasts with the LCs^+

TABLE 2: Solvent–Solute Interaction Energies (kcal/mol) in Bulk Solvents or at the Interface^a

		[BMI][Tf ₂ N]	chloroform	H ₂ O	total
In Bulk Solvents (Monophasic Systems)					
bulk IL ^b	LCs ⁺	−136			−136
	L	−86			−86
bulk chl ^c	LCs ⁺		−77		−77
	L		−68		−68
bulk wat ^c	LCs ⁺			−106	−106
	L			−84	−84
At The Interfaces (Biphasic Systems) ^d					
IL/wat	LCs ⁺	−128		−11	−139
	L	−65		−38	−103
Chl/wat	LCs ⁺		−65	−43	−108
	L		−57	−36	−93

^a Statistical fluctuations are about 5–10 kcal/mol. ^b Ref 33. ^c Ref 52. ^d Obtained from simulations with two LCs⁺ and two L species initially positioned at the interface (system F_{IL}; see Figure S9; after 20 ns at the IL interface and after 2 ns at the chloroform interface).

complexes and L ligands that are hydrophobic and prefer from the early steps of the dynamics IL-rich domains, to be finally shielded from water by “cages” of IL ions. The free calixarene L also prefers the IL over water, mainly due to specific interactions of its crown ether moiety with BMI⁺ cations, forming “inclusion complexes” in the bulk IL. These simulations confirm that there is no strong driving force to promote the diffusion of L and LCs⁺ species from the bulk IL to the interface or vice versa, because the IL is polar in nature and displays quite strong electrostatic attractions with these solutes (vide infra) which are therefore less attracted by water at the interface. This is not the case with a classical weakly polar solvent like chloroform. The partitioning between the two liquids and at the interface depends on many factors, like the surface tension and cavitation energy of the liquids⁶⁰ and, from the thermodynamics point of view, from entropic as well as from enthalpic components. Quantitative insights into the interface crossing by the studied species might be obtained, in principle, from PMF (potential of mean force) calculations,^{20,52} but these are presently hampered by the long relaxation times of the IL systems and related computational costs. It is, however, interesting to look at the results of the energy component analysis, comparing the solute–solvent interactions E_{int} in the different systems. The results (Table 2) show that the uncomplexed calixarene L interacts more strongly with its liquid environment at the interface than in the bulk IL ($E_{\text{int}} = -103$ and -86 ± 10 kcal/mol, respectively), whereas the LCs⁺ complex interacts equally well with the interface and the bulk IL ($E_{\text{int}} = -139$ and -136 ± 10 kcal/mol, respectively). These energies suggest that the complex is less surface-active than the L ligand at the IL interface, in keeping with its high extractability to the IL. With chloroform as the oil phase, both L and LCs⁺ clearly prefer the interface ($E_{\text{int}} = -93$ and -108 kcal/mol, respectively) over bulk chloroform ($E_{\text{int}} = -68$ and -77 kcal/mol, respectively), and LCs⁺ is more surface-active than L because it is more polar and more attracted by water ($E_{\text{int}} = -106$ and -84 kcal/mol, respectively, with pure water). Further comparison with the two oil monophasic systems shows that LCs⁺ interacts much better with the IL (by -136 kcal/mol) than with chloroform (-77 kcal/mol) and is therefore better solvated by the IL. In the case of the L ligand itself, interactions with IL and with chloroform (-86 and -68 kcal/mol, respectively) differ less, and these are weaker than the interactions at the corresponding interfaces (-103 and -93 kcal/mol). Generally speaking, the complexes should be less attracted at ionic liquid than at classical aqueous interfaces and thereby more easily transferred to the IL receiving

phase. This is fully consistent with the higher extraction efficiency to hydrophobic ILs compared to organic solvents.

Differences in interfacial activity may have deep effects on the cation complexation mechanism. In the case of classical interfaces, the fact that both ligands and their complexes are surface-active, and the negligible partitioning of ligands to water and of metal to the oil phase implies that the complexation process takes place “right at the interface”. With ILs as the receiving phase, the situation differs in many respects. First, the interfacial pressure is lower (about 13 mN/m with the neat water–IL interface⁶¹ and 27 mN/m with the neat water–chloroform interface⁶²), facilitating the interface crossing. Second, there are a non-negligible proportion of metal ions in contact with the interface or even in the IL phase, and these can be complexed by the ligands on the IL side of the interface or in the “bulk” IL. Even in the case where complexes form at the interface, they should transfer more easily to the IL than they do to molecular solvents, with which they interact less well. The effect of counterions also differs, as extraction to classical solvents generally requires neutralizing hydrophobic counterions, whereas extraction to ILs may proceed by a cation exchange mechanism without coextraction of anion to maintain the neutrality of the two phases.

Another important difference concerns the diffusion dynamics, much slower with ILs than with classical liquids,⁶³ and as a result, much longer simulation times (up to 60 ns in the case of the D_{IL} system with the calixarene complexes) are needed to equilibrate IL-containing systems, compared to their chloroform analogues (a few hundred picoseconds). Such issues are also observed experimentally with ILs, leading to slow kinetics and equilibration problems with possible aging effects. For instance, the interfacial tension of the biphasic [BMI][Tf₂N]/water system decreases from 15.9 to 13.7 dyne cm^{−1} after several hours when the two purified liquids were put in contact.⁶⁴ The water content of the IL also depends on time and differs after short contact (2–4 min) or several hours.⁶ The sampling difficulties we met, although dealing with much smaller time scales and “nanoscopic” solutions, are qualitatively consistent with these observations. To our knowledge, no such problems occur with classical molecular solvents, which also equilibrate faster in MD simulations.

The [BMI][Tf₂N] IL is quite heterogeneous and hygroscopic and may solubilize^{12,65–67} water in polar basins as isolated molecules or small clusters,^{28,68} increasing the diffusion of IL ions,¹⁴ as well as the extraction rate. Experimental investigations on a parent system (cation extraction by a crown ether to the [BMI][PF₆] IL)⁶ indicate that the extraction rates increase with the IL humidity, i.e., when the aqueous phase contains highly concentrated salts (~ 3 to 10 M; “salting out effect”) or/when the IL contains extractant molecules (“water dragging effect”⁶⁹). Our simulations with nitrate salts deal with a lower concentration (~ 0.25 M), and no significant change in IL humidity is observed relative to the neat interface,²⁸ in keeping with experiment. This contrasts with the case of LCs⁺-containing systems, where the amount of water in the IL is doubled, compared to the Cs⁺NO₃[−] solutions (there are ca. 30 extracted H₂O molecules in system A_{IL} and 60 extracted H₂O molecules in system C_{IL}; see Figure 5). In the case of chloroform-containing systems, the oil phase is dry, in keeping with the low polarity and hydrophobic character of this solvent.

To summarize, “apples to apples” comparative MD studies of electrolytes and extractant molecules at the water/ionic liquid versus water/chloroform interfaces provide microscopic insights into “what happens at the interface”¹⁴ in assisted ion extractant.

A number of analogies as well as interesting differences are pointed out. Our study should stimulate further experimental studies on the interfaces between water and ionic liquids and the surface activity of solutes transferred from one phase to the other.

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Supporting Information Available: Interaction energies between the solvents and the sodium and cesium nitrate salts (Table S1). Initial and final snapshots of the \mathbf{B}_{IL} , \mathbf{B}_{CLF} (Figure S1), \mathbf{F}_{IL} , \mathbf{F}_{CLF} (Figure S12) and \mathbf{D}_{IL} systems (Figure S10; system \mathbf{D}_{IL} simulated at 400 K). Snapshots of the \mathbf{C}_{IL} , \mathbf{C}_{CLF} , \mathbf{D}_{IL} , \mathbf{D}_{CLF} , \mathbf{E}_{IL} , and \mathbf{E}_{CLF} systems taken at different times during the dynamics (Figures S2–S7). Distance between calixarenes and the interface plotted as a function of time (Figure S8). Zooms on the complexes at the end of the \mathbf{D}_{IL} simulation (Figure S9). Solvent densities in the interfacial regions of selected systems (Figure S11). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Rogers, R. D.; Seddon, K. R. *Science* **2003**, *302*, 792.
- (2) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; VCH: Weinheim, 2002.
- (3) Rogers, R. D.; Seddon, K. R. *Ionic Liquids. Industrial Applications for Green Chemistry*; Rogers, R. D.; Seddon, K. R., Eds.; Washington, DC, 2002.
- (4) Visser, A. E.; Jensen, M. P.; Laszak, I.; Nash, K. L.; Choppin, G. R.; Rogers, R. D. *Inorg. Chem.* **2003**, *42*, 2197.
- (5) Cocalia, V. A.; Jensen, M. P.; Holbrey, J. D.; Spear, S. K.; Stepinski, D. C.; Rogers, R. D. *J. Chem. Soc., Dalton Trans.* **2005**, 1966.
- (6) Visser, A. E.; Swatloski, R. P.; Reichert, W. M.; Griffin, S. T.; Rogers, R. D. *Ind. Eng. Chem. Res.* **2000**, *39*, 3596.
- (7) Chun, S.; Dzyuba, S. V.; Bartsch, R. A. *Anal. Chem.* **2001**, *73*, 3737.
- (8) Dai, S.; Ju, Y. H.; Barnes, C. E. *J. Chem. Soc., Dalton Trans.* **1999**, 1201.
- (9) Luo, H. M.; Dai, S.; Bonnesen, P. V.; Buchanan, A. C.; Holbrey, J. D.; Bridges, N. J.; Rogers, R. D. *Anal. Chem.* **2004**, *76*, 3078.
- (10) Stepinski, D. C.; Jensen, M. P.; Dzielawa, J. A.; Dietz, M. L. *Green Chem.* **2005**, *7*, 151.
- (11) Jensen, M. P.; Beitz, J. V.; Neufeind, J.; Skanthakumar, S.; Soderholm, L. In *Ionic Liquids IIIA: Fundamentals, Progress, Challenges, and Opportunities, Properties and Structure*; Rogers, R. D., Seddon, K. R., Eds.; Washington, DC, 2005; Vol. 901, p 18.
- (12) Luo, H.; Dai, S.; Bonnesen, P. V. *Anal. Chem.* **2004**, *76*, 2773.
- (13) Dietz, M. L.; Dzielawa, J. A.; Laszak, I.; Young, B. A.; Jensen, M. P. *Green Chem.* **2003**, *5*, 682.
- (14) Watarai, H. *Trends Anal. Chem.* **1993**, *12*, 313.
- (15) Conboy, J. C.; Richmond, G. L. *J. Phys. Chem. B* **1997**, *101*, 983.
- (16) Girault, H. H.; Schiffrin, D. J. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Dekker: New York, 1989; Vol. 15, p 1.
- (17) Danesi, P. R.; Chiarizia, R.; Coleman, C. F. In *Critical Reviews in Analytical Chemistry*; Campbell, B., Ed.; CRC Press: Boca Raton, Florida, 1980; Vol. 10, p 1.
- (18) Szymanowski, J. *Solvent Extr. Ion Exch.* **2000**, *18*, 729.
- (19) Benjamin, I. *Acc. Chem. Res.* **1995**, *28*, 233.
- (20) Chang, T. M.; Dang, L. X. *Chem. Rev.* **2006**, *106*, 1305.
- (21) Wipff, G.; Lauterbach, M. *Supramol. Chem.* **1995**, *6*, 187.
- (22) Coupez, B.; Boehme, C.; Wipff, G. *J. Phys. Chem. B* **2003**, *107*, 9484.
- (23) Lauterbach, M.; Wipff, G. In *Physical Supramolecular Chemistry*; Echegoyen, L.; Kaifer, A. E., Eds.; NATO ASI Series, Vol. 485; Kluwer Academic Publishers: Dordrecht, 1996; p 65.
- (24) Baaden, M.; Berny, F.; Muzet, N.; Troxler, L.; Wipff, G. In *Calixarenes for Separation*; Lumetta, G.; Rogers, R.; Gopalan, A., Eds.; ACS Symposium Series 757; American Chemical Society: Washington, DC, 2000; p 71.
- (25) Sieffert, N.; Wipff, G. *J. Phys. Chem. B* **2006**, *110*, 4125.
- (26) Lynden-Bell, R. M.; Kohanoff, J.; Del Popolo, M. G. *Faraday Discuss.* **2005**, *129*, 57.
- (27) Chaumont, A.; Schurhammer, R.; Wipff, G. *J. Phys. Chem. B* **2005**, *109*, 18964.
- (28) Sieffert, N.; Wipff, G. *J. Phys. Chem. B* **2006**, *110*, 13076.
- (29) Halka, V.; Tsekov, T.; Freyland, W. *Phys. Chem. Chem. Phys.* **2005**, *7*, 2038.
- (30) Rivera-Rubero, S.; Baldelli, S. *J. Am. Chem. Soc.* **2004**, *126*, 11788.
- (31) Yan, T.; Li, S.; Jiang, W.; Gao, X.; Xiang, B.; Voth, G. A. *J. Phys. Chem. B* **2006**, *110*, 1800.
- (32) Lynden-Bell, R. M.; Del Popolo, M. *Phys. Chem. Chem. Phys.* **2006**, *8*, 949.
- (33) Sieffert, N.; Wipff, G. *J. Phys. Chem. A* **2006**, *110*, 1106.
- (34) Muzet, N.; Engler, E.; Wipff, G. *J. Phys. Chem. B* **1998**, *102*, 10772.
- (35) Casnati, A.; Pochini, A.; Ungaro, R.; Uguzzoli, F.; Arnaud, F.; Fanni, S.; Schwing, M. J.; Egberink, R. J. M.; de Jong, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 2767.
- (36) Varnek, A.; Wipff, G. *J. Comput. Chem.* **1996**, *17*, 1520.
- (37) Case, D. A.; Pearlman, D. A.; Caldwell, J. W.; Cheatham, T. E., III; Wang, J.; Ross, W. S.; Simmerling, C. L.; Darden, T. A.; Merz, K. M.; Stanton, R. V.; Cheng, A. L.; Vincent, J. J.; Crowley, M.; Tsui, V.; Gohlke, H.; Radmer, R. J.; Duan, Y.; Pitera, J.; Massova, I.; Seibel, G. L.; Singh, U. C.; Weiner, P. K.; Kollman, P. A. *AMBER7*, University of California, San Francisco, 2002.
- (38) Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Impey, R. W.; Klein, M. L. *J. Chem. Phys.* **1983**, *79*, 926.
- (39) Jorgensen, W. L.; Briggs, J. M.; Contreras, M. L. *J. Phys. Chem.* **1990**, *94*, 1683.
- (40) de Andrade, J.; Boes, E. S.; Stassen, H. *J. Phys. Chem. B* **2002**, *106*, 13344.
- (41) Canongia Lopes, J. N. A.; Padua, A. A. H. *J. Phys. Chem. B* **2004**, *108*, 16893.
- (42) Berny, F. Ph.D. Thesis, Université Louis Pasteur, Strasbourg, 2000.
- (43) Åqvist, J. *J. Phys. Chem.* **1990**, *94*, 8021.
- (44) Cornell, W. D.; Cieplak, P.; Bayly, C. I.; Gould, I. R.; Merz, K. M., Jr.; Ferguson, D. M.; Spellmeyer, D. C.; Fox, T.; Caldwell, J. W.; Kollman, P. A. *J. Am. Chem. Soc.* **1995**, *117*, 5179.
- (45) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Clarendon Press: Oxford, 1987.
- (46) Darden, T.; York, D.; Pedersen, L. *J. Chem. Phys.* **1993**, *98*, 10089.
- (47) Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W. F.; DiNola, A.; Haak, J. R. *J. Chem. Phys.* **1984**, *81*, 3684.
- (48) Engler, E.; Wipff, G. In *Crystallography of Supramolecular Compounds*; Tsoucaris, G.; Atwood, J. L., Lipkowski, J., Eds.; Kluwer Academic Publishers: Dordrecht, 1996; Vol. 480, p 471.
- (49) Humphrey, W.; Dalke, A.; Schulten, K. *J. Mol. Graphics* **1996**, *14*, 33.
- (50) Vayssiere, P.; Chaumont, A.; Wipff, G. *Phys. Chem. Chem. Phys.* **2005**, *7*, 124.
- (51) Lauterbach, M.; Wipff, G.; Mark, A.; van Gunsteren, W. F. *Gazz. Chim. Ital.* **1997**, *127*, 699.
- (52) Lauterbach, M.; Engler, E.; Muzet, N.; Troxler, L.; Wipff, G. *J. Phys. Chem. B* **1998**, *102*, 245.
- (53) Benjamin, I. *J. Phys. Chem. B* **2005**, *109*, 13711.
- (54) Winter, N.; Benjamin, I. *J. Chem. Phys.* **2005**, *122*.
- (55) Huang, X. H.; Margulis, C. J.; Li, Y. H.; Berne, B. J. *J. Am. Chem. Soc.* **2005**, *127*, 17842.
- (56) Chang, T. M.; Dang, L. X. *J. Chem. Phys.* **1996**, *104*, 6772.
- (57) Wick, C. D.; Dang, L. X. *J. Phys. Chem. B* **2006**, *110*, 6824.
- (58) Yan, T.; Burnham, C. J.; Popolo, M. G.; Voth, G. A. *J. Phys. Chem. B* **2004**, *108*, 11877.
- (59) This is supported by the results of MD simulations of the Cs^+ and NO_3^- ions in pure chloroform, in the [BMI][Tf₂N] ionic liquid, and in water, leading to interaction energies with the solvents of, respectively, −30, −106, and −97 kcal/mol for Cs^+ and −64, −110, and −123 kcal/mol for NO_3^- .
- (60) Pierotti, R. A. *Chem. Rev.* **1976**, *76*, 717.
- (61) Fitchett, B. D.; Rollins, J. B.; Conboy, J. C. *Langmuir* **2005**, *21*, 12179.
- (62) Dey, J.; Schwinté, P.; Darcy, R.; Ling, C. C.; Sicoli, F.; Ahern, C. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1513.
- (63) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2004**, *108*, 16593.
- (64) Toh, S. L. I.; McFarlane, J.; Tsouris, C.; DePaoli, D. W.; Luo, H.; Dai, S. *Solvent Extr. Ion Exch.* **2006**, *24*, 33.
- (65) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, *3*, 156.
- (66) Jacquemin, J.; Husson, P.; Padua, A. A. H.; Majer, V. *Green Chem.* **2006**, *8*, 172.
- (67) Luo, H.; Dai, S.; Bonnesen, P. V.; Haverlock, T. J.; Moyer, B. A.; Buchanan, A. C., III *Solvent Extr. Ion Exch.* **2006**, *24*, 19.
- (68) Cammarata, L.; Kazarian, S. G.; Salter, P. A.; Welton, T. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192.
- (69) Fan, W.; Tsai, R. S.; El Tayar, N.; Carrupt, P. A.; Testa, B. *J. Phys. Chem.* **1994**, *98*, 329.