CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200500741

Task-Specific Ionic Liquids Bearing 2-Hydroxybenzylamine Units: Synthesis and Americium-Extraction Studies

Ali Ouadi,*[a] Benoît Gadenne,[b] Peter Hesemann,[b] Joel J. E. Moreau,[b] Isabelle Billard,[a] Clotilde Gaillard,[a] Soufiane Mekki,[a, c] and Gilles Moutiers[c]

Abstract: The synthesis of two task-specific ionic liquids (TSILs) bearing 2-hydroxybenzylamine entities is described. These compounds are based on an imidazolium substructure onto which one hydrobenzylamine-complexing moiety is grafted. We have demonstrated that, whether pure or diluted, TSIL is able to extract americium ions. Furthermore, recovery of americium from the IL phase into a receiving phase can be achieved under acidic conditions. A possible mechanism for the metal-ion partitioning is presented, in which the extraction system is driven by an ion-exchange mechanism.

Keywords: americium · green chemistry · ion exchange · ionic liquids · solvent extraction

Introduction

Room-temperature ionic liquids (RTILs) are promising solvent alternatives for organic synthesis, catalysis, and electrochemistry.[1] In the field of separation processes, the usefulness of RTILs for the extraction of simple, neutral organic compounds, such as naphthalene,[2–4] has already been reported. Among industrial extraction processes, extraction and separation of actinides and lanthanides from nuclear waste is one of the most challenging fields, owing to the high activity of the solutions to be treated. Ionic-liquid phases are promising reception media for metallic species in liquid/liquid extraction processes as they show high stability under α- and γ-irradiation[5] and enhanced safety towards criticality.[6] However, the partitioning of charged metallic species is largely limited by the unfavorable complexation properties of hydrophobic ionic liquids: in general, RTILs are noncoordinating, and the highly hydrated metal ions remain in the aqueous phase.[7] Improvements in extraction efficiencies have been achieved by the addition of organic coordinating compounds, which significantly increase the distribution ratios of metal ions between the ionic-liquid and aqueous phases.[8–11] The extraction of various metallic species by using well-known ligands, such as crown ethers[12] or phosphates[13] dissolved in RTILs, such as 1-butyl-3-methylimidazolium bis-trifluorosulfonimide ([Bmim][Tf_2N]) **1a** or 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF_6]) **1b**, highlights the potential of these new solvents for extraction.

The introduction of RTILs into the nuclear-fuel cycle can be envisioned through two different approaches. Classically, RTILs can be considered as alternative solvents that replace the highly toxic and flammable kerosene mixtures currently in use.[14] The extraction of actinides (U^{VI}, Am^{III}) into RTIL phases by using tributylphosphate (TBP) or octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) has already been reported. Although such studies are scarce, it is clear that the extraction mechanism in a biphasic water/RTIL system is rather different from that observed in classical organic solvents. As demonstrated by Dietz et al., ion-exchange processes seem to play a significant role.[12]

Another very promising approach for metal extraction is the concept of task-specific ionic liquids (TSILs). These compounds, consisting of extracting entities grafted onto the cation of the ionic liquid, combine the properties of ionic liquids (e.g., nonvolatility, nonflammability) with those of classical extracting compounds. Upon grafting complexing

---

[a] Dr. A. Ouadi, Dr. I. Billard, Dr. C. Gaillard, S. Mekki
IReS, CNRS/IN2P3-ULP Chimie Nucléaire
B.P. 28, 67037, Strasbourg Cedex 2 (France)
Fax: (+33) 388-106-431
E-mail: ali.ouadi@ires.in2p3.fr

[b] Dr. B. Gadenne, Dr. P. Hesemann, Prof. J. J. E. Moreau
UMR 5076 CNRS/ENSCM
Hétérochimie Moléculaire et Macromoléculaire
8, rue de l'Ecole Normale
34296 Montpellier Cedex 05 (France)

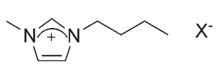
[c] S. Mekki, Dr. G. Moutiers
CEA Saclay, DEN/DPC/SCP/DIR
91191 Gif Sur Yvette Cedex (France)

substructures onto the organic cation of RTILs, the resulting TSILs would behave as both the organic phase and the extracting agent, suppressing the problems encountered through extractant/solvent miscibility and facilitating species extraction and solvent recovery. This concept has been the subject of very few studies in the field of separation. However, it has already been shown that TSILs bearing urea, thiourea, thioether,[7] or ethylene glycol[15,16] groups allow the partitioning of metal ions, such as Hg^{II} and Cd^{II}, from water.

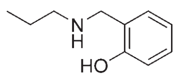
Here, we report the synthesis of functionalized hydrophobic ionic liquids bearing the 2-hydroxybenzylamine substructure, and their application in the liquid/liquid extraction of Am^{III}. The extraction abilities of these ionic compounds were compared with the molecular counterpart of the ionic liquids, the 2-propylaminomethyl-phenol. Finally, we propose a mechanism for the extraction of Am^{III} in biphasic ionic-liquid/water systems.

Results and Discussion

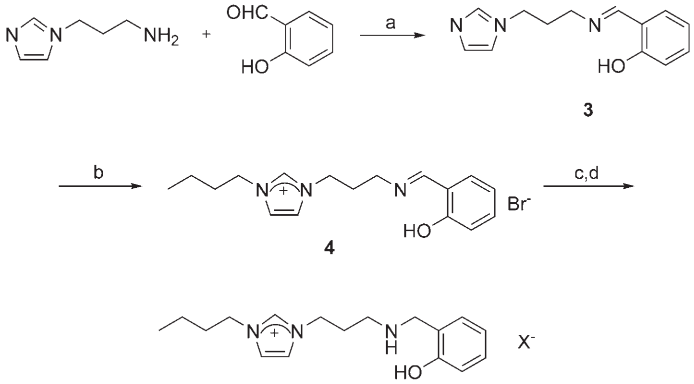
Synthesis of the functionalized ionic liquids 5a and 5b: 2-Hydroxy-benzylamine groups were grafted onto imidazolium substructures by using a three-step synthesis starting from salicylaldehyde and 3-aminopropylimidazole (Scheme 1). The product imine **3** was first alkylated by using 1-bromobutane, and the resulting ionic imine **4** was reduced with sodium borohydride. The water-soluble imidazolium bromide was finally transformed into the bis(trifluoromethanesulfonimide) **5a** and the hexafluorophosphate **5b** by using lithium bis(trifluoromethane)sulfonimide or potassium hexafluorophosphate, respectively. The water-immiscible imidazolium salts were isolated as viscous orange oils. The hexafluorophosphate **5b**, though much too viscous to be used in liquid/liquid extraction experiments ($\eta = 257000$ cP), has good solubility in the 1-butyl-3-methyl-imidazolium hexafluorophosphate. Notably, the compound **5a** shows a sufficiently low viscosity ($\eta = 2070$ cP) to be directly employed in liquid/liquid extraction experiments.



1a: X= $N(CF_3SO_2)_2^-$
1b: X= PF_6^-



2



5a: X= $N(CF_3SO_2)_2^-$
5b: X= PF_6^-

Scheme 1. Synthetic route to TSILs. a) EtOH; b) C_4H_9Br; c) $NaBH_4$, EtOH; d) $LiN(CF_3SO_2)_2$ or KPF_6.

Determination of pK_a: In water, both TSILs **5a** and **5b** are pH sensitive, owing to their functionalization by an amino and a phenolic group, respectively. An understanding of the acid-base behavior of these compounds is important in order to rationalize the chemical properties in separation processes. Hereafter, for the sake of simplicity, the TSILs will also be denoted as LH_2, with no mention of the counterion, unless necessary. The TSILs shown in Figure 1 may accept one proton at the nitrogen group to give $H_3(L)^+$. Because the complexing substructure contains two acidic protons, two deprotonation reactions need to be considered. However, as the pK_a values calculated for compounds **5a** and **5b** are very similar, we were not able to attribute them to the ammonium and phenol groups. The deprotonation steps are expressed for $H_3(L)^+$ in the equilibria below:

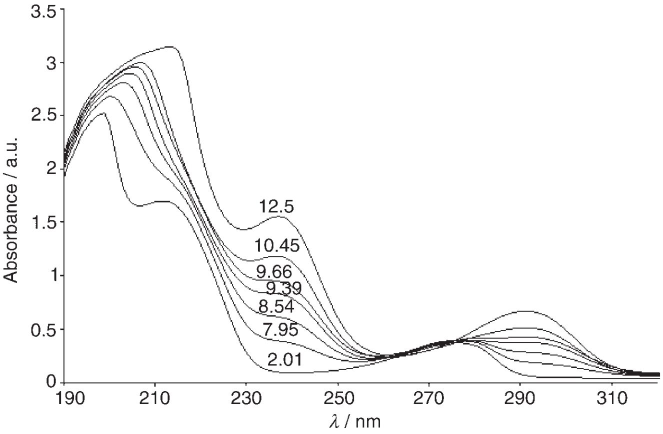


Figure 1. UV/Vis spectra of TSIL **5a** as a function of pH. The pH values are indicated on the spectra.

$$LH_3^+ \rightleftharpoons LH_2 + H^+, \text{ with } K_{a1} = [LH_2][H^+]/[LH_3^+]$$

$$LH_2 \rightleftharpoons LH^- + H^+, \text{ with } K_{a2} = [LH^-][H^+]/[LH_2]$$

Figure 1 displays the absorption spectra of **5a** within the range 190–330 nm as a function of pH range 2–12. Figure 2 shows the variation in absorption at two given wavelengths ($\lambda = 237$ and 290 nm) for the same pH range. The corre-

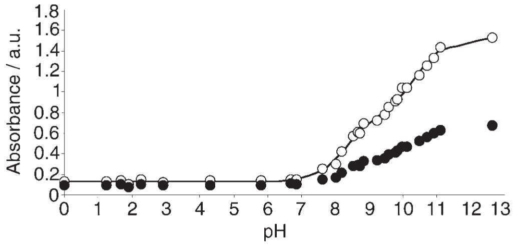


Figure 2. Variation in the absorbance of TSIL **5a** as a function of pH in water. ○: $\lambda = 237$ nm; ●: $\lambda = 290$ nm; the solid line represents the fit (see text).

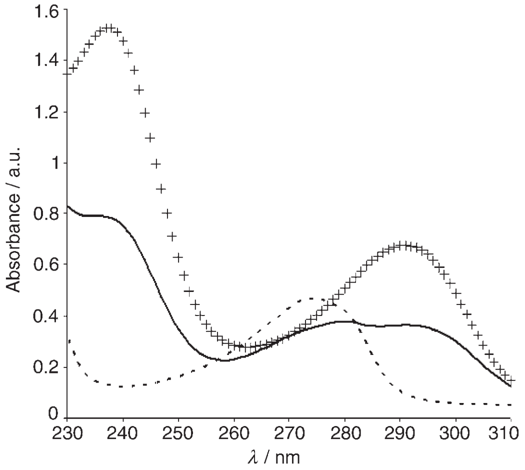


Figure 3. Calculated absorption spectra of the fully protonated LH_3^+ (---), neutral LH_2 (——), and deprotonated LH^- (+++) forms of TSIL **5a** in water.

Table 1. The pK_a values derived for the three compounds investigated in this work.

	Single wavelength fit	Chemometric analysis
TSIL **5b**	$pK_{a1} = 8.3 \pm 0.1$	$pK_{a1} = 8.32 \pm 0.01$
	$pK_{a2} = 10.4 \pm 0.1$	$pK_{a2} = 10.41 \pm 0.01$
TSIL **5a**	$pK_{a1} = 8.1 \pm 0.1$	$pK_{a1} = 8.1 \pm 0.1$
	$pK_{a2} = 10.3 \pm 0.1$	$pK_{a2} = 10.3 \pm 0.1$
compound **2**	$pK_{a1} = 8.4 \pm 0.1$	$pK_{a1} = 8.41 \pm 0.01$
	$pK_{a2} = 11.3 \pm 0.1$	$pK_{a2} = 11.15 \pm 0.04$

sponding data (not shown) for TSIL **5b** are very similar. In the case of the nonionic extractant molecule **2**, the wavelength range investigated is not large enough to reach absorbance saturation. The changes in the absorption spectra in response to pH variation are consistent with two successive deprotonations, which is in agreement with the chemical structures of the compounds **2**, **5a**, and **5b**.

The corresponding pK_a values can be determined from the change in absorption at a given wavelength (see Figure 2, data for TSIL **5a**). However, only the molecular absorbances of the three forms involved (LH_3^+, LH_2, and LH^-) at this particular wavelength can be derived in this way. Chemometrics[17] is a more complex mathematical treatment of the data that enables determination of 1) the number of independent species present in solution, 2) the pK_a values, and 3) the individual absorption spectra of each form (LH_3^+, LH_2, and LH^-) within the whole range investigated. This provides a much more complete set of information from the same set of experimental data.

The principal component analysis (PCA), which is the first step of a chemometric analysis, performed on the three sets of data confirms the presence of three independent species for TSILs **5a** and **5b**, however, the result is less clear for **2**. Table 1 presents the pK_a values derived from both mathematical treatments (chemometrics and "classical" fit) for the two TSILs and **2**, on the basis of a double deprotonation. Figure 3 displays the absorption spectra derived for the three independent species in the case of TSIL **5a** as an example (chemometrics analysis). The individual spectra derived for TSIL **5b** are very similar to those obtained for TSIL **5a**, however, in the case of **2**, the spectrum of the third species is mostly background. This phenomenon is attributed to the limited range of pH investigated in the case of **2**, which does not allow us to obtain the fully deprotonated form as a major component of the solution.

The values in Table 1 reveal very good agreement between the two methods of analysing the data. The pK_{a1} values, ranging from 8.10 to 8.44, are very similar for all three compounds, whereas the pK_{a2} values indicate that grafting the complexing pattern onto the IL skeleton induces a shift of almost one pK_a unit. This difference can be ascribed to the presence of the positive charge on the imidazolium ring, which is more strongly electron withdrawing than the aliphatic propyl chain in **2**.

Solubility of TSIL in water as a function of water pH: A known concentration of TSIL diluted in the corresponding RTIL (0.34 M) was introduced into water and the solubility of the TSIL in water was studied at different pH values. The absorbance was measured by using a UV-visible spectrophotometer; the TSIL concentration in water was then derived by using the Beer's law plots that were obtained previously for aqueous TSIL solutions of known concentrations. As shown in Figure 4, the solubility of TSIL increases as the pH of the aqueous phase increases.

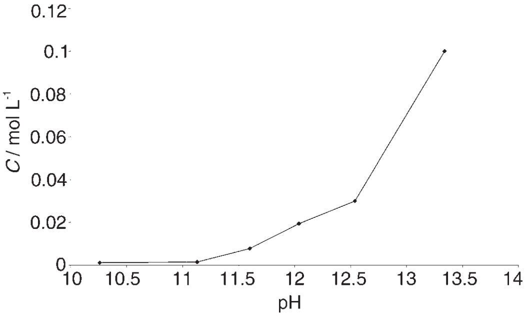


Figure 4. Solubilization of TSIL **5b** in aqueous phase at basic pH.

Distribution ratios for Am^{III} as a function of pH, TSIL concentration, and ionic strength: To determine the optimum conditions, the extraction of Am^{III} was performed at various pH values (Figure 5 shows the data for pure TSIL **5a** as an example). The variation in the distribution ratio D indicates that the coordinating and complexing abilities of pure TSIL **5a** are dependent on pH. At low pH values, the TSIL is in mainly its LH_3^+ (acidic) form, leading to a very low concentration of the Am–TSIL complex; at higher pH values, higher extraction efficiencies are obtained and the maximum extraction is obtained at around pH 10. The extraction efficiency decreases above pH 10, owing to the solubilization of the TSIL in the aqueous phase.

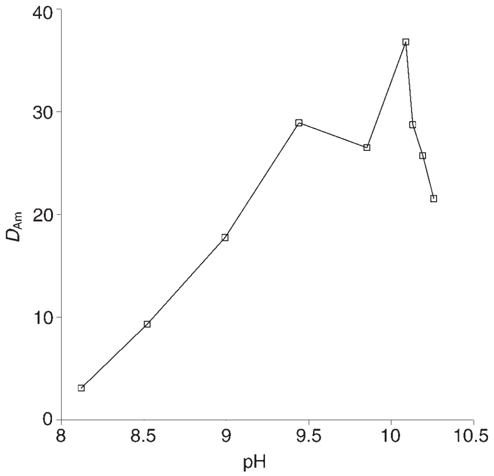


Figure 5. Variation in D_{Am} as a function of pH. Organic phase: pure TSIL **5a**.

In contrast to TSIL **5a**, which is a liquid at room temperature and has a moderate viscosity, TSIL **5b** is highly viscous. To investigate its metal-extraction efficiency, we dissolved this compound in [Bmim][PF_6] **1b**. The influence of pH on Am extraction upon using both TSILs and extractant **2**, dissolved in either [Bmim][Tf_2N] (TSIL **5a**) or [Bmim][PF_6] (TSIL **5b** and **2**), is shown in Figure 6. The extraction of trivalent americium with the different TSILs **5a** and **5b** displays the same behavior as previously presented for the pure TSIL **5a**. At identical concentrations, the functionalized RTILs extract americium more effectively than extractant **2**. Furthermore, the anionic part of the TSIL is shown to have an effect on the extraction efficiency. This can be ascribed to Tf_2N^- having a more hydrophobic character than PF_6^-.

The number of TSIL molecules that are present in the extracted moieties can be determined by plotting the distribution ratio (D) of the metal (at a constant pH value) as a function of the TSIL concentration; in a log versus log plot, the gradient of the slope is approximately equal to the number of TSIL molecules. At the constant pH value of 10, the graph of log$D$ against log$C$ is linear, with a gradient of 2 (Figure 7). Therefore, the stoichiometry of the extracted species (metal:extractant) is 1:2. Furthermore, the slope of the (log$D$ + logα_{Am}) versus pH plot indicates that two hydrogen ions participate in the extraction of metal ions (Figure 8).

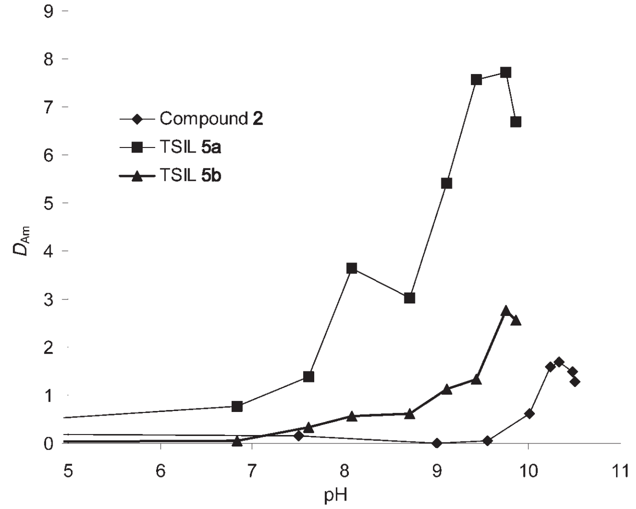


Figure 6. Comparison of D_{Am} for TSIL **5a**, TSIL **5b**, and **2** as a function of pH. Organic phase, 0.34 M: TSIL **5a** diluted in [Bmim][Tf_2N] **1a**, TSIL **5b** and compound **2** diluted in [Bmim][PF_6] **1b**.

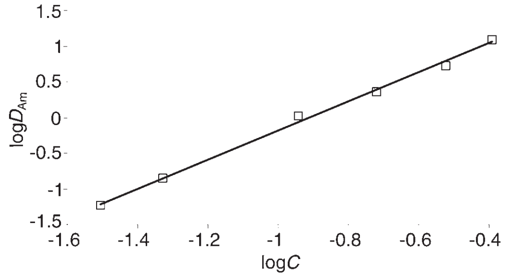


Figure 7. Plot of the logarithmic distribution ratios (logD_{Am}) for americium as a function of the logarithmic concentration of TSIL **5b** in [Bmim]-[PF_6] **1b**.

Finally, the performance of TSIL **5a** in extracting americium was evaluated in $NaClO_4$ medium (data not shown). The distribution coefficient of Am^{III} was determined at various $NaClO_4$ concentrations (0.05–1 M) at a fixed pH of 10. The distribution ratios increase linearly in this log/log plot, which suggests that the ClO_4^- ions participate in the extraction mechanism.

Determination of the extraction equilibrium equation: We attempted to fit the data of D versus pH (Figures 5 and 6) based on a chemical scheme describing the extraction process. The model we propose was conceived to reproduce as best as possible the experimental findings described above. Therefore, the proposed scheme takes into account 1) the first americium hydrolysis,[18] which is known to occur above pH 7; 2) the pH dependence of the variation in D, as displayed in Figure 6; and 3) the TSIL dependence (Figure 7) together with 4) the experimentally observed increased solu-

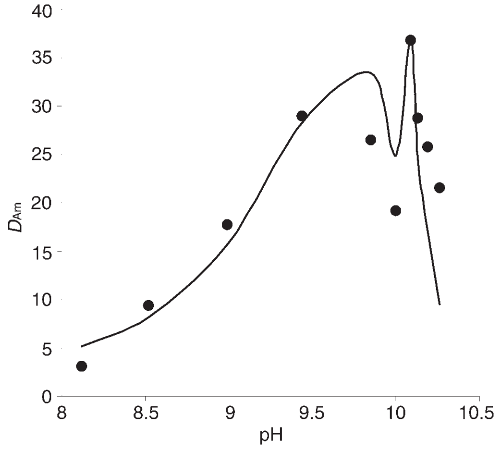


Figure 8. Plots of the logarithmic distribution ratios ($\log D + \log \alpha_{Am}$) for americium as a function of the aqueous pH. α_{Am} is the complexation coefficient of americium in the aqueous phase.

bilization of the TSIL in the aqueous phase at high pH. It also considers the effect of the ClO_4^- ions on the value of *D*. However, because we encountered some experimental difficulties (see below), the experimental indications are incomplete, and so many models could, in principle, reproduce the *D* variation. During the course of this work, we attempted fits of the data by using numerous models (data not shown), however, we restrict the following discussion to the best model that we tested.

By assuming that the predominant americium species in the perchlorate medium are Am^{3+} and $Am(OH)^{2+}$, the extraction equilibrium of Am^{III} by TSILs can be given as Equations (1)–(5),

$$\mathrm{Am^{3+} + 2\,ClO_4^- + \overline{LH_2} \rightleftharpoons \overline{Am(ClO_4)_2LH} + H^+} \tag{1}$$

$$\mathrm{Am^{3+} + H_2O \rightleftharpoons AmOH^{2+} + H^+} \tag{2}$$

$$\begin{aligned}&\mathrm{AmOH^{2+} + ClO_4^- + \overline{[Bmim][Tf_2N]} + 2\overline{LH_2} \rightleftharpoons}\\&\mathrm{\overline{AmOH(LH)_2ClO_4^-} + \overline{[Bmim]^+} + 2H^+ + Tf_2N^-}\end{aligned} \tag{3}$$

$$\mathrm{LH_2 \rightleftharpoons LH^- + H^+} \tag{4}$$

$$\mathrm{\overline{LH_2} \rightleftharpoons LH^- + H^+} \tag{5}$$

in which bars indicate species in the ionic-liquid phase. Each of the five equations is characterized by an equilibrium constant, K_1 to K_5. Equation (1) accounts for a possible extraction of americium below the hydrolysis pK_a of Am^{III}. Numerous numerical trials have shown that the shoulder observed in the *D* variation within the pH range 6–8.5 is best described by the introduction of such an extraction process for free Am^{3+} that involves a single LH_2 moiety. In fact, both the introduction of two LH_2 moieties in Equation (1) and the suppression of Equation (1) (i.e., $K_1 = 0$) lead to a steep increase in *D* from almost 0 to high values, without involving any intermediate values. Equation (2) corresponds to the Am hydrolysis. Equation (3) introduces the extraction of hydrolyzed forms of americium, the experimental effect of ClO_4^-, and is consistent with both of the slopes observed in Figures 7 and 8.

At equilibrium, the net charge of both the organic and aqueous phases must be zero, the negative charge of the complex anion in the RTIL phase must be balanced by transferring an anion from the organic phase to the aqueous phase.

To confirm this hypothesis of an anion exchange, spectroscopic studies of the extraction of europium at macro concentrations under the same conditions were carried out. The aim was to demonstrate the relationship between the Tf_2N concentration in the aqueous phase and the formation of a complex anion of europium in the RTIL phase. Unfortunately, at pH 10 and macro concentrations, Eu is completely hydrolyzed and precipitates, which prevents further reaction. Despite this problem, our work is consistent with the findings of Dietz et al.[12] and Jensen et al.,[19] who showed that an ion-exchange mechanism can function if TSIL is used as the organic phase together with a "classical" extracting moiety.

Finally, Equations (4) and (5) take into account the enhanced solubilization of the TSIL in water at high pH values, and the subsequent deprotonation that we observed. By definition, $pK_4 = pK_{a2}$. Owing to the limited pH range employed in this study, the presence of the additional aqueous species LH_3^+ was not considered; the other hydrolyzed Am products and carbonato–americium complexes were also neglected. Therefore, the mathematical model contains four unknown parameters. The mathematical treatment of the scheme is based on the classical mass action law, with no correction for ionic strength effect. The main hypothesis is that Am is present at the trace level.

To fit the curves, we first focussed on the TSIL **5a**/[Bmim][Tf$_2$N] **1a** series at either fixed or variable ionic strength. In the fit, the values of all four parameters were unfixed, however, it appears that fixing the value of K_2 to the value of the Am hydrolysis reported in the literature ($pK_a = 7.2$) does not significantly modify the quality of the fit, which is reasonable (not shown). In other words, the sensitivity of the model to the exact value of K_2 is poor. Similarly, owing to the few points above pH 9.5, the precision of K_5 is low. Interestingly, the impact of ClO_4^-, as included in the model, corresponds very well to that observed experimentally on the *D* versus pH plots obtained at variable ionic strength, for which the ClO_4^- concentration varies by almost four orders of magnitude (from 10^{-5} to 0.3 M), depending on the pH of the water phase before equilibration. This is a good indication that the model proposed is appropriate. For the fits, the K_4 value was fixed to the pK_{a2} value given in Table 1.

Secondly, we attempted fits of the series in which TSIL **5a** was used as a pure solvent. In the fitting procedure, the concentration of TSIL **5a** was changed from 0.34 to 2.5 M, which is the molar value of this solvent, and the ion-exchange mechanism of Equation (3), which is a crude approximation, was kept. In this case, fixing K_4 to its experimental values leads to an imperfect fit, whereas fixing K_4 to 0 allows satisfactory recovery of the data, as can be seen in Figure 9, which displays the fit of the D data on the basis of the model described above. The quality of the fit is rather good, although the ion-exchange mechanism [Eq. (3)] is modified and other physicochemical phenomena occur that are not properly described by the model. In particular, the viscosity is changed.

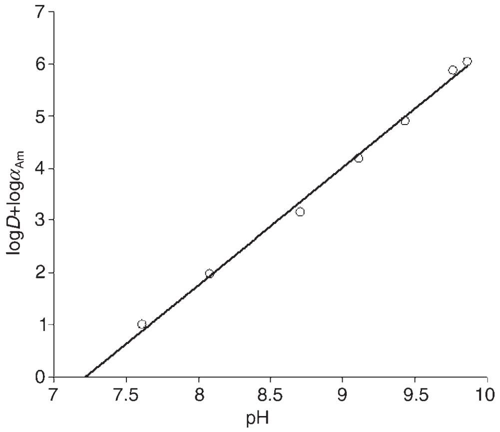


Figure 9. Fit of D_{Am} as a function of pH. Organic phase: pure TSIL **5a**.

Finally, we attempted fits of the TSIL **5b** series. In this case, no convincing adjustment of the data was possible (not shown). Am^{III}, either free or hydrolyzed, may be liable to complexation with PF_6^-, which would modify significantly the proposed complexation scheme.

Stripping test: Wei et al.[20] reported that neutral extractants, such as CMPO and crown ether, can extract metal ions under acidic conditions, whereas the use of neutral extractants leads to some difficulties in recovering the extracted metal. Subsequently, Luo et al.[21] reported the extraction of various alkali metals with alkyl aza crown ether, whereby the aza group provides a pH-switchable site and permits back-extraction at acidic pH. In the same way, the TSILs developed in our laboratory are pH sensitive and can be used for separation processes.

The americium loaded in the organic phase was back-extracted by contacting the organic phase with 1 M perchloric acid. At neutral or basic pH, the extraction efficiency is high, but at low pH, the amine group is protonated, reducing the binding constant for Am and, thus, allowing Am to be released into the aqueous phase. This extraction and stripping process was repeated three times. More than 99 % of the Am was recovered in the aqueous phase each time, indicating that a stripping process based on these TSILs is feasible. The IL phase could be reused for further liquid/liquid extraction of metal ions. As this process occurs at high pH, it may also be suitable for the extraction of other metal ions.

Conclusion

A solvent extraction system based on TSIL was investigated. This system presents innovative properties; the organic phase used is both the phase of reception for the actinide and the extracting agent. We have demonstrated that, whether pure or diluted, TSIL is able to extract americium ions, and that recovery of americium from the IL phase into a receiving phase can be achieved under acidic conditions.

A possible mechanism for the metal-ion partitioning is presented, in which the extraction system is driven by an ion-exchange mechanism.

Even though the TSILs developed in this work could be used for americium extraction under special conditions at basic pH, they are not well adapted for industrial processes at acidic pH. However, this work has allowed us to establish what a TSIL should *not* be with respect to actinide extraction. Firstly, we have confirmed the importance of the anion in lowering the viscosity of the TSIL. In addition to the problems of PF_6-based RTIL degradation that were encountered in many studies,[9,13] it appears that this anion is not suitable for fluid RTILs or TSILs. Although Tf_2N^- seems a good choice in this respect, other anions should be tested in the future so that the advantages of fluid and noncoordinating TSILs can be combined. Other possible weakly coordinating anions[22,23] might also be tried. Secondly, the extraction pattern may be changed to lower the effective extraction pH from basic to acidic values, or a neutral extracting pattern may be investigated. Finally, this complexing pattern could be grafted onto an RTIL-basis other than imidazolium, for example, tetraalkylammonium, which would interest the radiochemistry community because of the enhanced stability of radiolysis relative to that of imidazolim-based RTILs.

We are now attempting to apply these considerations to the synthesis of a more suitable TSIL.

Experimental Section

General remarks: All reactions were performed under an argon atmosphere and by using Schlenk-tube techniques as necessary. ^1H and ^{13}C NMR spectra in solution were recorded by using Bruker AC-200 and AC-250 spectrometers. $CDCl_3$, CD_3OD, and $[D_6]DMSO$ were used as NMR solvents. Chemical shifts are reported as δ values in ppm relative to TMS. IR spectra were recorded by using a Perkin–Elmer SPECTRUM 1000 FTIR spectrometer. Mass spectra were measured by using a JEOL MS-DX 300 mass spectrometer. All reagents were obtained from commercial sources and were used without purification. For experiments requiring dry solvents, THF, toluene, and diethyl ether were distilled over sodium benzophenone, DMF was distilled over CaH_2, dichloromethane was distilled over P_2O_5, and alcohols were distilled over Mg. [Bmim][Tf_2N] was synthesized and purified as previously reported;[24] [Bmim][PF_6] (purity = 99 %) was purchased from Solvionic (France).

2-[(3-Imidazol-1-yl-propylimino)-methyl]phenol (3): *N*-(3-aminopropyl)imidazole (2.05 g, 16.4 mmol) was added to a solution of salisaldehyde (2.00 g, 16.4 mmol) in absolute ethanol (20 mL). The homogeneous solution was stirred at RT for 30 min and then heated to reflux for 2 h. After cooling to RT, the solvents were pumped off. The resulting crystalline solids were purified by recrystallization from ethanol (3.55 g, 15.5 mmol, 95 %). ^{1}H NMR ($CDCl_3$): $\delta = 2.09$ (quintet, $J = 6.6$ Hz, 2H; CH_2), 3.45 (pseudo-t, $J = 6.6$ Hz, 2H; CH_2), 3.97 (pseudo-t, $J = 6.6$ Hz, 2H; CH_2), 6.77–6.94 (m, 3H), 7.00 (s, 1H), 7.14–7.30 (m, 2H), 7.39 (s, 1H), 8.23 (s, 1H; CH–N), 13.11 ppm (s, 1H; O*H*); ^{13}C NMR ($CDCl_3$): $\delta = 31.8$, 44.3, 55.8, 116.9, 118.5, 118.7, 118.8, 129.7, 131.4, 132.5, 137.1, 160.9, 166.1 ppm; IR (KBr): $\tilde{\nu}_{max} = 3435$, 3090, 2928, 1628, 1604, 1571, 1485, 1457, 1438, 1390, 1271, 1223, 1195, 1147, 1076, 1023, 976, 885, 804, 757, 657, 623, 466 cm^{-1}; HRMS (FAB+): *m*/*z*: calcd for $C_{13}H_{16}N_3O$ $[M+H]^+$: 230.1293; found: 230.1291.

1-Butyl-3-(3-{[1-(2-hydroxyphenyl)meth-(*E*)-ylidene]amino}propyl)-3*H*-imidazol-1-ium bromide (4): The imine (3.50 g, 15.3 mmol) was dissolved in 1-bromobutane (10 mL) and the mixture was heated to 80 °C for 10 h. After cooling to RT, the excess alkyl halide was eliminated by evaporation under vacuum and then by washing with diethyl ether (3 × 20 mL), yielding the product as a highly viscous orange oil (5.46 g, 14.9 mmol, 97 %). ^{1}H NMR (CD_3OD): $\delta = 0.94$ (t, $J = 7.3$ Hz, 3H; CH_3), 1.35 (septet, $J = 8.1$ Hz, 2H; CH_2), 1.80 (quintet, $J = 7.6$ Hz, 2H; CH_2), 2.34 (quintet, $J = 6.7$ Hz, 2H; CH_2), 3.75 (t, $J = 6.7$ Hz, 2H; CH_2), 4.14 (t, $J = 7.4$ Hz, 2H; CH_2), 4.40 (t, $J = 7.0$ Hz, 2H; CH_2), 4.80 (br s, 1H; OH), 6.81–6.91 (m, 2H), 7.26–7.40 (m, 2H), 7.64 (t, $J = 1.8$ Hz, 1H), 7.74 (t, $J = 1.9$ Hz, 1H), 8.52 (s, 1H; CH-N), 9.21 ppm (s, 1H); ^{13}C NMR (CD_3OD): $\delta = 13.9$, 20.6, 32.0, 32.9, 49.4, 50.7, 57.3, 117.9, 119.9, 120.0, 123.9, 124.0, 133.2, 133.9, 137.3, 162.6, 168.1 ppm; IR (KBr): $\tilde{\nu}_{max} = 3425$, 3130, 3071, 2950, 2870, 1628, 1560, 1495, 1457, 1276, 1209, 1161, 1120, 1023, 976, 833, 761, 638, 557, 457 cm^{-1}; HRMS (FAB+) *m*/*z*: calcd for $C_{17}H_{24}N_3O$ $[M^+]$: 286.1919; found: 286.1915.

1-Butyl-3-[3-(2-hydroxybenzylamino)propyl]-3*H*-imidazol-1-ium bis(trifluoromethane) sulfonimide (5a) and 1-butyl-3-[3-(2-hydroxybenzylamino)propyl]-3*H*-imidazol-1-ium hexafluorophosphate (5b): The alkylated compound (3.00 g, 8.2 mmol) was dissolved in methanol (20 mL). The resulting homogeneous solution was cooled to 0 °C and sodium borohydride (310 mg, 8.2 mmol) was slowly added under vigorous stirring. The resulting suspension was stirred for 3 h. The methanol was evaporated and the crude product was dissolved in water (50 mL). The aqueous solution was washed with diethyl ether (2 × 50 mL). A solution of *N*-lithiotrifluoromethanesulfonimide (2.58 g, 9.0 mmol) or potassium hexafluorophosphate (1.66 g, 9.0 mmol) in water (30 mL) was added to the aqueous solution of the functional imidazolium bromide. Demixation of the hydrophobic ionic liquid occurred immediately. The products were extracted with dichloromethane (50 mL). The organic layers were washed with water (3 × 30 mL) and dried (Na_2SO_4). Evaporation of the solvent yielded the title compounds as viscous brownish oils. Yields: **5a**: 4.48 g (7.9 mmol, 96 %), **5b**: 3.27 g (7.5 mmol, 92 %).

Physical data for 5b: Viscosity: $\eta = 257\,000$ cP; glass transition temperature: $T_g = -39$ °C; ^{1}H NMR ([D$_6$]DMSO): $\delta = 0.9$ (t $J = 7.2$ Hz, 3H; CH_3), 1.24 (sextet, $J = 7.6$ Hz, 2H; CH_2), 1.77 (quintet, $J = 6.8$ Hz, 2H; CH_2), 1.99 (quintet, $J = 7.3$ Hz, 2H; CH_2), 2.45 (m, 2H), 3.76 (s, 2H; CH_2–NH), 4.15 (m, $J = 7.1$ Hz, 2H; CH_2), 4.23 (m, $J = 7.2$ Hz, 2H; CH_2), 6.73 (m, 2H), 7.07 (m, 2H), 7.76 (s, 2H, Im$^+$), 9.15 ppm (s, 1H, Im$^+$); ^{13}C NMR ([D$_6$]DMSO): $\delta = 13.1$, 18.7, 29.1, 31.1, 44.5, 46.9, 48.5, 49.7, 115.4, 118.4, 122.3 (2C), 124.5, 127.7, 128.6, 135.9, 156.7 ppm; IR (KBr): $\tilde{\nu}_{max} = 3645$, 3320, 3157, 2937, 1585, 1561, 1461, 1252, 1161, 1104, 1033, 938, 842, 757, 638, 557, 452 cm^{-1}; HRMS (FAB+): *m*/*z*: calcd for $C_{17}H_{28}N_3O$ $[M]^+$: 288.2076; found: 288.2072.

Physical data for 5a: Compound **5a** shows similar spectroscopic properties to **5b**, except: Viscosity: $\eta = 2070$ cP; glass transition temperature: $T_g = -44$ °C; ^{13}C NMR: additional signal at 120.1 ppm (q, $J = 321$ Hz; $-CF_3$, $N(SO_2CF_3)_2$ anion); IR (KBr): $\tilde{\nu}_{max} = 3624$, 3329, 3149, 3114, 2965, 2938, 1590, 1565, 1492, 1468, 1350, 1256, 1203, 1139, 1057, 740 cm^{-1}.

2-Propylaminomethylphenol (2): Compound **2** was synthesized by a reaction sequence involving 1) the coupling of salicylaldehyde with propylamine and 2) the reduction of the imine formed with sodium borohydride. The crude product was purified by distillation under reduced pressure, yielding the title compound as a viscous yellow oil in nearly quantitative yield. ^{1}H NMR ($CDCl_3$): $\delta = 0.98$ (t, $J = 7.4$ Hz, 3H; CH_3), 1.59 (sextet, $J = 7.3$ Hz, 2H), 2.67 (t, $J = 7.1$ Hz, 2H), 4.01 (s, 2H; CH_2–N), 6.78–6.89 (m, 2H; Ar), 7.00–7.03 (m, 2H; Ar), 7.17–7.24 ppm (m, 1H; Ar); ^{13}C NMR ($CDCl_3$): $\delta = 11.5$, 22.6, 50.4, 52.5, 116.2, 118.8, 122.5, 128.1, 128.5, 158.3 ppm; IR (KBr): $\tilde{\nu}_{max} = 3320$, 3130, 3071, 2961, 2929, 2875, 1590, 1493, 1469, 1259, 754 cm^{-1}; HRMS (FAB+) *m*/*z*: calcd for $C_{10}H_{16}NO$ $[M+H]^+$: 166.1230; found: 166.1232.

Liquid/liquid extraction of americium: Ultrapure water (Millipore) was used in all cases. Aqueous solutions of $^{241}Am(ClO_4)_3$ at pH 3 were prepared. The ionic strength and pH values were adjusted by using $NaClO_4$, $HClO_4$, and NaOH (Aldrich, used as received). To avoid undesired metal complexation, no buffers were used for pH control. The pH of all samples was measured by using an ORION pH meter with an electrode (Orion). No attempts were made to dry any of the ionic liquids used, because of the equilibration with an aqueous phase during the course of the extraction experiments. The concentration of the TSILs in the corresponding ionic liquid was 0.34 M. The extraction protocol in the case of the pure TSIL phase was identical to that used for the ionic-liquid/TSIL solutions.

Distribution ratios of ^{241}Am were determined by mixing equal volumes (0.7 mL) of IL and an aqueous phase, followed by shaking on a vortex mixer apparatus at RT for 30 min, and centrifuging to equilibrate the phases. Owing to the variable solubility of the TSIL in water and its subsequent deprotonation, a large change in the pH value was eventually observed (in some cases, from pH 3 to pH 10).

Subsequently, ^{241}Am tracer (ca. 0.005 μCi, 2 μL) was added and extraction was performed by shaking and centrifuging to ensure that the phases were fully mixed and separated. No significant pH changes were observed after addition of the americium solution, owing to the very low volume added. Afterwards, 0.5 mL aliquots were taken from each phase and their γ-radioactivities were measured by using a well-type NaI(Tl) scintillation detector. The distribution ratio *D* was determined as the ratio of radioactivity of the organic phase to that of the aqueous phases.

Solubility of TSIL in water as a function of water pH: Each TSIL was shaken with an equal volume of water on a vortex mixer at 25 °C for 30 min. This was performed for water phases with various pH values. Each mixture was then centrifuged for 3 min to promote phase separation. Once each phase was separated, the aqueous phase was diluted with water by a factor of 10. The absorbance of this final solution at 291 nm was measured by using a UV/Vis spectrophotometer. The TSIL concentration in water was then derived by using the Beer's law plots obtained previously for TSIL aqueous solutions of known concentrations.

Determination of p*K*$_a$ values in water: Absorption spectra of aqueous solutions of **2**, **5a**, and **5b** of known concentrations (in the order of 1.8×10^{-4} M) within the range 190–800 nm were acquired by using an Uvikon 930 spectrophotometer at RT. The pH was varied by addition of aliquots of concentrated $HClO_4$ or NaOH aqueous solutions.

Stripping test: Back-extraction of Am^{III} with TSIL was performed by following a procedure similar to that described for the water/TSIL extraction. After equal volumes of the aqueous and RTIL solutions were mixed and shaken on the vortex mixer, so that Am^{III} was quantitatively transferred to the RTIL phase, a fresh aqueous solution containing 1 M perchloric acid was added. Both phases were mixed and shaken on the vortex mixer at 25 °C for 30 min. These mixtures were then centrifuged for 3 min to promote phase separation.

Fitting procedures and data analysis: The chemometric analysis was performed by using a program written under the Maple format, based on a program written previously by Pochon and co-workers.[25] The other fits were performed by using a Fortran subroutine included in the CERN package "MINUIT", which uses simplex and migrad algorithms for convergence.

Acknowledgement

We thank the GdR Paris for financial support.

---

[1] P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, **2003**, p. xvi, p. 364.

[2] J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, R. D. Rogers, *Green Chem.* **2001**, *3*, 156–164.
[3] L. A. Blanchard, D. Hancu, E. J. Beckman, J. F. Brennecke, *Nature* **1999**, *399*, 28–29.
[4] A. E. Visser, R. P. Swatloski, R. D. Rogers, *Green Chem.* **2000**, *2*, 1–4.
[5] D. Allen, G. Baston, A. E. Bradley, T. Gorman, A. Haile, I. Hamblett, J. E. Hatter, M. J. F. Healey, B. Hodgson, R. Lewin, K. V. Lovell, B. Newton, W. R. Pitner, D. W. Rooney, D. Sanders, K. R. Seddon, H. E. Sims, R. C. Thied, *Green Chem.* **2002**, *4*, 152–158.
[6] C. D. Harmon, W. H. Smith, D. A. Costa, *Radiat. Phys. Chem.* **2001**, *60*, 157–159.
[7] A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis, R. D. Rogers, *Chem. Commun.* **2001**, 135–136.
[8] A. E. Visser, M. P. Jensen, I. Laszak, K. L. Nash, G. R. Choppin, R. D. Rogers, *Inorg. Chem.* **2003**, *42*, 2197–2199.
[9] A. E. Visser, R. P. Swatloski, W. M. Reichert, S. T. Griffin, R. D. Rogers, *Ind. Eng. Chem. Res.* **2000**, *39*, 3596–3604.
[10] S. Dai, Y. H. Ju, C. E. Barnes, *J. Chem. Soc. Dalton Trans.* **1999**, 1201–1202.
[11] K. Shimojo, M. Goto, *Anal. Chem.* **2004**, *76*, 5039–5044.
[12] M. L. Dietz, J. A. Dzielawa, *Chem. Commun.* **2001**, 2124–2125.
[13] A. E. Visser, R. D. Rogers, *J. Solid State Chem.* **2003**, *171*, 109–113.
[14] J. N. Mathur, M. S. Murali, K. L. Nash, *Solvent Extr. Ion Exch.* **2001**, *19*, 357–390.
[15] L. C. Branco, J. N. Rosa, J. J. M. Ramos, C. A. M. Afonso, *Chem. Eur. J.* **2002**, *8*, 3671–3677.
[16] J. Fraga-Dubreuil, M. H. Famelart, J. P. Bazureau, *Org. Process Res. Dev.* **2002**, *6*, 374–378.
[17] M. J. Adams, *Chemometrics in Analytical Spectroscopy*, RSC, Cambridge, **1995**, p. 216.
[18] R. Guillaumont, T. Fanghanel, J. Fuger, I. Grenthe, V. Neck, D. A. Palmer, M. H. Rand, *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*, Elsevier, **2003**, p. 964.
[19] M. P. Jensen, J. Neuefeind, J. V. Beitz, S. Skanthakumar, L. Soderholm, *J. Am. Chem. Soc.* **2003**, *125*, 15466–15473.
[20] G. T. Wei, Z. S. Yang, C. J. Chen, *Anal. Chim. Acta* **2003**, *488*, 183–192.
[21] H. M. Luo, S. Dai, P. V. Bonnesen, *Anal. Chem.* **2004**, *76*, 2773–2779.
[22] I. Krossing, I. Raabe, *Angew. Chem.* **2004**, *16*, 2116–2142; *Angew. Chem. Int. Ed.* **2004**, *43*, 2066–2090.
[23] H. Suzuki, H. Naganawa, S. Tachimori, *Phys. Chem. Chem. Phys.* **2003**, *5*, 726–733.
[24] I. Billard, G. Moutiers, A. Labet, A. El Azzi, C. Gaillard, C. Mariet, K. Lutzenkirchen, *Inorg. Chem.* **2003**, *42*, 1726–1733.
[25] P. Pochon, P. Moisy, L. Donnet, C. de Brauer, P. Blanc, *Phys. Chem. Chem. Phys.* **2000**, *2*, 3813–3818.

Received: June 28, 2005
Revised: November 4, 2005