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Dramatic Changes in the Solubilities of Ions Induced by Ligand Addition in Biphasic System $D_2O/DNO_3//[C_1C_4im][Tf_2N]$: A Phenomenological Study

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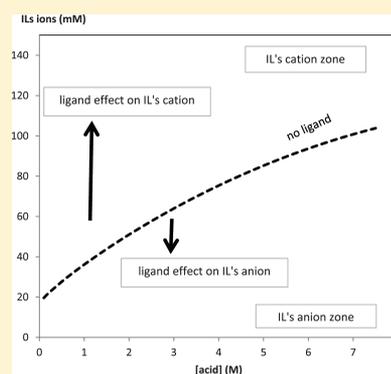
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ABSTRACT: The solubilities of $C_1C_4im^+$ and Tf_2N^- in nitric aqueous phases have been measured for several ligand types and concentrations (0.04 M tributylphosphine oxide, 0.05 M N,N' -dimethyl- N,N' -dibutylmalonamide, 0.10 M 1-methyl-3-[4-(dibutylphosphinoyl)butyl]-3H-imidazol-1-ium bis(trifluoromethylsulphonyl)imidate, and 1.1 M N,N -dihexyloctanamide). The data evidence a significant difference between the solubilities of the cations and anions of the ionic liquid as a consequence of several ion-exchange and/or ion-pairing mechanisms involving all ions present in the system as well as the protonation/nitric-extraction ability of the ligand.



1. INTRODUCTION

Since the excitement provoked by the first evidence of tremendous enhancement of metal-extraction efficiencies obtained by simply replacing molecular solvents by ionic liquids (ILs),¹ this new class of solvents, solely composed of ions and displaying melting points below 100 °C, has gained a clear legitimacy in the green chemistry portfolio.^{2–5} However, over the years, concerns have been raised on some questionable aspects of ILs such as the environmental benefits (or better to say hazards) they could bring.^{6,7} In particular, many papers now investigate the toxicity of such solvents to aquatic life,^{8–10} which is related to their biosphere dispersion as a consequence of possible industrial releases. On the other hand, the industrial potential of ILs spreads over many fields,¹¹ and liquid–liquid extraction of metal ions with the help of ILs is intensively studied; thus, a variety of techniques and topics (e.g., microextraction, nuclear waste management, biphasic systems, industrial-waste-water treatments, ultrasound-assisted extraction, recycling of urban mines, etc.) are worth mentioning.^{12–18} This is due to the unusual solvation properties of ILs that may help in resolving the long-lasting problems such as actinide/lanthanide¹⁹ and Ni/Co²⁰ separations. However, these unusual

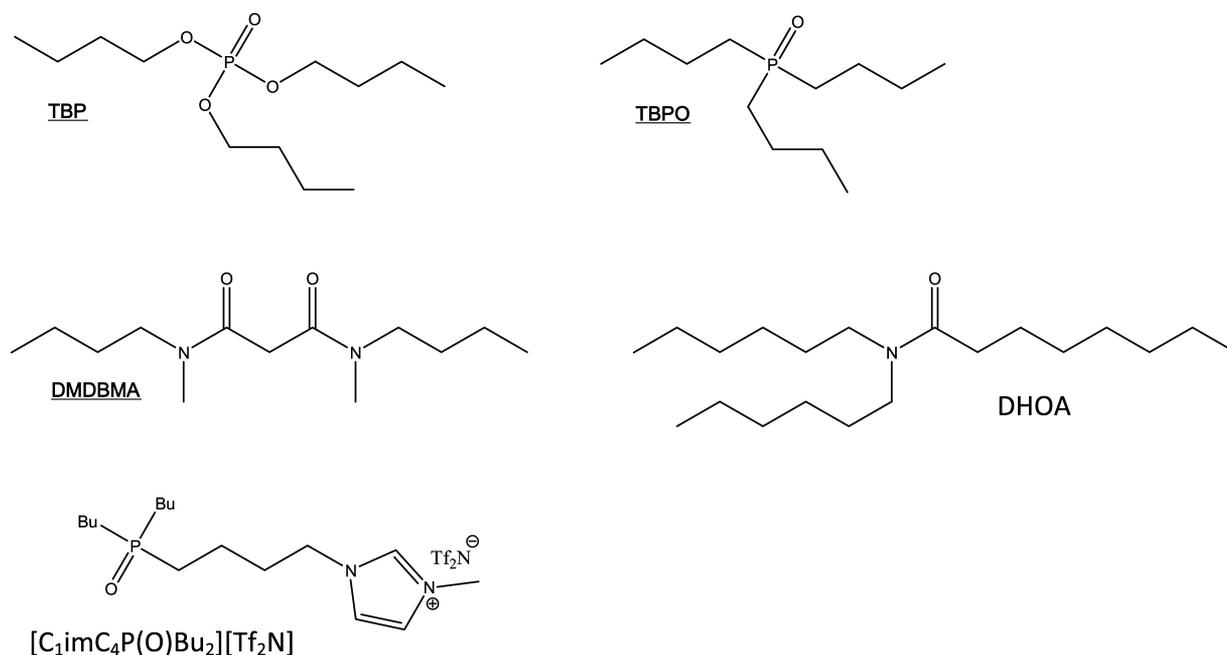
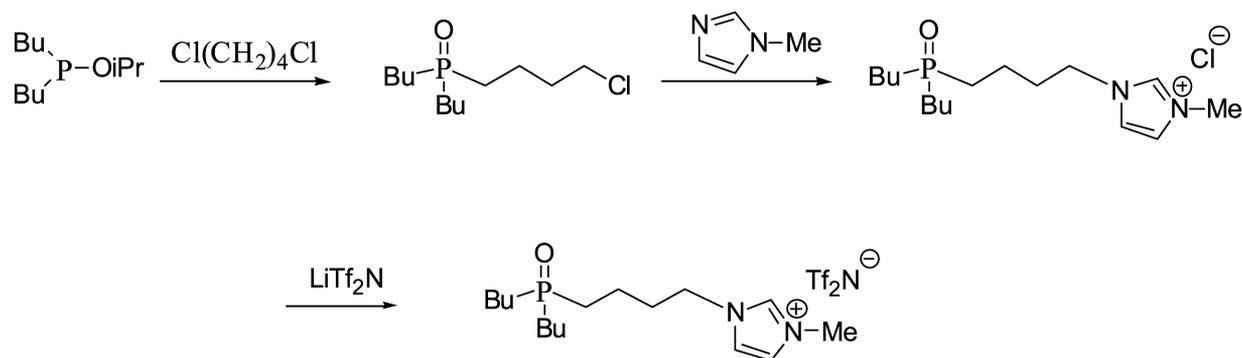
solvation properties have unexpected (as compared to those of molecular solvents) extraction mechanisms, based on cation/anion exchanges, ion-pair formation, and so forth.^{21,22} A way to tackle the undesired aqueous-phase pollution these ionic exchanges imply is toggling from an ion-exchange to ion-pairing mechanism,²³ hopefully maintaining the high extraction efficiencies for which ILs are famous. However, we believe that the search for ion-pairing extraction as a way to solve the problem of the solubility of ILs in aqueous phases is a misstated problem. This opinion is grounded on the fact that ILs being composed of ions, bringing them in contact with aqueous phases, even in the absence of metallic ions to be extracted, will unavoidably lead to partial solubility of water and any other component of the aqueous phase into the IL phase and to partial solubility of all of the species present in the IL phase, including the cations and anions of the IL. Two previous studies have examined the effect of added spectator ions²⁴ and salts having an ion in common with the IL of interest,²⁵

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Scheme 1. Chemical Structures of the Ligands in This Work

Scheme 2. $[C_1imC_4P(O)Bu_2][Tf_2N]$ Synthesis

showing that the main process of IL solubilization is ion exchange, leading to differences in the solubilities of the cations and anions of the ILs. The present work investigates the impact of several classical neutral ligands, such as tributylphosphate, tributyl phosphine oxide, and *N,N'*-dimethyl-*N,N'*-dibutylmalonamide, together with some less common ones. Our results confirm and extend these previous results, showing that ion exchange is the rule rather than the exception in such complex systems.

2. EXPERIMENTAL SECTION

2.1. Chemicals. The following short names will be used throughout this work: TBP for tributyl phosphate, TBPO for tributylphosphine oxide, DMDDBMA for *N,N'*-dimethyl-*N,N'*-dibutylmalonamide, DHOA for *N,N'*-dihexyloctanamide, and $[C_1imC_4P(O)Bu_2][Tf_2N]$ for 1-methyl-3-[4-(dibutylphosphinoyl)butyl]-3*H*-imidazol-1-ium bis(trifluoromethylsulfonyl)imidate. Scheme 1 shows the chemical structures of all of these compounds.

TBPO was purchased from Aldrich (95%). DHOA was provided by the Heavy Water Plant, Tuticorin, India. This ligand was vacuum-distilled before use, and the purity was checked by elemental analysis, NMR, and distribution ratio

measurements (by comparison with the reported distribution ratios for U and Pu²⁶). DMDDBMA was synthesized according to a published procedure.²⁷ 1-Methyl-3-butylimidazolium bis(trifluoromethanesulfonyl)imide, further denoted $[C_1C_4im][Tf_2N]$, was purchased from Solvionic, France (99.5% purity). Nitric and perchloric acids, deuterated or not, and D₂O were purchased from Sigma-Aldrich.

$[C_1imC_4P(O)Bu_2][Tf_2N]$ was synthesized as follows (see Scheme 2). Briefly, the synthesis of $[C_1imC_4P(O)Bu_2][Tf_2N]$ started with the Arbuzov reaction of 1,4-dichlorobutane with isopropyl-dibutylphosphinite giving the corresponding dibutyl-(4-chlorobutyl) phosphine oxide. At the next stage, 3-methylimidazole was alkylated with dibutyl-(4-chlorobutyl)-phosphine oxide; thus, dibutyl-4-(3-methylimidazolium)-butylphosphine oxide chloride ($[C_1imC_4P(O)Bu_2][Cl]$) was formed. The metathesis with LiTf₂N converted the chloride into bis(trifluoromethanesulfonyl)imide ($[C_1imC_4P(O)Bu_2][Tf_2N]$).

2.1.1. 4-Chlorobutyl-dibutylphosphine Oxide. The mixture of 1,4-dichlorobutane (40 mL, 0.365 mol) and isopropyl-dibutylphosphinite (5 g, 0.024 mol) was heated and stirred at 100 °C for 4 h. After vacuum evaporation of the excess of dichlorobutane, the residual liquid was distilled fractionally

under reduced pressure (0.01 mmHg). The fraction with boiling point 120–124 °C was collected (5.28 g, yield 87%).

^1H NMR (300.130 MHz, CDCl_3): δ 0.78 (t, 6H, $J = 7.5$ Hz, $-\text{CH}_2-\text{CH}_3$); 1.24–1.34 (m, 4H, $-\text{CH}_2-\text{CH}_2-\text{CH}_3$); 1.34–1.46 (m, 4H, $-\text{CH}_2-\text{CH}_2-\text{CH}_3$); 1.52–1.62 (m, 8H, P- CH_2-CH_2 and $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Cl}$); 1.69–1.79 (m, 2H, $-\text{CH}_2-\text{CH}_2-\text{Cl}$); 3.43 (t, 2H, $J = 6.3$ Hz, $-\text{CH}_2-\text{CH}_2-\text{Cl}$).

^{31}P NMR (121.421 MHz, CDCl_3): δ 50.7.

2.1.2. 1-Methyl-3-[4-(dibutylphosphinoyl)butyl]-3H-imidazol-1-ium Bis(trifluoromethylsulfonyl)imide. The mixture of 4-chlorobutyl-dibutylphosphine oxide (3 g, 0.012 mol) and 3-methylimidazole (1.1 mL, 0.013 mol) was heated in a sealed Pyrex ampule at 110 °C for 48 h. After cooling to room temperature, the ampule was opened and the crystalline imidazolium chloride was dissolved in water (30 mL). Then lithium bis(trifluoromethylsulfonyl)imide (3.7 g, 0.013 mol) was added and the reaction mixture was left for 12 h at 40 °C. The IL was extracted with dichloromethane (2×30 mL). The combined organic phases were washed with deionized water (7×30 mL) and evaporated under reduced pressure. The light brown liquid was dissolved in ethanol and decolorized with 0.5 g of activated charcoal. After filtration of charcoal, the solvent was evaporated and the product was dried under high vacuum. The spectral pure IL of light lemon color was obtained (5 g, total yield 72.5%).

^1H NMR (300.130 MHz, CDCl_3): δ 0.93 (t, 6H, $J = 7.5$ Hz, $-\text{CH}_2-\text{CH}_3$); 1.38–1.55 (m, 8H, $-\text{CH}_2-\text{CH}_2-\text{CH}_3$); 1.67–1.77 (m, 8H, P- CH_2-CH_2- and $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}$); 2.04–2.15 (m, 2H, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}$); 3.93 (s, 3H, N- CH_3); 4.24 (t, 2H, $J = 7.2$ Hz, $-\text{CH}_2-\text{N}$); 7.30 (s, 1H, C_5H in Im); 7.44 (s, 1H, C_4H in Im); 8.93 (s, 1H, N= $\text{CH}-\text{N}$).

^{31}P NMR (121.421 MHz, CDCl_3): δ 50.0.

2.2. Sample Preparation and NMR Measurements.

The IL was carefully degassed following a well-defined procedure²⁸ before sample preparation. All of the ligands were added by weight. The concentrations were set at 0.04 M (TBPO), 0.05 M (DMDBMA), 0.1 M ($[\text{C}_1\text{imC}_4\text{P}(\text{O})\text{Bu}_2][\text{Tf}_2\text{N}]$), and 1.1 M (DHOA). These values have been chosen in accordance with extraction experiments: U(VI) extracted with DMDBMA²⁹ or $[\text{C}_1\text{imC}_4\text{P}(\text{O})\text{Bu}_2][\text{Tf}_2\text{N}]$,³⁰ Ce(III) or In(III) extracted with TBPO,^{31,32} and Pu(IV) extracted with DHOA.³³

Equal volumes (ca. 0.8 mL) of the IL solution containing the ligand and of the acidified aqueous phase were mixed by mechanical shaking for 1 h and then centrifuged (1500 rpm). The upper phase (i.e., water-rich phase²⁵) was separated and analyzed to derive the $\text{C}_1\text{C}_4\text{im}^+$ and Tf_2N^- concentrations. Unless specified otherwise, the temperature was set to 21 ± 2 °C.

For TBPO, DMDBMA, $[\text{C}_1\text{imC}_4\text{P}(\text{O})\text{Bu}_2][\text{Tf}_2\text{N}]$ with nitric acid and for perchloric acid alone (no ligand), the NMR spectrometer was identical to that previously used (Bruker 300 MHz, equipped with a 5 mm quadrupole nucleus probe).²⁵ For the DHOA experiments, the cation and anion concentrations in the aqueous phases were determined on a Bruker Avance III 400 MHz NMR spectrometer equipped with a 5 mm broadband observe probe at 298 K. The NMR spectra were recorded with a 30° excitation pulse. All acquisition parameters are indicated in Table 1. For ^1H NMR, the frequency was 400.15 MHz and the spectral window was 0–15 ppm. For ^{19}F NMR, the frequency was 376.52 MHz and the spectral window was -50 to -180 ppm. Apart from this, the experimental NMR protocol was strictly identical to that

Table 1. Acquisition Parameters for the DHOA Samples

nucleus	number of scans	delay (s)	acquisition time (s)
^1H	32	22	2.71
^{19}F	150	0.45	2.75

previously published in ref 25, in particular, the internal standards used. The detection limit was 2 mM for both $\text{C}_1\text{C}_4\text{im}^+$ and Tf_2N^- , and the uncertainties were equal to 10% (IL cation) and 5% (IL anion).

2.3. Titration. The equilibrium concentration of H^+ in the aqueous (upper) phase ($[\text{HNO}_3]_{\text{init}} = 0.3$ M) after it came in contact with $[\text{C}_1\text{C}_4\text{im}][\text{Tf}_2\text{N}]$ phases, in which increasing concentrations of TBPO were dissolved (from 0 to 0.5 M), has been measured with an automatic titrator (titroline, Schott; error: $\pm 2\%$). Similar experiments were performed for $[\text{C}_1\text{imC}_4\text{P}(\text{O})\text{Bu}_2][\text{Tf}_2\text{N}]$ (ligand concentration range: 0–0.3 M) at $[\text{HNO}_3]_{\text{init}} = 0.296$ M. As regards the titration experiments using DHOA, 2 mL of 1 M DHOA solution in the IL was equilibrated with an equal volume of $\text{H}_2\text{O}/\text{HNO}_3$ (0.1–4 M acid). After centrifugation for 2 min, 1 mL of the IL phase was taken in a 100 mL conical flask containing 9 mL of neutralized ethanol (to which a phenolphthalein indicator was added) and 15 mL of deionized water was added. The mixture was titrated with standard alkali. These studies were carried out at 24 °C, and the measurements were performed in duplicate.

3. RESULTS AND DISCUSSION

Data are presented in terms of the ion concentration of the IL, $[\text{C}_1\text{C}_4\text{im}^+]$ and $[\text{Tf}_2\text{N}^-]$, as a function of the initial DNO_3 or DClO_4 concentrations and also, whenever necessary to the discussion, as the solubility product, defined as $[\text{C}_1\text{C}_4\text{im}^+] \times [\text{Tf}_2\text{N}^-] = k_s$, as a function of $[\text{DNO}_3]$. Figure 1 displays the $\text{C}_1\text{C}_4\text{im}^+$ and Tf_2N^- concentration variations in the absence of ligand and by use of DClO_4 , together with DNO_3 , using published values, for comparison purposes. Figure 2 shows the DHOA data for $\text{C}_1\text{C}_4\text{im}^+$ and Tf_2N^- as a function of $[\text{DNO}_3]$ (log scale on the y axis). For DMDBMA, TBPO, and

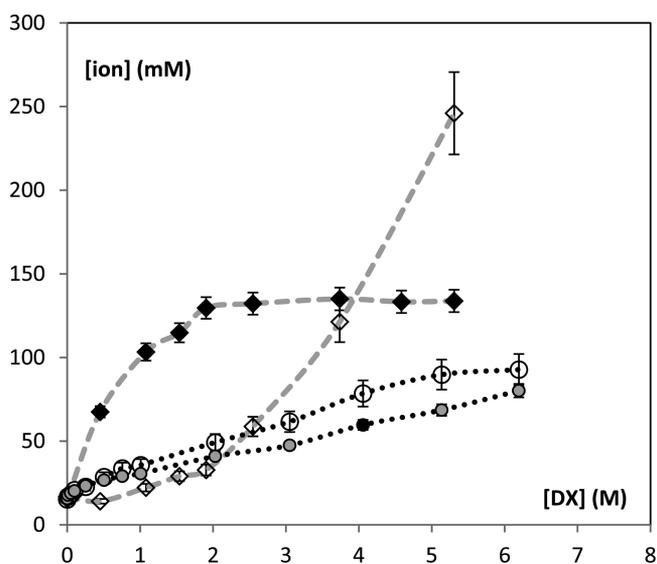


Figure 1. $[\text{Tf}_2\text{N}^-]$ and $[\text{C}_1\text{C}_4\text{im}^+]$ concentrations, in the absence of ligand, as a function of the initial acid concentration, $[\text{DX}]$. With DNO_3 : Tf_2N^- (●) and $\text{C}_1\text{C}_4\text{im}^+$ (○). With DClO_4 : Tf_2N^- (◆) and $\text{C}_1\text{C}_4\text{im}^+$ (◇). Dotted and solid lines are guides for the eye.

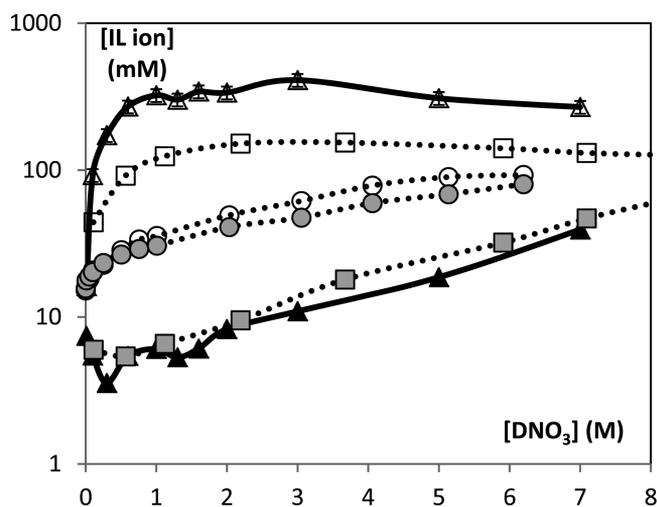


Figure 2. $[\text{Tf}_2\text{N}^-]$ and $[\text{C}_1\text{C}_4\text{im}^+]$ concentrations as a function of initial DNO_3 concentration. Without ligand: Tf_2N^- (●) and $\text{C}_1\text{C}_4\text{im}^+$ (○). With 1.1 M DHOA: Tf_2N^- (▲) and $\text{C}_1\text{C}_4\text{im}^+$ (△). With 1.1 M TBP: Tf_2N^- (■) and $\text{C}_1\text{C}_4\text{im}^+$ (□). Uncertainties are of the size of the symbols (see $\text{C}_1\text{C}_4\text{im}^+$ data with DHOA (△) as an example). Dotted and solid lines are guides for the eye.

$[\text{C}_1\text{imC}_4\text{P}(\text{O})\text{Bu}_2][\text{Tf}_2\text{N}^-]$, the $\text{C}_1\text{C}_4\text{im}^+$ and Tf_2N^- values as a function of $[\text{DNO}_3]$ are displayed in Figures 3 and 4,

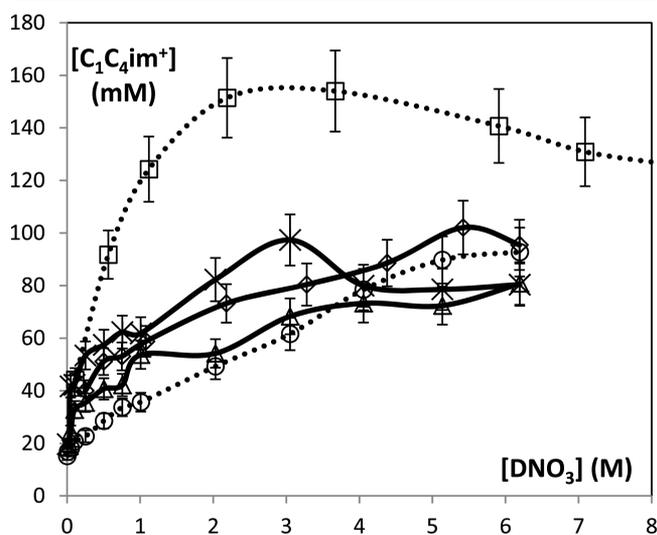


Figure 3. $\text{C}_1\text{C}_4\text{im}^+$ concentration variations as a function of initial DNO_3 concentration in the aqueous phase. □: TBP 1.1 M; *: $[\text{C}_1\text{imC}_4\text{P}(\text{O})\text{Bu}_2][\text{Tf}_2\text{N}^-]$, 0.1 M; ◇: DMDBMA 0.05 M; △: TBPO 0.04 M; ○: no ligand added. Dotted and solid lines are guides for the eye.

respectively (log scale for the y axis in Figure 4, for clarity reasons). For comparison purposes and because the concentration of ions from the IL varies over a large range, namely, from ca. 5 to 400 mM, Figures 2–4 also display the already published values obtained for 1.1 M TBP and/or in the absence of ligand.^{34,35} Titration results are shown in Figure 5a for TBPO and $[\text{C}_1\text{imC}_4\text{P}(\text{O})\text{Bu}_2][\text{Tf}_2\text{N}^-]$ and in Figure 5b for DHOA. Finally, the k_s variations (DNO_3 case) are shown in Figure 6 for DMDBMA, TBPO, and TBP and without ligand. The new data presented in this work correspond to both $[\text{C}_1\text{C}_4\text{im}^+]$ and $[\text{Tf}_2\text{N}^-]$ values in DClO_4 (no ligand added)

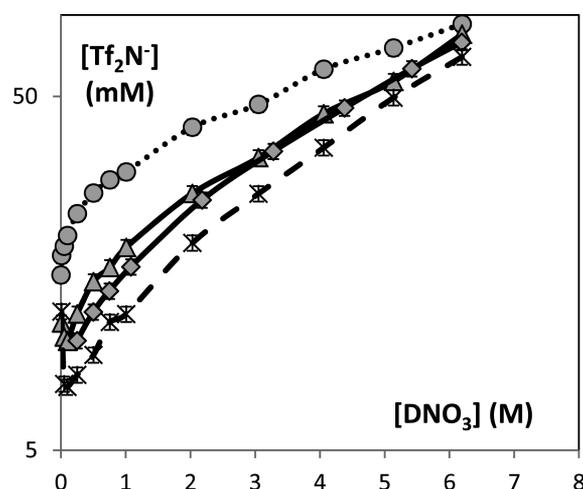


Figure 4. Tf_2N^- concentration variations as a function of initial DNO_3 concentration in the aqueous phase. *: $[\text{C}_1\text{imC}_4\text{P}(\text{O})\text{Bu}_2][\text{Tf}_2\text{N}^-]$, 0.1 M; ◇: DMDBMA 0.05 M; ▲: TBPO 0.04 M; ●: no ligand added. Dotted and solid lines are guides for the eye.

and in DNO_3 for TBPO, DMDBMA, DHOA, and $[\text{C}_1\text{imC}_4\text{P}(\text{O})\text{Bu}_2][\text{Tf}_2\text{N}^-]$ additions.

We recall that in the nitric acid concentration range 0–0.5 M and in the absence of ligand the solubilities of cations and anions are identical, within experimental uncertainties.²⁵ They increase as a function of acid concentration, starting from 15 mM at $[\text{DNO}_3] = 0$ M up to 28 mM at $[\text{DNO}_3] = 0.5$ M (average of the cation and anion values; see Figure 1 and Table 2). Above 2 M and up to ca. 5 M DNO_3 , the cation and anion concentrations differ by ca. 20 mM, a value which is significant as regards the experimental uncertainty, and finally tend to converge above 5 M DNO_3 . Figure 1 illustrates the drastic impact of the nature of acid on the cation and anion variations, in the absence of ligand. The values obtained in the present work for $[\text{C}_1\text{C}_4\text{im}^+]$ in the presence of DClO_4 match very well with those already published for this ion,³⁵ under identical chemical conditions. Our results can also be compared to solubility data obtained at low acid concentration (pH in the range 0.5–5, using DClO_4), without ligand and in the presence of increasing amounts of NaClO_4 .²⁴ Some of these experimental data are collected in Table 2. Data in Figure 1 and Table 2 confirm that without ligand and acid the aqueous solubilities of Tf_2N^- and $\text{C}_1\text{C}_4\text{im}^+$ are identical (ca. 16 mM). They also evidence an impact of the concentration and nature of the acid (DNO_3 vs DClO_4) and also an effect of changing H^+ into Na^+ .

Turning to data in the presence of added ligands, in Figure 2, the effect of addition of 1.1 M DHOA (as compared to that of 1.1 M TBP) on the $\text{C}_1\text{C}_4\text{im}^+$ concentration is striking, whereas the effect on the Tf_2N^- concentration is almost identical to that of 1.1 M TBP. At very high nitric acid concentration, cation and anion concentrations for DHOA and TBP seem to converge toward a single value at ca. 100 mM, toward which the data in the absence of ligand also apparently converge.

As presented in Figures 3 and 4, the addition of 0.04 M TBPO, 0.05 M DMDBMA, or 0.1 M $[\text{C}_1\text{imC}_4\text{P}(\text{O})\text{Bu}_2][\text{Tf}_2\text{N}^-]$ has a much smaller effect on the solubilities of $\text{C}_1\text{C}_4\text{im}^+$ and Tf_2N^- : the values are close to those obtained in the absence of ligand. This could be ascribed, at least in part, to the rather low concentrations of these ligands as compared to the DHOA and TBP concentrations. However, there is a significant difference

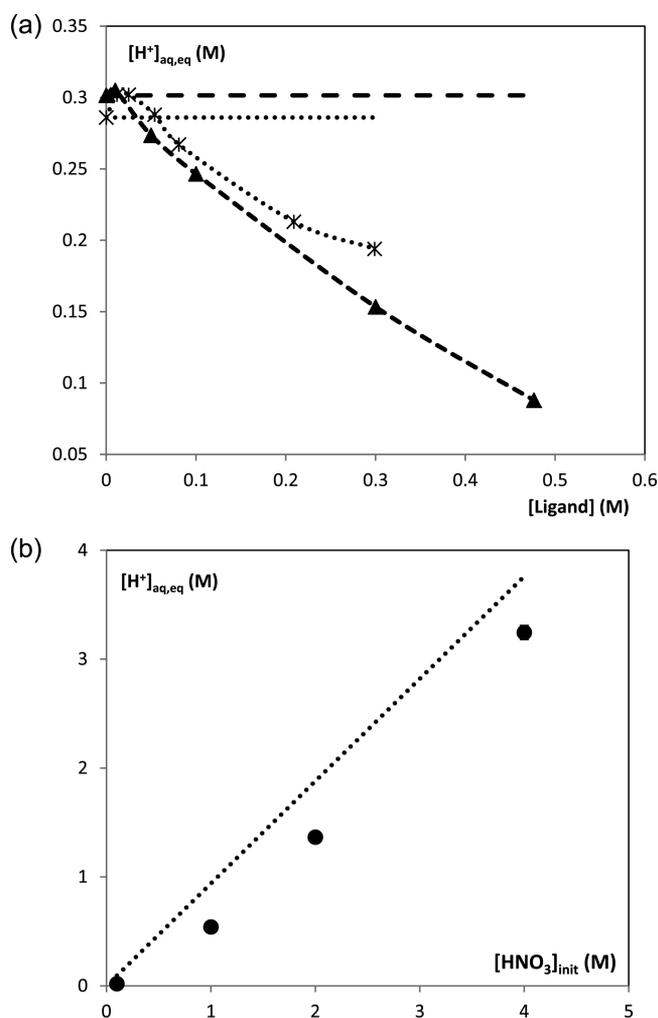


Figure 5. (a) Equilibrium H^+ concentrations in the aqueous (upper) phase when it came in contact with an acidic aqueous solution and $[C_1C_4im][Tf_2N]$ containing increasing concentrations of the ligand. \blacktriangle : TBPO; $*$: $[C_1imC_4P(O)Bu_2][Tf_2N]$. Horizontal dashed and dotted lines: 94% of the initial HNO_3 concentrations for the TBPO and $[C_1imC_4P(O)Bu_2][Tf_2N]$ cases, respectively. (b) Equilibrium H^+ concentrations in the aqueous (upper) phase when came into contact with an acidic aqueous solution of increasing acidity and $[C_1C_4im]-[Tf_2N]$ containing 1 M DHOA. Symbols: experimental data. Dotted line: 94% of the initial nitric acid concentration, no ligand protonation according to eq 2 (or 2bis). Uncertainties are of the size of the symbols.

between the solubilities of cations and anions, whatever the ligand is. Up to ca. 5 M, all anion values are significantly below those obtained in the absence of ligand, whereas all cation values are above or very close to the data in the absence of ligand. To further illustrate this difference, Table 3 collects the solubilities of cations and anions for DHOA, TBPO, and $[C_1imC_4P(O)Bu_2][Tf_2N]$ at $[DNO_3] = 0.01$ M and also data in the absence of ligand, for comparison purposes. As can be seen, the solubilities of cations at 0.01 M DNO_3 are more or less equal for all three ligands (average of 18 mM) and close to those in the absence of ligand. Conversely, a significant difference in the solubility of anions is observed upon addition of DHOA (7 mM), as compared to that in the case of TBPO or $[C_1imC_4P(O)Bu_2][Tf_2N]$ (average: 12 mM). One should not ascribe these results solely to the different ligand concentrations used because 1.1 M DHOA or TBP exhibits very different

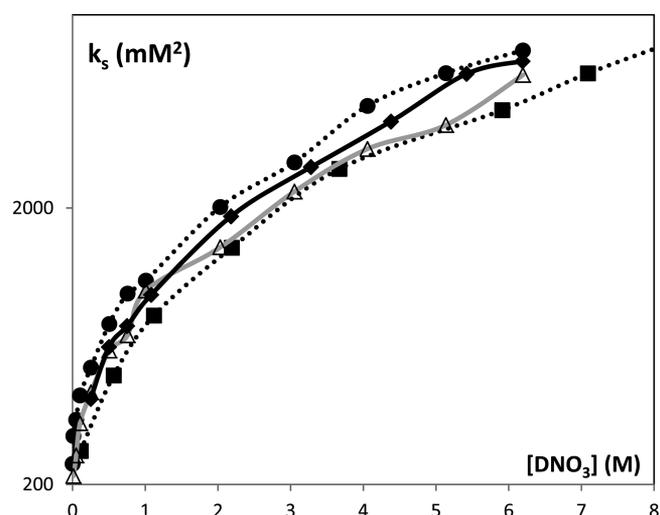


Figure 6. k_{s1} variations as a function of initial DNO_3 concentration in the aqueous phase. \bullet : no ligand added; \blacklozenge : DMDDBMA 50 mM; \triangle : TBPO 40 mM; \blacksquare : TBP 1.1 M. Dotted and solid lines are guides for the eye.

Table 2. Solubilities of Cations and Anions in the Absence of Ligand, for Two Concentrations Each of DNO_3 , $DClO_4$, and $NaClO_4$

acid/salt (M)	$[C_1C_4im^+]$ (mM)	$[Tf_2N^-]$ (mM)
$[DNO_3] = 0$	15 ^b	16 ^b
$[DNO_3] = 0.5$	29 ^b	27 ^b
$[DClO_4] = 0$	17 ^a	16 ^a
$[DClO_4] = 0.45$	14 ^a	68 ^a
$[NaClO_4] = 0$	16 ^c	17 ^c
$[NaClO_4] = 0.4$	<2 ^c	40 ^c

^aThis work. ^bRef 25. ^cRef 24.

Table 3. Solubilities of Cations and Anions for Several Ligands, at $[DNO_3] = 0.01$ M^a

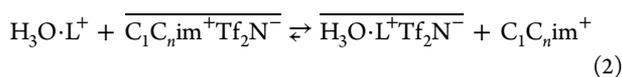
ligand	$[DNO_3]$ (M)	$[C_1C_4im^+]$ (mM)	$[Tf_2N^-]$ (mM)
no ligand	0	15	16
	0.01	17	18
DHOA 1.1 M	0.01	16	7
TBPO 40 mM	0.01	19	11
$[C_1imC_4P(O)Bu_2][Tf_2N]$ 0.1 M	0.01	20	12

^aData in the absence of ligand are from ref 25.

influences on the $[C_1C_4im^+]$ solubilities. Conversely, ligands from different chemical families, used at roughly the same concentration (TBPO and DMDDBMA), provide similar trends.

A few other groups have already observed such phenomena.^{36,37} Gutowski et al.³⁷ evidenced differences in the solubilities (as quantified through distribution ratios) of $C_1C_4im^+$ and Cl^- in the biphasic system arising from coming in contact with water, K_3PO_4 salt, and $[C_1C_4im][Cl]$. In this case, a phosphate salt is used instead of our organic ligands, but still this combination of chemicals induces different distribution ratios for $C_1C_4im^+$ and Cl^- in the salt-rich phase, although these ions have been introduced together, under exactly identical quantities. Rickert and collaborators³⁶ have first studied samples composed of several imidazolium-based ILs ($[C_1C_nim][Tf_2N]$, $n = 5, 8, \text{ and } 10$), nitric acid (1 M, fixed),

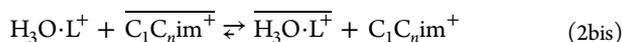
and a crown-ether ligand, dicyclohexano-18-crown-6, hereafter denoted DCH18C6. For their analysis, they only measured the solubility of $C_1C_nim^+$ and observed an increase in the aqueous solubility of $[C_1C_nim^+]$ with the concentration of several ligands. For example, the solubility in the aqueous phase for $C_1C_5im^+$ increases from 10^{-3} to 3×10^{-2} M as DCH18C6 varies from 10^{-2} to 0.31 M, whereas for 1.1 M TBP and 1 M nitric acid, $[C_1C_5im^+] = 50$ mM was obtained (data are corrected from the effect in the absence of ligand). Because of a large difference in ligand concentration (above 0.1 vs 0.04 M), data for TBPO from the two works cannot be easily compared. On the basis of their cation solubility data, Rickert et al. proposed a chemical model involving ligand protonation in the aqueous phase, followed by cation exchange between the aqueous protonated form of the ligand and the IL cation, $C_1C_nim^+$, as³⁶



where bars over the species correspond to those present in the IL phase and L stands for the crown ether. This proposal calls for three comments.

First, although the ligands of this work belong to several chemical families (phosphate: TBP, phosphine oxide: TBPO and $[C_1imC_4P(O)Bu_2][Tf_2N]$, amide: DHOA, and diamide: DMDBMA but also neutral (TBP, TBPO, DMDBMA, and DHOA) and ionic ligands ($[C_1imC_4P(O)Bu_2][Tf_2N]$)), they all can behave as acid extractants and thus follow eq 2. This is well known for TBP³⁸ and several tetraalkylmalonamides^{39–41} in molecular solvents as well. In the case when ILs are used as diluents, it has been repeatedly pinpointed that large amounts of water and H^+ are transferred to the IL phase when it came into contact with acidic aqueous solutions. For H_2O/HNO_3 in contact with $[C_1C_4im][Tf_2N]$, ca. 94% of the H^+ ions remain in the aqueous phase in the absence of ligand^{29,42} and an additional transfer of H^+ has been observed in the presence of TBP³⁵ and DMDBMA.²⁹ This is confirmed in this work for TBPO, $[C_1imC_4P(O)Bu_2][Tf_2N]$, and DHOA (see Figure S5a,b).

Second, written as such, the two species $C_1C_nim^+Tf_2N^-$ and $H_3O^+LTf_2N^-$ should be considered as neutral entities although the positions of the charges are indicated. Conductivity studies^{43,44} clearly show that imidazolium-based ILs are partially dissociated. Therefore, there is no reason to retain either neutral or dissociated forms in eq 2, but we nevertheless consider that, whenever possible, one would better avoid neutral moieties. Thus, we suggest rewriting eq 2 as

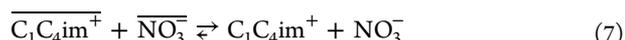
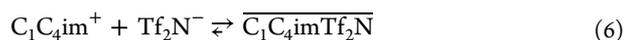


This form of eq 2, however, is still equivocal. As the ILs are water-saturated, water- or IL-separated ion pairs could be envisioned too. By analogy with the case of water, the protonated ligand indicated on the right-hand side of eq 2bis could also be written simply as $H_3O^+ + L$. These remarks are not merely typographical games but underline the impossible task of clearly representing the exact state of species in ILs.

Finally, and more importantly, this model assumes that the Tf_2N^- anions do not transfer to the aqueous phase, which is in clear contradiction with our data. We consider the ligand protonation, as first suggested by Rickert and co-workers, to

apply in our systems, but it should be completed by a description of the Tf_2N^- anion transfer.

Under the very high acidic conditions in this work, the fate of Tf_2N^- is impacted by several phenomena that are briefly discussed below. The acid association constant of HTf_2N in the aqueous phase is one of those, but a quantitative estimate of its importance would require a firm assessment of the pK_a value, as different values can be found in the literature: $pK_a = 1.2^{45}$ or 0.16.⁴⁶ To the best of our knowledge, the solubility of HTf_2N in ILs has not been investigated in detail, but there are indications that this could be important.³⁵ Then, one may also consider the transfer of Tf_2N^- to the aqueous phase as an anion exchange with NO_3^- and, last but not the least, the solubility of the ion pair $C_1C_4imTf_2N$. In addition to these chemical reactions directly implying the Tf_2N^- anion, one should not forget the aqueous solubility of the $[C_1C_4im][NO_3]$ IL and its association (in water) as well as the nitric acid association in water,⁴⁷ which modify the total ionic strength and effect the reactions listed above. All of these chemical processes can be described through the following equations



Although this set of seven additional equations, together with eq 2 (or 2bis), may appear reasonable in the sense that all of the mechanisms listed above do contribute to the observed experimental solubility values, it is clear that it cannot lead to a quantitative analysis of the data. Too many of the related equilibrium constants are unknown, and taking into account ionic-strength corrections is also very difficult. Furthermore, the chemical equations are interconnected, so it seems impossible to deduce qualitative trends. This theoretical impossibility is complemented with analytical problems. The equations above imply the presence of both associated and dissociated forms of the two acids (HNO_3 and HTf_2N) and a salt ($C_1C_4imNO_3$) in the aqueous phase, but the NMR (anions and cations of ILs) and titration (proton) data correspond to the overall ion concentrations, without being able to distinguish between free entities or associated ones. Thus there is some uncertainty on what is actually measured by titration and NMR. The very high ionic strength of our samples together with the rather low amounts of some of the ions/entities involved (IL ions in the range of 1 mM to 100 M) renders a precise analytical followup of the samples almost impossible. In particular, the uncertainties and detection limits of H^+/D^+ titration cannot match the uncertainties obtained by NMR for the cation and anion concentrations. Therefore, experimentally deciphering the multiple ion exchanges and transfers of all possible neutral couples (D^+ with NO_3^- and/or $C_1C_4im^+$ with Tf_2N^-), as listed in eqs 2–9, appears to be an almost impossible task in the absence of ligand. In case a ligand is added, the same experimental problems hold, and the situation is even more

intricate. For large ligand concentrations, such as those used for DHOA and TBP, the IL phase properties (viscosity, density, aqueous solubility, water loading maximum capacity, etc.) are modified in a manner hard to predict. For all of these reasons, we consider a quantitative theoretical description of the experimental data of this work to be out of our reach at the moment.

Another tentative approach to the data can be envisioned by considering the solubility product, k_s , as a function of acid concentration, as illustrated in Figure 6 (no ligand, TBP, TBPO, and DMDBMA). Although Figure 6 would indicate a general increasing trend, we do not think that this manner of considering the data is fruitful. As stressed above, the NMR data are unable to distinguish between associated and free cations or anions, so the k_s values as plotted in Figure 6 do not correctly represent the complexity of the system.

We,²⁴ and others,^{7,36} already pinpointed the problem raised by the solubilities of the IL components in aqueous phases as regards liquid/liquid extraction, a problem also connected to the question of IL recyclability.⁴⁸ As evidenced in this work, ion solubilities obey complex rules and are highly sensitive to chemical conditions. Therefore, it would be important to identify ways to drastically reduce or suppress them, if ever possible. On the constraint of maintaining an IL phase in the extraction system, few possibilities can be envisioned. Some authors have shed light on task-specific (TS) ILs, suggesting that these compounds could overcome the problem of aqueous phase pollution by IL components.⁴⁹ As demonstrated in our work for the $[C_{1}imC_4P(O)Bu_2][Tf_2N]$ case, this is not true if TSILs are used as solutes in an IL diluent. Therefore, TSILs should be used as pure phases, which, in many cases, is difficult because of their high viscosity. Another possibility might be to dissolve TSIL in molecular solvents,^{50–52} but in this case, the advantage of “green chemistry”, very often put forward to emphasize the interest in ILs and TSILs for metal extraction, fades away. Furthermore, to the best of our knowledge, the amount of IL ions dissolving in the aqueous phase of such systems has not been investigated. Another idea could be to use a diluent from which the dissolved IL components are easily eliminated. So far, supercritical CO_2 is the only diluent corresponding to this definition,⁵³ while offering appealing extraction efficiencies of metal ions.^{54–56}

4. CONCLUSIONS

New data on the aqueous solubilities of $C_1C_4im^+$ and Tf_2N^- as a function of the nature and concentration of ligands have been obtained. They evidence the great complexity of systems composed of acidic aqueous phases in contact with (ligand + IL) phases. In particular, a comprehensive understanding of the difference in the solubilities of IL cations and anions would require a minute analytical examination of phase composition at equilibrium, but this is rather difficult, if not impossible. Our data emphasize the difficulty in determining the ecological toxicity of ILs. One should also take into account the differences in the solubilities of cations and anions, depending on the nature of the aqueous phases in which they are prone to dissolve. On an applied perspective, these results raise additional concerns about the use of ILs. However, we would like to stress that this is not a definitive condemnation of ILs for two main reasons. First, a quantitative limit to what are considered as “acceptable” and “unacceptable” solubilities should be defined and is certainly dependent on the chemical structure of anions and cations. This difficult balance between

advantages and disadvantages should not consider only toxicity arguments. ILs are known to be very efficient extracting phases, after all, so they also provide benefits in terms of environmental safety, excluding economic concerns. For example, Janssen and co-workers note that “it is easy to imagine situations (e.g., the extraction of nuclear materials) in which this contamination represents a relatively minor inconvenience”.⁵⁷

On a more fundamental point of view, many metal-extraction mechanisms toward ILs obey an ion-exchange process,⁵⁸ therefore involving aqueous-phase pollution. It has been proposed that a means to counteract such an undesirable consequence of efficient metal-ion extraction would be to look for ion pairing as the dominant extraction process. However, this cannot solve the general question of ion solubilities of ILs, at least for the very low metal concentrations (in the range of traces up to ca. 10^{-4} M) that are used in fundamental works. This is because for the range of ligand concentration commonly used (from 1 M TBP to tens of mM DMDBMA, for instance), the “natural” (i.e., in the absence of metal) solubilities as evidenced in our work are at least ca. 2 orders of magnitude above those possibly avoided by the ion-pairing mechanism. Conversely, in case large amounts of metallic ions are used, there are chances that the solubilities of the IL components are largely different from those observed in the present work. Some indications are already found in the literature evidencing large effects of “spectator ions”²⁴ and metal counterions.⁵⁹

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Notes

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