DETERMINATION OF pK_{aIL} VALUES OF THREE CHELATING EXTRACTANTS IN ILs. CONSEQUENCE ON EXTRACTION PROCESS OF 4f-ELEMENTS

Maria Atanassova^{a,b} and Isabelle Billard^{a*}

^aInstitut Pluridisciplinaire Hubert Curien, UMR7178, Radiochimie, Rue du Loess 23, 67037
Strasbourg Cedex, France, E-mail: isabelle.billard@iphc.cnrs.fr

^bUniversity of Chemical Technology and Metallurgy, Department of General and Inorganic
Chemistry, 8 Kliment Okhridski blvd., 1756 Sofia, Bulgaria

Abstract Aqueous–ionic liquid (A–IL) biphasic systems have been examined in terms of water and acid solubilities in the IL-rich phase at ambient temperature. First, the biphasic mixtures were composed of acids of various concentrations (HCl, HNO₃, HClO₄ from 10⁻² to 10⁻⁴ M mainly) and four ionic liquids of the imidazolium family [C₁C_nim⁺][Tf₂N⁻], (n = 4, 6, 8 and 10). The effect of ionic strength (μ = 0.1 M, by use of NaCl, NaNO₃ or NaClO₄, according to the acid investigated), the nature of the IL cation as well as the nature of the acid on the mutual solubilities of (H₂O, H⁺, C₁C_nim⁺ and Tf₂N⁻) entities were determined. Then, three chelating compounds (HL), which belong to the β -diketone family (thenoyltrifluoroacetone (HTTA), 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (HP) and 4-benzoyl-3-phenyl-5-isoxazolone (HPBI)), were added to [C₁C₄im⁺][Tf₂N⁻], and subsequent determination of the H⁺ distribution between the two phases allowed the determination of their dissociation constants (pK_{aIL}) in the water-saturated ionic liquid phase. A very strong effect of the IL cation onto the HTTA pK_{aIL} value was observed from n = 4 to n = 10. The influence of this phenomenon on lanthanide extraction process is discussed.

Keywords Ionic liquids, Imidazolium, Tf₂N⁻, β -diketones, pK_a

1 Introduction

The first study of division of a substance between two immiscible solvents was carried out by Berthelot and Jungfleish in 1872 [1] and Nernst (1891) who were among the first to examine the partition coefficient as a purely physicochemical phenomenon. These scientists accurately measured the amounts present at equilibrium of both I₂ and Br₂ when distributed between CS₂ and water. They also measured the quantity of various organic acids, H₂SO₄, HCl and NH₃ when distributed between ethyl ether and water [2]. Recently Nash and Grimes [3] studied the acid dissociation constants for diethylenetriamine-N,N,N',N'',N'''-pentaacetic acid (DTPA), an octadentate aminopolycarboxylate complexing agent whose f-element complexes have found applications in diverse fields including nuclear fuel separation. The neutral DTPA molecule is pentabasic (H₅DTPA) in solution, though it has eight potential sites for H⁺ or metal ion association and three of the pK_a values are < 2 [3]. Safavi et al. [4] investigated the role of ionic liquids (ILs) in tuning the pK_{aw} values of two sulfonated indicators (methyl orange and azocarmine G). They have found that the presence of ILs leads to decreased pK_a values because of the stronger electrostatic interaction of cationic ILs with basic forms of the indicators with more negative charge. Clearly, when considering the influence of the solvent, the difference between the solvation energies of the protonated and dissociated acid forms influences the final pK_a values.

The acid dissociation constant is an important physicochemical parameter of a chelating substance and knowledge of this value is of fundamental significance in order to estimate its

application as an extracting ligand. In this respect, the β -diketone family provides many of the most widely investigated ligands in lanthanoid complexes [5, 6]. A β -diketone behaves as a monobasic acid, as the proton on the α -carbon of its β -diketone form or enol proton of β -keto-enol form can readily be deprotonated in an appropriate pH range, depending on its pK_a values. Thenoyltrifluoroacetone (HTTA) was introduced as an analytical reagent by Calvin and Reid in 1947 and has been extensively used as an extractant for lanthanoids [7]. Owing to the presence of the trifluoromethyl group it is highly acidic in the enol form, which in turn is useful in the extraction of many metals at low pH [8]. HTTA ($pK_a=6.23$) is less basic than acetylacetone ($pK_a = 8.82$) and hence yields more stable chelates. The next category of β -diketones is composed of 4-acyl-1-phenyl-3-methyl-5-pyrazolones (α -substituted β -diketones, pK_a : 2.5÷4) and their analogs of 3-methyl-4-acyl-5-isoxazolones [5, 9]. The later type has stronger acidities (lower pK_a values: 1.23) with high enhancing extraction power [10]. Finally, acylpyrazolones are an interesting class of β -diketones, containing a pyrazole fused to a chelating arm. These ligands have been used as advantageous chelating reagents for almost all metal ions. A great number of studies have appeared in the literature, but the investigations gave only selected data on acid dissociation constants of pyrazolones as well as metal complexes formation constants.

The fact that ILs appear to replace volatile molecular solvents in the field of liquid-liquid extraction of metals even before the REACH regulation is not surprising. The uniqueness of ILs derives in part from the variety of organic cations (e.g. imidazolium, pyridinium, ammonium derivatives) and small inorganic anions available. So, they are designer solvents in the sense that their physicochemical properties can be tuned by different combinations in view of a wide range of applications among them remarkable extraction media [11]. It has been apparent in the last few years that the process by which a metal ion is extracted into an IL is significantly more complicated than that observed with conventional molecular diluents [12]. In particular, it has been shown that such aqueous/IL biphasic systems experience mixing of all their components, in a way rather similar to the exchanges observed for aqueous/aqueous biphasic systems [13, 14] and that the presence of an extractant strongly influences such mutual solubilities [15]. Despite the progress in elucidation of the factors governing the extraction mechanism in ILs many aspects remain incompletely understood and, in particular, the factors determining the pK_a values of chelating extractants in such media. To the best of our knowledge, no protocol is defined yet to determine the pK_a of chelating extractants in IL media, although distribution ratios of HTTA in $[C_1C_n\text{im}^+][\text{Tf}_2\text{N}^-]$, ($n = 4, 6, 8$) have been measured quite recently [16].

We have thus performed a series of experiments aiming at studying the equilibrium state of biphasic mixtures of aqueous nitric, chloric and perchloric acid solutions (concentration range from 10^{-2} to ca. 10^{-4} M, mainly) and of four ionic liquids, 1-methyl-3-alkylimidazolium bis(trifluoromethylsulfonyl)imide $[C_1C_n\text{im}^+][\text{Tf}_2\text{N}^-]$, ($n = 4, 6, 8$ and 10), where Tf_2N^- stands for $(\text{CF}_3\text{SO}_2)_2\text{N}^-$. This anion was chosen because it is known to be very effective in producing hydrophobic ILs with low viscosity [17]. Other experiments focused on the effect of ionic strength ($\mu = 0.1$ M: NaCl, NaNO_3 , NaClO_4) on the solubilities of H_2O and H^+ in the lower phase. Impact of added traditional acidic extractants, such as β -diketones, onto the H^+ distribution was then investigated. For the first time, determination of pK_a values of HTTA, HPBI and HP chelating extractants in $[C_1C_4\text{im}^+][\text{Tf}_2\text{N}^-]$ has been performed. A change in the pK_a value for HTTA has been observed as n is turned from $n = 4$ to $n = 10$.

This research will provide new insights into the basic aspects of the behavior of the acidic ligands in ILs as an effort to design more efficient systems employing these innovative organic phases as medium for the solvent extraction of 4f-elements for example.

2 Experimentals

All throughout the text, we will use the following notations: $[H^+][A^-]$ is a mineral acid ($A^- = Cl^-$, ClO_4^- , NO_3^-); $C_1C_nim^+$ is the imidazolium cation of the ILs and $[Tf_2N^-]$ stands for $(CF_3SO_2)_2N^-$. The sodium salts used will be noted as $[Na^+][A^-]$ and ILs as $[C_1C_nim^+][Tf_2N^-]$ ($n = 4, 6, 8, 10$). Terms as initial H^+ concentration and H^+ concentration at equilibrium will refer solely to the aqueous phase quantities and will be noted by use of subscripts “init” and “eq” respectively. Biphasic systems of this study will be noted as $[H^+][A^-]/[Na^+][A^-]/[C_1C_nim^+][Tf_2N^-]$, omitting water for the sake of simplicity. In these systems, the upper phase is displayed on the left hand side of symbol //, indicating the existence of a meniscus.

2.1 Reagents

The commercial products 2-thenoyltrifluoroacetone (HTTA, Fluka, $\approx 99\%$), 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (HP, purity $> 99\%$, Fluka) and 4-benzoyl-3-phenyl-5-isoxazolone (HPBI, purity $> 97\%$, Fluka) were used as received. The solvents 1-butyl-3-methyl-imidazolium-bis(trifluoromethanesulfonyl)imide, 1-hexyl-3-methyl-imidazolium-bis(trifluoromethanesulfonyl)imide, 1-octyl-3-methyl-imidazolium-bis(trifluoromethanesulfonyl)imide, 1-decyl-3-methyl-imidazolium-bis(trifluoromethanesulfonyl)imide, (purity, 99.5%) were purchased from Solvionic (Toulouse, France). The ILs were dried under vacuum following a previously published procedure [18] prior to sample preparation. All aqueous solutions have been prepared with ultrapure water, apart those for NMR experiments, for which D_2O was used (see below). All other reagents were purchased from Merck and Fluka and used without any further purification. The structural formulas of the three chosen chelating ligands under study are presented in Scheme 1.

Scheme 1. Structural formulas of the chelating extractants (HTTA, HP and HPBI, respectively).

2.2 Apparatus and protocols

The H_2O amount in the IL phases was titrated by the Karl Fisher method with a coulometer (Mettler Toledo DL 32). The uncertainty is equal to $\pm 2\%$ for ca. 13000 ppm H_2O . The IL anion and cation solubilities in deuterated water were determined by NMR according to a protocol already published [14]. Limits of detection for both ions are in the range of 2 mM and uncertainties are equal to 10% for cations and to 5% for anions. The pH values of the aqueous solutions were measured by a Schott titrator (Titroline Easy) before, (as initial) and after, (as equilibrium), contact with the IL phases. The uncertainty is equal to ± 0.02 . Mechanical shaker model IKA Vibrax VXR was used as well as centrifuge Micro Star 12.

UV-vis spectra were recorded on a Cary 100 spectrophotometer, using 1 mm path length quartz cuvettes. Very good calibration curves were obtained for HPBI and HTTA dissolved in water (monophasic systems), at $\lambda = 310$ nm (HPBI, $\epsilon = 1400\text{ M}^{-1}\text{ cm}^{-1}$) and $\lambda = 267$ nm, (HTTA, $\epsilon = 763\text{ M}^{-1}\text{ cm}^{-1}$). By contrast, no calibration curve could be obtained for HP, because this compound does not

dissolve significantly in water (monophasic system). The calibration curves obtained for HTTA and HPBI were used to derive the concentration of the compounds in the equilibrated aqueous phases of this work.

Fitting of the data was performed by use of a FORTRAN subroutine specifically dedicated to the problem, by use of a minimization procedure, based on least square adjustment through the CERN library and software facilities.

2.3 Aqueous-ionic liquid biphasic systems, no chelating extractant

Equal volumes (0.8ml) of aqueous phase (containing or not 0.1 mol/dm^3 $[\text{Na}^+][\text{Cl}^-]$, $[\text{Na}^+][\text{NO}_3^-]$, $[\text{Na}^+][\text{ClO}_4^-]$ and adjusted to the desired pH with $[\text{H}^+][\text{Cl}^-]$, $[\text{H}^+][\text{NO}_3^-]$, $[\text{H}^+][\text{ClO}_4^-]$ or $[\text{Na}^+][\text{OH}^-]$ accordingly) and organic phase (different ILs) were equilibrated for 2 hours at 25°C by mechanical shaking. After centrifugation and phase separation, the pH of the aqueous phase was measured and taken as the equilibrium value.

2.4 Aqueous-ionic liquid biphasic systems, in the presence of chelating extractant

Equal volumes (0.8ml) of aqueous phase (containing 0.1 mol/dm^3 $[\text{Na}^+][\text{Cl}^-]$ and adjusted to the desired pH with $[\text{H}^+][\text{Cl}^-]$) and organic phase (containing HL at various concentrations in ILs, from $3 \times 10^{-2} \text{ M}$ to $5 \times 10^{-3} \text{ M}$) were equilibrated for 2 hours (1500 rpm) at 25°C . After centrifugation (5000 rpm) and phase separation, the pH of the aqueous phase was measured and taken as the equilibrium value.

3. Results

3. 1 Aqueous-ionic liquid biphasic systems, no chelating extractant

The question of water mixing with the IL will be regarded from the point of view that IL/water interface plays a key role in assisted ion extraction [19].

Figure 1 displays the amount of H_2O in ppm at equilibrium in the lower $[\text{C}_1\text{C}_6\text{im}^+][\text{Tf}_2\text{N}^-]$ phase for various $[\text{H}^+][\text{A}^-]$ and salt concentrations in the pH range from 0.5 to 3 chosen as a typical example of our data. The solid line corresponds to the average of all collected data (10 600 ppm). The results obtained from Karl Fischer titration for the other three ILs are presented in Supporting Information (Figures S1–S3) and evidence a similar absence of influence of the aqueous phase composition ($[\text{H}^+][\text{A}^-]$ or $[\text{Na}^+][\text{A}^-]$) on the water amount at equilibrium in all four ILs. Our study demonstrates that the water dragging to the IL phase does not depend significantly on the acid or salt anion nature in the aqueous phase in this pH range. By contrast, the average water amount strongly depends on the IL nature, as illustrated in Figure 2, which shows an almost linear decrease with increasing length of the IL cation, from 12 200 ppm down to 8 350 ppm ($n = 4$ to 10).

The average value of 12 200 ppm of water in $[\text{C}_1\text{C}_4\text{im}^+][\text{Tf}_2\text{N}^-]$ obtained in our work compares well with the value already published by our group in the absence of any acid or added salt (ca. 12 000 ppm, no acid, same IL) [18]. Note that the average values of 12 200 ppm of H_2O dissolved in $[\text{C}_1\text{C}_4\text{im}^+][\text{Tf}_2\text{N}^-]$ displayed in Figure 2 is lower than what has been measured for higher acidity of the aqueous phases (14 500 ppm [14] at 0.2 M H^+) REF IS MISSING, an effect ascribed to the different acidity values. Our results as a function of n (Figure 2) also agree with data obtained for D_2O equilibration experiments, where it was found that the amount of D_2O transferred to the lower phase is not negligible with a trend following that of the hydrophobicity the ILs' cations: $[\text{C}_1\text{C}_{10}\text{im}^+] > [\text{C}_1\text{C}_4\text{im}^+] > [\text{Me}_3\text{BuN}^+]$ (trimethylbutylammonium) [14].

The aqueous solubilities of $C_1C_4im^+$ and Tf_2N^- were then determined as a function of initial pH in the range 0.5 – 4. Both ions display a constant solubility value in this pH range, at ca. 17 mM (data not shown), whatever the chemical condition ($[D^+][NO_3^-]$ or $[D^+][Cl^-]$, in the presence or not of $[Na^+][NO_3^-]$ or $[Na^+][Cl^-]$). This value is in very good agreement with our previous determination in pure water [14].

In a third step, for pH ranging from 0.5 to 10, the equilibrium pH was measured as a function of the initial pH using all four ILs. Data are displayed in Figure 3 for $[C_1C_4im^+][Tf_2N^-]$. As for the H_2O amount results, no impact of the aqueous phase composition (acid, salt) could be observed as all data lie on the same continuous line. Therefore, we used identical symbols for all data points (all four acids, in the presence or absence of the corresponding sodium salt). Using $[C_1C_4im^+][Tf_2N^-]$, one observes a striking departure from the line $y = x$ (i. e. $pH_{init} = pH_{eq}$) above $pH_{init} = 2$, as the signature of a non-negligible solubility of H^+ in the IL phase, that tends to increase the equilibrium pH value. For $pH_{init} > 7$, the equilibrium pH remains equal to 7.

By contrast, similar experiments performed for $n = 6, 8$ and 10 show that pH_{init} and pH_{eq} are perfectly equal up to at least a value of 3 (see Figure 4 for $[C_1C_6im^+][Tf_2N^-]$ and Figures S4-S6 for the other ILs). As previously observed for $[C_1C_4im^+][Tf_2N^-]$, the chemical composition of the aqueous phase has no effect on the equilibrium pH value.

3.2 Aqueous-ionic liquid biphasic systems in the presence of chelating extractant

The effect of adding chelating compounds to the IL phase ($n = 4$) onto the H^+ distribution (pH at equilibrium as a function of pH_{init}) was examined in the pH range 1÷3.5. Considering the absence of effect of the aqueous phase composition as displayed in Figure 3, only one aqueous composition was thus investigated in this case ($[H^+][Cl^-]$ and $[Na^+][Cl^-] = 0.1$ M). The obtained results are presented in Figure 5 (HTTA), Figure 6 (HP) and Figure 7 (HPBI). Addition of any of the three ligands has a large impact onto the pH_{eq} values, which decrease so that the pH_{eq} vs pH_{init} plot lies below the curve obtained in the absence of ligand. In the case of HPBI, some values are even below the line $pH_{eq} = pH_{init}$.

Finally, the same type of experiments was performed for thenoyltrifluoroacetone addition in $[C_1C_{10}im^+][Tf_2N^-]$ and the results are displayed in Figure 8. As for the data in the absence of ligand, our results evidence a clear difference of behavior between $[C_1C_4im^+][Tf_2N^-]$ and $[C_1C_{10}im^+][Tf_2N^-]$. Using the latter IL, all data points, either with or without HTTA, lie on the same $y = x$ line.

4. Discussion

4.1 Aqueous-ionic liquid biphasic systems, no chelating extractant

Because ILs are composed of ions, interactions with dipolar water molecules are expected, and consequently, water transfer to IL phases with which they are contacted, as is the case in our experiments, is not surprising [14]. Conversely, transfers of the IL cations and anions towards the aqueous phase are expected. Although they are considered as immiscible with water, because of the existence of a meniscus, all $[C_1C_nim^+][Tf_2N^-]$ used in this work appear in fact highly hygroscopic and the solubility of water in ILs, in mole fraction units, is several orders of magnitude higher than the solubility of ILs in water [20], under a large range of aqueous phase composition. Furthermore, water and IL ion solubilities appear to be independent of pH value and chemical composition, although the nature of the IL cation influences the water solubility. By contrast, the H^+ solubility in $[C_1C_4im^+][Tf_2N^-]$ is highly dependent on pH_{init} , while it is independent on the type of acid and on the presence or absence of sodium salt. Therefore, we can consider the plot displayed in Figure 3 as a

‘universal’ plot describing the distribution of H^+ ions between the $[C_1C_4im^+][Tf_2N^-]$ phase and the acidic aqueous phase. Qualitatively speaking, the data presented in Figure 3 can be explained as follows: at very acidic values and up to $pH \approx 2$, H^+ transfer to the IL phase is either nil or below detection limits. Above $pH 2$ the total H^+ amount available in the system is such that even a small transfer to the IL phase induces large changes in pH values. As pH tends toward 7, the equilibrium and initial pH values merge because no H^+ is present in the biphasic system anymore. Above $pH 7$, the constant equilibrium pH value observed implies that OH^- ions also migrate to the IL phase. On a quantitative basis, any tentative description of these results would at minimum imply considering equilibria with carbonates provided by CO_2 of the atmosphere, in both the aqueous and the IL phase. Knowledge of the gas solubility (CO_2 , H_2) in this new family of liquid solvents can be found for example in the work of Jacquemin et al. [21], who showed that carbon dioxide (10^{-2} mole-fraction solubility) is two orders of magnitude more soluble than hydrogen in three ionic liquids based on the bis(trifluoromethylsulfonyl)imide anion. They also found that changing the cation of the IL has only a minor effect on the CO_2 solubility. Finally, the situation is very different when using $[C_1C_{10}im^+][Tf_2N^-]$ and we can safely assume that H^+ solubility in $[C_1C_{10}im^+][Tf_2N^-]$ is very low, although water still migrates to this IL.

It was found by Genov and Dukov [22, 23] that the extractability of the acids changes in the sequence: HCl , HNO_3 and $HClO_4$ in molecular solvents (C_8H_{18} , CCl_4 , C_6H_6 , $CHCl_3$) with high-molecular amines. An increase of the anions’ radius induces a decrease in free hydrogenation energy, which facilitates the transition into the organic phase. When solvent with the greatest solvating capacity ($CHCl_3$) was used, the difference in the extraction of different acids is greatest. It was found that when solvents with a lower solvating capacity (C_8H_{18} , CCl_4 , C_6H_6) were applied, this difference is smaller [22, 23]. In this respect, ILs appear very different, as neither effect of acid nature nor of ionic strength could be evidenced. Furthermore, no specific extracting agent is required to obtain large water/acid solubilities. In these points, except for $n = 4$, the ILs’ cation effect is equalized and the different acids are not significantly extracted using $[C_1C_nim^+][Tf_2N^-]$, when $n = 6, 8$ and 10 , Figures S4–S6.

4.2 Aqueous-ionic liquid biphasic systems, in the presence of chelating extractant

Addition of a ligand to the IL phase has no effect onto the water solubility. For example, the average water content in $[C_1C_{10}im^+][Tf_2N^-]$ in the presence of HTTA is 8500 ppm, to be compared to an average value, in the absence of ligand, equal to 8350 ppm. Similar results were obtained for the other two ligands (data not shown). By contrast, adding any of the ligand has a clear impact onto the H^+ distribution curve in case of $[C_1C_4im^+][Tf_2N^-]$ (see Figures 5, 6 and 7): the more ligand is introduced, the more acidic the aqueous phase becomes, at any initial pH value. For such experiments, a clear effect of the IL nature is also observed, as addition of HTTA to $[C_1C_{10}im^+][Tf_2N^-]$ does not change the H^+ distribution ratio (see Figure 8).

We can ascribe the results in Figures 5 to 7 to two different phenomena: First, the acidic ligand in the IL phase is actually a potential reservoir of H^+ ions, in addition to those already present in the system owing to the initial $[H^+][Cl^-]$ value. Should the ligand dissociate in the IL phase, even partially, according to its (yet unknown) pK_{aIL} value, then the total H^+ amount available in the system is increased, which results in an updated distribution of the total H^+ amount between the two phases according to the universal distribution curve as displayed in Figure 3. Second, the possible solubilisation of the neutral ligand in the aqueous phase, followed by its partial dissociation, according to the pK_{a_w} value in water can also be the reason for a decrease in pH_{eq} . The combination of these two phenomena (i.e. dissociation in IL or solubility in the aqueous phase and subsequent dissociation), is the driving force explaining our data. In principle, both effects can occur simultaneously and can be

different from one ligand to the other. A technique that is still considered as the most accurate for determination of pK values in water between ca. pH 2 and 12 is potentiometric titration [24, 25] although a broad range of experimental methods was applied in the past decades [24, 26]. However, in IL phases, no easy-to-use technique is available at the moment.

In the case of HTTA, experimental results by Kidani and co-worker [16] show that, under the chemical conditions of our work, HTTA dissociation in IL and subsequent release of H^+ is the only significant process. This team has studied HTTA distribution between an acidic/basic aqueous phase (pH range: 1 – 13) and various imidazolium ILs $[C_1C_nim^+][Tf_2N^-]$ ($n = 4, 6, 8$). Below $pH_{eq} = 6$, the HTTA distribution ratio is equal to ca. 44 (average $\log D = 1.64$) for all three ILs. In other words, below $pH_{eq} = 6$, HTTA is poorly soluble in water, while it dissolves more effectively above $pH_{eq} = 6$. This result is in line with the pK_{aw} value of HTTA, which is equal to ca. 6.3 [7]. Our experimental HTTA data, as illustrated in Figure 5, correspond to pH_{eq} values below 5 except one point ($pH_{eq} = 6.14$). Therefore, in a first approximation, we can consider that the very low fraction of HTTA which transfers to water is not significantly dissociated and thus is not the cause of the increased H^+ amount observed. As a consequence, HTTA dissociation in the water-saturated $[C_1C_4im^+][Tf_2N^-]$ IL is solely responsible for the decreased pH values as compared to the same system without HTTA. The results of Kidani and Imura also show that HTTA is similarly poorly water-soluble when $[C_1C_{10}im^+][Tf_2N^-]$ is used. However, as evidenced in Figures S6, H^+ is not soluble in this IL so that HTTA dissociates to a very low extend. This explains why no change in H^+ distribution ratio is observed in Figure 8.

The situation is very different for the other two acidic extractant additions because these two compounds display very low pK_{aw} values as compared to HTTA: HPBI $pK_{aw} = 0.68$ [27] and HP $pK_{aw} = 3.92$ [28]. Thus, should solubilisation of the compound in the aqueous phase occur, this would lead to massive dissociation under the chemical conditions of our study, providing part of the additional H^+ observed in Figure 4. For the HP and HPBI cases, we could not find in the literature any data similar to those of Kidani et al. [16] giving the experimental ligand solubility in our biphasic systems. We therefore collected UV-vis spectra aiming at determining the ligand water solubility under our experimental conditions (see experimental section). Typical UV-vis. data are displayed in Figure 9 for the three ligands of this work. The HTTA UV-vis spectra were acquired in view of comparison with Kidani's work. As regards thenoyltrifluoroacetone, we found a distribution ratio very close to that of Kidani and collaborator: $D = 50$. The UV-vis. spectrum of HPBI is in good agreement with a previous determination in $[H^+][Cl^-]$ medium [27]. It turns out that HPBI is also poorly soluble in the aqueous phase, with D values equal to ca. 53 up to $pH_{init} = 3.5$. As explained in the experimental section, no distribution ratio could be obtained for HP but this compound is not soluble in water below $pH = 2.9$ (no UV-vis. signal).

Owing to its almost complete dissociation in water, even the low amount of HPBI in the aqueous phase significantly contributes to the decrease in pH value. As an example, using an initial HPBI concentration of 3×10^{-2} M and an initial pH value of 3.4, HPBI solubilisation in the aqueous phase and subsequent dissociation additionally provides ca. 5.6×10^{-4} M H^+ , which would correspond to a final pH value equal to ca. 3.02. Our experimental value is equal to 2.23, which indicates an additional contribution of HPBI dissociation in the IL phase but clearly, direct dissociation of the ligand in water is no more negligible for the HPBI case.

Based on this qualitative discussion, it appears that our results with $[C_1C_4im^+][Tf_2N^-]$ are an almost ideal case to determine the dissociation constant of the ligands in the water-saturated $[C_1C_4im^+][Tf_2N^-]$ IL phase. To this end, taking into account the dissociation of the ligand in the IL phase is easy through the mass action law derived from the chemical equilibrium:

$$Ka_{IL} = \frac{[\overline{H^+}][\overline{L^-}]}{[\overline{HL}]} \quad (2)$$

Where HL denotes any of the three ligands of this work, and K_{aIL} is the dissociation constant of the ligand in the water-saturated IL phase. Solubility of the ligand and its dissociation constant in water are taken into account according to our UV-Vis data (HTTA and HPBI). As regard the HP case, we assumed no solubilisation in the whole pH range investigated ($D = \infty$), a reasonable estimate considering the UV-Vis data. Then, a correct analytical description of the universal curve displayed in Figure 3 is necessary, to link the total amount of H^+ to pH_{eq} . As already stressed, this is not easily feasible by considering the multiple chemical equilibria, such as those involving CO_2 . Instead, we decided to limit ourselves to the use of a purely empirical expression relating pH_{init} to pH_{eq} as:

$$\text{pH}_{\text{eq}} = 2.32\text{arctang}(1.62\exp(0.39\text{pH}_{\text{init}} + 1.19\text{pH}_{\text{init}} - 7.1) - 0.05\text{pH}_{\text{init}} + 4)$$

The calculated curve, which recovers the data in a very satisfactory way, is displayed in Figure 3 as a solid line. On this basis, the theoretical expression of pH_{eq} , in the presence of the ligand, which contains as unique unknown parameter K_{aIL} , was fitted to the experimental data for all three ligands (Figures 5 to 7). The minimization procedure leads to $\text{p}K_{\text{aIL}} = 3.0$ (HTTA) $\text{p}K_{\text{aIL}} = 2.0$ (HPBI) and $\text{p}K_{\text{aIL}} = 3.5$ (HP). The corresponding fitted curves are displayed as solid lines in Figures 5 to 7.

Agreement between experimental and calculated curves is quite satisfactory for HTTA and the HP case corresponds to a fair agreement. We thus conclude that the assumptions we made are correct for HTTA and HP. By contrast, agreement is not so good for HPBI, although the decreasing trend as a function of ligand concentration and initial pH is correct. We ascribe the discrepancy between the calculated and experimental data to the dissociation/equilibration process which is quite different for HPBI as compared to HTTA and HP. In fact, the underlining hypothesis of these calculations is the equilibration of H^+ entities between the aqueous and IL phases, owing to ligand dissociation in the IL and water phases. This of course requires transfer of other entities in order to ensure the electroneutrality of each phase. In case of H^+ departure from the IL towards the aqueous phase, electroneutrality can be achieved by several mechanisms: i) aqueous solubilisation of Tf_2N^- ii) back transfer of NO_3^- that may have dissolved in the IL phase iii) back transfer of $\text{C}_1\text{C}_4\text{im}^+$ ions from the aqueous to the IL phase and finally, iv) joint transfer of the deprotonated ligand, L^- . Obviously, all these processes can occur simultaneously to some extent. For the HTTA case, a large contribution of process iv) can be safely ruled out because HTTA is not significantly dissociated in water. Similarly, for HP, D is very high so no deprotonated HP entities are to be found in the aqueous phase. Consequently, the curve displayed in Figure 3 is valid. By contrast, although HPBI is only slightly soluble in water, its low $\text{p}K_{\text{aw}}$ value induces an almost complete dissociation and we suspect the presence of PBI^- moieties to distort the plot on which our calculation is based.

Note that the relative contributions of processes i) to iii) cannot be easily derived. For example, in our experiments, the most striking effect of HTTA on the equilibrium pH values is observed for $\text{pH}_{\text{init}} = 3.35$, with an initial HTTA concentration of 3×10^{-2} M, for which the expected equilibrium pH is ca. 6.8 (Figure 3) and the measured pH_{eq} value is equal to 3.2. This corresponds to 6.3×10^{-4} M of H^+ in addition to those already introduced by $[\text{H}^+][\text{Cl}^-]$ and thus to the same amount of any other charged entity transferring from one phase to the other (at maximum). Clearly, such a low amount cannot be detected by NMR (Tf_2N^- or $\text{C}_1\text{C}_4\text{im}^+$) or by UV-vis. for nitrate determination [29, 30].

The $\text{p}K_{\text{aIL}}$ values we obtained correspond to the ligand dissociation abilities in a water-saturated $[\text{C}_1\text{C}_4\text{im}^+][\text{Tf}_2\text{N}^-]$ phase. Although the HP value cannot be taken for granted, it is nevertheless an as good as possible estimate of the exact value. Comparison with the corresponding $\text{p}K_{\text{aw}}$ values of the three ligands evidences a levelling off of the acidic abilities in $[\text{C}_1\text{C}_4\text{im}^+][\text{Tf}_2\text{N}^-]$ around $\text{p}K_{\text{aIL}} \approx 3$. The factors that affect $\text{p}K_{\text{a}}$ are: i) the strength of the H–A bond because the stronger the H–A bond, the harder it is for the acid to donate a proton, and ii) the ability of the solvent at stabilizing the ions formed. In traditional molecular solvents, the delocalization of the negative charge

after removing a proton influences also the values of pK_a as it is seen from Table S2: for HClO_4 the negative charge is delocalized over 4 oxygens and as a result the pK_a value diminishes significantly as compared to the other HClO_x compounds ($x = 1$ to 3). Our results indicate that ILs offer a very different surrounding for the acidic ligands. First, ILs are composed of ions so that $[\text{C}_1\text{C}_4\text{im}^+][\text{Tf}_2\text{N}^-]$ accommodates H^+ entities, irrespective of the counter-anion (TTA^- , PBI^- or P^-). However, this is strongly correlated to the IL cation nature, as demonstrated by our results for HTTA in $[\text{C}_1\text{C}_{10}\text{im}^+][\text{Tf}_2\text{N}^-]$.

4.3 Consequences for lanthanoid ions extraction

As a group of typical metal elements, lanthanoids (Lns) can form chemical bonds with most of nonmetal elements. From a soft-hard acid-base point of view, 4f-elements are hard bases and they tend to form chemical bonds with atoms that belong to the hard acid group (such as F, O and N), example, oxygen and Lns form $\text{Ln}-\text{O}$ bonds and have high coordination numbers. The β -diketone acts as a mononegative $\text{O}-\text{O}'$ bidentate ligand to coordinate to lanthanoid ions and forms stable complexes [5, 6, 8-10, 31-33]. These complexes are the most popular and the most intensively investigated rare-earth coordination compounds. Umetani and Matsui [28] have investigated the substituent effect of eight 4-acyl-3-methyl-1-phenyl-5-pyrazolones (Table S1) on the acid dissociation and partition constants between aqueous and cyclohexane phases. Some relationships between pK_{aw} values and the extraction constants obtained for Zn(II) ion using two series of reagents having an aromatic and aliphatic substituents at the 4-position of 5-pyrazolone were postulated. It is established that the substituted pyrazolones in para-position cause quantitative changes in the synergistic extraction of lanthanoids with CHCl_3 [32]. The obtained $\log K_{L,S}$ with 4-fluorophenyl terminal group (an electron withdrawing substituent) are larger than the case when electron donating ($-\text{CH}_3$) groups are introduced in the benzoyl moieties. So, acid dissociation constants are important parameters for a quantitative understanding of complex equilibria. In fact, the acid dissociation constant as a compound property is considered as being among the most commonly used chemical properties by chemists nowadays [24].

Consequently, in liquid-liquid extraction of Lns with molecular solvents, great attention has been paid to the exact pK_{aw} value of the ligand and this parameter has been carefully adjusted by introduction of various substituents, thanks to the synthetic ability of organic chemists. Because of the ionic compositions and the corresponding physicochemical properties and characteristics of ILs, the extraction of metal ions is more significant in IL systems than in conventional volatile organic diluents (VOCs) from the aqueous solution employing strong monobasic acids. ILs provide a very different scenario because they allow direct /immediate dissociation of acidic ligands in their water-saturated bulk to an extent that does not seem to depend much on the chemical structure of the ligand. Therefore, there is no need to take advantage of the chemical versatility of β -diketonates in view of extraction, because similar amounts of L^- would be available in the IL phase, irrespective of the ligand solubility in water and independent of the ligand structure. Thus we would conclude that thenoyltrifluoroacetone and 4-acylpyrazolone will extract lanthanoid ions similarly if dissolved in $\text{C}_1\text{C}_4\text{imTf}_2\text{N}$, by contrast to the large differences evidenced in molecular solvents. However, this rather deceiving prediction has to be modulated according to the IL nature and we predict that in $\text{C}_1\text{C}_{10}\text{imTf}_2\text{N}$ the extraction peculiarities of HTTA and HP would be observed again, owing to their negligible deprotonation in the IL phase.

5. Conclusion

According to the above experiments, the high efficient procedure of the extraction of metal ions using ILs can be developed with respect to their phenomenology, drawbacks and even shortcomings.

Additional ideas for conclusion.

Acknowledgements The authors are grateful to FP7-PEOPLE-Marie Curie Actions-IEF for the financial support of the project INNOVILLN (622906) 2014-2016. The authors would like also to acknowledge the contribution of the COST Action CM1206 (EXIL).

Figure 1. H_2O amount (ppm) in the lower phase vs pH_{eq} of the aqueous phase using $[\text{C}_{11}\text{C}_6\text{im}^+][\text{Tf}_2\text{N}^-]$ as organic medium. Δ : $[\text{H}^+][\text{ClO}_4^-]$, $\circ$: $[\text{H}^+][\text{ClO}_4^-]$ and $[\text{Na}^+][\text{ClO}_4^-]$, $\square$: $[\text{H}^+][\text{Cl}^-]$, $\diamond$: $[\text{H}^+][\text{Cl}^-]$ and $[\text{Na}^+][\text{Cl}^-]$, $+$: $[\text{H}^+][\text{NO}_3^-]$; $\times$: $[\text{H}^+][\text{NO}_3^-]$ and $[\text{Na}^+][\text{NO}_3^-]$. Dotted line: average of all values.

Figure 2. H_2O average amount (ppm) in the lower phase vs n , the length of the IL cation. Solid line is a guide for the eye only.

Figure 3. pH_{eq} vs pH_{init} using $[\text{C}_1\text{C}_4\text{im}^+][\text{Tf}_2\text{N}^-]$ as organic medium. Dotted line: $y = x$. Solid line: empirical fit (see text).

Figure 4: pH_{eq} vs pH_{init} using $[\text{C}_1\text{C}_6\text{im}^+][\text{Tf}_2\text{N}^-]$ as organic medium. Dotted line: $y = x$. $\circ$: $[\text{H}^+][\text{Cl}^-]$ and $[\text{Na}^+][\text{Cl}^-]$; $\square$: $[\text{H}^+][\text{Cl}^-]$; Δ : $[\text{H}^+][\text{ClO}_4^-]$; $+$: $[\text{H}^+][\text{ClO}_4^-]$ and $[\text{Na}^+][\text{ClO}_4^-]$; $\diamond$: $[\text{H}^+][\text{NO}_3^-]$; $\times$: $[\text{H}^+][\text{NO}_3^-]$ and $[\text{Na}^+][\text{NO}_3^-]$.

Figure 5. Effect of increasing concentrations of HTTA dissolved in $[C_1C_4im^+][Tf_2N^-]$ on the H^+ concentration at equilibrium, in the pH range 0.5 – 3.5. $\circ$: $[HTTA] = 7 \times 10^{-3}$ M; $\square$: $[HTTA] = 1.5 \times 10^{-2}$ M; Δ : $[HTTA] = 3 \times 10^{-2}$ M. Dotted line: $y = x$. Dashed line: in the absence of ligand. Solid lines: fits (see text).

Figure 6. Effect of increasing concentrations of HP dissolved in $[C_1C_4im^+][Tf_2N^-]$ on the H^+ concentration at equilibrium, in the pH range 0.5 – 3.5. $\circ$: $[HP] = 5 \times 10^{-3}$ M; $\square$: $[HP] = 10^{-2}$ M; Δ : $[HP] = 3 \times 10^{-2}$ M. Dotted line: $y = x$. Dashed line: in the absence of ligand. Solid lines: fits (see text).

Figure 7. Effect of increasing concentrations of HPBI dissolved in $[C_1C_4im^+][Tf_2N^-]$ on the H^+ concentration at equilibrium, in the pH range 0.5 – 3.5. $\circ$: $[HPBI] = 5 \times 10^{-3} M$; $\square$: $[HPBI] = 10^{-2} M$; Δ : $[HPBI] = 3 \times 10^{-2} M$. Dotted line: $y = x$. Dashed line: in the absence of ligand. Solid lines: fits (see text).

Figure 8. Effect of increasing concentrations of HTTA dissolved in $[C_1C_{10}im^+][Tf_2N^-]$ on the H^+ concentration at equilibrium, in the pH range 0.5 – 3.5. $\circ$: $[HTTA] = 7 \times 10^{-3} M$; $\square$: $[HTTA] = 1.5 \times 10^{-2} M$; Δ : $[HTTA] = 3 \times 10^{-2} M$. Dotted line: $y = x$.

Figure 9: UV-Vis spectra of the aqueous equilibrated phases containing HP (dashed line; $[\text{HP}]_{\text{init}} = 0.03 \text{ M}$, $\text{pH} = 4.79$); HPBI (solid line, $[\text{HPBI}]_{\text{init}} = 0.01 \text{ M}$, $\text{pH} = 2.59$); HTTA (dotted line, $[\text{HTTA}]_{\text{init}} = 0.015 \text{ M}$, $\text{pH} = 2.57$).

References

1. M. Berthelot, Jungfleisch: Sur les lois qui président au partage d'un corps entre deux dissolvants (expériences). *J. Ann. Chim. Phys.*, 26 396 (1872).
2. A. Leo, C. Harnsch, D. Elkins: Partition coefficients and their use. *Chem. Rev.*, 71 525-616 (1971).
3. T. Grimes, K. Nash: Acid dissociation constants and rare earth stability constants for DTPA. *J. Sol. Chem.*, 43 298-313 (2014).
4. A. Safavi, H. Abdollahi, N. Meleki, S. Zeinali: Investigation of the role of ionic liquids in tuning the pKa values of some anionic indicators. *J. Sol. Chem.*, 38 753-761 (2009).
5. K. Binnemans, Rare-Earth beta-diketonates, in: K.A. Gschneidner, J.C.G. Bünzli (Eds.) *Handbook on the Physics and Chemistry of Rare Earths*, Elsevier, Amsterdam, 2005.
6. C. Pettinari, F. Marchetti, A. Drozdov, β -diketones and related ligands in: *Comprehensive coordination chemistry II*, Elsevier, 2003.
7. A.K. De, S.M. Khopkar: *J. Sci. Ind. Des.*, 21A 131-135 (1962).
8. M. Atanassova, I. Dukov: A comparative study of the solvent extraction of trivalent elements of the lanthanoid series with thenoyltrifluoroacetone and 4-benzoyl-3-methyl-1-phenyl-2pyrazolin-5-one using diphenylsulphoxide as synergistic agents. *J. Sol. Chem.*, 38 289-301 (2009).
9. F. Marchetti, C. Pettinari, R. Pettinari: Acylpyrazolone ligands: synthesis, structures, metal coordination chemistry and applications. *Coord. Chem. Rev.*, 249 2909 (2005).
10. M. Atanassova, V.I. Lachkova, N.G. Vassilev, S.G. Varbanov, I. Dukov: Complexation of trivalent lanthanoid ions with 4-benzoyl-3-phenyl-5-isoxazolone and p-tert-butylcalix[4]arene fitted with phosphinol pendant arms in solution during synergistic solvent extraction and structural study of solid complexes by IR and NMR. *Polyhedron*, 29 655 (2010).
11. I. Billard, Ionic liquids: new hopes for efficient lanthanide/actinide extraction and separation?, in: J.C.G. Bünzli, V.K. Perchasky (Eds.) *Handbook on the Physics and Chemistry of Rare earth*, Elsevier, 2013.
12. S.L. Garvey, C.A. Hawkins, M.L. Dietz: Effect of aqueous phase anion on the mode of facilitated ion transfer into room-temperature ionic liquids. *Talanta*, 95 25-30 (2012).
13. M.P. Jensen, M. Borkowski, I. Lazak, J.V. Beitz, P.G. Rickert, M.L. Dietz: Anion effects in the extraction of lanthanide 2-thenoyltrifluoroacetone complexes into an ionic liquid. *Sep. Sci. Technol.*, 47 233-243 (2012).
14. V. Mazan, I. Billard, N. Papaiconomou: Experimental connections between aqueous aqueous and aqueous ionic liquid biphasic systems. *RSC Advances*, 4 13371-13384 (2014).
15. P.G. Rickert, D.C. Stepinski, D.J. Rausch, R.M. Bergeron, S. Jakab, M.L. Dietz: Solute-induced dissolution of hydrophobic ionic liquids in water *Talanta*, 72 315-320 (2007).
16. K. Kidani, H. Imura: Solvent effect of ionic liquids on the distribution constant of 2-thenoyltrifluoroacetone and its nickel(II) and copper(II) chelates and the evaluation of the solvent properties based on the regular solution theory. *Talanta*, 83 299-304 (2010).
17. T.J. Bell, Y. Ikeda: The application of novel hydrophobic ionic liquids to the extraction of uranium(VI) from nitric acid medium and a determination of the uranyl complexes formed. *Dalton Trans.*, 40 10125-10130 (2011).
18. I. Billard, S. Georg: Reactivity of the radiolysis products of the ionic liquid C4-mimTf2N and effect of water : A TRLFS preliminary study. *Helv. Chim. Acta*, 92 2227 (2009).
19. A. Chaumont, G. Wipff: Solvation of uranyl and europium(III) cations and their chloro complexes in a room temperature ionic liquid. A theoretical study of the effect of solvent humidity. *Inorg. Chem.*, 43 5891 (2004).
20. M.G. Freire, P.J. Carvalho, R.L. Gardas, I.M. Marrucho, L.M.N.B.F. Santos, J.A.P. Coutinho: Mutual solubilities of water and the [Cnmim][Tf2N] hydrophobic ionic liquids. *J. Phys. Chem. B*, 112 1604-1610 (2008).
21. J. Jacquemin, P. Husson, V. Majer, M.C. Gomez: Influence of the cation on the solubility of CO₂ and H₂ in ionic liquids based on the bis(trifluoromethylsulfonyl)imide anion. 36 967-979 (2007).
22. L. Genov, I. Dukov: Extraction of some strong single-base acids with di-2-ethylhexylamine. *Comptes Rendus Acad. Bulg.Sci.*, 25 621-624 (1972).

23. L. Genov, I. Dukov: Effect of solvents in extraction of some strong monobasic acids with high-molecular amines. *Comptes Rendus Acad. Bulg.Sci.*, 26 1041-1044 (1973).
24. S. Babic, A. Horvat, D. Pavlovic, M. Kastelan-Macan: Determination of pka values of active pharmaceutical ingredients. *Trends Anal. Chem.*, 26 1043-1061 (2007).
25. Z. Szakacs, G. Hägele: Accurate determination of low pk values by ¹H NMR titration. *Talanta*, 62 819-825 (2004).
26. J. Reijenga, A.v. Hoof, A.v. Loon, B. Teunissen: Development of methods for the determination of pka values. *Anal. Chem. Insights*, 8 53-71 (2013).
27. M. Bouby, I. Billard, G. Duplâtre, J.P. Simonin, O. Bernard, J.P. Brunette, G. Goetz-Grandmont: Determination of the thermodynamic acidity constant of 3-phenkly-4-benzoylisoxazol-5-one (HPBI) using the binding mean spherical approximation model. *Phys. Chem. Chem. Phys.*, 1 3765-3769 (1999).
28. S. Umetani, M. Matsui: Liquid-liquid distribution of 4-acyl-3-methyl-1-phenyl-5-pyrazolones and their zinc complexes. *Bull. Chem. Soc. Japan*, 56 3426-3429 (1983).
29. C. Gaillard, V. Mazan, S. Georg, O. Klimchuk, M. Sypula, I. Billard, R. Schurhammer, G. Wipff: Acid extraction to a hydrophobic ionic liquid: the role of added tributylphosphate investigated by experiments and simulations. *Phys. Chem. Chem. Phys.*, 14 5187-5199 (2012).
30. I. Billard, A. Ouadi, E. Jobin, J. Champion, C. Gaillard, S. Georg: Understanding extraction mechanism in ionic liquids: UO₂²⁺/HNO₃/TBP/C4-mimTf₂N as a case study. *Solv. Ext. Ion Exchange*, 29 577-601 (2011).
31. Y.A. Zolotov, N.M. Kuzmin, *Extraction of metals by acylpyrazolones*, Nauka, Moscow, 1977.
32. M. Atanassova, V. Kurteva, L. Lubenov, S. Varbanov, I. Dukov: Behavior of mixed systems based on para-substituted 4-aroil-5-pyrazolones in the presence of phosphorus containing calix[4]arene toward lanthanoids: synergistic solvent extraction and separation. *Sep. Pur. Technol.*, 95 58-63 (2012).
33. C.H. Huang, *Rare earth coordination chemistry. Fundamental and applications*, Jon Wiley&Son, Asia, 2010.