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The crucial performance of mutual solubility among water and ionic liquids in the time of liquid-liquid extraction of metallic species

Academic Publications, Sofia
2020

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2020, English language, First Edition

Scientific Reviewers:

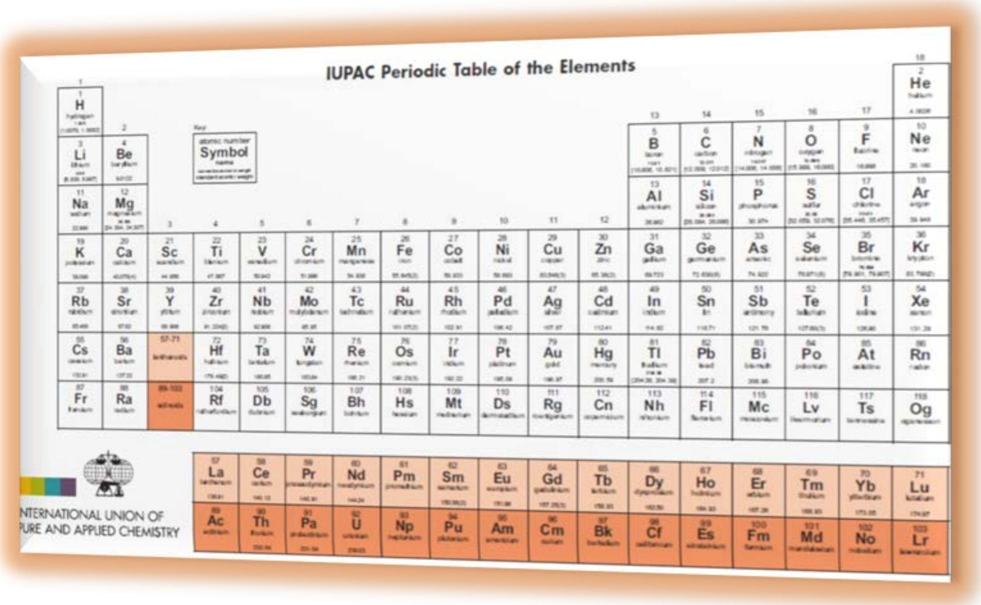
Assoc. Prof. Eng. Alexander Lirkov, PhD
Assoc. Prof. Eng. Alexander Zahariev, PhD

ISBN: 978-954-2940-23-4

Sofia, 2020

The photo on cover page was taken in the Aqua World Oarai Aquarium, Japan, from Dr. Maria Atanassova.

Dedicated to 150th anniversary of the discovery of the Periodic Table of chemical elements by Dmitry Mendeleev and 100th anniversary of IUPAC celebrated in 2019 year



IUPAC Periodic Table of the Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	57-71	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	89-103	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

"By presenting my book to the scientific community, I know there are flaws and shortcomings in it, but I hope that people will be recalled to know that science is immense and that the human mind is limited."
Dmitry Ivanovich Mendeleev

Preface

Inasmuch as ionic liquids (ILs) were reported firstly in the literature in late 1914, there has always been a parallel amid academic scientific research and industrial interest that covers an increasingly diverse range of technological fields, especially for water stable liquid compounds. The proposed overview addresses the investigations of the mutual solubilities between ILs and water attempting to relate them with the chemical nature and structure of these liquid compounds. For the two-phase liquid system, the question arises about how much of each of the pure liquid components dissolves in the other at equilibrium at a given temperature and pressure. Focusing on the employment of more benign and sustainable technological process, this class of chemical reagents have found a large-scale application in solvent extraction process under various appearance *id est* extracting compounds, additives, modifiers, pure diluents, etc. Nevertheless, the more "green" character ascribed to ILs in comparison to conventional molecular diluents is critically assessed nowadays, more than ever. To this end, the number of studies focused on the effect of several IL chemical structural characteristics through their phase behavior with water, namely the IL anion nature, the cation core, the alkyl side tail length attached to cation, and the presence of structural/positional isomers has been expanding in the past few years. Thus, in the course of phase transfer equilibrium reaction during liquid-liquid metal extraction into IL phase the substantial loss of the IL cation and/or anion to the aqueous phase may occur that automatically diminished the putative "greenness" of this class of organic diluents, the main moot consideration. A possibility to overcome this disrespect to be called "green", the magnitude of mutual solubility enclosed by aqueous−IL biphasic systems, and the factors influencing it, have been explored hitherto within the present state of scientific knowledge. Almost all of the presented solvent extraction systems exhibit an upper critical solution temperature (UCST, more common behavior for pairs of liquids), in other words, a biphasic liquid scheme will be envisioned. Brief presentation of mechanistic models with ILs in the role of extracting phase towards variety of metal ions will be given. Why not "tune" the efficiency of extraction process of a target metallic species into an IL by simple adjusting of water content in the equilibrated ionic phase? The ultimate goal is to create general rules for the design of as more hydrophobic as possible ILs for a given extraction task and reaction mechanism with an acceptable environmental footprint.

Contents

1. Introduction

In liquid-liquid extraction processes of metallic species, the two phases should be immiscible as they can be mixed together in all proportions forming two separate appearances at ambient temperature and pressure in the act of lucid criterion.[1-4] In practice, as a rule, one of the phases is aqueous, while another one is organic (solvent: a liquid or solid phase containing more than one substance, solvent = diluent + extractant + modifier…).[5] Whereas the organic phase is commonly quite a complex solution of one or more organic liquids containing one or more extractants and possibly modifiers of various kinds, as well as a diluent, particular care has been taken over the definitions applicable to these various components.[6,7] The solvent extraction circuit should have only two phases: aqueous and organic, because the third phase formation (the organic phase separates into two layers with different densities) can significantly interrupt the interfacial properties of the system leading to *inter alia* deterioration in phase disengagement. In the two phases, the solute is surrounded by water or diluent molecules, thus it is in hydrated and solvated form. The extraction of a metallic complex is a function of two steps: i) transfer by means of collapsing the cavity in the aqueous phase and breaking the bonds between water molecules and the complex; ii) dissolving of the complex into the organic phase and creation of a cavity (space in the liquid where a species can be placed) in its bulky volume, followed by the interactions with diluent molecules.[8] To ensure good mass transfer of the extracted or stripped species across the aqueous-organic interface, a sufficient contact between the two liquids is necessary. Once the two phases have been mixed adequately ensuring excellent kinetics, they have to be separated easily inasmuch as the solvent extraction is an interfacial phenomenon. Actually, the choice of an organic diluent is imperative for a solvent extraction process and this goes without saying.

However, 250 years ago, only a few pure diluents seemed to be acknowledged: besides natural water and oils of course, only alcohol, ether and "etheric oils" were known, Fig. 1. Classical diluents are low molecular weight organic substances that belong to two different broad chemical families: hydrocarbons (aliphatic, cyclic, aromatic) and oxygenates (esters, ethers). Despite the fact that it is difficult to trace them far back in history, really enormous compounds were synthesized since the early nineteenth century. Nowadays, approximately 600 conventional molecular diluents applied in chemical industry are recognized. Y. Marcus has categorized numerous diluents in five classes:[2] 1) liquid capable to form three-dimensional networks of strong hydrohen bonds (e.g., water); 2) protic liquids that have both active hydrogen atoms and donor atoms (O, N, F), but do not form three-dimensional networks; 3) liquid molecules containing donor atoms except active hydrogen i.e. dipolar aprotic substances; 4) liquids composed of molecules with an active hydrogen atom but no donor atoms, e.g. chloroform; 5) liquids with no hydrogen bond forming capability and no donor atoms e.g. carbon tetrachloride or supercritical carbon dioxide. During a screening, the aliphatic diluents are often considered to produce the most efficient systems in order to obtain high distribution ratios, easy handling and effortless manufacturing. They form no hydrogen bonds, have a low polarity and a low dipole moment, and cannot react directly with inorganic compounds forming extractable organic complexes in contrast to cyclohexanone, for example.[9] Water solubility is low in aliphatic molecules and higher in polar ones. High water solubility in the organic phase is definitely a decreasing factor for extraction ability.[10] Thus, liquid-liquid extraction method suffers from a significant drawback: the requirement of water-immiscible organic diluents that are often toxic, flammable or volatile. The analyte distributes itself between the two liquids according to its hydrophobic/hydrophilic character.[11,12] Quantitatively speaking, the distribution ratio of metallic species (M) could be defined as

$$D = \frac{[M]_{(o),eq}}{[M]_{(aq),eq}}\ x\ \frac{V_{aq}}{V_O} \qquad (1),$$

where V_{aq} and V_o are the volumes of the two liquid phases. This means: the ratio of total analytical concentration of a solute in the extract (regardless of its chemical form) to its total analytical concentration in the other phase (aqueous).[5] Consequently, the diluent miscibility chart is a suitable tool for determining which diluents are not soluble in water and therefore can be potential candidates for application in solvent extraction chemistry, Fig. 2. As one exemplification, solubility of water in several diluents in mol·dm^{-3} unit (often abbreviated as M) decrease in the order: 1,2-dichloroethane(0.1262)>$CHCl_3$(0.0738)>C_6H_6(0.0349)>toluene(0.027)≈*p*-xylene(0.021)>CCl_4(0.0087)>C_6H_{12}(0.0029).[13] It is known that the solubility of water in heptane is extremely low (0.0003% w/w or 3 mg L^{-1} or 3×10^{-5} M). Although the two diluents (usually the inorganic water and the organic one) may form two visibly distinct phases when mixing together, they are often somewhat soluble in each other and will, in fact, become mutually saturated. Both parameters (solubility/partition coefficient) are often not equivalent (*via* inverse relationship) and should be consulted when selecting an extraction diluent pair.[13, 14] For example, 0.68% of the diluent *n*-butyl acetate is soluble in water. Conversely, water is 1.2% soluble in its bulky volume. R. Ney ranks water solubility as low (less than 10 ppm), medium (between 10 and 1000 ppm) and high (greater than 1000 ppm).[15] Another important consideration through the list of nearly 16 desirable properties must be taken into account when selecting an extraction diluent is its density in addition to low volatility. The reader is referred to the excellent Perry's chemical engineering handbook on this topic.[16,17] Any organic compound having at 20°C a vapour pressure of 0.01 kPa or more is volatile, VOC. The modern chemical trend is generally towards diluents containing aromatic components, e.g. C_6H_6, because of their lower boiling and flash points, higher volatility and toxicity, carcinogenic properties, greater flammability, and the need to limit carbon emissions in compliance with the applicable environmental legislation, including higher aqueous-phase solubility. The organic molecular compounds that are denser than water (0.9982 g/ml) will form the lower layer of the pair i.e. heavier phase when mixed together, while the less dense will form the upper, lighter layer, or "float" on water. For example, benzene has a density of 0.8765 g/ml at 20°C and would constitute the upper phase when combined with water. On the other hand, the density of $CHCl_3$ is 1.4892 g/ml at 20°C. Therefore, water would form the top layer in an aqueous-chloroform pair, Fig. 3. For a specific application, diluents could be blended occasionally to achieve distinct properties, but in terms of tailored assets, no single "multifunctional" chemical reagent can be perfect in every technological respect.

Figure 1. Alchemy laboratory in Suntory whiskey museum in Hokuto, Japan.[18]

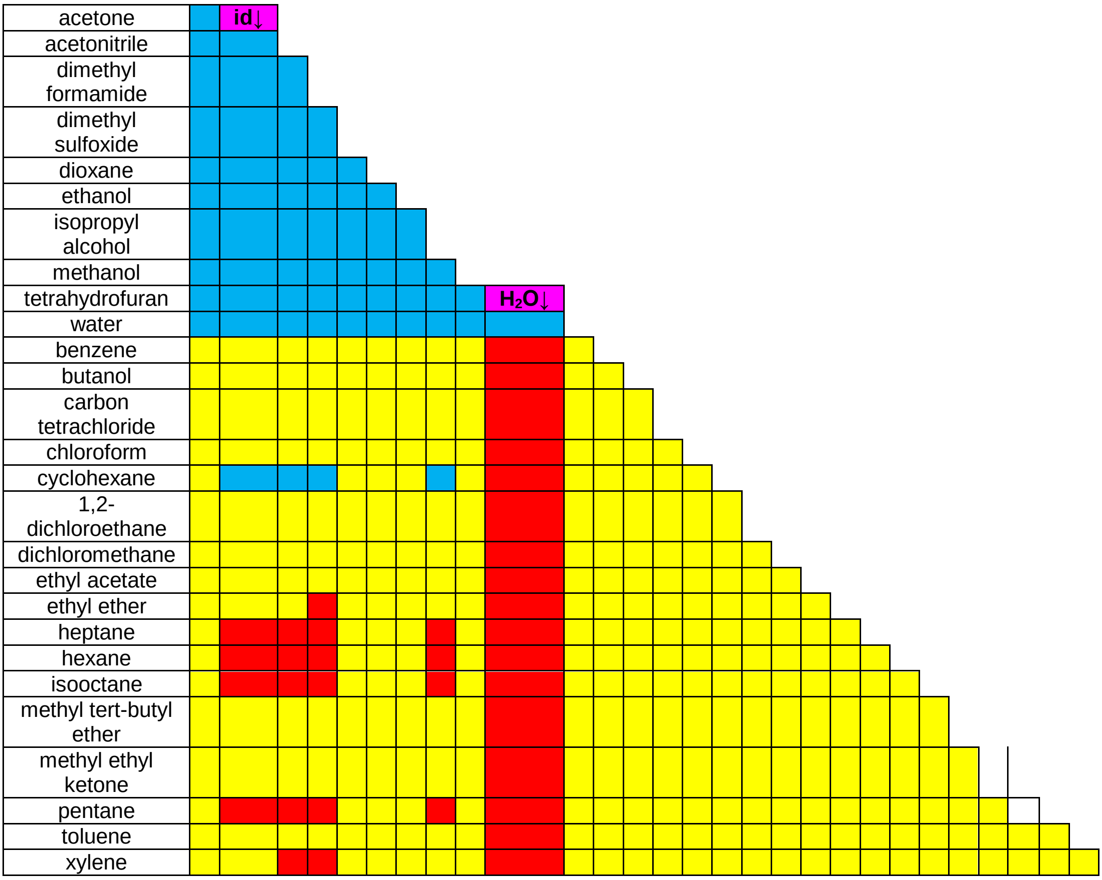


Figure 2. Diluent miscibility chart: 🟨 – missible, 🟥 – immisible and 🟦 – missible/in water.

Figure 3. Aqueous biphasic systems obtained by $CHCl_3$ and C_6H_6, where aqueous liquid phase is colored by $CuSO_4 \cdot 5H_2O$.

Undoubtedly, great volumes of contaminated diluents are generated almost always in the course of traditional liquid-liquid extraction processes. In terms of increased safety, prevention of pollution and improvement of extraction efficiency, the research, development and implementation of innovative chemical technologies are indispensable entering alternative to these detrimental, volatile organic chemicals. The use of a new class of reagents named ionic liquids (ILs) presented usually as "environmentally friendly alternative diluents", because they are nonvolatile, nonflammable, eco-friendly, biodegradable and even edible, with unique chemical and physical properties, increased tremendously in the last ten years not only in the field of solvent extraction chemistry.[19] Most of them have high ignition points, so they do not generate explosive air-vapor mixtures. Ionic liquids are organic salts with melting temperature below 100°C (the boiling point of water) due to their ions' delocalized charge and asymmetrical structure that prevent crystallization. Hereinafter, the principal recognition of ILs abides absolutely in their liquid state, and according to the definition, ILs are media composed of ions. They are presumed to be known since 1914, i.e. for alredy 106 years, when the first compound ethyl ammonium nitrate $[(C_2H_5)NH_3^+][NO_3^-]$ was synthesized by Paul Walden with melting point of 12°C, while he has trying to find a replacement of the nitroglycerine.[20] This chemical was obtained by simple addition of concentrated nitric acid to ethylamine, after which the water was removed by distillation to give a pure salt in a liquid state at room temperature. In order to highlight the ionic character of these alike reagents, they are usually denoted as $[Cat^+][Ani^-]$ considering the ILs' bulky organic cations with a basic cyclic structure and smaller inorganic or organic anions. The abbreviations and structures of all ionic chemicals cited herein are provided at the end of this book in section 8. Due to the cation structure there are five basic classes of ILs: ammonium, phosphonium, imidazolium, pyridinium and pyrrolidinium. Among the large variety of organic or inorganic anions (halides, hexafluorophosphates, tetrafluoroborates, alkyl sulfates, tosylates, methanesulfonates and bis(trifluoromethylsulfonyl)imides) have been distinguished, Fig. 4.

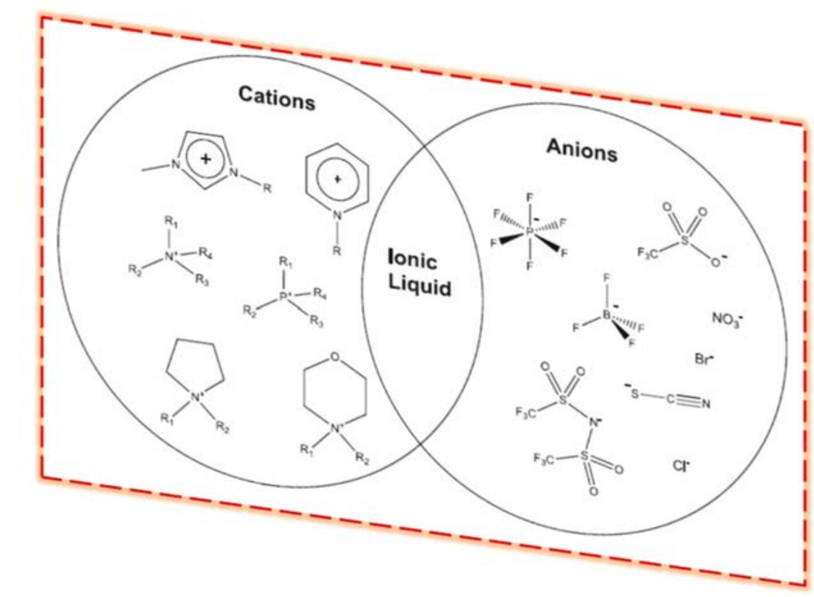


Figure 4. Several widely used cations and anions for synthesis of ILs used as diluents. Adapted from Ref. 21.

Based on the chemical behavior, ILs can be divided in two categories: aprotic and protic. The structure of the premier subclass is mainly based on bulky organic cations (*ex*. imidazolium or pyridinium), whereas the protic are produced through proton transfer from a Brønsted acid to a Brønsted base. To date, the aprotic ILs have received unachievable attention than the protic varieties. Considering the large structural variability of their cations and anions (often estimated as nearly 10^{18}), ILs can cover a wide range of properties, for instance from strongly hydrophilic to extremely hydrophobic chemical nature. One of the most essential properties of the liquid-liquid two-phase systems formed by a hydrophobic ionic liquid and water is the mutual solubility, since ILs are salts having certain solubility in water similar to the traditional one (*ex*. NaCl).[22-26] The huge potential of these novel fluids as diluents, however, has completely overshadowed their fundamental scientific examination as normal, new chemical salts. The applications of ILs in separation solvent extraction processes usually presenting them as a panacea, the point to which everyone agrees (or almost), have been summarized in a number of excellent books[27-30] and reviews.[31-39] A qualitative view of the period 1930−2015 gives an indication that the number of patents focused on ILs as a product *per se* is decreasing over time, while the expansion of the number of patents directed to the new areas of technology illustrates how the transfer of knowledge from academic labs to the industrial sector has been developed and where this scientific research is leading to.[40] Mirroring the optimistic results provided by the academic world and patents which appeared in the last two-decades, it seems that this is very much the end of the beginning regarding technologies implementing ILs, and not the beginning of the end.

The present book covers the literature sources that recognized the existence of a hydrophilic effect, considering the influence of this property on the distribution of a solute between "immiscible" aqueous−ionic liquid phases during solvent extraction of various metallic species. To the best of our knowledge, no book or review highlighting this specific issue caused by ionic liquid molecules in solvent extraction has been previously published in such an intricate way. An increasing number of new exotic or simple ionic types of reagents and an accumulating knowledge of novel metal extraction systems based on ILs have been elaborated in the past decade. Although part of them are not treated comprehensively in this survey, their contribution to the progress of separation science is really fascinating.[41-44] It is worth mentioning the recently proposed concept of an IL−IL separation system for rare-earth minerals (monazite, bastnäsite, ankerite, calcite, dolomite) using a phosphate/ammonium based IL as a droplet phase dispersed into a second immiscible IL.[45] It is of great importance to hint that the thermomorphic behavior of ILs compounds will not be overlooked herein.[42] There are pairs of liquids that are completely miscible at certain temperatures but not at others, ergo, they have critical solution temperatures, T_{CS}. In this approach, ILs with both an upper critical solution temperature (UCST, the system is monophasic upon heating) and a lower critical solution temperature (below LCST, the system is monophasic) could be used for the extraction of metal ions *via* an homogeneous state, i.e. atop change from monophasic to biphasic phase and *vice versa*, Fig. 5.

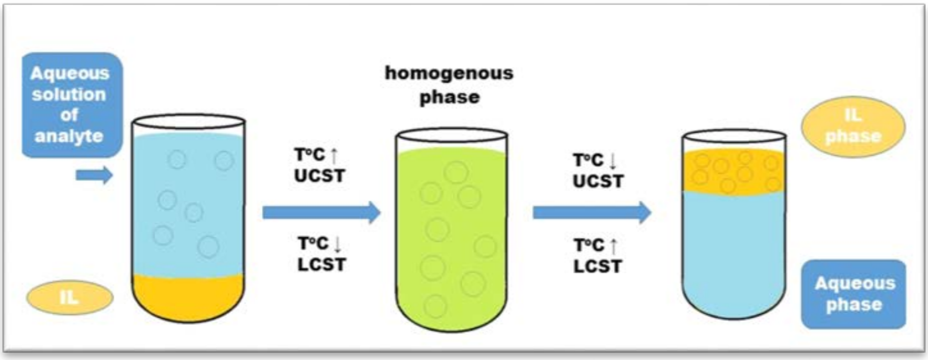


Figure 5. Thermomorphic behavior of ILs with UCST and LCST.

To see detailed fundamental comments on the above, the reader is referred to one book[2] and several publications of prof. Binnemans' group. In parallel to these academic evolutions appears the non-aqueous solvent extraction process, i.e. solvometallurgy with only a handful of available papers at the moment.[21, 46] Needless to say, an obvious advantage is the reduced use of water and the avoidance of the wastewater treatment problems posterior.

The following discussion is divided into different sections regarding: i) the mutual solubility of water and various ionic liquids commonly applied as alternatives to the VOCs; ii) the transfer of ILs' ions (cation/anion) into the aqueous phase in the presence of metallic species due or not due to the corresponding extraction mechanism; iii) the influence of the chemical nature of the dissolved extracting moieties presented in the organic ionic environment, which is also considered in a more simplistic view concerning ILs solubility in the opposite phase; iv) particularly relevant are the investigations focused on the design of new task-specific ionic liquids and their possible application as an organic medium, taking into account the hydrophobic effect; v) a meaningful comparison of the existing relationship between extraction efficiency and water content in the organic phase (IL or conventional molecular diluent) will be done as well. Finally, all collected results, in what concerns the mutual solubility of water and ILs during the extraction process and its crucial role on observed efficiency and selectivity of these analyzed systems, are further critically outlined and addressed in comparison to the available literature data. The opportunity of tunable physicochemical properties has endowed ILs as a particular *sui generis* phase in solvent extraction separation processes, and as a key hunk of today's green chemistry, distinguished them from the traditional molecular systems.

2. Water dragging to the ionic liquid phase at equilibrium stage

Despite the fact that the application of ILs in numerous chemical processes complies with some of the twelve principles of green chemistr, their release through accidental spills or as effluents after industrial waste processing to aquatic environments could cause serious coincidental hazards. This escape of ILs' components is a serious environmental problem and should be controlled, limited to a minimum or avoided if possible, because all ILs cannot be considered environmentally benign, just as an advocacy, one critical review.[47] Regrettably, nowadays the green image of ILs is misplaced a little bit because a great deal of information has been accumulated by the research studies apropos water solubility and diverse toxicological estimation.[48-56] In addition, the physico-chemical properties of individual ILs can be tuned over wide ranges by adequately manipulating the constituent cations or anions and, as consequence, understanding the risk and threats for biota becomes much more complicated in spite of the fantastic variety of attainable chemical structures. The authors also pointed out that hydrophobicity, which corresponds to the increasing alkyl chain substituent length on the IL cation, is found to induce peril toxicity, i.e. ILs with C_8 were found to be more harmful that those with C_6 and C_4 tails regardless of the cation type.[26, 48] The anion can also contribute to toxicity but, in most cases, anion effects are less drastic compared to the side chain effect and the role of anion type remains somehow unclear. In any case, hydrophilic ILs (those that are completely water soluble at room temperature) normally have lower toxicity than hydrophobic ones. Undoubtedly, the knowledge of the mutual solubilities of water and ILs or CO_2 solubility in ILs is of key importance as regards their applications as pure diluents in the chemical engineering field.[57,58] ILs turn out to be very normal organic diluents in which diversified chemical reactions could be accomplish. Such investigations are of interest to the field of metallic removal but also on a wider perspective, in order to predict their eco impact and to overcome their leaching drawback by adjusting their chemical composition. Therefore, the requirement for first-hand mutual solubility experimental data in aqueous biphasic systems in view of solvent extraction is really an essential topic. Stability of IL−water mixtures is an important factor revealed not a long ago by microscopy images with FE-SEM monitoring that shows a stepwise sequence of the extraction process in depth.[59]

2.1. *Applicability of diverse ILs in view of their hydrophobicity*

The solvation of water in ILs is found to depend mainly on the electrostatic water-ion interaction strength that can be determined by two factors: basically, by the size of the ions subordinated to the amount of charge on the ion surface that is coordinated with water.[60] In the case of imidazolium-based ILs and water mutual solubilities, the nature of anions largely determines the macroscopic behavior of these mixtures. On ideal illustration, $[C_1C_4im^+]$−based ILs, in combination with hydrophilic anions $[Cl^-]$, $[Br^-]$, $[CF_3SO_3^-]$ or $[BF_4^-]$, are fully miscible with water, but those combined with $[C(CN_3)^-]$, $[CH_3(C_2H_4O)_2SO_4^-]$, $[PF_6^-]$, $[N(CN)_2^-]$ or $[N(SO_2CF_3)_2^-]$ present phase split at room temperature.[61] On the other hand, note that the solubility could be adjusted to a specific goal if the alkyl side of the cation becomes sufficiently long if, $n>4$, then [BF_4^-] anion can form a biphasic system. Thus, the anion has a primary effect on water miscibility and the cation a secondary sequence. Motivated by the urgent requirement of finding an alternative, more environmentally benign diluents, under the driving forces of the new European chemical regulation REACH (stands for Registration, Evaluation, Authorization and Restriction of Chemicals, in force as of 2007), for the purposes of extraction of valuable compounds their high production costs were not regarded principally as a major disadvantage, both for industrial purposes and for academic research.[62] The structural characteristics of ILs have determined their principal utilization. Those containing expensive functionalized ions have been designed with the aim to be used in small amounts for applications featuring very high added value. Moreover, ILs composed of fluorinated anions are more expensive, i.e. the hydrophobic ones due to the costs of raw materials needed for their production, for example the price of 50 g [Li^+][Tf_2N^-] salt is around EUR 240, Fig. 6. For this purpose, the recovery and reusability of ILs are vital issues in terms of both supporting the economic viability and minimizing the environmental footprint of the proposed chemical processes.[19,63]

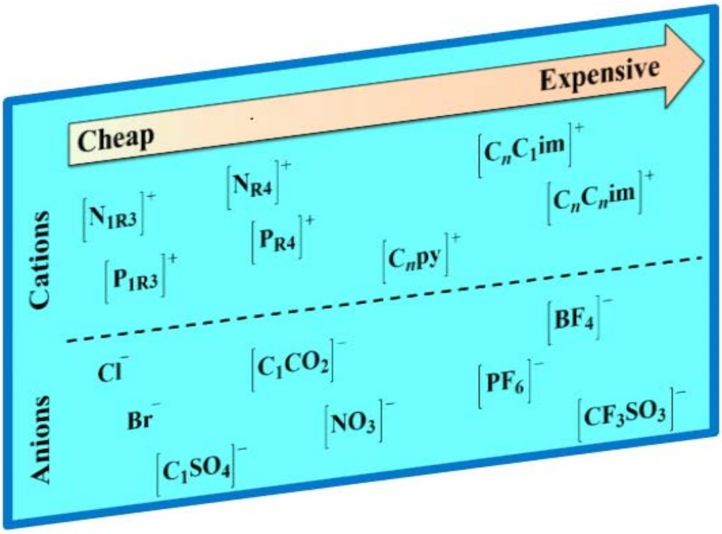


Figure 6. Schematic illustration of the cost of some widely used ILs. Adapted from Ref. 63.

Most ILs are more complicated and more costly to be synthesized than the traditional organic diluents. However, IL−water systems have one distinct feature in comparison to molecular diluents: when two liquids are brought into contact, the ILs ions start dissolving into aqueous phase like typical salts despite being organic. Most ILs used for extraction studies have relatively high solubility in water, in the order of a few tens of millimolar (~10^{-2} M). Strongly hydrophobic ILs are 3 orders of magnitude less soluble in water (1×10^{-5} M), while the moderately soluble ones are in between, at a few millimolar.[64, 65] Under such a frame, the mole fraction solubilities of ILs in water vary from 10^{-4} to 10^{-5}, while vice versa the water dragging to ILs is in the order of 10^{-1}.[66] Thus, if the water−rich phase is considered nearly pure when the dissolved IL is infinitely diluted, the IL−rich phase cannot be premeditated being so pure. In the following sections, both parameters are discussed depending on their availability in the articles under consideration. In the work of Carda-Broch, $[C_1C_4im^+][PF_6^-]$ (*n*-alkyl-3-methylimidazolium cation, hereinafter referred to as $[C_1C_nim^+]$) was selected as a typical example of an IL forming a biphasic liquid system with water.[67] Nevertheless, a decrease in viscosity by an order of magnitude was observed, affected by water saturation: the measured water content in the pinpointed IL is 19 g L^{-1}, 1.05 M, 0.21 mole fraction or 1.8% v/v.

The solubility of water in the ionic-liquid phase was usually determined by the coulometric Karl-Fisher technique invented in 1935 by the German chemist,[66] excluding one study based on OECD guideline 105 for testing chemicals (a set of internationally accepted specifications for testing chemicals, decided by the Organization for Economic Co-operation and Development).[24] Table 1 lists the mutual solubility of water and some ILs at 25°C.[65] For comparison, it lists also the mutual solubility of water and some traditional molecular diluents that have been used for studying the liquid-liquid extraction equilibria. One can see that the degree of solubility of the highly hydrophobic ILs in water is much smaller as compared to typical nonpolar aprotic diluents ($CHCl_3$). That is why meticulous drying protocols and inert environments are frequently employed vis-à-vis traditional organic diluents and similar precautions have been taken into account through elaboration of drying procedures for ILs too, Fig. 7.[68-72] A careful degassing procedure is applied under reduced pressure of nearly 3.5×10^{-2} mbar and heating at 60°C for 2 h, then no heating but still under depression for 1 h to allow the warming of the sample to room temperature. This has proved a perfect control of the amount of H_2O remaining in the IL, with a final average value of approximately 30 ppm or 2.4×10^{-3} M measured by Karl-fisher tirtration with a gobal uncertainty ±2%.[71]

Table 1. Mutual solubility of water and moderately hydrophobic ionic liquids as well as molecular diluents at 25°C.[65]

IL	Solubility	of water	in IL	Solubility	of IL	in water
	Wt %	mol kg^{-1}	χ_W^{IL}	Wt %	mol kg^{-1}	χ_{IL}^{W}
$[C_1C_2im^+][Tf_2N^-]$	1.94	1.08	0.298	1.81	4.6×10^{-2}	8.38×10^{-4}
$[C_1C_4im^+][Tf_2N^-]$	1.48	8.2×10^{-1}	0.257	0.716	1.72×10^{-2}	3.07×10^{-4}
$[C_1C_6im^+][Tf_2N^-]$	1.05	5.83×10^{-1}	0.208	0.23	5.3×10^{-3}	9.56×10^{-5}
$[C_1C_8im^+][Tf_2N^-]$	0.87	4.83×10^{-1}	0.187	8.87×10^{-2}	1.87×10^{-3}	3.36×10^{-5}
$[C_1C_{10}im^+][Tf_2N^-]$				0.014		
$[C_1C_4im^+][PF_6^-]$	2.19					
$[C_1C_6im^+][PF_6^-]$	1.47					
$CHCl_3$				0.8		
CCl_4				9.9×10^{-3}		
dodecane				3.67×10^{-7}		
1,2-dichloroethane	0.15			0.81		
nitrobenzene	0.26			0.20		

Figure 7. Snapshot of water removing under reduced pressure using vacuum pump during $[C_1C_4im^+][Tf_2N^-]$ synthesis.

A falling film evaporator operated in a continuous mode has been used also to separate water from IL/water solutions, but it is essential for the process to determine the favorable parameters.[73] These investigations were found to be very promising in terms of achieved water contents < 1×10^{-3} g_{water}/g_{total} at moderate process conditions: 120°C, 50 mbar, specific heat flux < 15 kW m^{-2}, etc. Falling film evaporators are commonly used in chemical engineering technology for separating thermally sensitive products, e.g. fruit juices, milk or sugar syrup. Furthermore, a dependency of viscosity to water content and temperature showed the possibility to utilize the viscosity as a parameter to monitor water contents online. The dehydration process was studied by Wellner et al. for two commercially available IL at different feed rates and water concentrations at the inlet: dimethyl-dihydroxy-ethylammonium methylsulfonate belongs to the ammonium group molten salts, while 1-ethyl-3-methylimidazolium ethylsulfate is based on imidazole cyclic structure.[73] Water contents from 0.0086 to 0.0121 g_{water}/g_{total} could be reached with only one objectionable future, colorless and transparent ILs turned to be yellow transparent over the experiment duration.

The solubility of water in the ILs increased from pyridinium to imidazolium−based ILs due to their aromatic character and is higher compared to pyrrolidinium and piperidinium type of ILs, because they can potentially interact with water molecules (OH…π or O…π).[66] It is apparent from Table 1 that the longer is the alkyl chain (*ex.* $[C_1C_8im^+][Tf_2N^-]$), the smaller is the solubility of water in ILs and also that of ILs in water, meaning that the ILs polarities decrease with the alkyl chain length increase of the cation. The ILs with a larger molecular size had lower densities and polarities, which contribute to a lower IL solubility.

By contrast, to what could be apprehending, it is not perfect to say that ILs for handling in solvent extraction processes should be immiscible with water. All scientific contributions contradict this statement. Besides the fact that hydrophobic ILs tend to form a second liquid phase with water, they are highly hygroscopic. Howbeit, the idiom “totally immiscible” is merely a question of instrumental detection limits and scientific tangibility. On that account, the use of terms “upper” and “lower” liquid phase after mixing a biphasic sample seems to be overall more meaningful than“water rich” and “IL−rich” or “oily” phase etc., as frequently delineated in the field. Note that the densities of ILs are generally higher than water. In the following discussion, subscripts “aq” and “o” in the notation that correspond to the aqueous and organic phase will be designated.

The biphasic mixtures composed of three monobasic mineral acids often used in liquid/liquid extraction of metallic species (DCl, DNO_3, $DClO_4$ from 10^{-2} to 10^{-4} M) and of their corresponding sodium salts (μ=0.1 M NaCl, $NaNO_3$ and μ=0.1, 0.2 and 0.4 M $NaClO_4$) were investigated by Atanassova et al., with the aim to assess the water dragging to the lower oil “ubiquitous” phase ($[C_1C_nim^+][Tf_2N^-]$, n = 2,4,6,8 and 10) and the loss of IL components in the upper aqueous phase too.[74] The solubility of $[D^+]$ in $[C_1C_nim^+][Tf_2N^-]$ series of ILs was determined as a function of initial pD value, and suchlike pD_{eq} *vs* pD_{in} obtained results are unprecedented in the literature, as only few data have appeared in the studied pH/pD range, Fig. 8. When $[C_1C_4im^+][Tf_2N^-]$ and $[C_1C_6im^+][Tf_2N^-]$ were applied, a clear declination from the line y = x (i.e. $pD_{in} = pD_{eq}$) is seen, as a result of a solubility of $[D^+]$ in the lower organic phase, that leads to an increase of the equilibrium pD values in the upper aqueous phase. At the same time, no $[D^+]$ transfer was detected when $[C_1C_8im^+][Tf_2N^-]$ or $[C_1C_{10}im^+][Tf_2N^-]$ has been used, Fig. 8. It is evident that the chemical composition of the aqueous phase (NO_3^-, ClO_4^-, Cl^-) did not influence this appearance. Apart from this, samples with sodium perchlorate concentrations equal to 0.2 M and 0.4 M deviate from the y = x line above pD_{in} = 3.2, with a plateau at pD_{eq} = 6.2, Fig. 8.

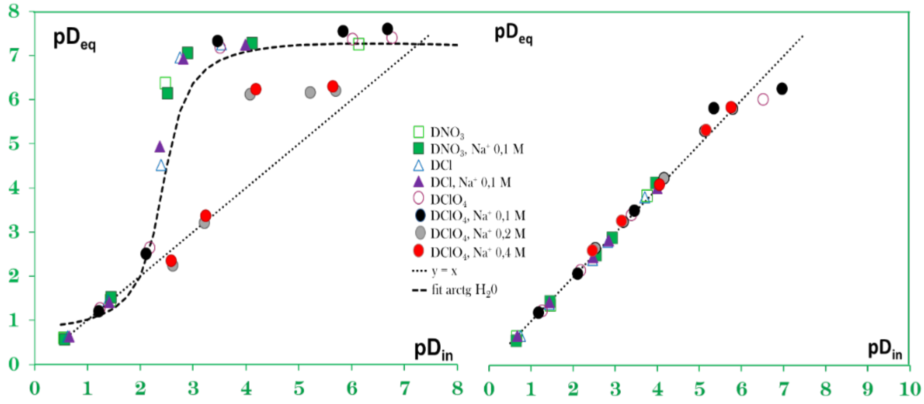


Figure 8. pD_{eq} *vs.* pD_{in} of the aqueous phases using $[C_1C_4im^+][Tf_2N^-]$ and $[C_1C_{10}im^+][Tf_2N^-]$ as organic medium. Re-drawn from Ref. 74.

No significant effect of D^+/Na^+ composition of the aqueous phase into D_2O transfer to the IL was observed in the pD range investigated (0.6–7) for a given IL, and the corresponding average values were calculated, Fig. 9. The decrease in water solubilisation can be clearly seen as a function of ***n*** (approximately more than -60 % in D_2O solubility altering $[C_1C_2im^+]$ with $[C_1C_{10}im^+]$ cation. This is ascribable to the increase in hydrophobicity of the IL phase by changing the cation, keeping the same anion $[Tf_2N^-]$: $C_1C_2im^+ > C_1C_4im^+ > C_1C_6im^+ > C_1C_8im^+ > C_1C_{10}im^+$, Fig. 9.

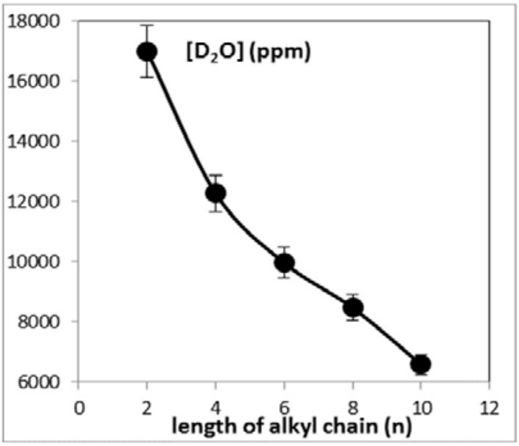


Figure 9. D_2O average amount (ppm) in the lower phase *vs. n* (the length of the IL cation C_1C_nim$^+$). Adapted from Ref. 74.

This order, as concerns the hydrophilicity of the ILs' cation ([C_1C_{10}im$^+$]>[C_1C_4im$^+$]>[Me_3BuN$^+$], see section 8 denoted to notations), is maintained as added DNO_3 amount increases significantly up to 6 M, but the D_2O transfer is more or less constant up to 3 M DNO_3 referable to inorganic acid partial association, Fig. 10, and then increases for the three studied series by authors.[75] Therefore, clear picture emerges from the published solubilization results implementing [$C_1C_{\mathbf{n}}$im$^+$][Tf_2N^-] ILs. Beyond doubt, it is perceptible at low acidic pH range and proceeds monotonously up to 7 M solutions of nitric acid, which is commonly applied as a salting-out agent.

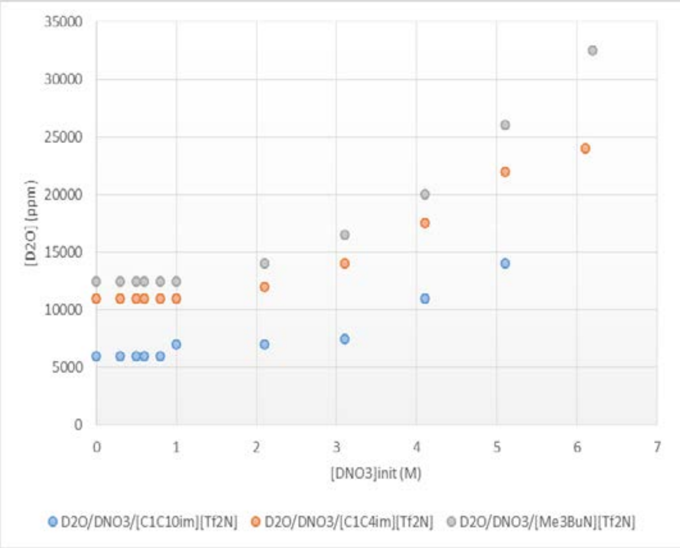


Figure 10. D_2O amount in the lower phase. Adapted from Ref. 75.

However, the effect of DCl acid presence (0–8 M) on the water solubility in long alkyl chain ILs $[C_1C_nim^+][Tf_2N^-]$, $n = 6$ and 8 differs from these results, obtained in the same research laboratory, where nitric acid increases distinctly the water content.[76] Since the two mineral acids HNO_3 and HCl showed dissimilar water dispersion profiles, the authors had no valid in a common sense, explanation of the observed trends. It was found by Genov and Dukov[77, 78] that the extractability of the inorganic acids changes in the sequence HCl, HNO_3 and $HClO_4$ in molecular diluents (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 liquid phase. The diluent with the greatest solvating capacity ($CHCl_3$), in which the difference in the extraction of different acids is greatest and passing through diluents with a lower solvating capacity (C_8H_{18}, CCl_4, C_6H_6), with which this difference is smaller, an ideal case is attained, where the absolutely inert diluent has no solvating capacity whatever and the extraction of different acids is equalized.[77,78] Henceforward, the water uptake into $[C_1C_2im^+][Tf_2N^-]$ equilibrated with 7.1 M DCl solution was reported to be 2.2 M, which decreases to 1.0 M into its $[C_1C_4im^+]$ homologue, to 0.48 M into $[C_1C_6im^+]$ representative, and finally to 0.32 M into $[C_1C_8im^+][Tf_2N^-]$.[76] It is noticeable that the increase of aqueous DCl concentration (from 0 to 8 M) leads to the continual and significant rise of equilibrium water content above 3 M in $[C_1C_2im^+]$ and $[C_1C_3pyr^+]$ $[Tf_2N^-]$, while it remains almost constant in the $[C_1C_4im^+][Tf_2N^-]$ sample. It is interesting to elucidate that this addition of mineral acid results in lower water dragging into $[C_1C_4im^+]$– and $[C_1C_8im^+][Tf_2N^-]$ layers as compared to the case when $H[Tf_2N^-]$ acid compound was employed for acidifying the aqueous phase. The maximum acid concentration was limited to 2 M because if greater fixation than 3 M was introduced into aqueous phase, the formed biphasic system with $[C_1C_4im^+][Tf_2N^-]$ would become monophasic, unfortunately. It is apparent from the published data that the increase of aqueous $H[Tf_2N^-]$ concentration from 0 M (0.94 M and 0.58 M for n=4 and 8) to 2 M provokes the water uptake in ILs to the amounts of *ca*. 3.8 and 1.8 M, respectively.

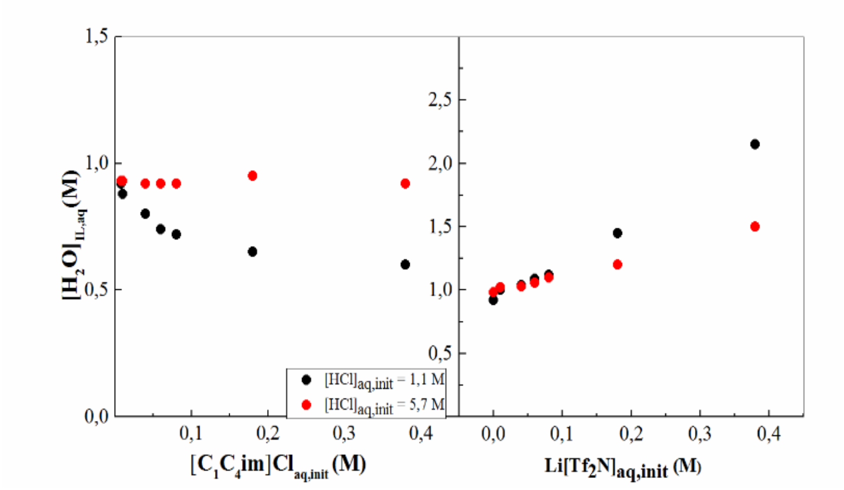


Figure 11. Equilibrium water content in $[C_1C_4im^+][Tf_2N^-]$ ionic liquid as a function of the salt concentration in the aqueous hydrochloric acid solution. Adapted from Ref. 76.

Furthermore, the experimental results on the solubility of water into $[C_1C_4im^+][Tf_2N^-]$ that was equilibrated with aqueous hydrochloric acid solutions with two chosen concentrations, 1.1 and 5.7 M, in the presence of various quantities of the salts $[C_1C_4im^+][Cl^-]$ and $[Li^+][Tf_2N^-]$ equal to 0.4 M, i.e. two chemical compounds bearing the same ions (cation/anion) as the studied IL phase, are shown in Fig. 11.[76] The introduction of these salts has opposing influences on water dragging into organic ionic layer, much more pronounced at the higher aqueous HCl concentration of course. The insertion of $[C_1C_4im^+]$ cation leads to a very slight decrease of water transfer, while the presence of $[Li^+][Tf_2N^-]$ obviously increases water solubility, more remarkable likely with 0.4 M applied salt concentration and 1.1 M HCl acidity.

Although $[C_1C_nim^+][Tf_2N^-]$(n = 2, 3, 4, 5, 6, 7 and 8) are among the most hydrophobic classes of ILs known, this statement is in fact a little bit misleading. The solubility of water in these compounds is surprisingly high, ranging from 0.17 to 0.36 mole fraction, while the solubility of ILs in water is much lower, in the range from 3.2×10^{-5} to 1.1×10^{-3} in mole fraction, measured in the temperature range from 288.15K to 318.15K at atmospheric pressure.[22] Another worthy example is the typical liquid-liquid behavior of increasing miscibility between both phases, with the temperature increase as shown on Fig. 12. Particularly relevant are the results focused on the larger cross-contamination of water−ILs systems at higher temperatures.

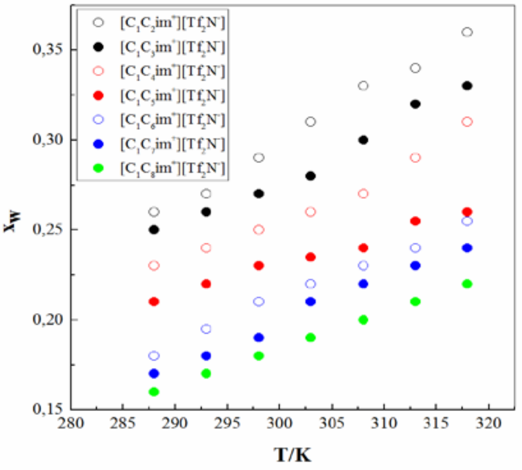


Figure 12. Mole fraction solubility of water (χ_W) as a function of temperature in the ILs. Drawn from data reported in Ref. 22.

Freire et al. have examined the impact of ILs' structural modification like the cation family, its chain length and the number of substitutions, as well as the anion identity influence in their liquid-liquid phase behavior with water.[79] The experimental results show that there is a hydrophobic tendency that increases due to the cation family in the order $[C_1C_nim^+]$< $[C_1C_npy^+]$ < $[C_1C_npyr^+]$ < $[C_1C_npip^+]$. Thus, the imidazolium-based cations present the higher solubility of water, followed by pyridinium-, pyrrolidinium- and at last the piperidinium- type of compounds. The higher solubility of the first two cations seems to be due to the interaction of water with the π systems of those cations, while no electrons are available for privileged interaction in the latter two varieties. Furthermore, the inclusion of a third methyl group replacing the most acidic hydrogen at C2 position in the imidazolium cation showed to have different impacts in both "rich" liquid phases, which was addressed supplementary to the hydrogen bond. It leads to a strong decrease of water solubility to a value closer to that obtained for $[C_1C_8im^+][PF_6^-]$ form. Insights into the relative strength cation-anion interaction were given, substantiated by ESI-MS-MS measurements.[79] It was found that such an interaction decreases as the alkyl side chain length increases for both $[C_1C_nim^+]$ and $[C_1C_npy^+]$ cation families. This is because of an increase in the hydrogen-to-fluorine distance with the corresponding carbon chain. Particularly relevant is the work focused on the effect of both structural and positional isomerism of cation, namely its alkyl chain length and structural isomers, and the position of the second alkyl substitution, on the six pyridinium-based ILs with $[Tf_2N^-]$ anion: the investigated thermophysical properties were evaluated by Oliveira et al.[72] Given the importance of the water content on the corresponding physical properties, water-saturated ILs samples were analyzed in the temperature range from 298K to 363K, again at atmospheric pressure, Table 2.

Table 2. Molecular weight (M_{IL}), mole fraction solubility (χ_w), and weight fraction (W_w) saturation of water in each IL at 298.15K and atmospheric pressure.[72]

IL	M_{IL}		
	$g \cdot mol^{-1}$	χ_w	W_w
$[C_3\text{-}3\text{-}C_1py^+][Tf_2N^-]$	416.37	0.238	0.013
$[C_4\text{-}3\text{-}C_1py^+][Tf_2N^-]$	430.39	0.214	0.011
$[C_4\text{-}4\text{-}C_1py^+][Tf_2N^-]$	430.39	0.244	0.013
$[C_4py^+][Tf_2N^-]$	416.37	0.248	0.014
$[C_6py^+][Tf_2N^-]$	444.42	0.233	0.012
$[C_8py^+][Tf_2N^-]$	472.48	0.197	0.009

The same research group has studied the IL's anion impact on the mole fraction solubility of water as a function of temperature. The authors concluded that the hydrophobicity of the examined anions increases in the order: $[BF_4^-] < [CH_3(C_2H_4O)_2SO_4^-] < [C(CN)_3^-] < [PF_6^-] < [N(SO_2CF_3)_2^-]$.[61] Another worthy example shows the water-saturation of what the chemist researchers call "hydrophobic ILs" incorporating $[PF_6^-]$ and $[BF_4^-]$ anions, Fig. 13. As a rule, in the presence of the first negatively charged ion, ILs dissolve less water than $[BF_4^-]$ anion variety, and the solubility decreases with the increasing alkyl chain length of imidazolium cation as well, even though not so impressively.[68]

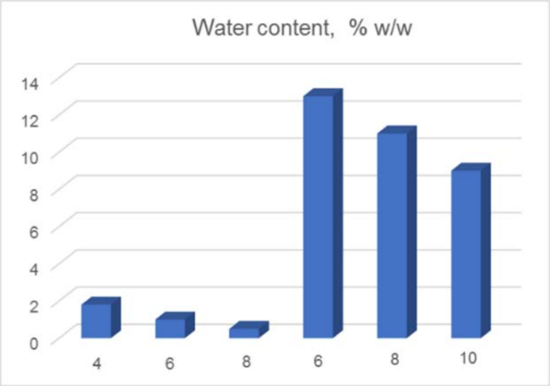


Figure 13. Water content on saturation at ambient temperature (*ca*. 22°C) for $[C_1C_n\text{im}^+][PF_6^-]$, ($n$=4, 6 and 8) and for $[C_1C_n\text{im}^+][BF_4^-]$, ($n$ = 6, 8 and 10). Drawn from data reported in Ref. 68.

It can be clearly seen that IL's solubility depends so strongly on the inorganic anion of the IL employed. Other similar examples display that enhanced diffusion of water into $[C_1C_4\text{im}^+][PF_6^-]$. Fig. 14 represents the UV spectra of $[C_1C_4\text{im}^+]$ cation in water equilibrated with three ILs.[80] The exact quantitative results of these dialkyl imidazolium ILs are summarized in Table 3. The loss of $[\text{BETI}^-]$ containing sample into water was estimated to be 25-fold less than that of the $[C_1C_4\text{im}^+][PF_6^-]$ variety. Water partitioning into ILs also decreases with IL anion hydrophobicity.

Table 3. Effect of different IL anions on water content and solubility of ILs in water. 1ml of IL was contacted with 10 ml of H_2O for 1 hour.[80]

	$[C_1C_2\text{im}^+]$		$[C_1C_4\text{im}^+]$		
	$[Tf_2N^-]$	$[\text{BETI}^-]$	$[PF_6^-]$	$[Tf_2N^-]$	$[\text{BETI}^-]$
Density (g/L)	1.50	1.53	1.37	1.42	1.45
H_2O content in "dry" ILs (ppm)	350	223	513	240	143
H_2O content in "wet" ILs (ppm)	19400	10600	20700	13600	7070
IL solubility in H_2O (mM)	45.3	8.93	86.6	19.0	3.41

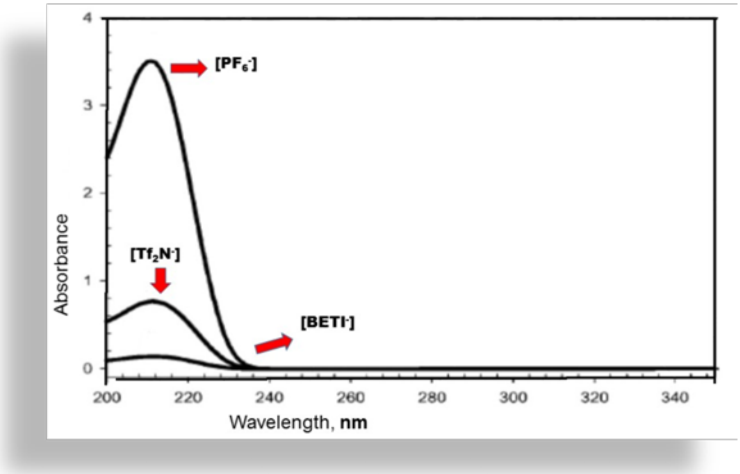


Figure 14. Determination of imidazolium cation concentration ($[C_1C_4im^+]$) in water employing $[PF_6^-]$, $[Tf_2N^-]$ and $[BETI^-]$ anions *via* UV-vis spectra of equilibrium aqueous phases. Adapted from Ref. 80.

The anion effect of ILs has more pronounced impact on solvent extraction processes for the more highly charged metal cations. This idea is given further weight by subsequent investigation of selectivity between alkali and alkaline earth s-ions by the authors. Increasing anion hydrophobicity of ILs with unlike aliphatic tails increases Sr/Cs selectivity for low *n* lengths, but decreases Sr/Cs selectivity for high *n* value.[80] The significant differences among the three anions pinpointed above are relatived to hydrophobicity and can also be seen from the data summarized in Table 4 for longer alkyl chain $n = 5$, 8 and 10.[81]

Table 4. Effect of IL anion on the water content and water solubility of various $[C_1C_{\mathbf{n}}im^+][Ani^-]$.[81]

	$[C_1C_5im^+]$ $[Ani^-]$			$[C_1C_8im^+]$ $[Ani^-]$			$[C_1C_{10}im^+]$ $[Ani^-]$		
	$[PF_6^-]$	$[Tf_2N^-]$	$[BETI^-]$	$[PF_6^-]$	$[Tf_2N^-]$	$[BETI^-]$	$[PF_6^-]$	$[Tf_2N^-]$	$[BETI^-]$
Mr (g/mol)	298.1	429.4	529.5	340.3	443.5	575.5	368.1	503.5	603.5
Density” dry” (g/ml)	1.29	1.35	1.51	1.22	1.28	1.45	1.18	1.29	1.38
H_2O in “dry” ILs (ppm)	425	< 10	–	< 10	< 10	–	< 10	< 10	–
H_2O in “wet” ILs (ppm)	19260	17100	3880	15883	11500	4000	11375	10400	5600

ILs solubility in H_2O (ppm)	11262	2150	3779	2158	990	227	736	310	114

For these solubility measurements, 1 ml aliquot of IL was contacted with 10 ml portion of deionized water, 10 min vortex followed by stand ~1 h undisturbed to equilibrate the samples. UV-visible absorption was applied too, i.e. only the solubility of $[C_1C_nim^+]$ was checked in reality. The choice of counterion, in particular its hydrophobicity, for $[C_1C_nim^+]$–based ILs could strongly influence the balance among the various possible pathways for extraction equilibrium of s-elements, and it affects both efficiency and selectivity of the process. The overall conclusion is that higher IL anion hydrophobicity is accompanied by a greater tendency towards an ion exchange mode of reaction employing macrocyclic polyether compound as ligands diluted in the IL media. Unfortunately, the available data for $[PF_6^-]$ ionic liquid salts are rather scattering.[47] In spite of the fact that $[PF_6^-]$–based ILs form a biphasic system with water, they are extremely moisture sensitive and produce volatiles such as HF, POF_3 or crystalline decomposition product, for example $[C_1C_4im^+]F{\cdot}H_2O$:

$[PF_6^-] + 4H_2O = 5HF + F^- + H_3PO_4$.[82]

Specifically, the IL $[C_1C_8im^+][PF_6^-]$ is easily decomposed in contact with ≥ 5 M nitric acid solution. When $[C_1C_4im^+][PF_6^-]$ was exposed to moisture, two types of PF_2X_n species ($X = Cl^-$ or OH^-) were detected by ^{31}P NMR analysis.[83] The formation of PF_2 moieties was based on the assumption that the equatorial **F** ligands of $[PF_6^-]$ are relatively easily substituted compared to the apical **F** atoms.

Quite clearly, one of the reaction product of anion hydrolysis $[BF_4^-]$ is also a hydrogen fluoride:

$[BF_4^-] + H_2O = [BF_3OH^-] + HF$. Thus, one can refer only to the average solubility of $[C_1C_8im^+][BF_4^-]$ in water, reported to be 0.065 mol kg^{-1} at room temperature.[70] At the same time, $[C_1C_4im^+][BF_4^-]$ is completely water soluble, but at 0°C the solubility decreases. In respect to the environmentally responsible design of novel diluents, the fluorine-containing ILs with well-established instability towards hydrolysis are unacceptable just like the two highlighted reagents. The decomposition recation leads to the formation of toxic HF. As already pinpointed, it is widely accepted in the literature that the toxicity of ILs are proportionately related with their hydrophobicity.

The water content of air-saturated and water-saturated series of ILs was measured after exposing them for one-week to air humidity or after mixing them with water for 24 hours and living in contact with fresh water after centrifugation for another 24 h in order to reach an equilibrium. The reported data in weight percents with ±7% precise are given in Table 5.[84]

Table 5. Water content **m** in % of selected air- and water-saturated ILs, including relative humidity (RH) at 25°C.[84]

IL	RH/%	m(air−sat)/%	m(water−sat)/%
$[4Mopy^+][BF_4^-]$	49	1.81	11.3
$[3Mopy^+][BF_4^-]$	48	1.25	13.6
$[Opy^+][Tf_2N^-]$	49	0.13	0.86
$[2Mopy^+][Tf_2N^-]$	49	0.31	0.78
$[4Mopy^+][Tf_2N^-]$	49	0.10	0.73
$[4Mopy^+][BETI^-]$	49	0.20	0.52
$[4Mopy^+][TfO^-]$	49	0.23	17.2
$[4Mopy^+][N(CN)_2^-]$	49	1.84	54.9
$[4Mopy^+][AsF_6^-]$	49	0.25	0.90

The high solubility in water has been obtained for $[BF_4^-]$, $[TfO^-]$ and $[N(CN)_2^-]$−ILs. All other studied ILs have lower contents: 0.10, 0.20 and 0.25 % for air saturated $[4Mopy^+]$ cation based types combined with $[Tf_2N^-]$, $[BETI^-]$ and $[AsF_6^-]$ anions, respectively. It should be noted that when the methyl group on the octylpyridinium cation was replaced from ortho to para position, the water content decreased for $[Tf_2N^-]$−ILs. For example, for air saturated $[2Mopy^+][Tf_2N^-]$ and $[4Mopy^+][Tf_2N^-]$, the decrease is from 0.31 to 0.10%, respectively. At the same time for the similar water-saturated samples, this influence was negligible: the water content difference was 0.05%. Considering the anion chemical structure, it should be noted also that ILs containing fluorinated spherical anions are much more hygroscopic. Hereinafter, the solubility of these liquid salts could be easily modified by relevant molecular design. The same experimental protocol has been applied for monitoring the water solubility influenced by pyrrolidinium and piperidinium cations when they were attached to the $[Tf_2N^-]$ anion in order to form the IL compounds.[85] The collected results are listed in the following Table 6.

Table 6. Solubilities of selected ILs in water and water solubility in ILs at a relative humidity of 40% and in liquid-water saturated systems. Mass fraction (w) is in ppm.[85]

IL	w (sol. in water)	w(air−sat.)	w(water−sat.)
$[MPpyr^+][Tf_2N^-]$	8200-9900	5190	13200
$[MBpyr^+][Tf_2N^-]$	5900-6100	3450	11700
$[MOpyr^+][Tf_2N^-]$	500-540	2930	8370
$[MPpip^+][Tf_2N^-]$	6900-8000	4220	11700
$[MBpip^+][Tf_2N^-]$	3600-4400	3610	10050
$[MOpip^+][Tf_2N^-]$	< 200	2260	6590
$[MOpip^+][N(CN)_2^-]$	ND	49330	>50000

There is a little influence of alkyl-chain length or nature of the cation ring on the water contents of ILs accommodating pyrrolidinium or piperidinium type of cations. The last one appears to have lower water absorption capacity than its pyrrolidinium homologue. However, the chemical nature of cations has more pronounced impact on the solubility of ILs in water. Increase of the alkyl chain tail from butyl to octyl, leads to a decrease by one order of magnitude in the solubility in water. Here again, piperidinium variety shows lower solubility in water compared to pyrrolidinium kind of compounds. The appropriate toxicity investigation was also conducted in the cited work of Salminen et al.[85]

The lower toxicity of the ammonium compounds in comparison to their phosphonium counterparts supports the suggestion that they future a lower hydrophobic nature.[86] Under such a frame, the impact of non-aromatic and non-cyclic cation N-alkyl-triethylammonium $[N_{R,222}^+][Tf_2N^-]$, where $R = 6$ to 12) on the mutual solubility with water and with water/methanol mixture (1:1 weight ratio) was investigated by va olumetric and cloud-point method respectively.[87] The authors summarized that the solubility of water in IL is fairly high, of approximately 0.25 to 0.35 in mole fraction unit, independent from the cation length. On the other hand, the solubility of ILs in water drops by an order of magnitude in the aqueous phase with increasing of the alkyl chain length on the ammonium cation $R = 6$ to 12 for each higher member of the homologous series. Note that in the work of Machanova et al.,[87] this finding was noticed in a /methanol binary system as well. Generally, this decrease of ILs solubility in water influenced by the chain length (for similar anion-based ILs) was explained to be driven by the decrease of the entropy of dissolution, and depends on their molecular volume either.[79] The observed temperature trend of solubility also changes slightly while editing the cation structure: the solubility dependence on temperature is less pronounced in higher members of the homologous series.[87]

To the best of our knowledge, there are only few reports providing the reciprocal solubilities of ammonium- sulfonium- and phosphonium-based ILs, published by prof. Coutinho's group.[88] As a result of the high hydrophobic nature of $[N_{1888}^+][Tf_2N^-]$ and $[P_{1888}^+][Tf_2N^-]$, their solubility in water is very low, below the detection limit of the conductivity method applied in this study. Therefore, only the water presence in the lower phase has been reported. The most noticeable result described by authors is that the binary system composed of $[P_{1888}^+]$ $[Tf_2N^-]$ exhibits the widest immiscibility gap, followed by $[N_{1888}^+][Tf_2N^-]$, $[N_{4441}^+][Tf_2N^-]$, $[S_{222}^+][Tf_2N^-]$, $[N_{4111}^+][Tf_2N^-]$ and $[S_{221}^+][Tf_2N^-]$. As a whole, comparing ILs with the same central atom, the mutual solubilities decrease from $[S_{221}^+]$ to $[S_{222}^+]$, and from $[N_{4111}^+]$ via $[N_{4441}^+]$ to $[N_{8881}^+]$. This is a well-established, déjà vu trend by which an increase in the size of the aliphatic moieties attached to the cyclic cation core leads to an increase in the IL hydrophobicity. Moreover, phosphonium-based ILs are more hydrophobic than their ammonium-based counterparts, i.e., $[P_{1888}^+][Tf_2N^-]$ exhibits a lower solubility of water than $[N_{1888}^+][Tf_2N^-]$. It is interesting also to highlight that the binary mixtures composed of $[S_{222}^+][Tf_2N^-]$ were found to exhibit a wider immiscibility gap compared to $[N_{4111}^+]$–IL, despite the fact that the former has a lower number of total carbon atoms (or methylene groups) at the cation (6 and 7 carbon atoms, respectively). This is a clear indication that the joint solubilities between water and ILs are not only related to the increase in the hydrophobic character of the cation, but are also governed by other factors, such as charge distribution of the central atom and consequent charge distribution at the aliphatic moieties, and further accessibility of water to the charged part of the cation.[88] To get a deeper insight into the molecular mechanisms which rule the liquid-liquid phase behavior, the researchers used COSMO-RS calculations, additionally. The main conclusion was that, besides the IL hydrophobicity afforded by the size of the aliphatic tails, the hydrogen-bonding ability of the IL cation towards water molecules also seems to play an important role. Howeve, $[S_{221}^+]$, $[S_{222}^+]$, $[N_{4111}^+]$, and $[N_{4441}^+]$–ILs were considered to be hygroscopic (with a mole fraction solubility of water in the order of 10^{-1}). The low mole fraction in $[N_{1888}^+]$ and $[P_{1888}^+]$–ILs (in the order of 10^{-2}) is low enough to be accepted as infinite dilution. The high positive enthalpies calculated by Kurnia et al. for the solution of water in $[N_{1888}^+][Tf_2N^-]$ and $[P_{1888}^+][Tf_2N^-]$ at 298.15 K indicate that the interaction between H_2O and these ionic compounds is very weak due to their bulky alkyl chains. Hence, the small solubility differentiation between the two ILs, with [N_{1888}^{+}] and [P_{1888}^{+}] cations, is ruled by the small distinction in the enthalpy of solution that is higher (more positive) for an IL with a lower solubility of water, i.e. [P_{1888}^{+}]. The higher and almost non-contrast entropy of the solution of water in both ILs reflects the entropy increment of water molecules in the IL solution, when compared to water in the bulk phase.[88]

2.2. *Influence of ILs hydrophobicity on the extraction mechanism of metallic species in ionic media*

It can be assumed that the solubility of water in imidazolium-based ILs is dependent on both the cation and anion hydrophobicity, but the anion plays the crucial role in their phase behavior. In fact, the cationic factors could be employed for fine-tuning of the solubility properties and toxicities as they appear to be directly related to ILs lipophilicity. The last entry in Table 1, which shows that the solubility of water in ILs is high as 1 mol kg^{-1} in the case of [$C_1C_2im^+$][Tf_2N^-], propones that the IL phase may be seen as a concentrated aqueous solution of a salt, although the number of water molecules is one in three or four [$C_1C_2im^+$][Tf_2N^-] pairs. Nevertheless, exactly this IL was applied successfully by Okamura et al. for removal of the strontium cation (Sr^{2+}) from water by using a novel macrocyclic receptor composed of diaza-18-crown-6 and two-β-diketone fragments, which further leads to improved extraction performance, Fig. 15.[89] The magnitude of the intramolecular cooperative effect was higher exactly in [$C_1C_2im^+$][Tf_2N^-], with about a 500-fold increase in extraction performance relative to the chloroform system and higher in comparison to other two studied ILs: [$C_1C_4im^+$][Tf_2N^-] and [$C_1C_6im^+$][Tf_2N^-].

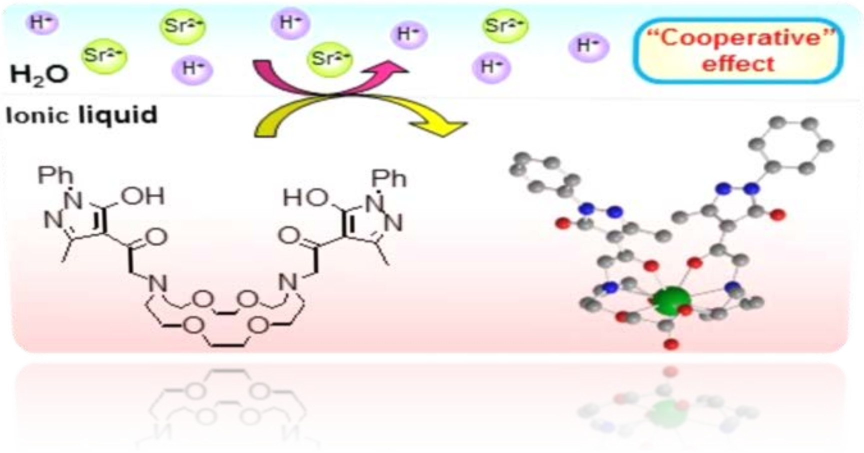


Figure 15. Specific cooperative effect of a macrocyclic receptor for metal ion transfer into ILs, $[C_1C_\mathbf{n}im^+][Tf_2N^-]$, $n = 2$, 4 and 6. Re-drawn from Ref.[89]

The intramolecular cooperative effect denotes a phenomenon: combination two different types of ligands leads to an increase of the extraction performance due to their cooperative interactions within the molecule, which is discriminated from the general synergistic effect. Slope analysis and ponetentiometric titration confirmed that identical combined extraction mechanisms of cation-exchange and proton exchange reactions operated in both IL and chloroform systems indicating, that one ligand molecule (DBzDA18C6) was required to extract Sr^{2+} in a 1:1 complex:

$$Sr^{2+}_{(aq)} + H(DBzDA18C6)^+_{(o)} + [C_1C_2im^+]_{(o)} \rightleftharpoons Sr(DBzDA18C6)^{2+}_{(o)} + H^+_{(aq)} + [C_1C_2im^+]_{(aq)} \qquad (2)$$

To elucidate the involvement of $[C_1C_2im^+]$ cation in Sr^{2+} extraction, the dependence of D_{Sr} *vs*. $[C_1C_2im^+]$ concentration in the aqueous phase was investigated, showing a slope of *ca*. -1.09±0.02.[89]

Furthermore, it was confirmed that the presence of water molecules affects the rates and selectivity of chemical reactions involving (or carried out in) ILs. Hawkins et al. have evaluated a series of 1,3-dialkylimidazolium-based ILs and their 1-(ω-hydroxyalkyl) analog, and concluded that the extent of strontium metal extraction into the ILs in the presence of a crown ether molecule scales depends linearly with IL phase water content.[90] As suggested by the authors, this pattern, based on the missibility between ILs and water, has a decisive impact on the extraction efficiency of the process. The extraction of Sr^{2+} from nitric acid solution into $[C_1C_\mathbf{n}im^+][Tf_2N^-]$, $n =$ 2-8 by dicylohexano-18-crown-6 (CE, DCH18C6) was examined by Dietz et al.[91] The published results strongly suggested that the mechanism of strontium ion partitioning between two liquid phases is fundamentally different, with far exceeding efficiency from the one observed in 1-octanol extraction system. They concluded that the phase transfer reaction proceeds through cation exchange:

$$\mathrm{Sr{\cdot}CE^{2+} + 2\,[C_1C_{\mathbf{n}}im^{+}]_{(o)} \rightleftharpoons Sr{\cdot}CE^{2+}_{(o)} + 2\,[C_1C_{\mathbf{n}}im^{+}]_{(aq)}} \tag{3}$$

$$\mathrm{Sr^{2+} + 2NO_3^{-} + DCH18C6_{(o)} \rightleftharpoons Sr(NO_3)_2{\cdot}DCH18C6_{(o)}} \tag{4}$$

A significant decrease in cation partitioning was found to accompany the increased hydrophobicity of the IL as the alkyl chain of IL cation becomes longer. For a given IL anion, D_{Na} and D_{Sr} (0.1 M DCH18C6) fall as the hydrophobicity of IL cation increase (from n=5 to n=10) and is consistent with the greater difficulty encountered in transferring a more hydrophobic IL cation to the aqueous phase, Eq. 3.[92] After this proof of principle, countless works latter on confirmed this assumption.[23, 93, 94]

The efficiency of extraction of strontium ion by DCH18C6 from aqueous nitric acid solution into four families of oxygenated aliphatic diluents (alcohols, ketones, esters, and carboxylic acids) was found to be correlated with the water content in the organic phase, i.e. higher water concentrations yields greater metal extraction.[95] Two families of imidazolium-based ILs were studied (N-(1-hydroxyalkyl-N'-alkylimidazolium and N,N'-dialkylimidazolim cations combined with [$\mathrm{Tf_2N^-}$] anion), compared to five *n*-alcohols concerning the effect of the absorbed equilibrium water concentration (molar) *vs*. the conditional extraction constant of Sr(II), which comprises 1 M $\mathrm{HNO_3}$ and 0.050 M DCH18C6 at 25ºC by Hawkins and co-researchers.[95] In the course of this investigation, it has become evident that doubling the IL phase water content leads to doubling the $K_{\mathrm{ex,Sr}}$. The same linear relationship between $K_{\mathrm{ex,Sr}}$ and $\mathrm{[H_2O]_{IL}}$ was observed for ILs, regardless absence or presence of a hydroxyl group in the cation's structure. This observation stands in contrast to analogues molecular diluents, where the absence of an oxygenated functional group leads to only a little dissolution of water in the organic phase. As consequence negligible metal ions extraction has been obtained in such cases. In other words, the linear trend across two analogues studied ILs series indicates that the employment of so-called hydrophobic ILs, which anywhay dissolve a considerable amount of water, will enhance significantly the extraction of strontium-nitrato-crown-ether complexes.

Accompanying ion exchange mechanism is the appearance of the IL cation in the aqueous phase in a one-to one ratio, in view of the target ion.[96-98] $\mathrm{La^{3+}}$ extraction by lower rim partially substituted phosphorus-containing calix[4]arene (S) in [$C_1C_4im^+$][Tf_2N^-] proceeds through cationic exchange according to the following equilibrium:[99, 100]

$$Ln^{3+}_{(aq)} + S_{(o)} + 3\,[C_1C_4im^+]_{(o)} \rightleftharpoons [LnS]^{3+}_{(o)} + 3[C_1C_4im^+]_{(aq)} \qquad (5)$$

It is now acknowledged, in contrast to conventional molecular diluents, that the metal extraction in aqueous−IL systems proceeds mainly by ion exchange (either cationic or anionic), not only in the presence of O-donors ligands, and is not at all a good sign for a sustainable extraction processes. Although sometimes neutral metal species have been also established in the organic ionic phase, *ex*. in [$C_1C_{10}im^+$][Tf_2N^-], i.e. the more hydrophobic one.[93] A strongly hydrophobic IL cation will cut off the reactions involving exchange of cationic metal complex, and a hydrophobic IL anion will probably restrain the exchange of anionic metal complexes.[101-103] Thus, the "greenness" of environmentally benign metal ion separation systems employing ILs is somehow questionable ever and again. In an effort to answer this interrogation, several investigations were carried out *vide infra*. The hydrophobicity of the IL component ions procures strong influence on the mechanism of metal transfer *via* two possible modes: through limitation of water content of the IL, and through suppression of ion exchange reactions. Janssen et al. have demonstrated and clearly discussed this phenomenon.[104] The former is so important, because metal coordination complexes in the IL phase can also incorporate water molecules in some rare cases. Water content of the so-called "hydrophobic phase" is known to be important in traditional molecular liquids[10, 95, 105, 106] too. Simulation scrutiny[107,108] has shown that the solvation energy and coordination state of metal complexes in an IL can be more sensitive to the quantity of water present in its bulky volume. However, this picture is somehow incomplete and should be born in mind when the equilibrium mechanisms for metal solvent extraction in different ILs are suggested and subsequently interpret.

2.3. *Solubility of water into task specific ionic liquids, TSILs*

A special class of IL compounds incorporating functional groups in their chemical structure, namely task specific ionic liquids (TSILs), which can stably bond metal ions, have been designed in order to be used either as new extractants dissolved in molecular or ionic diluents, or solely as new organic media.[109] ILs may be either inert, i.e. acting only as pure diluents, or can be designed to actively participate in a specific chemical reaction. More rational and cheaper way to use them in combination with classical ILs (commercially available) rather than in pure form is mainly due to the fact, that TSILs often have a higher melting point and a higher viscosity than conventional ILs. Whatever the reason, it is quite inaccurate to consider TSILs as a new class of organic diluents. The presence of water has obviously an effect on the physicochemical and coordination properties of TSIL compounds as well.[110] The increase of water content leads to the decrease of densities and viscosities for series of trialkylmethylammonium TSILs saturated with water, as applied by Sun et al. for solvent extraction purpose (1 ml of dried IL was equilibrated with 3 ml of water at 20°C), Table 7.[111]

Table 7. Solubility of water in TSILs. [111]

TSILs	[A336] [P204]	[A336] [P507]	[A336] [CA-12]	[A336] [CA-100]	[A336] [Cyanex272]	[A336] [Cyanex302]
Wt %	1.03	0.87	1.03	0.94	1.39	0.55

The clue as given in Table 7 can be helpful in a general valuation of the influence of the ILs structure on their lipophilic character, but not forgetting that the solvent extraction systems typically include also various solutes in each liquid phase. Another work in relation with the above is the use of tetraoctylammonium cation in order to form water-immiscible halogen−free ILs with dodecylsulfate and dodecylbenzenesulfonate anions, with reported solubility of water at 25°C in them being 2.8% and 4.0%, respectively.[112] The possible use of tetraoctylammonium dodecylsulfate as a duluent for solvent extraction of divalent transition metal cations was positively tested using the β-diketone thenoyltrifluoroacetone as an extractant. The water contents in three specially prepared, “fusion” extractive compounds $[TBA^+][DEHP^-]$, $[TOMA^+]DEHP^-]$ and $[THTP^+][DEHP^-]$ have been determined to be 1.2%, 1.0% and 0.3%, respectively, according to the Karl-Fisher titration carried out in the ref. 113. The phosphonium-based IL, i.e. $[THTP^+][DEHP^-]$, is much more hydrophobic than the two ammonium functionalized ILs, where $DEHP^-$ is the anion of di(2-ethylhexyl)phosphoric acid.

The ability of a TSIL, a cationic ester derivative of betaine (tri(n-butyl)[2-ethoxy-2-oxoethyl)ammonium, $[BuGBOEt^+]$) in combination with the coordinating dicyanamide anion ($[Dca^-]=[C_2N_3^-]$), to remove heavy metals (Cu^{2+}, Cd^{2+}, Ni^{2+} and Pb^{2+}) from water has been evaluated when dissolved in its homologue, the TSIL $[BuGBOEt^+][Tf_2N^-]$, as possessing a non-coordinating anion.[114] In order to conceive more environmentally friendly systems, a workable way is to use the mixture of $[BuGBOEt^+][Dca^-]$ and a less soluble in water TSIL, $[BuGBOEt^+][Tf_2N^-]$. Before extraction experiments the chemical stability of the cationic part of the IL ester in aqueous solutions *vs.* time was checked by analysis of the total organic carbon (TOC) after 24 h contact of equal volumes (aq/o). The cation has hydrolysed solely at high acidic or alkaline media, i.e. 1.5<pH>11.5, while at intermediate pH the cation showed stability for several days, without exact cited precision. Generally, the solubility of the TSIL with [Tf_2N^-] anion in water is lower than its homologue TSIL-[Dca^-] and is quite similar to the IL [$C_1C_4im^+$][Tf_2N^-]. The reported TOC release in aqueous solution from this TSIL mixture is around 11.8 $g.L^{-1}$ with 10% [$BuGBOEt^+$][Dca^-] content. If its concentration in mixture increases to 30%, the TOC reaches a value of *ca.* 16.4 $g.L^{-1}$, while for pure samples of [$BuGBOEt^+$][Dca^-] or [$BuGBOEt^+$][Tf_2N^-] the measured values are 38.9 $g.L^{-1}$ and 5.2 $g.L^{-1}$, respectively. Thus, a real environmental benefit was achieved in favor of ion-pairing mode of solvent metal extraction. The replacement of [Tf_2N^-] by [Dca^-] as anionic constituent of the IL brings drastic modifications in the coordination metal behavior as the extraction yields obtained are higher than 90% in all experiments done, while at the same time [$BuGBOEt^+$][Tf_2N^-] is a very weak extractant compound.

2.4. *New approach in solvent extraction − solvometallurgy*

In view of solvometallurgy as a new approach in solvent extraction with no water consumption, being a process based on various non-aqueous diluents like lower alcohols, polyalcohols, ethers, ketones etc. is created to be an alternative to hydrometallurgy where water is in the main role. On the grounds that no water will be consumed in such chemical processes, more environmental issues connected to generated wastewater usually produced and its treatment could be solved. Ionic liquid-ionic liquid solvent extraction systems that consist of two-mismatched immiscible ILs permit the reinforcing of these new separation processes despite the fact that a more nuanced perspective is required concerning their appropriateness. Recently, another method was introduced for group separation of heavy from light rare earths by successful replacement of water with the polar organic diluent ethylene glycol in the presence of $LiNO_3$ up to 1 M or LiCl up till 4 M, while the extracting organic phase consists of Cyanex 923 dissolved in *n*-dodecane.[21, 115, 116] The achieved efficient separation is highly pronounced in comparison to water samples, per contra it is impossible to omit the moderate toxicity of the proposed organic entity and the relative expense of the process. Since two organic immiscible phases were used for solvent extraction, being aware of this point their mutual solubility was also estimated by the authors in like manner applying ^{31}P NMR and gas chromatography. The mutual solubility of ethylene glycol and n-dodecane was measured by recording the ^{1}H NMR spectra of both phases after 30 min equilibrium of equal volumes (5 ml), with no resonance lines observation revealing completely immiscible liquids. ^{31}P NMR spectra indicates no loss of extractant Cyanex 923 in the ethylene glycol phase. However, it was found that about 24.5 $g \cdot L^{-1}$ of ethylene glycol was co-extracted into 1 M Cyanex/*n*-dodecane estimated by GC-FID. This co-extracted content has decreased to 20.8 $g \cdot L^{-1}$ by addition of 1 M $LiNO_3$ and 10 $g \cdot L^{-1}$ La(III) to the ethylene glycol phase.[115] The solubility/co-extraction of ethylene glycol diluent by 1 M Cyanex 923/(+10% v/v 1-decanol)/*n*-dodecane was measured to be significant: 46.3 $g \cdot L^{-1}$ (1-decnol was added as phase modifier). This value decreases to 29.7 $g \cdot L^{-1}$ uppon addition of 2 M LiCl and was further suppressed to 23.5 $g \cdot L^{-1}$ when extractions were carried out from feed solutions of 50 $g \cdot L^{-1}$ rare earths together with 2 M LiCl. Perhaps it is important to underline that co-extraction of water and ethylene glycol are comparable.[116] In addition, the Binnemans's group has investigated the extraction mechanism in detail with two metallic ions Yb^{3+} and Nd^{3+}, under the same experimental protocols, by slope analysis method and EXAFS. The established extracted species in the Cyanex 923(L)/*n*-dodecane phase are different and demonstrate divergent coordination: $YbCl_3 \cdot 4L$ and $Nd(NO_3)_3 \cdot 3L \cdot EG$, where EG is ethylene glycol molecule. However, the recycling of these organic diluents is mandatory from ecological and economic point of view, as they are much more expensive than the natural product water.

3. Transfer of IL's ions into the aqueous phase during aqueous-biphasic equilibrium

Qualitatively, the dilution of IL in water was similar to the one observed for *n*-alkanes, for example heptane, and other organic compounds that are anyway principally insoluble in water.[66] Admitting that the concentration of $[C_1C_4im^+]$ cation in the aqueous phase has been usually determined spectrophotometrically at 210 nm *via* UV spectroscopy (Fig. 14), for example in the excellent work of Jensen and co-researchers, while that of the anion $[Tf_2N^-]$ has been determined as colored ion bis[(trifluoromethyl)sulfonyl)]imide bis(2,9-dimethyl-1,10-phenantroline)copper (I) in ethyl acetate at 456 nm.[101] The researchers have examined the reaction mechanism of 4f-ions in ionic organic media with the widely used chelating β-diketone compound, *videlicet* thenoyltrifluoroacetone (HTTA). As illustrated in Fig. 16, the added sodium ions (1 M $NaClO_4$) do not participate in the equilibrium process, while at the same time the extraction of Ln^{3+}–tta^{-} complexes does cause a linear increase in the aqueous phase concentration of the anion species $[Tf_2N^-]$ ($[0.0139\ M]_{in}$), with a slope close to 1.1. For this reason, it was supposed that one entity of the IL anion probably participates in the equilibrium reaction, Eq. 6. The anion exchange mechanism leading to the formation of anion $[Ln(TTA)_4^-]$ entities in organic diluents is not reserved to ILs solely: it was seen already in traditional molecular media:[117, 118]

$$Ln^{3+}_{(aq)} + 4HTTA_{(o)} + [C_1C_4im^+][Tf_2N^-]_{(o)} \rightleftharpoons$$

$$[C_1C_4im^+][Ln(TTA)_4^-]_{(o)} + 4H^+_{(aq)} + [Tf_2N^-]_{(aq)} \qquad (6)$$

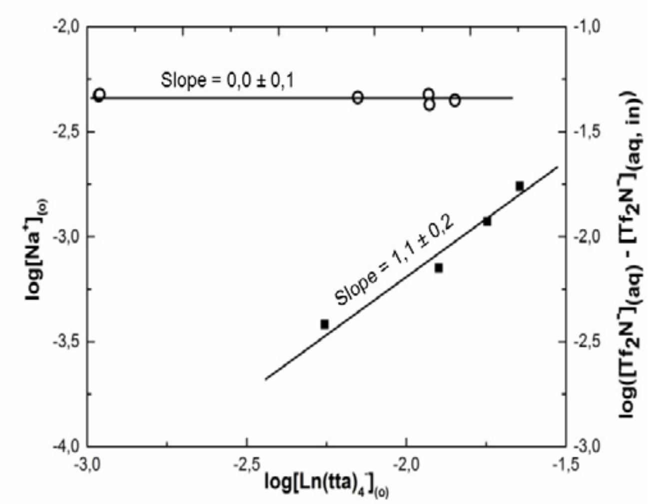


Figure 16. The dependence of partitioning of Na^+ into $[C_1C_4im^+][Tf_2N^-]$ on the organic phase concentration of $[Eu(TTA)_4^-]$ (○, 1.0 M $NaClO_4$) as well as the dependence of partitioning of $[Tf_2N^-]$ into the aqueous phase on the organic phase concentration of $[Nd(TTA)_4^-]$ (■, 1.0 M NaCl). Lines indicate best fit of data by linear least-squares regression. Re-drawn from Ref. 101.

Solubilities of ILs containing $[Opyr^+]$ or $[4Mopyr^+]$ cations in water were obtained by recording the UV spectra at 254 nm, while 265 nm wavelength was used for intensity of absorption corresponding to the $[2Mopyr^+]$–IL.[84] The solubility in water for $[4Mopyr^+][TfO^-]$ and $[4Mopyr^+][N(CN)_2^-]$ ILs is found to be 1.59% and 5%. The first value is very close to the one registered for $[4Mopyr^+][BF_4^-]$. The borate anions of the pairs $[4Mopyr^+][BF_4^-]$ and $[C_1C_8im^+][BF_4^-]$ have shown almost the same solubility in water, as well as the $[4Mopyr^+]][BF_3Ph^-]$ (0.49%) and its homologue $[C_1C_8im^+][BF_3Ph^-]$ (0.53%). The reported water solubilities are 0.013%, 0.022%, 0.036%, and 0.027% for [4Mopyr$^+$][BETI$^-$], [4Mopyr$^+$][Tf$_2$N$^-$], [4Mopyr$^+$][NfO$^-$] and [4Mopyr$^+$][AsF$_6$$^-$], respectively. ILs possessing [Opyr$^+$] cations appears to be slightly more soluble in water, taking into account the published results, than [4Mopyr$^+$]−type of IL. Considering the anion, water solubilities obtained for [Opyr$^+$][Tf$_2$N$^-$] and [Opyr$^+$][NfO$^-$] are close to 0.035% and 0.046%. In addition, the ILs incorporating [2Mopyr$^+$] cations have shown higher solubility in water. For example, 0.10% was obtained for [2Mopyr$^+$][Tf$_2$N$^-$] compared to 0.035% and 0.020% for the two structural varieties [Opyr$^+$][Tf$_2$N$^-$] and [4Mopyr$^+$][Tf$_2$N$^-$].[84]

Another elegant idea proposed for one more rare earth ion, the extraction of Sc(III), handling an aqueous biphasic system presaturated with 16 wt % NaCl in combination with a nonfluorinated functionalized IL, merits to be mentioned too.[119] Depuydt et al. have reported a higher solubility of the IL cation ([P$_{444}$C$_1$COOH$^+$], tri-*n*-butyl(carboxylmethyl)-phosphonium) in water rich phase at lower measured pH *via* ^{1}H NMR, with an internal standard phenol, Fig.17.

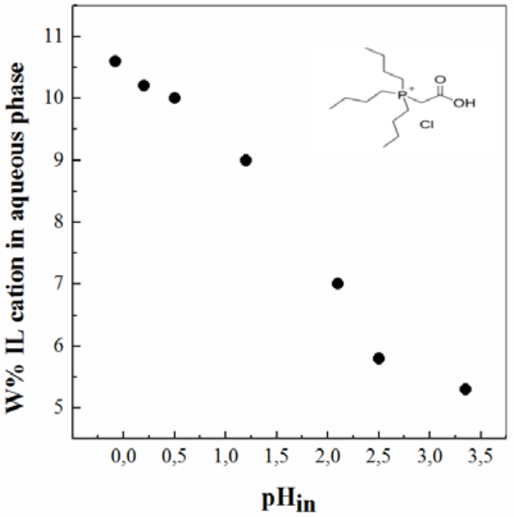


Figure 17. Solubility of the IL cation [P$_{444}$C$_1$COOH$^+$] in the water-rich phase. Drawn from data reported in Ref. 119.

Based on certain number of experimental evidences, it is now generally acknowledged, as already pinpointed in the previous section, that metal extraction in aqueous−IL systems proceeds mainly by ion exchange, either cationic or anionic, although neutral metal species were also established sometimes. This escape of ILs' components to the aqueous phase linked to the solvent extraction mechanism has been particularly treated in the literature source inasmuch as a serious environmental problem. No doubt, it should be controlled, limited to a minimum and even avoided if possible, because all ILs cannot be considered environmentally benign. That is why the efforts to examine chloride, nitrate and perchlorate-based aqueous phases by Atanassova et al. *via* methodical Q−NMR study, in contact with liquid salts commonly used as a model ($[C_1C_{\mathbf{n}}im^+][Tf_2N^-]$, $n = 2, 4, 6, 8$ and 10) have started with the determination of the concentrations of cation $[C_1C_{\mathbf{n}}im^+]$ and anion $[Tf_2N^-]$ entities in the upper aqueous phase at low but not very strong acidity (1×10^{-4} – 1.5 M DX^-, where X^- is the acid anion: Cl^-, NO_3^- or ClO_4^-), Fig. 18.[74] The mineral acids are DCl (35%), DNO_3 (65%) and $DClO_4$ (68%) (in D_2O, 99 atom % D).

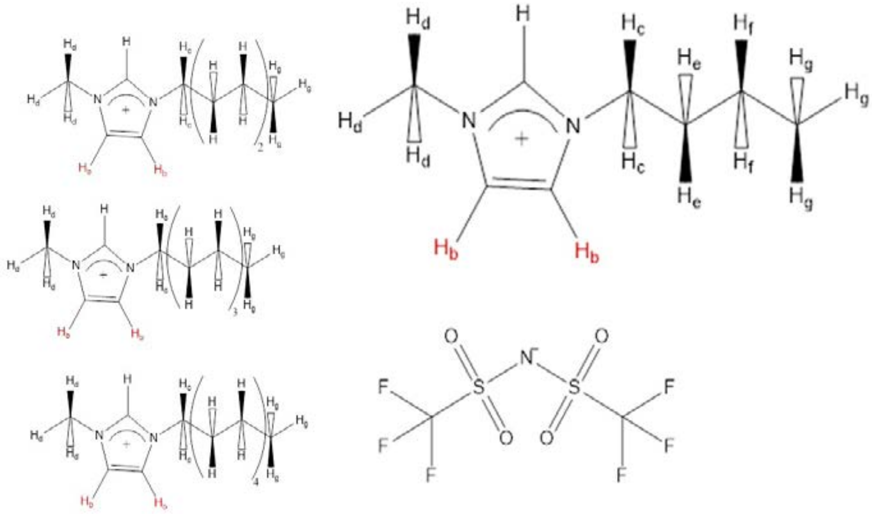


Figure 18. Chemical structures of the IL cations and anion used in the study[74] ($[C_1C_{\mathbf{n}}im^+][Tf_2N^-]$, $n = 4, 6, 8$ and 10).

Nearly 70 years after the observation of proton nuclear magnetic resonance (^1H) in liquid water, NMR spectroscopy is the preeminent tool for structural elucidation of the chemical compounds. It is the only physical method used routinely that can provide quantitative valuable information at the molecular level concerning analysis of complex mixtures from various sources in diverse fields such as medicine, biology, pharmacy, and food science including living systems (*in vivo* studies) used in many scientific analytical laboratories. Fluorine-19 NMR analysis provides a highly specific method for quantification of fluorine containing drugs due to several significant advantages: short longitudinal relaxation times (T1), 100% natural abundance, and high sensitivity (83% of the proton). NMR is most powerful when used quantitatively, as the integrated intensity of a resonance signal is directly proportional to the number of nuclei represented by this signal. NMR quantitative analysis has special characteristics, which are uniquely suitable for analysis of mixtures in an adequate deuterated diluent. The ILs under study have several magnetically active nuclei that can be used for analysis (e.g. ^{13}C, ^{1}H, ^{15}N, ^{33}S and ^{19}F), but ^{1}H and ^{19}F have the best response. The internal standard used in ^{1}H NMR is trisodium citrate dehydrate ($C_6H_5Na_3O_7{\cdot}2H_2O$). It is chosen because its protons are well separated from those of the studied IL's cations, while the chemical standard used in ^{19}F NMR is sodium trifluoroacetate, (CF_3CO_2Na). The measurements of absolute concentrations involve the presence in the spectrum of a reference signal of known concentration to provide a calibration standard. This is why standards were introduced together with the samples in the NMR tube (conventional 5 mm tube, with a total sample volume of 600µL). In order to perform a reliable quantitative determination of ILs' components transferred into the aqueous phase concentrations, it is very important that all spins have relaxed in between two-excitation pulse. What's more, the longitudinal relaxation times, T1, for ^{1}H and ^{19}F samples and standards should thus be carefully determined as a function of the chemical conditions that could eventually influence their values. In this study[74] the T1 determinations were performed at 3 M $[D^+][NO_3^-]/D_2O$ using $[C_1C_8im^+][Cl^-]$. The T1 values are displayed in Table 8. Considering the collected data, the following NMR spectra were recorded with a 30^{o} excitation pulse, and all acquisition parameters are indicated in Table 9. In solution, the concentrations of the analytes are calculated habitually by comparing the analyte ($[C_1C_{\mathbf{n}}im^+]$: B protons, Table 10) and reference integrals (I) corrected from the number of contributing nuclei (N) in their respective resonance, as well as taking into account the purity of the used standards (P):[120]-[122]

$$C = \frac{I}{Istd}\,x\,\frac{Nstd}{N}\,x\,\frac{Pstd}{P}\,x\,\frac{Vstd}{V}\,x\,C_{std}.$$

A precise protocol that considers and controls the aspects of both the measurement procedure and the spectra processing and evaluation is responsible for good quantitative investigations. The uncertainty of the cation concentrations is equal to 10 % and to 5% for anions, with detection limits equal to 1 mM for each compound.

Table 8. Results for determination of T1 using $[C_1C_8im^+][Cl^-]/D_2O/3M\ DNO_3/C_6H_5Na_3O_7\cdot 2H_2O$.

Proton	δ (ppm)	Io	error	T1(s)	error
A	proton	acid is	unutilisable	for	Q-NMR
B	6.505	2.91e+07	7.394e+05	3.82	0.1948
B	6.498	3.11e+07	9.564e+05	3.29	0.2079
C	3.231	2.28e+07	5.014e+05	0.811	0.05852
D	2.954	1.14e+07	4.549e+05	1.91	0.1719
citrate	2.164	1.57e+07	2.980e+05	0.564	0.04480
citrate	2.111	2.74e+07	4.869e+05	0.564	0.04189
citrate	1.992	2.76e+07	4.290e+05	0.553	0.03643
citrate	1.938	1.57e+07	2.821e+05	0.550	0.04203
E	0.891	8.36e+07	3.186e+05	0.68	0.09520
F	0.329	2.70e+07	1.146e+05	0.776	0.1109
F	0.269	2.66e+07	1.153e+05	1.19	0.1366
F	0.264	2.87e+07	1.232e+05	1.01	0.1248
G	-0.138	3.62e+07	1.255e+05	1.75	0.1399

Table 9. NMR acquisition parameters with 30° excitation pulse, 298K, 300MHz.

Ion	Number of scan	Delay (s)	Record time (s)	Signal recovery (%)
$[Tf_2N^-]$	150	0.45	3	96.5
$[C_1C_4im^+]$	32	22	2.71	99.5
$[C_1C_6im^+]$	32	22	2.71	99.5
$[C_1C_8im^+]$	32	22	2.71	99.5
$[C_1C_{10}im^+]$	32	22	2.71	99.5

Table 10. Chemical shift of the ^1H or ^{19}F nuclei.

Cations (protons B)/anions	Shifts in ppm (D_2O)
$[C_1C_4im^+]$ Doublet of doublet	δ= 7-7.8
$[C_1C_6im^+]$ Doublet of doublet	δ= 7.43-7.45
$[C_1C_8im^+]$ Doublet of doublet	δ= 7.45-7.41
$[C_1C_{10}im^+]$ Doublet of doublet	δ= 7.13-7.85
Sodium citrate 4 protons Doublet of doublet	δ= 2.4-2.8
$[Tf_2N^-]$	δ= -79.16
Sodium trifluoroacetate	δ= -76.6

The quantities (mM) of the IL's entities transferred from the lower oil to the upper aqueous phase were measured by inspection of the corresponding ^{1}H and ^{19}F NMR spectra, as illustrated on, Fig. 19. It is so important to recall that ion distributions between the two liquid phases can lead to non-identical amounts of $[C_1C_{\mathbf{n}}im^+]$ and $[Tf_2N^-]$ in the upper phase, Figures 20 and 21. Indeed, the latter consideration was not accepted in most of the cited works discussed in the previous section, where only IL cation transfer was evaluated indeed *via* UV-vis technique. For the lower alkyl chain lengths (n = 6, 4, 2), the IL cation solubilities obtained are similar for all pD_{eq} values and present a decreasing trend as ***n*** increases, in accordance with the hydrophobicity of the cation: $[C_1C_2im^+]_u \approx [Tf_2N^-]_u = 40$ mM, $[C_1C_4im^+]_u \approx [Tf_2N^-]_u = 17$ mM and $[C_1C_6im^+]_u \approx [Tf_2N^-]_u = 6$ mM. All collected data for n = 10 and 8 are below the detectable limit of the applied method, Fig. 22.[74, 123-126]

These results are in complete agreement to those in distillated/deionized water reported for $[C_1C_{\mathbf{n}}im^+][Tf_2N^-]$, n = 2, 4, 6 and 8 ILs, corresponding to 48.9, 15.7, 7.2 and 4.1 mM, respectively, obtained by analysis of the UV absorbance spectrum of the IL cation.[26] Furthermore, it was observed that $[BETI^-]$−ILs have a lower solubility than the $[Tf_2N^-]$−IL for a cation of the same alkyl chain length: 9.2, 4.5, 1.4 and 0.4 mM, at n = 2 to 8. This trend was explained by the existence of additional fluorinated carbon group, $-CF_2-$, in the $[BETI^-]$ anion structure. This proof of the principle demonstrates that, for a series of $[C_1C_{\mathbf{n}}im^+]$ cations, increasing the alkyl chain length from ethyl to decyl increases significantly the hydrophobicity and the viscosity of the IL, whereas densities and surface tension values decrease and could be accepted as a promising tool to better understand how the ionic environment sustains the ILs.[127]

The extraction of 4f-ions has ussually carried out at low acidity (pH: 1−4). The conclusion based on findings presented by Atanassova et al.[74] is that the quantity (mM) of the IL's entities ($[C_1C_4im^+]$, $[Tf_2N^-]$) transferred from "oil" to the "water-rich" solution is independent from the chemical composition of the aqueous phase. This is valid in the cases when DNO_3, DCl or $DClO_4$, deuterated mineral acids, were exploited including the examination at constant ionic strength, i.e. $\mu=0.1$ (NaCl or $NaNO_3$), so that the solubility of IL constituents remains approximately constant: ~14-17 mM. However, it is worth noting that an addition of sodium perchlorate salt induces a large increase in $[Tf_2N^-]$ solubility. The latter rises to 22 mM, 31 mM and 43 mM for 0.1 M, 0.2 M and 0.4 M concentrations of $NaClO_4$ salt added to $DClO_4/D_2O$ solution, respectively, as it can be seen from the data presented on Fig. 23.

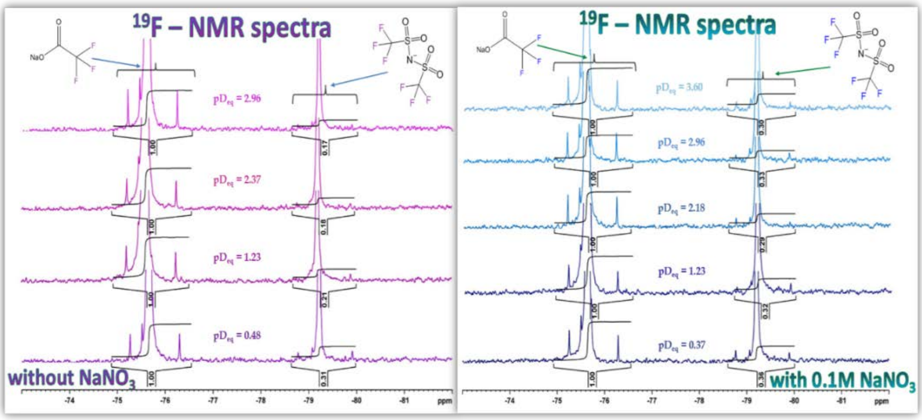


Figure 19. ^{19}F spectra obtained using the system $\mathrm{DNO_3/[C_1C_8im^+][Tf_2N^-]}$ and $\mathrm{DNO_3}$/0.1M $\mathrm{NaNO_3/[C_1C_8im^+][Tf_2N^-]}$ in Ref. 74.

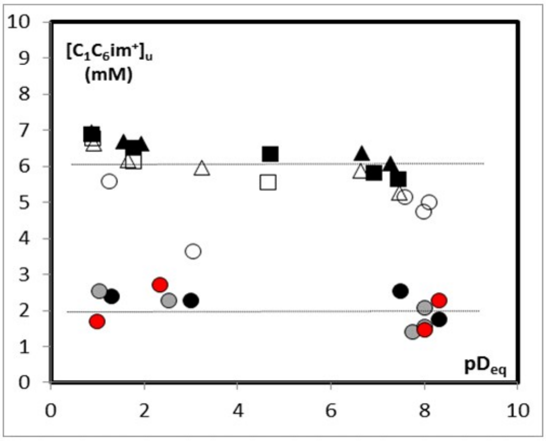


Figure 20. $\mathrm{[C_1C_6im^+]_u}$ *vs.* $\mathrm{pD_{eq}}$ of the aqueous phases using $\mathrm{[C_1C_6im][Tf_2N]}$ as an organic medium. □: $\mathrm{DNO_3}$. ■: $\mathrm{DNO_3}$ and $\mathrm{NaNO_3}$ 0.1 M. Δ: DCl; ▲: DCl and NaCl 0.1 M; ○: $\mathrm{DClO_4}$; ●: $\mathrm{DClO_4}$ and $\mathrm{NaClO_4}$ 0.1 M; ○: $\mathrm{DClO_4}$ and $\mathrm{NaClO_4}$ 0.2 M; 🔴: $\mathrm{DClO_4}$ and $\mathrm{NaClO_4}$ 0.4 M. Dashed lines: averages at 6 mM and 2 mM. Adapted from Ref. 74.

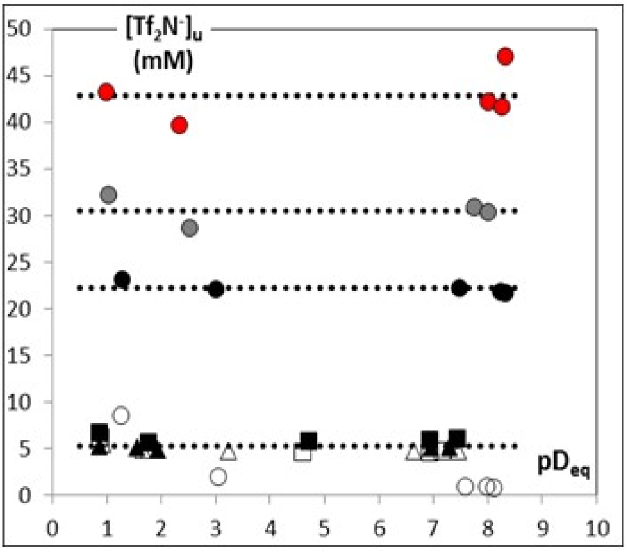


Figure 21. $[Tf_2N^-]_u$ *vs.* pD_{eq} in the aqueous phases using $[C_1C_6im^+][Tf_2N^-]$ as an organic medium. □: DNO_3. ■: DNO_3 and $NaNO_3$ 0.1 M. Δ: DCl; ▲: DCl and NaCl 0.1 M; ○: $DClO_4$; ●: $DClO_4$ and $NaClO_4$ 0.1 M; ○: $DClO_4$ and $NaClO_4$ 0.2 M; ○: $DClO_4$ and $NaClO_4$ 0.4 M. Dotted lines are average of individual series. Adapted from Ref. 74.

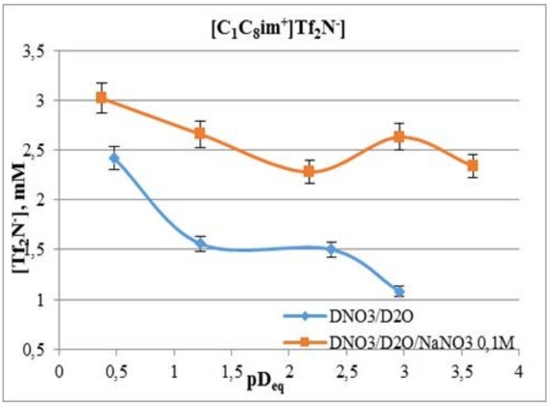


Figure 22. $[Tf_2N^-]_u$ *vs.* pD_{eq} in the aqueous phases using $[C_1C_8im^+][Tf_2N^-]$ as an organic medium. Detection limits for $[Tf_2N^-]$ are in the range of 1−2 mM.

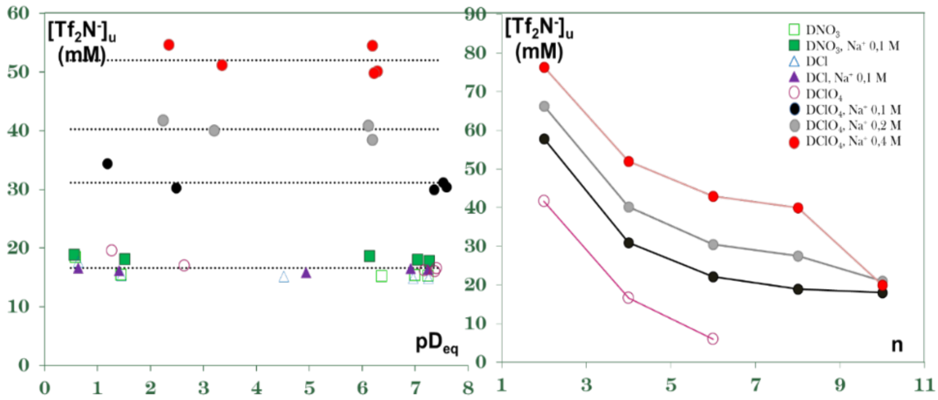


Figure 23. $[Tf_2N^-]_u$ *vs.* pD_{eq} in the aqueous phases using $[C_1C_4im^+][Tf_2N^-]$ as an organic medium. Average values of $[Tf_2N^-]$ solubility in the upper aqueous phase, as a function of length of the alkyl chain, for the various applied sodium perchlorate concentrations. Re-drawn from Ref. 74.

On the other hand, for a given aqueous phase composition, $[Tf_2N^-]$ solubility in the upper aqueous phase decreases as ***n*** increases, Fig. 23. Addition of sodium perchlorate salt seems to induce a limited decrease in $[C_1C_nim^+]$ amount, of *ca.* 4 – 6 mM (*n* = 2 and 4). Experimental results established by Gaillard et al. have already evidenced that aqueous solutions containing large amounts (in the molar range, from 0.5 M to 6 M) of perchloric acid, when contacted with $[C_1C_4im^+][Tf_2N^-]$ behave somewhat differently in comparison with nitric, hydrochloric and perrhenic acids employed in the study.[128] To gain microscopic insights into interfacial behavior of the water, IL, HA acids and ligand TBP components of the studied systems, molecular dynamics “MD” simulations have also been performed on related biphasic IL/water model systems, with HNO_3 and $HTcO_4$ acids with and without the presence of TBP. Inter-miscibility of diluents in biphasic systems clearly evidenced an enhanced water/IL interaction concomitant to water acidification (from 0 to 6-7 M), as large quantities of water are dragged to the IL phase during equilibration (3 ml, a/o, 1 h) except HCl, where $[H_2O]_{(o),eq}$ remains constant in the whole range of $[HCl]_{aq,in}$ investigated. For the other acids, $[H_2O]_{(o),eq}$ increases up to 3 M for $HReO_4$, 2.5 M for HNO_3 and 1.8 M for $HClO_4$, with different extraction curve shapes acidifying the aqueous phase $[X^-]_{aq,in}$= 6.5-8 M. The amount of dragged water is not proportional to the total acid concentration, but obviously depends on the mineral acid’s nature. Marked differences were observed among the inorganic acids that could be related to their associated/dissociated state in the aqueous phase. The $[C_1C_4im^+]$

concentration at equilibrium in the aqueous phase (by UV-visible spectroscopy at 211 nm, except for HNO_3 and $HReO_4$ solutions whose anions interfere with $[C_1C_4im^+]$ spectrum) has reached a maximum of 0.35 M for $[HClO_4]$ = 6 M and 0.12 M for [HCl] = 8 M. There is thus more cation $[C_1C_4im^+]$ transfer to water acidified with $HClO_4$ than with HCl acid.[128]

The $[Tf_2N^-]$−quaternary ammonium IL ($R_1=R_2=R_3=CH_3$, $R_4=CH_2CH_2OMe$) was syntesized by Bell and Ikeda for the purposes of liquid-liquid U(VI) extraction from nitric acid solution by tributylphosphate (TBP), the key extractant molecule in the uranium cycle.[129] This IL was sligthly soluble in the aqueous phase, approximately 0.3%, while around 3 to 5 % of the avilable water was somehow distributed in the lower layer according to the proportion of acid concentration (0.1 M HNO_3: 25 992 ppm, 3 M HNO_3: 36 857 ppm and at 6 M HNO_3: 45 208 ppm). Additionaly, it was found that around 7.9×10^{-3} M of nitric acid, i.e. 79 % of the total amount available has been trasferred to the IL layer as well. In order to determine the exact extraction mechanism of U(VI) that occurs as a fomation of neutral, cationic or anionic complexes, the authors have examined the IL $[Cat^+]$ and $[Ani^-]$ solubility in the aqueous phase with the corresponding ^1H and ^{19}F NMR spectra, as well as the mole number of uranium (1.5 to 3×10^{-2} M) extracted from aqueous to the IL phase at 0.01 M and 6 M HNO_3, respectively, Fig. 24. A straight line with a slope of 1 was obtained in both cases, indicating that a cationic and an anionic exchange mode occurred with one cation and one anion entity from the IL involved in the reaction processes:

$$UO_2^{2+}{}_{(aq)} + 3TBP_{(o)} + [Cat^+]_{(o)} + H^+{}_{(o)} \rightleftharpoons UO_2^{2+}\cdot(TBP)_{3(o)} + [Cat^+]_{(aq)} + H^+{}_{(aq)} \tag{7}$$

$$UO_2^{2+}{}_{(aq)} + 3NO_3^-{}_{(aq)} + TBP_{(o)} + [Tf_2N^-]_{(o)} \rightleftharpoons UO_2^{2+}(NO_3^-)_3\cdot(TBP)_{(o)} + [Tf_2N^-]_{(aq)} \tag{8}$$

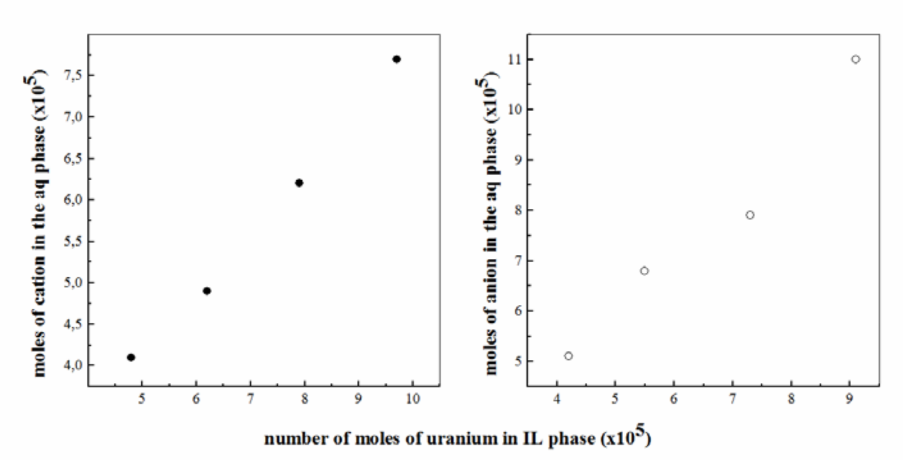


Figure 24. Solubility of IL's cation ($[(CH_3)_3NCH_2CH_2OMe^+]$ and anion ($[Tf_2N^-]$) in the aqueous phase *vs*. concentration of U(VI) extracted in the IL phase at 0.01 M and 6 M HNO_3 acidity, employing the standard sodium acetate for cationic component and trifluoroacetic acid for anionic NMR measuring concentraions of IL, respectively. Drawn from data reported in Ref. 129.

Even in the absence of uranium species, the IL was diluted in the aqueous phase at same extent. The solubility of a chemical compound in water is generally affected by the presence of an electrolyte. The $[C_1C_2\text{im}^+]$ cation solubility as a function of sodium or potassium chloride concentration was measured by Toh and co-researchers, and the results are shown in Table 11.[26] It is evident that the solubility of $[C_1C_2\text{im}^+]$ initially increased with addition of non-complexing electrolyte (inorganic salts) but further increases in salt concentration that decreased markedly the solubility. However, the threshold level is different for the two added salts, when eventually the IL $[C_1C_2\text{im}^+][Tf_2N^-]$ began to precipitate.[26]

Table 11. Solubility of $[C_1C_2\text{im}^+]$ cation (mM, standard deviation ± 0.3-11 mM) as a function of salts concentrations at room temperature and ambient pressure.[26]

Solubility $[C_1C_2\text{im}^+]$ (mM)	water	NaCl			KCl			
		0.5 M	1 M	3 M	0.5 M	1 M	2 M	3 M
	48.9	57.5	38.5	20.3	73.9	61.2	52.7	38.6

Because of the very low solubility obtained for $[C_1C_{\mathbf{n}}\text{im}^+][Tf_2N^-]$($n$ = 2, 3, 4, 5, 6, 7 and 8) in water, the ILs in the "water-rich" phase may be considered to be at infinite dilution, as suggested by Freire and coworkers, Table 12.[22] Aside from the fact that in this scintific contribution the solubility of ILs was determined by UV-spectroscopy, i.e. by a method providing an adequate description of the exact cation solubility dependence only, without an automatic reference to the anion performance.

Table 12. Experimental mole fraction solubility of $[Tf_2N^-]$–based ILs in water as a function of temperature (standard deviation ± 0.01-0.08).[22]

T/K	[C1C2im+]	[C1C3im+]	[C1C4im+]	[C1C5im+]	[C1C6im+]	[C1C7im+]	[C1C8im+]
	$10^4(\chi_{IL})$	$10^4(\chi_{IL})$	$10^4(\chi_{IL})$	$10^4(\chi_{IL})$	$10^5(\chi_{IL})$	$10^5(\chi_{IL})$	$10^5(\chi_{IL})$
288.15	7.66	5.15	2.86	1.84	8.90	4.85	3.17
293.15	8.03	5.27	2.92	1.88	8.96	4.98	3.23
298.15	8.38	5.40	3.07	1.96	9.56	5.09	3.36
303.15	8.75	5.68	3.18	2.01	9.73	5.28	3.55
308.15	9.33	6.04	3.44	2.18	10.2	5.81	3.68
313.15	9.85	6.49	3.94	2.32	11.7	6.87	3.94
318.15	10.5	7.01	4.70	2.53	13.2	7.93	4.55

The phenomenon known as “salting-out” effect was observed initially by Gutowski et al. who discovered that water-soluble ILs can be removed from aqueous solutions with water-structuring salts such as K_3PO_4.[130] The first attempt to present in detail the magnitudes of the salting-in and salting-out effects assessed by changing either the cation or the anion, in a large series of salts, as well as the influence of salt concentration, was done by Freire et al. at 298.15K and atmospheric pressure.[123] A maximum UV absorption wavelength of 211 nm was again used for the studied hydrophobic IL $[C_1C_4im^+][Tf_2N^-]$. For a series of various chloride salts, it was observed that they promote the IL salting-in phenomenon at low concentrations, followed by a salting-out effect at higher concentrations. At a salt concentration equal to 1.5 mol kg^{-1}, the IL solubility salting out decrease order is in the following sequence: $Sr^{2+}>Ca^{2+}>Mg^{2+}>Na^+>Li^+\approx K^+$. On the contrary, for three salts, the 1.5 mol kg^{-1} molality induces an increasing salting-in effect of the IL in water following the cation order: $NH_4^+<H^+<(CH_3)_4N^+$. It was confirmed that the influence of the inorganic ions on the IL solubility has followed exactly the well-known Hofmeister series in chemistry. However, the increase of the salt concentration in the water-rich phase reduces the chemical potential of the main molecule, H_2O, resulting in the decrease of the solubility of water into the IL. The influence of the pH in the mutual solubilities was reported to be marginal in the studied cases. The results obtained by Freire and co-workers for both liquid phases with several sodium-based salts (NaCl, $NaCH_3CO_2$, $NaHCO_3$, $NaHSO_4$, NaH_2PO_4, Na_2SO_4, Na_2CO_3, Na_3PO_4 and $Na_3C_6H_5O_7$) have shown that the salting-in region appears at low concentrations followed by salting-out at higher concentrations.[123] The decreasing of IL solubility was found at a 1.5 mol kg^{-1} salt molality with an anion change in the following order: $C_6H_5O_7^{3-} > CO_3^{2-} > SO_4^{2-} > H_2PO_4^{-} > CH_3CO_2^{-} \approx HSO_4^{-} > Cl^{-}$. The experimental data indicate that the anion inducing the strongest salting-out effect was PO_4^{3-}, and the anion that brings the strongest salting-in effect is SCN^{-}. The solubility data of the same IL $[C_1C_4im^+][Tf_2N^-]$ in aqueous solutions of ten different salts at molalities up to 1.5 mol kg^{-1} at 298.15K and 1 bar were also determined.[25] In these cases, the salting-out of the IL from aqueous media was observed at salt molalities higher than 0.20 mol kg^{-1}. At fixed salt concentration of 1.5 mol kg^{-1}, the strength of this effect was reported to decrease in the following order: $ZnSO_4 > K_3C_6H_5O_7 > KNaC_4H_4O_6 > K_3PO_4 > Mg(CH_3CO_2)_2 > K_2HPO_4 > MgSO_4 > KH_2PO_4 > KCH_3CO_2$. The inorganic salt $Al_2(SO_4)_3$ at concentration of *ca*. 0.75 mol kg^{-1} concentration, close to its saturation solubility in water, causes the strongest salting-out effect observed by the research team. The detailed measured data and respective standard deviations, in weight fraction and molality units, can be found in the respective two cited papers. The trivalent ion Al^{3+} with higher cation's valence (III) induces a stronger salting-out impact than the divalent Mg^{2+} and Zn^{2+} ions, followed by the monovalent K^+ cation.[25]

Unfortunately, all presented results indicate that even in the absence of any metal ion solvent extraction process, appreciable loss of IL can occur as a result of the possible additional interaction in aqueous-biphasic system, even in pure water.

4. *Mutual solubility of ionic liquids and water in the presence of metallic species as a part of extraction mechanism*

Majority of these modern, innovative ionic diluents have no supplementary functional groups attached to their chemical structure that could directly coordinate to metal ions. In molecular diluents, it is impossible to extract directly the metallic species from an aqueous phase without the help of suitable ligands in order to perform the transfer into the organic layer. Even through, in particular cases, ILs can extract metallic species alone, unaccompanied with ligand moieties by an ion-pair formation mechanism. Incorporating this concept, an attempt was made to provide a narrow overview of the valuable literature examples influencing metal partitioning in the absence of a classical extractant or any additional molecular compound. Firstly, the use of undiluted ILs acting as both an extractant and a hydrophobic phase in traditional solvent extraction processes is unveiled. This is a complete renewal concept of the philosophy of solvent extraction: "task specific" diluents that can act as an extracting phase. Several research groups, mainly in Europe and Asia, have investigated the solvent extraction behavior of “classical” hydrophobic room temperature ILs based on imidazolim, piperidinium, pyrrolidinium and pyridinium cations for different s-, d- and f-ions, including precious metals from aqueous solutions.[131-141] Furthermore, many heavy metal ions are recognized to be toxic or cancergenic, and accordingly the pollution, caused by their presence is scrutinized as a major environmental threat for biota today. The removal of heavy metal ions from aqueous phase by extraction techniques with ILs is a research topic with promising perspectives allowing to evaluate them as innovative and sustainable extracting agents.[131] For the first time, liquid phase micro extraction with ILs was applied to industrial and communal wastewater samples.[142] The elimination of the metal(oid)s Ag, As, Cd, Cr, Cu, Hg, Pb, Pt, Sn, Zn and the cancerostatic platinum compounds cisplatin and carboplatin was screened, using two classes of ILs based on quaternary ammonium- and phosphonium-cations. Modifying the ionic composition of Aliquat 336 and Cyphos IL 101 by appending a metal-ion ligating functional group, like the following set-up of anions (SCN^-, $CH_3(CH_2)_4COO^-$, salisylate, thiosalicylate, benzoate, 2-(methylthio)benzoate), the selective extraction of solute metals have been favorably adjusted. The extraction efficiencies for Hg ranged from 80 to 100 %, for all tested ILs, without obvious trends regarding IL’s functionality. In model solutions at environmentally relevant concentrations applied, extraction effectiveness ≥95 % was reached for Ag, Cu, Hg and Pt with ILs bearing a sulphur atom in their anionic part, while other metals have been extracted to a lower extent (7-79 %). The obtained results clearly demonstrated that not only a simple “task specificity” of the evaluated ILs is responsible for the metal distribution, but also their physico-chemical properties, as well as the matrix composition as a whole. Supplementary, waste electrical (e-waste) and electronic equipment also represents an important secondary source of critical and valuable metals and must be viewed as a potential resource within the context of the circular economy.[143] More than a decade, the generated e-waste stream at a worldwide level seemed to cause serious environmental issues, which encouraged the recycling of valuable metals.[144] From the literature reviewed, it seems that most investigations deal with no real waste products. This is because model aqueous solutions and mimicking mixtures prepared in laboratory and consisting of the target metal species close to “real-waste” samples have been usually applied.[35, 145-150] A total number of 12 chloride ILs with various cations were transformed into corresponding trichloride ILs [Cl_3^-].[151] Moreover, these trichloride ILs can selectively dissolve some metals while leaving other metals in mixtures untouched.

For example, easy separation could be achieved for highly valuable metals like Au and Pt.

The aqueous biphasic system based on 1-hexyl-3-methyl-imidazolium tetrafluoroborate $[C_1C_6im^+][BF_4^-]$ and sodium chloride as a salting-out agent has been utilized for an efficient extraction of cobalt(II) ions from neutral media without adding any complexing agents.[152] As a third phase, aqueous solutions containing different inorganic additives suc as NaCl, $NaPF_6$, HCl, Na_2SO_4, NaH_2PO_4 were tested. The use of a diluted solution of the chaotropic salt $NaPF_6$ was found to be most effective for both the extraction and regeneration processes of the IL phase, and was further considered as a “flywheel”. The exact extraction mechanism of Co(II) by an ion-pair creation between the anionic metal complex and the cation of the IL could be described as:

$$2\,[C_1C_6im^+][BF_4^-]_{(o)} + 2CoCl_4^{2-}{}_{(aq)} \rightleftharpoons 2[C_1C_6im^+][CoCl_4^-]_{(o)} + 2[BF_4^-]_{(aq)} \qquad (9)$$

IL−based three phase partitioning was achieved by the creation of an additional solid phase in the two-phase systems, presented in Fig. 25, i.e. top IL-rich phase and bottom salt-rich phase. The third phase exhibits a pink color characteristic for hexaaquacobalt $Co(H_2O)_6^{2+}$ entities.

Figure 25. Influence of the aqueous biphasic system composition on the phase separation. Adapted from Ref. 152.

Papaiconomou et al.[153] have investigated the solvent extraction of Cu^{2+}, Hg^{2+}, Ag^{+} and Pd^{2+} from an aqueous chloride solution at pH 7 with ten imidazolium, piperidinium and pyrrolidinium ILs comprising typical anions, like $[BF_4^-]$, $[Tf_2N^-]$, trifluoromethyl sulfonate $[TfO^-]$ or nonafluorobutyl sulfonate $[NfO^-]$. Moreover, pyridinium or pyrrolidinium cations enhance low D values as compared to imidazolium or piperidinium positive charged parts in ILs. In fact, only Hg^{2+} has been extracted (D>24) with imidazolium and pyridinium ILs.

Definitively, the so called "supply" of toxic heavy metals in the aquatic environment is nowadays trully a remarkable issue, which explains the appropriate demand for innovative techniques targeted to achieving efficient elimination of toxic metals and their compounds from municipal and industrial wastewater streams, in order to comply with legal requirements and to prevent eventual risks for biota and human population.[131] Germani et al. investigated several ILs $[C_1C_n im^+][PF_6^-]$ as extracting agents for mercury leaching from aqueous solutions with pH equal to 4.68.[154] A general conclusion was made by the authors as the obtained results strongly indicated that the alkyl chain length of the IL cation, having firstly hydrophobic and secondly hydrophilic features, taken together affect the metal ion association and the extraction process of the whole system, e.g. the hydrophobicity of ILs and anion concentration in the aqueous phase. A similar behavior can be seen during the removal of Fe(III), Zn(II), and Cd(II) (0.1 g/L) from hydrochloric acid solutions (1 M) by a series of ILs. In that study, the extraction efficiency of ILs for Zn(II) and Cd(II) has increased in the sequence $[Tf_2N^-]<[PF_6^-]<[BF_4^-]$, in typical observed accordance with the hydrophilicity of the IL anions.[155] On the other hand, the prolongation of the alkyl chain of the cation resulted in the increase of the extraction ability of imidazolium based ILs, n=4 and 8.

Protic ILs have been used relatively rarely for the extraction of metals, despite their advantage to eliminate the need for the inclusion of a chelating agent in the process.[156] The protic ILs applied in the study of Janssen et al. are based on trialkylammonium cations (trihexyl- $[T_6A^+]$ and trioctylammonium $[T_8A^+]$) and linear alkanoate anions (hexnoate $[C_5COO^-]$, octanoate $[C_7COO^-]$ and docanoate $[C_9COO^-]$), because the Cu(II) ion coordinates strongly with carboxylate and amine ligands. The distribution of metal contents is generaly non-surprising, with the more strongly hydrophobic $[T_8A^+]$ cations (*ex*. $[T_8A^+][C_7COO^-]$ dragged 1.22 % water, $[T_8A^+][C_5COO^-]$ – 1.04%) leading to lower levels of water saturation than the $[T_6A^+]$–species $[T_6A^+][C_9COO^-]$ –1.43%, $[T_6A^+][C_7COO^-]$ – 1.29% and $[T_6A^+][C_5COO^-]$ –2.76%). The significant water amount for last one, which absorbs roughly twice more water by mass than any other IL, was reported to be due to the difference of two carbons in the anion alkyl chain. Examination of the change balance indicates that neutral metal extraction is the dominant mechanism in all studied cases, as it avoids the degradation of the IL phase associated with the ion exchange mechanism. A key insight of this work is the presence of the Hofmeister effect that probably plays an important role in the metal solvation in ILs: NO_3^- >Cl>SO_4^-. The anion of the metal salt strongly influences the extraction of copper, which is related to different solubility of inorganic anions in the IL phase. Thus, one might expect that the water content of the water-saturated IL should change the dissolution of the copper salt.

The experimental findings of competitive solvent extraction tests for various s-, d-cations and La(III) ion by pure oil phase i.e. $[C_1C_4im^+][Tf_2N^-]$ were not a surprise, as it is shown on Table 13. In this case, no solute (a dedicated organic ligand) was added to the IL to perform the target metal extraction. This particular IL is very effective for stripping selectivity of Fe^{3+} ion and a few s - elements as well from such an aqueous metal soup, whereas the simultaneous partial transfer of other heavy metallic species (except Mn^{2+}) including La^{3+}, is practically nil.[157] These results are fascinating in the sense that, it is possible to save the costly polydentate ligands possessing unsymmetrical NH-urea fragment applied in the cited paper. Also, it might compensate the use of costly IL, but if used in a rather small quantity only. In as much as the addition of a ligand is not a "*conditio sine qua non*" for solvent extraction of a couple metal ions like Fe^{3+}.

Table 13. Competitive extraction of various M^{n+} ions using the pure IL $[C_1C_4im^+][Tf_2N^-]$: a volume of 2.5 ml of aqueous solution containing various M^{n+} metal ions ($M^{n+}(NO_3)_n$//$M^{n+}(NO_3)_n \cdot xH_2O$) with $pH_{initial}$ *ca*. 2.61 was equilibrated for 2 h with 2.5 ml organic oil phase.[157]

M^{n+}	Na^+	K^+	Ca^{2+}	Ba^{2+}	Fe^{3+}	Zn^{2+}	Pb^{2+}	Cr^{3+}	Mn^{2+}	Ni^{2+}	Co^{2+}	La^{3+}
C_{in},mg/L	8.05	18.69	94.32	13.02	8.89	2.49	3.89	0.54	24.47	1.03	3.29	2.92
E (%)	0.0	5.1	20.3	5.5	45.2	0.0	0.0	0.0	5.3	0.0	0.0	0.0

The aqueous biphasic system incorporating $[C_1C_4im^+][PF_6^-]$ IL and a hydrochloric acid solution containing Pt(IV), Pd(II) and Rh(III) was scrutinized by Zhang et al. in order to develop stable three-layered liquids, a coexisting mixture, as a selective technique for platinum metal ions upon addition of S201-nonane organic solution (diisopentyl sulfide).[158] The experimental results have registered that most of Pt(IV) was extracted into the bottom IL phase, thus admitting the lower partition of other two metallic species, Pd(II) and Rh(III), Table 14. The almost negligible distribution of Rh(III) into $[C_1C_4im^+][PF_6^-]$ layer was attributed to the quick hydration of $RhCl_6^{3-}$ species influenced by HCl media that hinders the process of transfer. Par contra, the opposite is valid for $PtCl_6^{2-}$ anions, i.e. slower hydration kinetics in combination with lower charge density.

Table 14. Metal partition behaviors in two phase systems of $[C_1C_4im^+][PF_6^-]$/water at 1:6 ratio, and at [HCl]=1 M acidity.[158]

Metals	Pt	Pd	Rh	Pt/Pd	Pt/Rh	Rh/Pd	Pt/Pd/Rh
w% aq phase	29.33	92.3	93.2	27.9/90.7	28.5/93.8	92.7/93.9	26.9/91.7/93.5
w% in org IL phase	70.67	7.7	6.8	72.1/9.3	71.5/6.2	7.3/6.1	73.1/8.3/6.5

Moreover, the authors have observed that the biphasic system prepared with 6 M HCl concentration became a monophasic solution after setting for several hours, due to HCl transfer into the bottom organic layer that promotes the degradation of the oil phase, according to the reaction:

$$H^+ + PF_6^- + 6H_2O + 3HCl \rightarrow H_3PO_4 + 6HF + 3HCl + 2H_2O.$$

As already pinpointed, in addition to hydrolysis such chemical compounds should be avoided in spite of the uncontestable excellent results achieved for Pt(IV) species, as shown in Table 14.[158]

The extraction behavior of Ce(IV) by the similar IL $[C_1C_8im^+][PF_6^-]$ was particularly studied along with Th(IV) and other trivalent lanthanoids like Ce, Gd and Yb from nitric acid aqueous medium.[159] Two interesting investigations were carried out by the authors to provide a supplementary proof for the possible anion exchange mechanism. Insofar as the IL anion, $[PF_6^-]$, may be exchanged into the aqueous phase according to the proposed chemical reaction for Ce(IV), the total phosphorus amount in the equilibrated aqueous phase was determined using ICP-MS technique. Fig. 26 shows that, with increasing Ce(IV) concentrations in the IL phase, the phosphorus (existing as $[PF_6^-]$ and partly in a hydrolytic form) in the aqueous phase increases almost linearly too. The observation indicated that probably more of the $[PF_6^-]$ entities would be exchanged into the aqueous solutions when more Ce(IV) ions entered into the IL phase at the time of equilibrium. The second solution based investigation supporting the anion exchange mechanism during metal solvent extraction is the need of NO_3^- anions for the formation of $Ce(NO_3)_m^{n-}$ species in the organic phase. As a consequence, Fig. 27 gives a strong dependence of the extraction of Ce(IV) ions on the aqueous NO_3^- concentration. The following consideration is coincident with the acidity study done and additionally proves that Ce(IV) was not extracted into the IL phase as free Ce(IV) cations but as a coordination compound of Ce^{4+} and NO_3^-, that is, a $Ce(NO_3)_m^{n-}$ species.

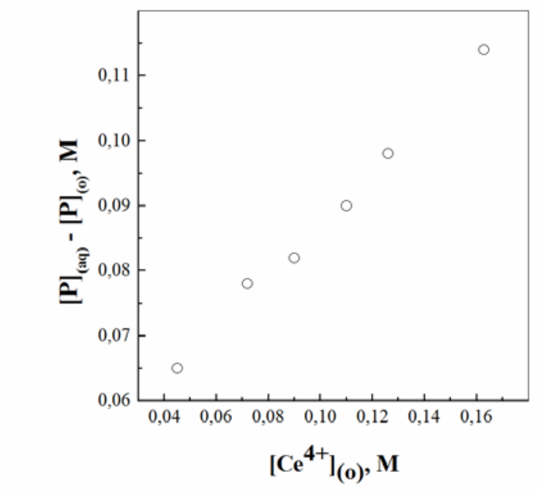


Figure 26. Dependence of aqueous Δ[P] on the concentration of Ce(IV) in the organic phase. $[HNO_3]_{in}$=1.36 M, $[Ce(NO_3)_4]_{in}$ = 0−0.09 M, $[P]_{(o)}$ refers to the concentration of aqueous total prosphorus when $[Ce(NO_3)_4]_{in}$ = 0. Adapted from Ref. 159.

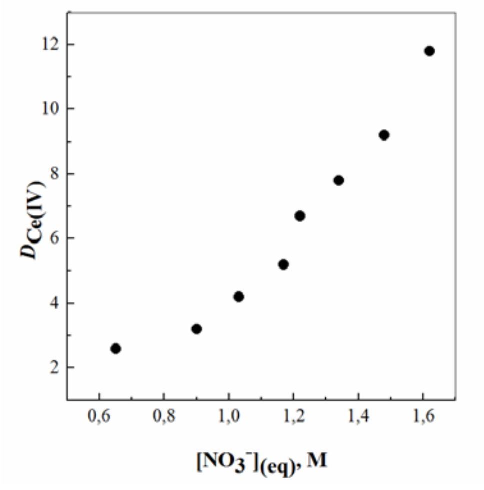


Figure 27. Dependence of $D_{Ce(IV)}$ on the equilibrated concentration of nitrate ions. $[Ce(NO_3)_4]_{in}$ = 0.0268 M, $[HNO_3]_{in}$=1.36 M, $[NaNO_3]_{in}$=0−0.7 M. Adapted from Ref. 159.

The reported average equilibrium constant of the reaction, log K_{ex}, is about -2.70:

$$Ce^{4+}_{(aq)} + 2[C_1C_8im^+][PF_6^-]_{(o)} + 6NO_3^-{}_{(aq)} \rightleftharpoons [C_1C_8im^+]_2[Ce(NO_3)_6^{2-}]_{(o)} + 2[PF_6^-]_{(aq)} \quad (10)$$

The obtained considerable selectivity of Ce/Th pair (~ 100) was very similar to that observed for DEHEHP/*n*-heptane (di(2-ethylhexyl)2-ethylhexyl phosphate) extracting phase, i.e. when the ligand was dissolved in a molecular diluent, Table 15.

Table 15. Separation factors of Ce(IV) versus Th(IV) obtained at various acidity of the aqueous phase.[159]

$[HNO_3]$, M	SF (Ce^{4+}/Th^{4+})
0.91	158
1.44	122
1.97	108
2.50	97.9
3.06	87.2

The effortless stripping process of Ce(IV) conducted by water from $[C_1C_8im^+][PF_6^-]$ phase was explained to be due to the hydrolysis of $Ce(NO_3)_6^{2-}$ in a diluted solution. Despite the anion exchange mechanism that results in IL loss during the extraction process, Eq. 10, the recycle test of IL demonstrated that the destruction could be controlled *via* adding of $[C_1C_8im^+][Cl^-]$ salt to the initial $Ce(NO_3)_4$ aqueous solutions and/or using KPF_6 as a stripping compound. According to the authors, this is an interesting phenomenon: the IL $[C_1C_8im^+][PF_6^-]$ can act as a liquid anion exchanger during the metal solvent extraction process. Then the anion could be recovered in the following stripping process.[159]

The absence of chelating agents is reported also for complete removal of the mercury ion by hydrophobic ILs.[160] Several parameters were studied deeply, in particular the anionic component of IL used. The resulting data seem to suggest that the metal ion partition into $[C_1C_8im^+]$ salts involves neutral and/or anionic Hg(II) species, since the rate of the process strongly depends on the experimental conditions, such as the working temperature, nature of the anionic component of the IL, the buffer solution and the counterion of Hg(II) (Br^-, SO_4^{2-}, $(CH_3COO)^-$). The highlight process kinetics of the mercury transfer in IL was in the following order: $[Tf_2N^-] < [PF_6^-] < [BF_4^-]$. The required time for 50 % metal ion transferring in the organic phase is approximately 4 h for $[Tf_2N^-]$–imidazolium IL, compared to 90 % complete extraction rate obtained in 24 h for its $[PF_6^-]$ analog. In fact, the designated water solubility of both anions of the corresponding imidazolium liquid salt progressively decreases in the same order: $[Tf_2N^-]$ < $[PF_6^-]$ < $[BF_4^-]$.[160]

The effect of the alkyl chain length of $[C_1C_\mathbf{n}im^+][Tf_2N^-]$ ILs was evaluated by Prof. Goto's group in order to use them undiluted as an extracting phase towards precious metal ions, namely Pt (IV) and Pd(II).[161] Fig. 28 shows that, with increasing ***n***, the extraction of Pt(IV) significantly increased, while that of Pd(II) *a priori* increasing very slightly. It is worth mentioning that the separation factor of the metal pair Pt/Pd can reach the value of *ca*. 312 at optimum experimental conditions. The anion exchange reactions for Pt(IV) solvent extraction were shown to be as follows:

$$PtCl_6^{2-}{}_{(aq)} + 2[C_1C_8im^+][Tf_2N^-]_{(o)} \rightleftharpoons [C_1C_8im^+]_2[PtCl_6^{2-}]_{(o)} + 2[Tf_2N^-]_{(aq)} \quad (11)$$

$$HPtCl_6^-{}_{(aq)} + [C_1C_8im^+][Tf_2N^-]_{(o)} \rightleftharpoons [C_1C_8im^+][HPtCl_6^-]_{(o)} + [Tf_2N^-]_{(aq)}, \quad (12)$$

when [HCl] > 0.01 M.

That is, chloro metal complex anions were transferred to the oil phase, while $[Tf_2N^-]$ anions of IL were released to the aqueous phase during the equilibrium process.

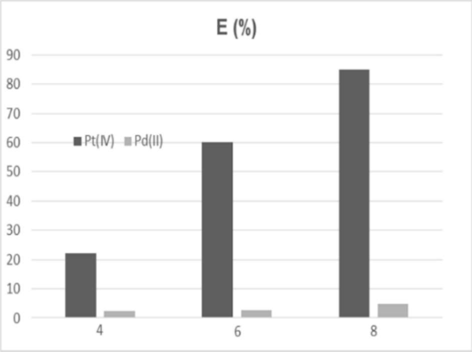


Figure 28. Effect of alkyl chain length of IL on the extraction percentage of Pt(II) and Pd(IV) ions in a single component extraction system. Aqueous phase: [HCl] = 1 M, $[M^{n+}]$ = 1 mM; Extracting phase: $[C_1C_\mathbf{n}im^+][Tf_2N^-]$, V_{aq}/V_{IL} =2. Drawn from data reported in Ref. 161.

The highly hygroscopic IL compound such as $[Hbet^+][Tf_2N^-]$ can form a two-phase system with water at and slightly above room temperature, while a one-phase system could be formed easily upon heating with an upper consolute point at *ca*. 55.5±0.2°C. This is shown on the phase binary system diagram presented on Fig. 29.[162] Betaine is an inner salt with a zwitterionic structure, which trivial name is 1-carboxy-N,N,N-trimethylmethanaminium hydroxide. The measurement by equilibrating the [Hbet$^+$][Tf$_2$N$^-$]–water mixture at a given temperature, followed by an analysis of the components in the [Hbet$^+$][Tf$_2$N$^-$]–rich phase (lower layer) and in the water–rich phase (upper layer) have been conducted by Nockemann et al. The composition of the phases was determined by distilling out the water and comparing the original mass with the remaining (nonvolatile) IL mass. The obtained mass fraction of the IL near the critical concentration was reported to be *ca.* 0.519 ± 0.001.

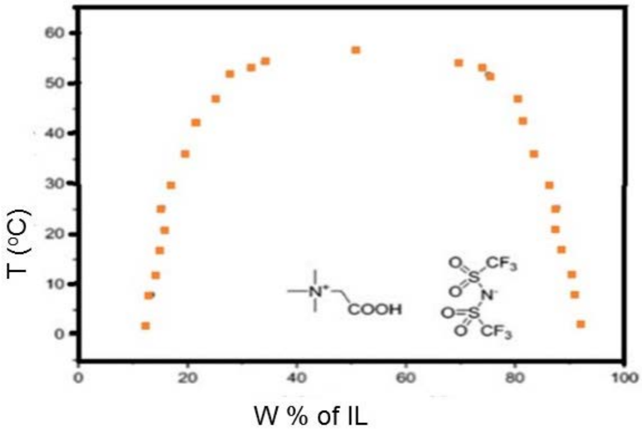


Figure 29. Liquid-liquid equilibrium phase diagram of the binary mixture [Hbet$^+$][Tf$_2$N$^-$]–water. Re-drawn from Ref. 162.

Although the existence of a thermomorphic phenomenon is clearly acknowledged for this IL compound in the literature, it is not necessary to take advantage of it during metal extraction procedures, which are usually conducted at room temperature. In the other cases, the extraction protocols involve heating above the UCST (at 60°C) of the samples, and then cooling them back to room temperature in order to achieve liquid phase separation or better process efficiency *via* homogeneous state. However, the large water uptake of nearly 13 wt%, as well as the large solubilization of [Hbet$^+$][Tf$_2$N$^-$] in water of up to 15 wt%, for equal volumes of the two liquids put into contact at room temperature render the potential of such a metal extraction system rather complicated for utilisation with such an intense ion exchange between the two liquid phases.[162]

The phase behaviour of the binary mixture of symmetrical dialkyl imidazolium IL (1,3-dihexylimidazolium nitrate) with water was investigated by Depuydt et al. The study showed that the water content into

IL phase after presaturation seems to be 24 wt% at 25°C, while the amount of IL dissolved in the water phase was calculated to be nearly 6 wt%, i.e. approximately 4 times difference.[42] The high salt concentration added to the aqueous phase 6 M $NaNO_3$ actually lowers the water solubility in the IL to 11 wt% instead of 24 wt%, hence a significant reduction was obtained. The IL−water system was reported to be still biphasic, with an ionic liquid solubility of 0.5 wt% in the aqueous phase, if the IL was put in contact with 6 M concentration of $NaNO_3$ salt. The preferential solvent extraction of rare earths (Sc^{3+}, Y^{3+}, La^{3+}, Nd^{3+}, Sm^{3+}) over 1st row transition metals in the Periodic Table was observed by the Binnemans' research group applying this symmetrical dihexyl nitrate−IL. As a final point in this study, the authors further exploited the separation of Sm/Co and La/Ni metal pairs relevant for recycling of the end-of-life products, more specificaly $SmCo_5$ magnets and nickel metal hydride batteries.[42]

The solvent extraction of such a presious metal as Au(III) from 0.1 M HCl aqueous phase into various aprotic ILs was investigated by Katsuta et al., with a very high distribution ratio accomplished, i.e. > 100.[163] Quantitatively, the authors explained the metal D dependencies on the IL species as a function of the solubility product of the IL used, Fig. 30. The equilibrium model, as suggested by the authors, comprise the ion pair extraction of $[AuCl_4^-]$ species with the IL cation in the aqueous layer, so the ion exchange of $[AuCl_4^-]$ with the IL anion in the oil phase was further considered. Although the extractability of gold(III) greatly depends on the type of IL, it is possible to estimate the extraction efficiency of any aprotic IL from the K_{sp} value if it is available.

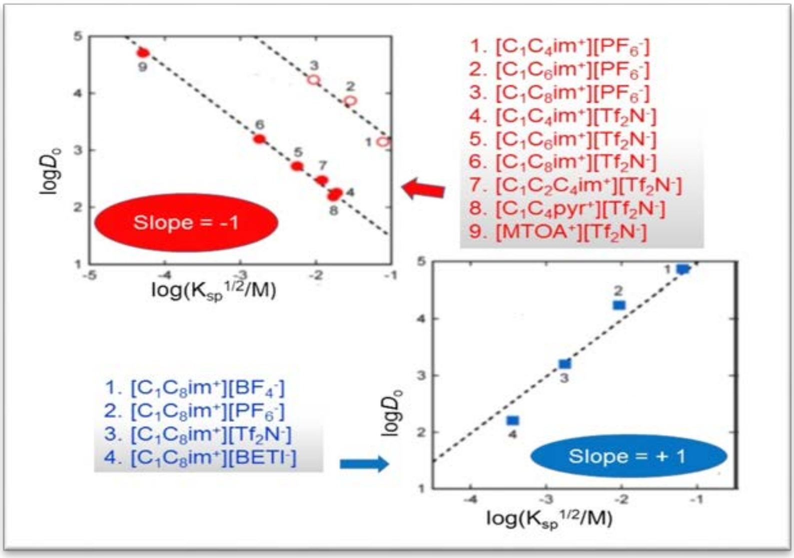


Figure 30. Relationship between logD_o and log$K_{sp}^{1/2}$. Adapted from Ref. 163.

Extraction of tetrachloroaurate or tetrabromoaurate anions has been carried out at relatively low acidic aqueous solutions with pHs in the range from 1 to 4 with several hydrophobic ILs bearing halide or [Tf_2N^-] anions and cations specifically, 1-octyl-3-methylimidazolium, 1-octylpyridinium or 1-methyl-1-octylpyrrolidinium.[134] The liquid–liquid extraction process carried out for target anionic gold complexes has achieved D ratios in the range from 3×10^2 to 3×10^4. Thus, gold was successfully extracted from water whatever the pH was applied and the variety of IL in use. Investigation on the solvent extraction mechanism has revealed an anion exchange between one anionic gold complex and one [Tf_2N^-] anion of the IL. In the studied case, with a tetrahalogenoaurate anion, one could expect an exchange of IL anion, according to the reaction in 1 to 1 ratio:

$$[AuX_4^-]_{(aq)} + [Tf_2N^-]_{(o)} \rightleftharpoons [AuX_4^-]_{(o)} + [Tf_2N^-]_{(aq)} \qquad (13)$$

It should be pointed out that the proposed equation is somehow compatible with the reaction mechanism involving the precipitation of an IL containing [AuX_4^-] species. This wass investigated too, through the chemical analysis done by the research team. Since, the latter is formed with a cation from the hydrophobic IL, the concentration of this cation in water automatically decreases. But, if the description of the solubility products of [$C_1C_8im^+$][Tf_2N^-] could be written like $K_{IL} = [C_1C_8im^+]^{final} \times [Tf_2N^-]^{final}$, i.e. this implies a mandatory solubilisation in water of some of the IL from the lower organic phase. In turn, this is due to the overall increase of the concentration of $[Tf_2N^-]$ anions related to the precipitation of gold species. Assuming that an anion exchange occurs as written in the foregoing equilibrium, the new authors'suggestion for *D* have resulte in the following expression:

$$D = \frac{K_{ext}\,[Tf_2N^-]_{(O)}}{[Tf_2N^-]_{(aq)}} \tag{14}$$

The solvent extraction process carried out for $[AuCl_4^-]$ entities from aqueous phase at pH ~1.5 with $[C_1C_8im^+][Tf_2N^-]$, applying various concentrations of $Li[Tf_2N^-]$ salt dissolved in water confirms the deducted assumption made by the authors. A good linear correlation was reported to be obtained by the authors between *D* and $1/[Tf_2N^-]_{(aq)}$ ($r^2 = 0.990$), which undoubtedly indicates that the liquid–liquid extraction of gold with ILs, therefore, involves certainly an anion exchange mechanism.[134]

Since the cation $[C_1C_8im^+]$ is a so-called strong anion exchanger, highly similar to the salt Aliquat 336, the liquid-liquid extraction of $PtCl_6^{2-}$ metallic species from 1 − 12 M HCl aqueous solutions was described by the formation of an ion pair:

$$2[C_1C_8im^+]_{(o)} + PtCl_6^{2-}{}_{(aq)} \rightleftharpoons [C_1C_8im^+]_2[PtCl_6^-]_{(o)} \tag{15}$$

However, the formation can be hindered, thus yielding a poor extraction of Pt(IV), if there is a lack of available IL cation. On the contrary, when $[C_1C_8im^+]$ is in excess compared to the metallic species, the extraction process of $PtCl_6^{2-}$ will be more than efficient.[164] All investigations reporting the extraction mechanism of a metallic anion (mono- or multivalent) towards an IL phase could be equally described as an anion exchange or an ion pair, according to the researchers, and are usually linked *via* the aqueous solubility product of the IL and its chemical nature (for review on that point, see chapter 9 in ref. 29).

Another interesting alternatives are phosphonium- and ammonium-based ILs for the extraction of transition metallic species incorporating a distinct anions like a thiosalycilate or thiocyanate, for example. The performance of eight new water immiscible halogen-free ILs, which were synthesized to possess a functionalization component from the corresponding trialkylamine, have been evaluated and further compared to trioctylmethylammonium thiosalicylate (a highly efficient commercial IL), as extracting agents for heavy metal cations.[165] The removal of d-cations, such as nickel, copper, lead, zinc, and cobalt from the aqueous solution with an initial concentration of 25 ppm at neutral pH was reported to be highly efficient: from 93 to nearly 99 %, while for the Cu (II) cation it has reached almost 100 %. The variation of the anionic part of the ILs has significant effect on the quantitative metal leaching efficiency, while at the same time the cationic part does not cause such a pronounced influence. The metal extraction percentages when using trioctylmethylammonium-based ILs were reported to increase in the following sequence: [Azelate] ≤ [Thiosalicylate/Salicylate] ≈ [Dodecanedioate] < [Oxalate], which could be probably in agreement with the formation of an anion chelate complex sequence. Furthermore, it was established that the increase in the cation chain's length of IL does not affect the extraction process, despite the lack of a mechanistic search in this published article.

Mixtures of two protic ILs were investigated as an extracting organic phase for platinum group elements by Katsuta and co-researchers.[166] The mixture of 10 wt % $[TOAH^+][NO_3^-]$ (trioctylammonium cation) dissolved in $[TOAH^+][Tf_2N^-]$ has a relatively low viscosity and low aqueous solubility (2.6×10^{-5} M when the cation was tested). With this applied IL combination, Pd(II) and Pt(IV) were extracted almost quantitatively from 0.1 M HCl aqueous solutions. Under the same experimental conditions other metal cations like Na(I), Mg(II), K(I), Ca(II), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ru(III), Rh(III), and Cd(II) were only slightly extracted. It was found that the extraction of Pd and Pt increases with increasing $[TOAH^+][NO_3^-]$ content in the organic ionic liquid mixture. The study proved that the proposed extraction systems provide an efficient separation method for Pd(II) and Pt(IV) species, and that their organic phases are recyclable, easy to handle, safe, and environmentally friendly.

The IL $[C_1C_{16}im^+][Cl^-]$ dissolved in the molecular diluent $CHCl_3$ was investigated for Au(III) extraction from 0.5, 1 and 2 M HCl solutions.[167] The so composed system IL salt dissolved in $CHCl_3$ shows high affinity towards Au(III) and high selectivity over some other d-metals such as Cu(II), Co(II), Ni(II), Fe(III), Al(III) and Sn(IV). As suggested by the authors, the anion-exchange mechanism according to the experimentaly obtained Job plot was further confirmed by the method of continuous variation, UV-Vis and infrared spectrum analysis leading always to the formation of a neutral complex:

$$AuCl_4^-{}_{(aq)} + [C_1C_{16}im^+][Cl^-]_{(o)} \rightleftharpoons [C_1C_{16}im^+][AuCl_4^-]_{(o)} + Cl^-{}_{(aq)} \qquad (16)$$

In 2014, the same research group has investigated one more precious metallic ion Pd(II), under the same experimental protocol, with another cyclic IL cation $[C_1C_{16}pyr^+][Cl^-]/CHCl_3/HCl$, i.e. supported by a pyridinium–based IL.[168] It is interesting to note in the report of Tong et al. that when the mole ratio of $[C_1C_{16}pyr^+][Cl^-]$ to Pd(II) is above 4, the extraction yield of Pd(II) is almost 100 %. Moreover, mixed hydrophilic–

hydrophobic ILs, $[C_1C_nim^+][Cl^-]$ (n = 12, 14 and 16)/ $[C_1C_nim^+]PF_6^-]$, (n = 4, 6, and 8) and $[C_1C_8im^+]Tf_2N^-]$ are tested to precipitate Pt(IV) from hydrochloric acid medium in additional step done by the group.[169] Under the optimal conditions, the $[C_1C_{16}im^+][Cl^-]/[C_1C_8im^+]PF_6^-]$ mixed system shows high extractability and outstanding selectivity for Pt(IV) over several base metals (Mn(II), Cu(II), Co(II), Ni(II), Fe(III), and Al(III)). By a reductive stripping process, Pt(IV) in the organic phase can be stripped in the form of platinum powders using hydrazine hydrate as long as $[C_1C_{16}im^+][Cl^-]$ is at the same time regenerated in the organic phase.

A new 1-butyl-3-benzimidazolium−functional IL ($[HBBIm^+][Br^-]$) has been exploited to be utilized in the same classical approach, i.e. diluted in the molecular diluent $CHCl_3$ in order to reduce the viscosity of the organic phase as usually done.[170] Some ILs are rather viscous, with values in the range of 40 cP or above. Therefore, the mass transfer process at the liquid-liquid interface may occur to be too slow. It was found that the $[HBBIm^+][Br^-]$/chloroform system showed effective dissimilar behavior for selective extraction of Pd(II), as the formed metal complex shows excellent solubility in chloroform and, at the same time, the Pt(IV) entities have been precipitating. According to the obtained X-ray structure of the solid product, the extraction mechanism of Pd(II) could be represented by the following equation:

$$2[HBBIm^+][Br^-]_{(o)} + PdCl_4^-{}_{(aq)} \rightleftharpoons [PdBr_2{\cdot}2BBIm]_{(o)} + 2H^+{}_{(aq)} + 4Cl^-{}_{(aq)} \quad (17)$$

Single crystal X-ray diffraction method was applied for structural examination of the IL−Pd monodentate symmetrical complex: $[PdBr_2{\cdot}2BBIm]$, Fig. 31. In fact, only one bonding site in the ligand of the $[HBBIm^+]$−cation exists: the nitrogen atom. The stoichiometric number of IL and Pd(II) during the solvent extraction procedure was determined to be 2:1. Consequently, the Pd(II) atom has shared two bonding nitrogens provided by the two isolated $[HBBIm^+][Br^-]$ molecules.

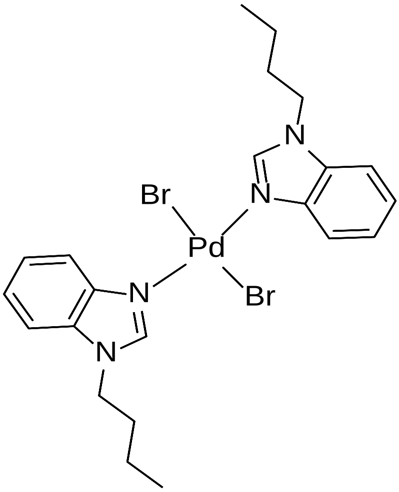


Figure 31. Re-drawn molecular structure of [$PdBr_2$·2BBIm].[170]

It was found that only the concentration of H^+ could inhibit the separation of Pt(IV), because the H^+ ion could attract the metallic anion $PtCl_6^{2-}$ to some extent. Thus, the anion exchange mechanism between the two-anion moieties $PtCl_6^{2-}$ and Br^- was prevented in this case. However, the concentration of both H^+ and Cl^- can obviously inhibit the extraction of Pd(II) insofar as these two ions are the products. This is because the chemical reaction and the simple increase of their concentration could frustrate the progress of the reaction, i.e. coordination mechanism.

A novel 2-mercaptobenzothiazole-functionalized IL (a bicyclic heteroatomic molecule, which exhibits sulfur and nitrogen atoms acting as chelating agent) has been synthesized for selective extraction of Pd(II) over Pt(IV). This has been done in a system where $[C_1C_8im^+][Tf_2N^-]$ was the diluting agent in order to escape from the poisonous molecular organic diluents typically involved in solvent extraction processes betraying the notion of the green chemistry.[171] The performance of this system over other metal ions such as nickel, aluminium, cobalt, rhodium, and ruthenium was assessed as well. Nearly 100 % extraction efficiency was achieved for Pd(II) ion, and approximately 99 % stripping recovery from the loaded organic phase with combination of 0.5 M thiourea and 1.0 M hydrochloride acid was further reported. According to the scientific discussion, the extraction mechanism could be represented by the following equation:

$$2PdCl_4^-{}_{(aq)} + 2\{[C_{10}(mim)_2{}^{2+}]2[MBT^-]\}_{(o)} \rightleftharpoons$$

$$[Pd(MBT)_2]_{2(o)} + 2[C_{10}(mim)_2Cl_2]_{(aq)} + 2Cl^-{}_{(aq)} \qquad (18)$$

As it can be seen on Fig. 32 the peaks of the IL cation have vanished on the recorded ^{1}H NMR spectrum of the obtained isolated metallic complex. This observation was consistent with the measured FT-IR spectra as well.

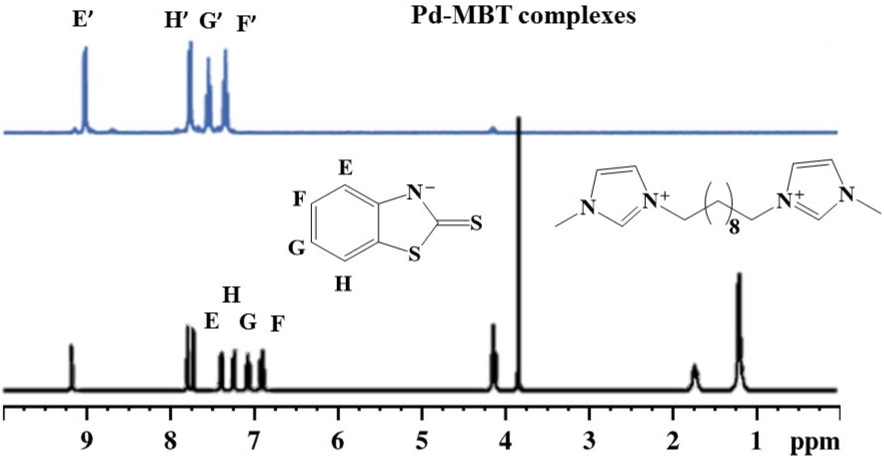


Figure 32. ^{1}H NMR spectra of {[$C_{10}(mim)_2^{2+}$]2[MBT^-]}and Pd-MBT complex. Re-drawn from Ref. 171.

Uncomplicated and smooth, the selective extraction process was proposed for three precious metals, Au(III), Pt(IV), and Pd(II), applying the Aliquat 336/C_6H_6 organic extractant phase, by Wei et al., with schematical representation on Fig. 33.[172] The reason why C_6H_6 was actually chosen is that it is a good nonpolar diluent that is very unreactive. Nevertheless, attention is need: it is estimated to be human carcinogen and laboratory experiments have shown its mutagenic effects. At room temperature, the liquid benzene evaporates easily into the air and can be dissolved in water. Therefore, it should be handled in accordance with the applicable first-rate laboratory hygiene and safety practices ensuring adequate ventilation. Overall, it may cause cancer and genetic defects.

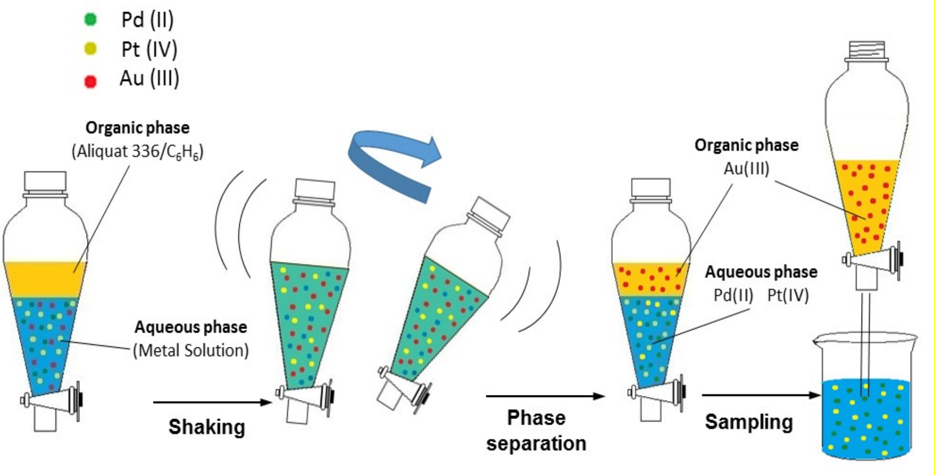


Figure 33. Schematically presentation of extraction process for precious metals using Aliquat 336. Re-drwn from Ref. 172.

Moreover, the results of the found selectivity coefficient as a function of pH have showed that pH 1 (0.1 M HCl solution) was the optimum for quantitative recovery of Au(III). The solvent extraction process of these three precious metallic anionic species can be expressed with equilibrium as follows:

$$[R_3CH_3N^+][Cl^-]_{(o)} + AuCl_4^-{}_{(aq)} \rightleftharpoons [R_3CH_3N^+][AuCl_4^-]_{(o)} + Cl^-{}_{(aq)} \quad (19)$$

$$2[R_3CH_3N^+][Cl^-]_{(o)} + PtCl_6^{2-}{}_{(aq)} \rightleftharpoons [R_3CH_3N^+]_2[PtCl_6^{2-}]_{(o)} + 2Cl^-{}_{(aq)} \quad (20)$$

$$2[R_3CH_3N^+][Cl^-]_{(o)} + PdCl_4^{2-}{}_{(aq)} \rightleftharpoons [R_3CH_3N^+]_2[PdCl_4^{2-}]_{(o)} + 2Cl^-{}_{(aq)} \quad (21)$$

It was mentioned that the established metal complexes with a lower charge density like those of $AuCl_4^-$ attract less water molecules in order to form a smaller hydration shell, which is very beneficial scenario for anion-exchange reactions. That is why, Au(III) exhibits much higher selectivity than the other metal ions, Pt(IV) and Pd(II).

Beyond the environmental and health concerns, the recovery of noble metals is relevant because of their current cost. As an example, approximately 40 000 euros/kg is the asking price for platinum and gold.[173] Boudesocque et al. have tried to develop greener methodology, which enables the substitution of molecular organic diluents and cyanide salts used usually to recover precious metals like Au(III), Pt(III) and Pt(IV). Several ILs were tested by the research team bearing tetrahexylammonium

([THN$^+$]) or tetraoctylammonium ([TON$^+$]) cations and halide [Br$^-$], dicyanide [DCA$^-$], thiocyanato [SCN$^-$], and [Tf$_2$N$^-$] anions. Whatever the IL was used towards gold the values of extraction yield exceed 95% from water. The solubility of ILs in water has been determined by ^{1}H NMR technique using the compound terabutylammonium bromide at 1 mM concentration as an external reference for analysis. The obtained solubility of [THN$^+$][Tf$_2$N$^-$] and [TON$^+$][Tf$_2$N$^-$] is found to be less than 0.01 %, while [DCA$^-$] and [SCN$^-$]–based ILs are more soluble with the percentage values of around 0.04 %. The reported *D* values have evidenced a lower affinity of [AuCl$_4^-$] ions for [Tf$_2$N$^-$] based ILs in comparison with other organic liquid phases [DCA$^-$], [Br$^-$] or [SCN$^-$] that generate D>1000. Thus, the higher hydrophobicity of [Tf$_2$N$^-$] anion renders the anion exchange process with [AuX$_4^-$] much more difficult. The liquid-liquid extraction of Pt(IV) was reported to be efficient with bromide, dicyanamide and thiocyanate ILs close to 100% and *D* higher than 1000 (the experimental limits of the method). The process efficiency depends on the hydrophilicity of the anion, the more exchangable anion leads to higher extraction yield, ex. for Au(III): [Tf$_2$N$^-$]<[DCA$^-$]<[SCN$^-$]. Consequently, the [Tf$_2$N$^-$] containing ILs may be used effectively to carry out the separation process between Au and Pt metal pair from mixed solutions because these ILs compounds do not extract Pt(II) or Pt(IV).

Solvent extraction of La(III) from acidic nitrate aqueous medium has been studied with [A336$^+$][NO$_3^-$] diluted in kerosene.[174] Maximum extraction of La(III) equal to 82 % was achieved when 0.6 M concentration of IL [A336$^+$][NO$_3^-$] was adjusted. The proposed reaction mechanism by authors includes no transfer of IL components into the aqueous phase under the employed experimental conditions:

$$La^{3+}{}_{(aq)} + 3NO_3^-{}_{(aq)} + [R_3R'N^+][NO_3^-]_{(o)} \rightleftharpoons [R_3R'N^+][La(NO_3)_4^-]_{(o)} \qquad (22)$$

About 98 % of the metal has been recovered using 0.2 M HNO_3 solution as a stripping agent. The calculated separation factor of La(III) and Sm(III) was reported to be *ca*. 65.2 using 0.1 M [A336$^+$][NO$_3^-$] solution.

The IL, triethyl-4-hexylphosphonium-[Tf$_2$N$^-$] has been exploited for the extraction of Pt(IV) using tri-n-octylamine (TOA, R_3N, $R=(CH_2)_7CH_3$) hydrochloride, followed by direct electrodeposition as Pt metal from organic phase.[175] The following anion exchange extraction mechanism of Pt(IV) with the ligand TOA has been established:

$$[PtCl_6^{2-}]_{(aq)} + 2[R_3N\cdot HCl]_{(o)} \rightleftharpoons [R_3NH^+]_2[PtCl_6^-]_{(o)} + 2Cl^-{}_{(aq)} \qquad (23)$$

with K=1.8118±0.397×10^5 for the condition of 0.5 to 1.5 M HCl aqueous solution.

A new methodology for recovering and purifying ammonium-based ILs applying the addition-phase method was proposed by Vergara and collaborates, after the solvent extraction of metal cations like cadmium, copper and lead with initial concentration of 50 to 100 ppm under neutral pH conditions at 30°C, with 1:20 weight ratio between two liquid (o/a) phases.[176] The extraction percentage was reported to be above 90% for all investigated cases and after five continuous cycle tests. The two synthesized halogen-free ILs are trioctylmethyl ammonium camphorate and trioctylmethyl ammonium dodecanedioate that displayed relatively low hydrophilicity confirmed by the TGA spectrum showing water concentration below 2%. In this sense, it is important to mention that the ion exchange of the anionic part of IL forming bonds with the metal ions was the main equilibrium chemical scheme. For the recovery of ILs, some organic molecular diluents such as ethanol or acetone (1:1 mixture ratio), with polarity indexes between 4.3 and 5.1 were proposed by the research team.

D_{Nd} higher than 10^5 and approximately 100% extraction was obtained after an equilibrium time of 30 minutes in the cases when the HNO_3 concentration is greater than 6 M applying undiluted and non-fluorinated ILs as extracting phase: (1-octyl-1-methylpiperidinium octylphosphite, 1-octyl-1-methylmorpholinium octylphosphite and 1-octyl-1-methylpyrrolidinium octylphosphite (P_{ip18}–OP)).[177] Solvation mechanism was suggested to occur during the extraction process, with involvement of three molecules of IL to one Nd^{3+}-nitrate complex, as shown on Fig. 34.

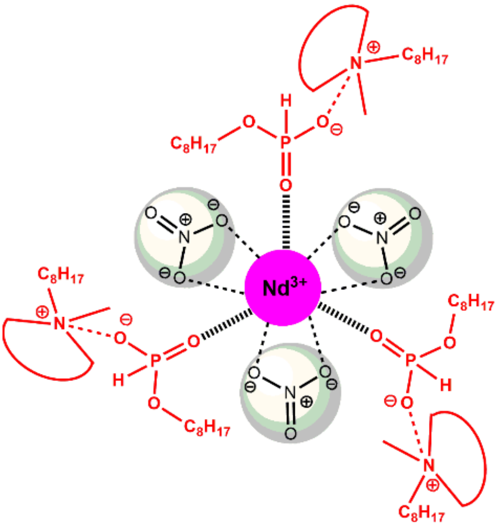


Figure 34. Proposed structure of Nd^{3+} nitrate complex and its coordination environment with P_{ip18}–OP. Re-drawn from Ref. 177.

High separation factors (> 7 5000) have been found for Co/Sm pair when undiluted ILs $[A336^+][Cl^-]$, $[A336^+][SCN^-]$, $[A336^+][NO_3^-]$ without the addition of any organic molecular or ionic liquid diluents were applied.[178] The achieved extraction/scrubbing/stripping efficiencies were found to be high already after a single contact of the phases. Eventually, the cited study could contribute directly to SmCo magnets recycling by solvent extraction technique.

Preliminary results on Rh(III) and Ru(III) solvent extraction with phosphonium IL–containing (Cyphos IL 101 and IL 104) organic phases carried out by Rzelewska and collaborators have shown that there is no significant difference in performance of each organic phase though they differ in the type of the attached IL anion.[179] This observation could be explained by the similar hydrophobicity of both anions: bis(2,4,4-trimethylpentyl)phosphinate and chloride. Unfortunately, Rh(III) transport has appeared to be inefficient under applied experimental condition, while over 70 % of Ru(III) was extracted from 3 M HCl solution as an example. The stoichiometry of the extracted Ru(III) species with Cyphos IL 101 (0.005 M solution in toluene) from both 0.1 and 5 M HCl aqueous phases could be represented by the following anion exchange equation, in which water molecule in the chloro-complex was skipped ($RuCl_5 \cdot (H_2O)^{2-}$):

$$RuCl_5^{2-}{}_{(aq)} + 2[R_3R'P^+][Cl^-]_{(o)} \rightleftharpoons [R_3R'P^+]_2[RuCl_5^-]_{(o)} + 2Cl^-{}_{(aq)} \qquad (24)$$

Trihexyl(tetradecyl)phosphonium chloride (Cyphos 101, $[P_{66614}^{+}][Cl^{-}]$) is a commercially available, non-fluorinated IL consisting of an organophosphorus-based cation combined with a chloride anion – *cf.* Table 23. $[P_{66614}^{+}][Cl^{-}]$ IL has already proved to be a very promising extracting organic phase for a variety of metal ions: Zn(II), Fe(II/III), Co(II), Lns(III), Au(III), Hg(II), Pd(II), Pt(IV), Bi(III), Re(IV) and U(IV).[143]

The results presented in the supplementary paper of Rzelewska et al., published one year before the above mentioned, have indicated that Cyphos IL 167 is the best extractant for extraction of Ru(III) from single-metal feeds compared to Cyphos IL 101 or Cyphos IL 104.[180] The measured distribution ratio of Ru(III) is equal to almost 3 for 1 M HCl concentration in the feed, but the main disadvantage was the formation of emulsion, which in some extent could eliminate this IL from future application as an extractant.

The extractant phase incorporating Cyphos IL 101/xylene has shown good selective co-extraction of Pd(II) and Pt(IV) leaving the Rh(III) entities in the raffinate.[181] One more aromatic hydrocarbon diluent, xylene is a mixture of three different isomers meta-, ortho- and para-dimethylbenzene. The main sequence of inhaling xylene vapour is depression of the central nervous system, generally referred to as “organic diluent syndrome”, with symptoms in the same manner with headache, dizziness, nausea or vomiting effects beging to occur with exposure to air levels of about 100 ppm. The complexation of $[PtCl_6^{2-}]$ by liquid anion exchanger $[P_{66614}^{+}][Cl^{-}]$ occurs according to the following equation:

$$[PtCl_6^{2-}]_{(aq)} + 2[P_{66614}^{+}][Cl^{-}]_{(o)} \rightleftharpoons [P_{66614}^{+}]_2[PtCl_6^{2-}]_{(o)} + 2Cl^{-}_{(aq)} \qquad (25)$$

The formation of $[P_{66614}^{+}][PdCl_3^{-}]$ species in the organic phase at low HCl concentration (0.1 M) was detected schematically *op. cit.* as exemplified below:

$$[PdCl_4^{2-}]_{(aq)} + [P_{66614}^{+}][Cl^{-}]_{(o)} \rightleftharpoons [P_{66614}^{+}][PdCl_3^{-}]_{(o)} + 2Cl^{-}_{(aq)} \qquad (26)$$

Or, due to the rapid equilibrium between the two entities $[PdCl_3^{-}]$ and $[PdCl_4^{2-}]$ in the aqueous phase, so in this way the reaction could be described as:

$$[PdCl_3^{-}]_{(aq)} + [P_{66614}^{+}][Cl^{-}]_{(o)} \rightleftharpoons [P_{66614}^{+}][PdCl_3^{-}]_{(o)} + Cl^{-}_{(aq)} \qquad (27)$$

On the other hand, very different extraction mechanism was proposed at 4 M HCl/Cl^{-} acid concentration with no detection of 1:3 metal: ligand stoichiometry in the oranic solution:

$$[PdCl_4^{2-}]_{(aq)} + 3[P_{66614}^{+}][Cl^{-}]_{(o)} \rightleftharpoons$$

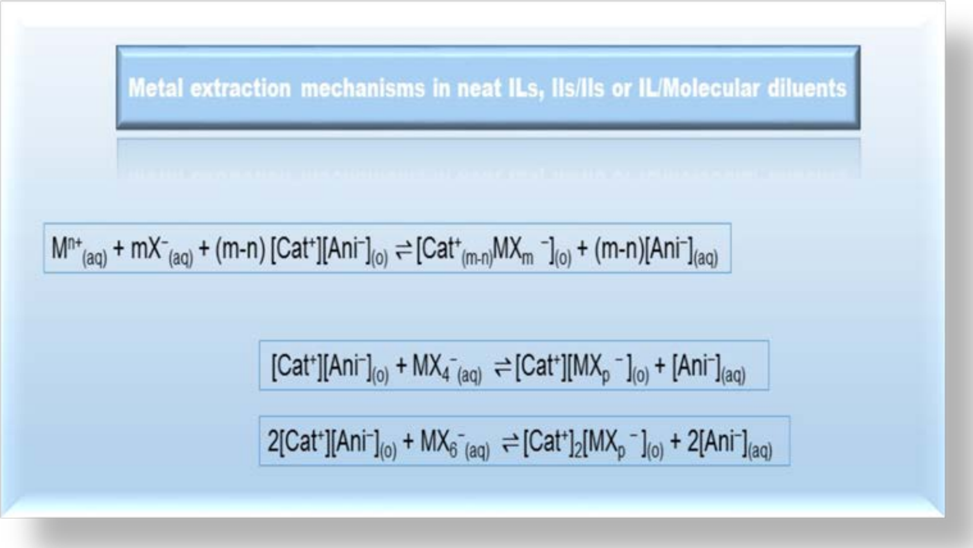
$[P_{66614}^{+}]_2[PdCl_4^{2-}]\cdot[P_{66614}^{+}][Cl^{-}]_{(o)} + 2Cl^{-}_{(aq)}$ (28)

where $[P_{66614}^{+}][Cl^{-}]$ can play the role of anion exchanger and solvating agent in the same time. [181]

The established metal complexes in the IL/xylene phases (0.08−0.7 $g.L^{-1}$) *via* anionic exchange mechanism were further characterized by ^{1}H and ^{31}P NMR spectroscopies. Maybe, it is essential to underline that, this integrated process based on the use of Cyphos IL 101 as an extractant and on the use of NaSCN and thiourea/HCl as stripping agents for Pt(IV) and Pd(II) is highly effective and leads to the recovery of these two precious metals over 99.9 %(w) for Pt(IV) *vs.* Pd(II)+Rh(III), as well as for Pd(II) *vs.* Pt(IV)+Rh(III).
The influence of the hydrophobicity of IL component ions could be less direct on the reaction mode. One representation, Luo et al.[80] have observed a cation exchange mechanism during the extraction of strontium cations to an IL that increases quietly along the IL anion hydrophobicity. The noticed effect was ascribed by authors to be due to the anion impact on the solubility product of the IL into an aqueous phase[104]

$K_{sp} = [Cat^{+}]_{(aq)}[Ani^{-}]_{(aq)}$,

where Cat^{+} and Ani^{-} are the cation and anion of the IL, respectively. If the IL has a relatively high solubility in the aqueous phase, then the presence of Cat^{+} in this liquid phase will probably inhibit the cation exchange mechanism by means of simple ion effect. When the hydrophobicity of the anion increases, the value of K_{sp} was reduced and, as consequence, the cation exchange mechanism normally will be enhanced.[104] Based on the all studies above it appears, that the different mechanisms can be controlled by elementary manipulating the hydrophobicity of IL components, this can lead to well-established adjustment apropos extraction efficiency. Nevertheless, it is more than clear in the cases when enhance process design is seeking, one must consider both the performance of metal complexes in the IL extracting phase and the presence of IL components transferred into the aqueous phase.[104] Principally, the solvent extraction mechanism implicating a loss of ILs components into the aqueous phase, i.e. aquatic ambiance provides the “greenness” of the whole chemical process rather questionable.[43, 182] Obviously, an ionic exchange is unavoidable process in aqueous/IL biphasic systems because owing to the polarity of water and the presence of ions as IL constituents, there will always be interactions between ions from the two liquid phases. After all, maybe initially applied as pure diluents exclusively for precious metallic species, ILs are highly likely not inert diluents, because their active contribution in the extraction mechanism cannot be negligible. From the various experimental examples presented above, one may have the feeling that reaction mechanism in M^{n+}/HX//IL biphasic systems without analog in molecular diluents, although with a very large diversity of patterns, might be considered at all no so confusing, even simple at first glance in some cases. In the presented investigations in brief, where no special ligands are added to the organic phase, i.e. neat IL, IL+molecular diluent or IL+IL were applied as extracting phase, the extraction mechanism of metallic species can be discussed in one possible way: hydrophobic ion pair formation or anion exchange reaction, Fig. 35. In this mode of chemical equilibrium, an anion of the IL compound is transferred to the aqueous phase and as a result, the metal complexation in the organic phase is possible with the participation of the cation part of the IL in its complex entity *via* formation of a hydrophobic ion pair. Obviously, this reaction scheme is not possible for neat organic molecular diluents. In view of metal extraction in order to avoid hydrolysis and/or precipitation, the acidic conditions of reaction medium are clearly an advantage. Thus, metal cations could formed negatively charged complex ions with inorganic anions presented in the aqueous phase (ClO_4^-, Cl^-, NO_3^-, SO_4^{2-}) originated from the mineral acid or added inorganic salt (to have a constant ionic strength). For instance, it is typical for many d- and 5f-metal ions to form vaious types of polychlorometallate complexes depending on the concentration of the acid HCl in the aqueous phase. The implementation of neat ILs in these cases is more than efficient for extracting such anionic metallic species. Through an ion exchange mechanism, the IL cation is released to the aqueous phase to compensate the incoming positive charge of the metal complex, Eq. 18.



Metal extraction mechanisms in neat ILs, Ils/Ils or IL/Molecular diluents

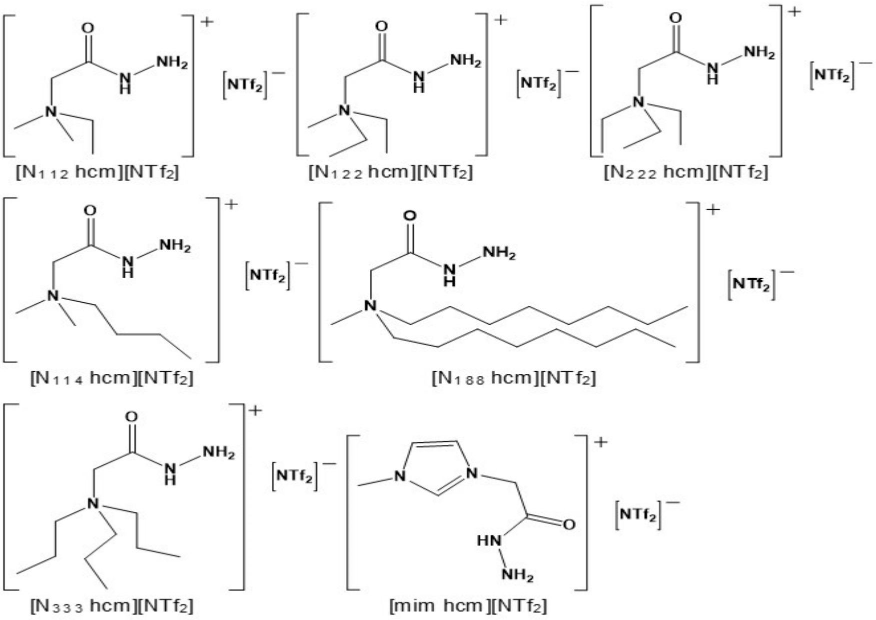
$$M^{n+}_{(aq)} + mX^{-}_{(aq)} + (m\text{-}n)\,[Cat^{+}][Ani^{-}]_{(o)} \rightleftharpoons [Cat^{+}_{(m\text{-}n)}MX_{m}{}^{-}]_{(o)} + (m\text{-}n)[Ani^{-}]_{(aq)}$$

$$[Cat^{+}][Ani^{-}]_{(o)} + MX_{4}{}^{-}{}_{(aq)} \rightleftharpoons [Cat^{+}][MX_{p}{}^{-}]_{(o)} + [Ani^{-}]_{(aq)}$$

$$2[Cat^{+}][Ani^{-}]_{(o)} + MX_{6}{}^{-}{}_{(aq)} \rightleftharpoons [Cat^{+}]_{2}[MX_{p}{}^{-}]_{(o)} + 2[Ani^{-}]_{(aq)}$$

Figure 35. Simplified schematic mode of metallic species extraction into ionic extracting phase.

A series of ILs based on Girard’s reagents, referred to colloquially known molecular structure introduced in the 1930s, containing the heteroatom-rich polar hydrazide group (-CONHNH$_2$-) was synthesized by Blesic and co-workers, Fig. 36.[183] Their tunable thermomorphic behavior with water was examined in detail providing a novel media for isolating both organic and inorganic species from water, i.e. removal of water-soluble dyes and scavenging metal ions. In this context, the high performance of ILs will open new horizons for implementation as dyes are widely utilized in textile, leather and food, cosmetic and printing technologies among other industrial chemical processes.



[N112 hcm][NTf2] [N122 hcm][NTf2] [N222 hcm][NTf2]

[N114 hcm][NTf2] [N188 hcm][NTf2]

[N333 hcm][NTf2] [mim hcm][NTf2]

Figure 36. A library of new synthesized Girard's ILs presented in the work 183.

The phase behavior of $[N_{xyz}hcm^+][Tf_2N^-]$−water mixtures has been studied as a chosen example and the corresponding T−χ diagram measured through cloud-point temperature determination was shown in Fig. 37. It should be stressed that all bistriflamide ILs−water systems revealed upper critical solution temperature (UCST) that strongly depends of the length and structure of the alkyl chains attached to the IL cation with T_C values varying from *ca.* 5 to 95°C. Thus, the most hydrophobic cation member $[N_{1888}hcm^+][Tf_2N^-]$ (see chemical structures on fig. 36) is almost immiscible, conversely to $[mimhcm^+][Tf_2N^-]$−water system with no phase splitting even at temperatures close to the freezing point of water. This behavior could be attributable to the two hydrogen-bond acceptors and three hydrogen-bond donors in the hydrazide functionality. It should be noticed that this is one of the rare examples of $[Tf_2N^-]$−IL that is soluble in water at room temperature at all compositions. For the other studied ILs see Fig. 37, the immiscibility envelopes (defined by the binodal curves) was strongly influenced by the total number of carbon atoms in the alkyl chains, and their distribution. So, it was concluded that, increasing the number of carbon atoms in the alkyl chains of the cations leads to an increase in critical temperature, and to a decrease in the critical composition. Interestingly, the two structural studied isomers $[N_{222}hcm^+][Tf_2N^-]$ and $[N_{114}hcm^+]$ $[Tf_2N^-]$ (both having the same total number of carbon atoms in the alkyl chains) were compared additionally, and their UCST behavior was found to be markedly different as well. A reasonable explanation for the observed difference could be the closer packing of alkyl chains in $[N_{222}hcm^+]$ cation and formation of van der Waals contacts between these chains creating a smaller cavity in the water, and hence, decrease the number of water molecules forced to be in contact with hydrophobic chains.

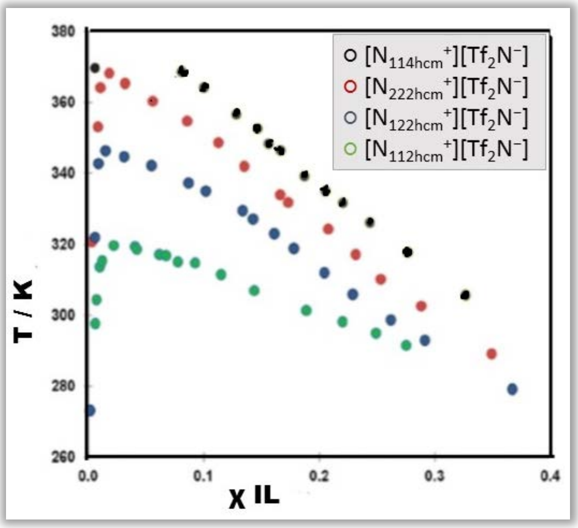


Figure 37. Cloud-point temperature, T, as a function of composition (mole fraction, $\chi_{\text{ionic liquid}}$) of ILs in water. Immiscibility regions are located below the curves. Adapted from Ref. 183.

The viability of one of the Girard's ILs as pure metal complexing reagents towards four common metal ions was tested *via* stirring an aqueous solution of metal salt (initial concentration 10 mM and counter-anions $CH_3CO_2^-$, and NO_3^- for Cr(III)) together with the IL, forming the homogeneous phase for nearly 20 min stirring at 60°C. The ICP technique was applied after cooling down the samples (T=20°C) and the mixture phase-separation of course, Fig. 38.

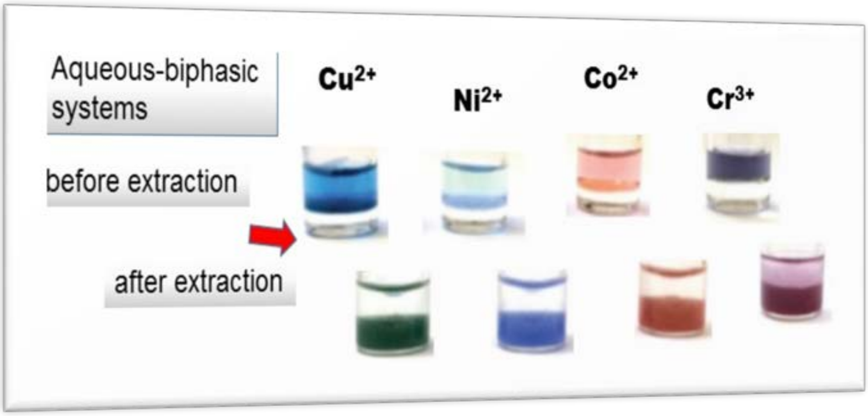
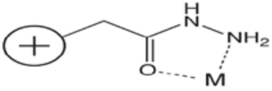


Figure 37. Metal extraction of an aqueous solution of metal salts ($[Ni(H_2O)_6]^{2+}$, $[Co(H_2O)_6]^{2+}$, $[Cu(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{3+}$ into $[N_{222hcm}{}^{+}][Tf_2N^{-}]$. The aqueous phase forms the upper layer, in all cases. Adaptation from Ref. 183.

The established low value of D_{Cr} was explained by authors in terms of the kinetic inertness of the low-spin d^3 electronic configuration in an octahedral ligand field, Table 16. For the metal complexes in the +2 oxidation state, the reflection to the well-known Irving-Williams series was demonstrated concerning the order of obtained distribution ratios: Cu(II)>>Ni(II)>Co(II).

Table 16. Distribution ratios of some d-ions at 20°C applying $[N_{222hcm}{}^{+}][Tf_2N^{-}]$ and the suggested coordination mode of this IL.[183]

Metal ion	D_M	Suggested coordination mode
Ni(II)	767	
Cu(II)	28 586	
Co(II)	36	
Cr(III)	5.4	

Untill now in the discussion only biphasic systems are cited predominantly, nevertheless, beyond this restriction one publication merits a recognition as well. Inside into the recycling of some rare earth elements like La, Ce, Nd, Y and several base metals has been presented from recycling slag powders of nickel metal hydride batteries.[184] The leaching process has been studied by $[Him^{+}][HSO_4^{-}]$ IL compound chosen among six acidic IL diluted in water 30 % (v/v) i.e. no second liquid phase was implemented in the described investigation proposed by Sahin and co-workers.

5. Mutual solubility of ionic liquids and water in the presence of ligands in the organic ionic phase

The scientific data on the solubility of ILs in pure water or aqueous phase including electrolytes could be helpful but the organic phase may constitutes of solutes as well. As an example, a commonly applied class of hydrophobic ILs in solvent extraction are those embodied [Tf_2N^-] anion. Howeve, these ILs requires the addition of an extracting molecule to increase the hydrophobicity of the metal complex in order to facilitate the leaching of hydrated metal cations, *cf*. Table 13. Nowadays, a wide range of available library of extracting compounds exists with cation or anion exchange properties, or chelating reagents that could complex the metallic species of interest by solvation as well. Various other components can be added into the organic phase with special purpose to ameliorate the interfacial characteristic of the biphasic system like synergistic agents, phase modifiers, antioxidants capable to retard or prevent degradation of diluted molecules, or phase-transfer catalysts in order to improve the process kinetics in a similar way to classical molecular systems (molecular ligand + molecular diluent). Thus, the application of IL as a hydrophobic diluting phase in conjunction with neutral or acidic chelating ligands should be discussed and taken into consideration as well. One may conclude that, the solubility of ILs' components in the aqueous phase does not depend on the presence of the organic molecule usually used as an extracting agent for solvent extraction (to name a few: 2-thenoyltrifluoroacetone (HTTA), benzoylacetone, N,N-diisobutyl-2-(octylphenylphosphoryl)acetamide (CMPO), and p-*tert*-butylcalix[4]arene) for 4f-ions, their concentration, and the chemical nature (acidic and neutral reagents or acidic/neutral synergistic combination).[185, 186] Table 17 has collected the data of the cation and anion solubility of [$C_1C_4im^+$][Tf_2N^-] IL incorporating mixture of two ligands after contacting with aqueous phase with different acidity (1×10^{-4} – 1.5 M DNO_3). It is interesting to mention that approximately the same values were calculated in the cases when one ligand was dissolved in the [$C_1C_4im^+$][Tf_2N^-] phase applying the same concentrations without regard of its nature (acidic or neutral molecule) and without difference on the IL's cation or anion solubilities, i.e. $[C_1C_4im^+]_{aq,eq} \approx [Tf_2N^-]_{aq,eq}$, Fig. 39. Moreover, these values can be consider as equal to those in the absence of ligand for $D_2O/DNO_3/[C_1C_4im^+][Tf_2N^-]$ system: *ex*. 16.7 mM and 15.4 mM are the reported quantities for [$C_1C_4im^+$] and [Tf_2N^-] ions at pH ~2.[74] The established results confirm that without ligand and without mineral acid, the $[C_1C_4im^+]_{aq,eq} = [Tf_2N^-]_{aq,eq}$ aqueous solubilities are almost identical (*ca*. 16 mM). Therefore, a clear picture emerges from data obtained at $\geq$ 0.1 M acid concentration and the presence of extractant compound in the organic phase at $\leq$ 1 M applied concentration. The quality of the solubility data may in some cases be questionable and less reliable at inorganic acid concentrations above 5 M due to the partial decomposition of IL compound. The possible reactions between solutes in the two phase must be taken into account and not to forget the probable transfer of diluted ligand in organic phase into the aqueous phase in some extent during equilibration, too.[187]

Table 17. [$C_1C_4im^+$] and [Tf_2N^-] ions concentrations in the aqueous phase at different acidity using mixture of HTTA − CMPO at $8x10^{-3}$ and $2x10^{-3}$ M concentrations, respectively.[188]

[DNO_3], M	[$C_1C_4im^+$], mM	[Tf_2N^-], mM
0.0001	14.2	13.9
0.001	14.3	13.8
0.01	14.5	14.6
0.1	21.4	20.3
0.5	26.3	27.0
1	29.6	28.2
1.5	30.8	30.3

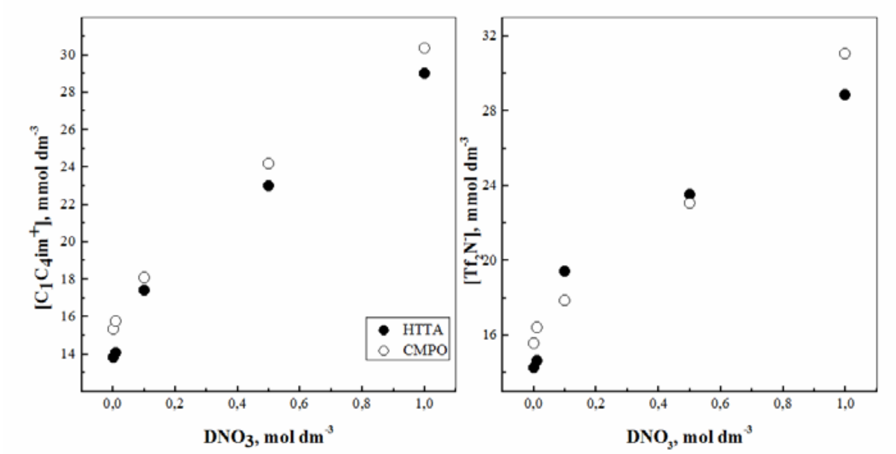


Figure 39. $[C_1C_4im^+]_u$ or $[Tf_2N^-]_u$ vs. $[DNO_3]$ of the aqueous phase using $[C_1C_4im^+][Tf_2N^-]$ as organic medium and $[HTTA]=8x10^{-3}$ M and $[CMPO]=2x10^{-3}$ M ligands. Adapted from Ref. 188.

However, the data presented on Fig. 40 show that the IL cation and anion solubilities in water are very different in strong HNO_3 and $HClO_4$ acidic aqueous media in the presence of CMPO ligand in the organic phase. Moreover, for the $HClO_4$ medium, the $[Tf_2N^-]$ solubility displays a plateau above *ca.* 3.8 M acid concentration, and somehow this correlates with the change in curvature of the variation of D_U found by authors as well.[189]

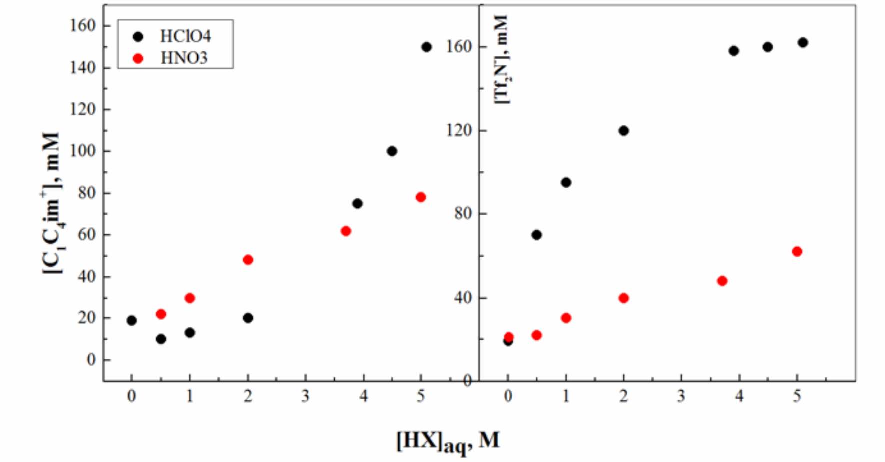


Figure 40. Concentrations of the IL ions in acidic HNO_3 and $HClO_4$ solutions in the presence of CMPO ligand concentration 13 mM. Drawn from data reported in Ref. 189.

It is important to remember that, as a whole, addition of a ligand to the IL phase has no significant effect onto the water solubility. For example, the average water content in $[C_1C_{10}im][Tf_2N]$ IL, in the presence of HTTA molecule diluted in it is ~ 8500 ppm, to be compared to an average value, in the absence of ligand, equal to 8250 ppm, Fig. 41.

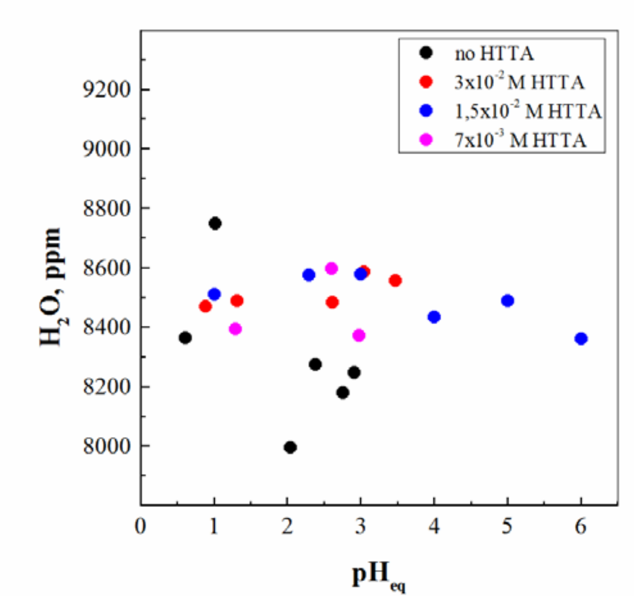


Figure 41. H_2O amount in the lower organic phase *vs*. pH_{eq} of the aqueous phase (0.1 M NaCl/HCl) using $[C_1C_{10}im^+][Tf_2N^-]$ as organic medium and different concentration of HTTA compound.

The average value of 12 200 ppm of water in $[C_1C_4im^+][Tf_2N^-]$ obtained in the work of Atanassova and Billard[23] compares very well with the value published previously in the absence of any mineral acid or added inorganic salt (*ca*. 12 000 ppm, no acid, same IL).[71] Note that this average value of 12 200 ppm of H_2O dissolved in $[C_1C_4im^+][Tf_2N^-]$ is lower than what has been measured for higher acidity of the aqueous phases (14 500 ppm[75] at 0.2 M H^+ concentration and 13 900 ppm at pH = 7)[22], an effect ascribed to the different acidity values investigated. Almost the same effect was observed upon addition of three chelating ligands (with chemical structures presented on fig. 42) in the organic ionic phase $[C_1C_4im^+][Tf_2N^-]$ at various concentrations. It can be seen from Fig. 43, that a little increase of water content was observed ~ 1000−1500 ppm upon change of the cation of IL, i.e. *n*=10 with *n*=4.

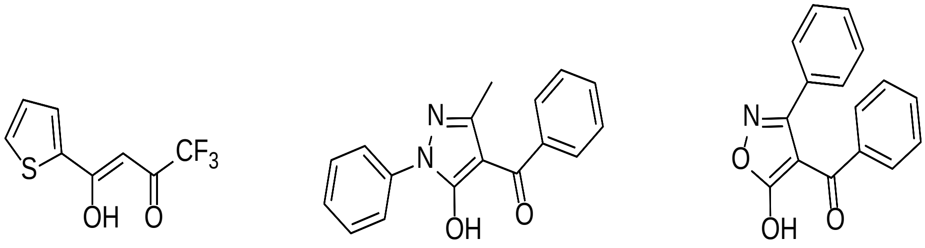


Figure 42. Structural formulas of the chelating extractants (HTTA, HP and HPBI, respectively).

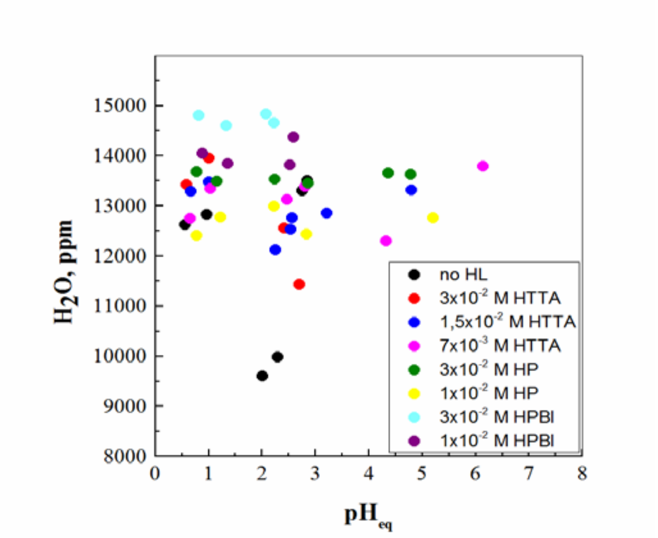


Figure 43. H_2O amount in the lower organic phase *vs*. pH_{eq} of the aqueous phase (0.1 M NaCl/HCl) using $[C_1C_4im^+][Tf_2N^-]$ as an organic medium and different concentrations of the three chelating compounds (HL, thenoyltrifluoroacetone (HTTA), 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (HP) and 4-benzoyl-3-phenyl-5-isoxazolone (HPBI)).

Depending on the water content into $[C_1C_4im^+][Tf_2N^-]$ bulky volume, the keto-hydrated/enol equilibrium[185, 190] kinetics of the β-diketone compound, HTTA could last up to tens of hours dissolved in this ionic environment despite its viscosity, because this IL displays relatively faster kinetics than the molecular cyclohexane diluent for comparison.[191]

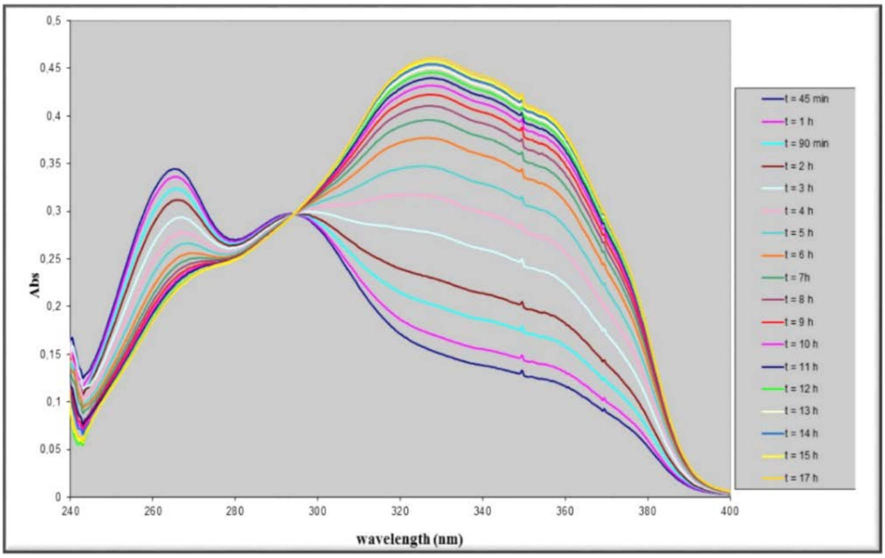


Figure 44. Absorption of HTTA in $[C_1C_4im^+][Tf_2N^-]$ as a function of time at $[H_2O]$=860 ppm. Adapted from 191.

The values of the isobestic points observed for two diluents ionic and molecular one were presented in Table 18 together with the exact water amount and the β-diketone concentration in its keto-hydrate form dissolved in their volumes. The recorded UV-vis spectra as a function of time recorded for sample with $[H_2O]$=860 ppm was displayed on Fig. 44, as an example.

Table 18. Values of the water amount, HTTA concentration in its keto-hydrate form and the position of detected isobestic points.[191]

diluent	$[H_2O]$, (ppm or M)	[HTTA], (10^{-5} M)	Isobestic point (nm)
$[C_1C_4im^+][Tf_2N^-]$	$50/3.9\times10^{-3}$	3.5	293
	$860/6.8\times10^{-2}$	4.25	293
	$1600/1.3\times10^{-1}$	3.8	294
	$2150/1.7\times10^{-1}$	4.1	294
	$3000/2.4\times10^{-1}$	3.8	294
	$5900/4.6\times10^{-1}$	3.95	294
	$7100/5.6\times10^{-1}$	4.25	296
	$8650/6.8\times10^{-1}$	4.25	–
	$11\,900/9.4\times10^{-1}$	4.25	301
cyclohexane	≈20	0.8	293

According to obtained data in the presence of higher water amount in the ionic diluent, the enol/hydrate equilibrium is reached in faster way. Thus, the keto-hydrated form could release one H_2O molecule in order to turn in its enol analog, which equilibrium was given by the existence of an isobestic point and depending strongly from the polarity of the diluent. As it was reported by Billard et al. at equilibrium, the dominant keto form exists at [H_2O]=11 900 ppm, while the enol is the major component for [H_2O]=50 ppm quantity dissolved in the diluent [$C_1C_4im^+$][Tf_2N^-].[191]

The enol content, or enol fraction (f_e) greatly depends on the polarity of diluents, e.g. f_e=0.9-1 for nopolar, and f_e=0.01-0.8 for polar diluents. To determine f_e of HTTA molecule in [$C_1C_{\mathbf{n}}im^+$][Tf_2N^-] IL, the UV spectrophotometry has been applied by Kidani and Imura taking into account that the observed peaks in the vicinity at 265 and 290 nm are usually attributed to the keto or keto hydrate form, while the peak at 340 nm to the enol form of β-diketones.[192] The authors have recorded that the absorbance at 334 nm gradually decreases with increasing time, whereas the increase at 269 nm is due to the transformation of enol to the keto form occurrence in [$C_1C_4im^+$][Tf_2N^-]. It was deducted that f_e value increases with the increase in 1-alkyl chain length, which in fact is the decreasing order of polarity of the [$C_1C_{\mathbf{n}}im^+$][Tf_2N^-] ILs. Thus, the f_e values become a little larger with the lowering in the IL's polarity: 0.43±0.01, 0.55±0.02 and 0.72±0.01, respectively for **n** equal to 4, 6 and 8. On the other hand, the enol fraction of HTTA in benzene solution *ca.* 0.95±0.02 was calculated according to the ^1H NMR spectrum.

The NMR spectra of another β-diketone molecule, benzoylacetone (HBA) in chloroform at 293K, 0.5 h after its dissolution showed the presence of two forms, 97 % of the preferable keto-enol and 3 % of diketo tautomer with characteristic methylene resonance at 4.1 ppm, Fig. 45.[185] This ratio was changed to 95:5 and 93:7 within 3 h and 24 h, which confirms that the signals of the minor component belong exactly to a tautomeric form, not to an impurity, Fig. 46. The same ratio, 7% minor component, was measured after 3 days showing that 24 h are enough to establish the tautomeric equilibrium in the specific experimental conditions. In this respect, it seems that IL behaves as classical organic diluents, with its specific future that the ratio enol/hydrate can be tuned by monitoring the absorbed water amount.

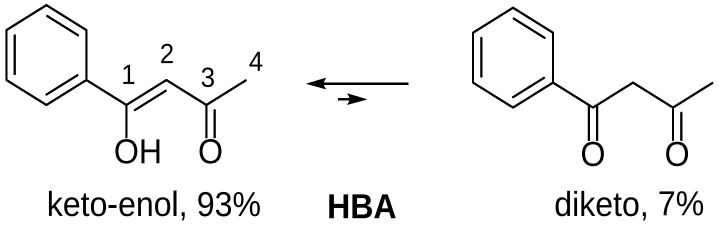


Figure 45. Tautomeric forms of benzoylacetone (HBA) in $CDCl_3$ in equilibrium at room temperature.[185]

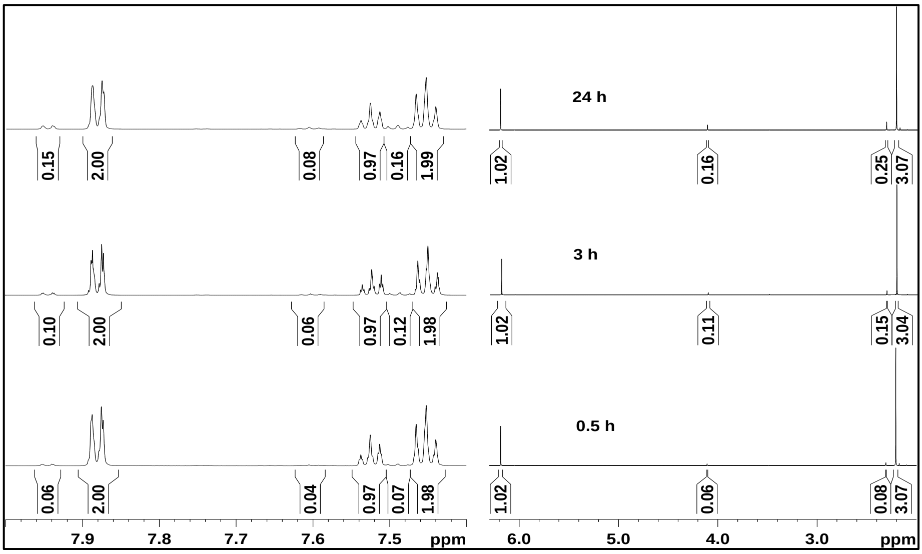


Figure 46. Parts of ^{1}H NMR spectra of HBA in $CDCl_3$ within 0.5 h, 3 h and 24 h after dissolution. Adapted from Ref. 185.

Variation of the water amount in $[C_1C_4im^+][Tf_2N^-]$ liquid phase as a function of $[HNO_3]_{aq}$ = 0−7.4 M concentrations for various values of TBP ligand loading (0.18 M, 0.55 M and 1.1 M) has been studied in detail by Billard et al. too.[193] The observed increase is not so linear, as it becomes significant above *ca*. 3 M of $[HNO_3]_{aq}$, and reaches a maximum of *ca*. 32 000 ppm of water absorbed at 7.4 M HNO_3 concentration, corresponding roughly to a factor of 3.4 more water than for 0 M HNO_3 sample. The influence of TBP loading could be represented for 4 M HNO_3 as the measured water content is ~13 000 ppm, with 0.18 M TBP ligand. This value increases to ~16 000 ppm, *via* 22 000 ppm at 0.55 M ligand concentration, and reaches approximately 25 000 ppm water content in the bottom layer when the presence of TBP compound is around 1.1 M in the organic phase. Under the experimental conditions of the cited work, it was established that at 7.4 M HNO_3 acidity the water amount in the lower organic phase is almost independent of the TBP loading i.e. the four variations seem to reach a value of approximately 30 000 ppm. Attention about the fact that mineral acid extraction is competing with the extraction of metallic cation at high acid concentration applied, thus lowering the process efficiency.

Therefore, a full discussion foregoes that focus on what these examinations reveal about the nature of ILs and the extracting organic moieties. In comparison with the extraction behaviors of conventional molecular systems (molecular extractant and molecular diluent), the metal ions under study in ionic liquid plus molecular extractant organic phase exhibit very high complexities. It is a general accepted statement that depending on the type of extracted metal complex, being anionic or cationic, anions or cations of the IL diffuse to the aqueous phase in exchange for the extracted metal complex.[43] Moreover, Fu et al. pointed out that due to the formation of a metal neutral complex in the extraction process, losses of IL components can be avoided, which somehow seems a little bit to be a misstated approach.[194]

Significant solubilization of ostensibly water-immiscible ILs in strong acidic aqueous phases is induced by the presence of any of a variety of neutral extractants.[195] The apparent results of the formation of the protonated form of the ligand due to the nitric acid and its subsequent exchange for the cationic component of the IL, resulting in loss of the IL component to the aqueous phase:

$$H_3O^+_{(aq)} + DCH18C6_{(aq)} \rightleftharpoons H_3O{\cdot}DCH18C6^+_{(aq)} \qquad (29)$$

$$H_3O{\cdot}DCH18C6^+_{(aq)} + [C_1C_nim^+][Tf_2N^-]_{(o)} \rightleftharpoons$$
$$[H_3O{\cdot}DCH18C6^+][Tf_2N^-]_{(o)} + [C_1C_nim^+]_{(aq)} \qquad (30)$$

A log-log plot of IL solubility versus DCH18C6 neutral ligand concentration yields approximately a line for each of the three IL systems ($[C_1C_nim^+][Tf_2N^-]$, $n = 5$, 8 and 10) contacted with an acidic (1 M HNO_3) aqueous phase, Fig. 47. It must be noted that the presented solubilities were corrected taking into account the results in the absence of any crown ether molecule (1.9×10^{-2} M, 1.4×10^{-3} M and 2.6×10^{-4} M for $n = 5$, 8 and 10 respectively).

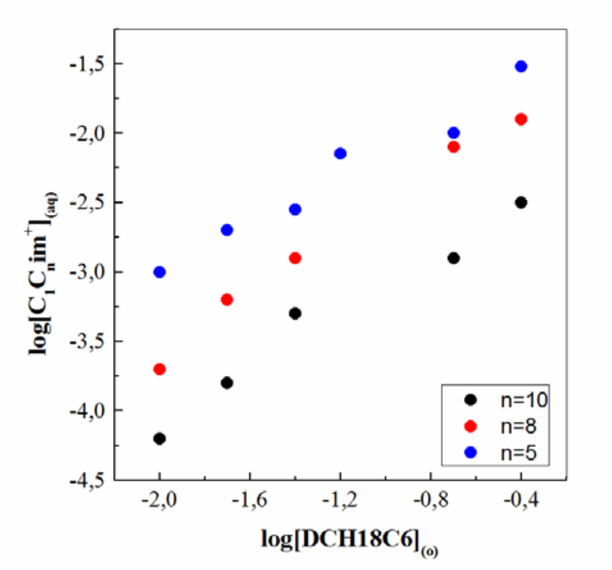


Figure 47. The effect of DCH18C6 ligand concentration on the solubility of $[C_1C_n im^+]$ cations into the acidic aqueous phase 1 M HNO_3 (T=25ºC, slopes close to 0.85, 1.10 and 1.0 from *n* = 5 to 10). Adapted from Ref. 195.

The increase in the initial concentration of the crown ether in IL is accompanied by a corresponding increase in the solubility of the IL cation in the aqueous phase. Rickert et al. have determined the $[C_1C_n im^+]$ content in the aqueous phase only by ^1H NMR analysis left out $[Tf_2N^-]$ anion aside, after dryness of a known aliquot of the aqueous phase on a rotary evaporator and dissolution of the residue in d-toluene. It would be anticipated, that as the hydrophobicity of the IL increased, the above exchange process would become progressively more difficult and the solubility effect of the ligand molecule diminished. For purposes of comparison, the effect of the addition of four neutral organophosphorus reagents upon the solubility of $[C_1C_5 im^+]$ in the acidic aqueous phase (1 M HNO_3) was determined too. Similarly, to the DCH18C6 case, the increase of the ligand concentrations is associated with a proportional increase in the solubilization of the IL cation. For example, $[C_1C_5 im^+]$ concentration increases from 10^{-3} to 3×10^{-2} M as [CE] = 10^{-2} changes to 0.31 M, while for 1.1 M concentration of the ligand TBP nearly $[C_1C_5 im^+]$ = 50 mM was released in the aqueous phase. In addition, the variation in solubility effect with ligand follows the extractant basicity (TBP (ti-*n*-butylphosphate) < DBBP (dibutyl butylphosphonate) < BDBP (butyl dibutylphosphinate) < TBPO(tributyl phosphine oxide)), i.e. the order of increasing basicity of the phosphoryl oxygen.[195] However, no appreciable difference was detected by the authors in the solubility of [$C_1C_{10}im^+$] cation in the aqueous phase (*ca.* 8×10^{-4} M) upon addition of an acidic organophosphorus compound bis-(2-ethylhexyl)phosphoric acid (HDEHP) with varies concentration over the same range (0.25−1.1 M).

Different inner-sphere coordination environments have been observed for the uranyl nitrate complexes formed with CMPO and TBP neutral ligands in one molecular diluent, dodecane and two ILs [$C_1C_4im^+$][PF_6^-] or [$C_1C_8im^+$][Tf_2N^-] by Visser and collaborators.[196] The existence of hexagonal bipyramidal complex $UO_2(NO_3)_2\cdot(CMPO)_2$ and coordination number of around 4.5 for a net stoichiometry of $UO_2(NO_3)(CMPO)^+$ were reported grace on measured EXAFS data, Fig. 48. Furthermore, the data concerning the IL solubility shown in Table 19 demonstrated clearly that the formation of the corresponding complex in ionic media coincides with a one-for-one exchange of the IL cation into the aqueous phase. The amount of IL cation transferred into the aqueous phase was quantitated by UV-visible absorption spectra. It is evident that less amount of the more hydrophobic cation was leached into the aqueous phase, as consequence lower distribution ratios of target metal were obtained.

Table 19. Concentration of [$C_1C_nim^+$] transferred into the aqueous phase.[196]

composition of the aqueous phase	[$C_1C_4im^+$], M	[$C_1C_8im^+$], M
water	0.024	0.011
1 M HNO_3	0.520	0.290
20 mM $UO_2(NO_3)_2$ + 1 M HNO_3	0.537	0.317
40 mM $UO_2(NO_3)_2$ + 1 M HNO_3	0.553	0.334
60 mM $UO_2(NO_3)_2$ + 1 M HNO_3	0.571	0.352

Seemingly, two or three water molecules would also be attached with the UO_2^{2+} entity, if the two analyzed ligands are monodentate. In the opposite case, bidentate ligand attachment with a maximum of one additional water molecule would be present in the inner coordination sphere of metal complex.

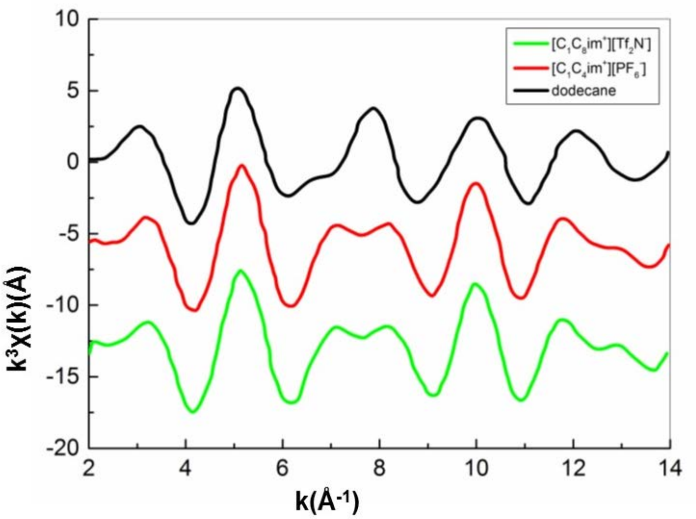


Figure 48. k^3 weighted EXAFS data over the range 2.5−13.5 Å for UO_2^{2+} species extracted into dodecane and two ILs, where solid line is data and symbols, fit. Redrawn from Ref. 196.

Attenuated Total Reflectance Fourier Transform Infra-Red spectroscopy has proved to be useful for $[Tf_2N^-]$ transfer determination in the aqueous phase due to its signal in the range of 1000-1300 cm^{-1} (peaks at 1059/1140/1205 cm^{-1}). Nevertheless, the small contribution of nitrate ions must be taken into account in such a case (peak at 1040 cm^{-1}).[193] The obtained results by Billard et al. have demonstrated that $[Tf_2N^-]$ anion solubility in pure water is independent of the ligand TBP loading, with an average value equal to *ca.* 0.049 M $[Tf_2N^-]_{aq,eq}$. However, at $[HNO_3]$ = 7 M strong acidity the experimental uncertainty is maybe larger, nevertheless the reported average value is equal to $[Tf_2N^-]_{aq,eq}$= 0.041 M. Therefore, the authors have assumed that IL anion solubility of $[C_1C_4im^+][Tf_2N^-]$ IL into the aqueous phase is not affected by either TBP (up to 1.1 M) or mineral acid HNO_3 loadings under the experimental conditions applied. On the other hand, Gaillard et al. have demonstrated that the solubility of each IL ion in the aqueous phase is different concluding that it is never possible to consider $[C_1C_4im^+]_{aq,eq}$ = $[Tf_2N^-]_{aq,eq}$ in the presence of organic solutes diluted in IL volume.[197] The introduction of 1.1 M TBP molecule into the IL phase has led to dramatic increase in the cation IL solubility up to 0.13 M at $[DNO_3]$ = 8 M concentration, while in the absence of this organic molecule at $[DNO_3]$ = 6 M, the $[C_1C_4im^+]$ solubility reaches a value of nearly 0.1 M. This research group observed the opposite trend for anion IL solubility in strong acidic aqueous phases from 0 to 9 M DNO_3, i.e. the presence of TBP molecule strongly reduces the transfer of IL's anions regardless the initial nitric acid concentration. At $[DNO_3]$= 2, 4 and 6 M acidifying the aqueous phase the $[Tf_2N^-]$ solubility is found to be approximately 0.01, 0.02 and 0.03 M in the presence of 1.1 M TBP molecules. While without this ligand the IL anion detected concentration in the aqueous phase under cited acidic conditions is around 0.04, 0.06 and 0.08 M. This trend was confirmed by measurements at a constant 3.7 M DNO_3 acidity and varied TBP concentration, Fig. 49. The experimental results have shown an increase of the amount of $[C_1C_4im^+]$ cation and a decrease of $[Tf_2N^-]$ anion concentrations in the aqueous phase, with an increase of the extractant concentration in the lower ionic phase.

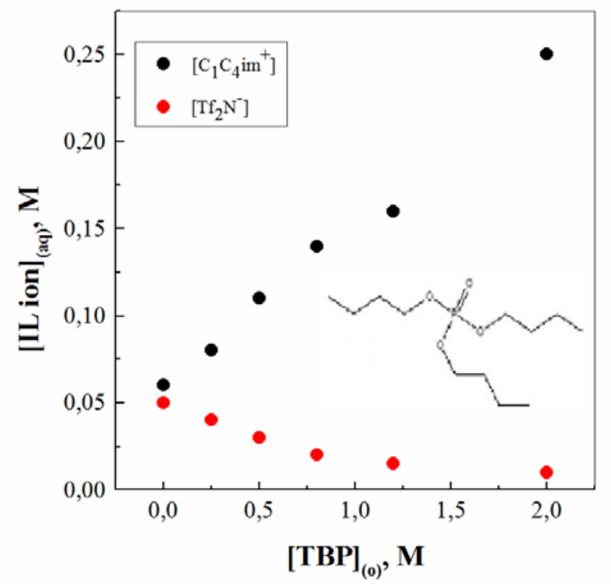


Figure 49. Evolution of the $[C_1C_4im^+]$ and $[Tf_2N^-]$ concentration in the aqueous phase in 3.7 M HNO_3 solution at equilibrium as a function of the TBP concentration in the IL phase, $[C_1C_4im^+][Tf_2N^-]$. Adapted from Ref. 197.

The impact of several ligands on the solubilities of IL ions in the biphasic system $D_2O/DNO_3/[C_1C_4im^+][Tf_2N^-]$ has been investigated recently. Nowadays most of workable solvent extraction studies for various metallic species are fixed likely on $H_2O/[C_1C_4im^+][Tf_2N^-]$ corresponding to a very stable aqueous-biphasic system: extractant investigated concentrations (0.04 M tributylphosphine oxide (TBPO), 0.05 M N,N'-dimethyl-N,N'-dibutylmalonamide (DMDBMA), 0.10 M 1-methyl-3-[4-

(dibutylphosphinoyl)butyl]-3H-imidazol-1-ium bis-trifluoromethyl-sulphonylimidate-[$C_1imC_4P(O)Bu_2$][Tf_2N] and 1.1 M N,N-dihexyloctanamide (DHOA).[198] The data evidence a significant difference between the IL's cation and anion solubilities, as a consequence of several ion exchange and/or ion pairing mechanisms involving all ions present in the biphasic system, but taking into account also the protonation/nitric extraction ability of the ligand, Fig. 51. Turning to data presented in Fig. 50, the effect of addition of 1.1 M concentration of N,N-dihexyloctanamide (DHOA) reagent as compared to that of 1.1 M TBP ligand case on the [$C_1C_4im^+$] solubility is astonishing, whereas the effect on the IL anion is almost identical. At very high nitric acid, concentration above 6 M, IL cation and anion concentrations in the aqueous phase in the presence of DHOA and TBP used as ligands seem to converge toward a single value of *ca.* 100 mM, toward which the data in the absence of ligand also apparently focalize, Fig. 50.

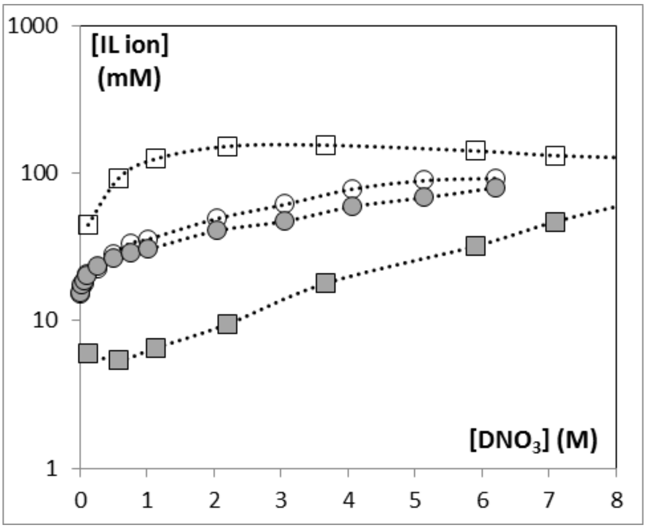


Figure 50. [Tf_2N^-] and [$C_1C_4im^+$] concentrations as a function of initial DNO_3 concentration. Without ligand: Tf_2N^- (●) and $C_1C_4im^+$ (○). With TBP 1.1 M: Tf_2N^- (■) and $C_1C_4im^+$ (□). Adapted from Ref. 198.

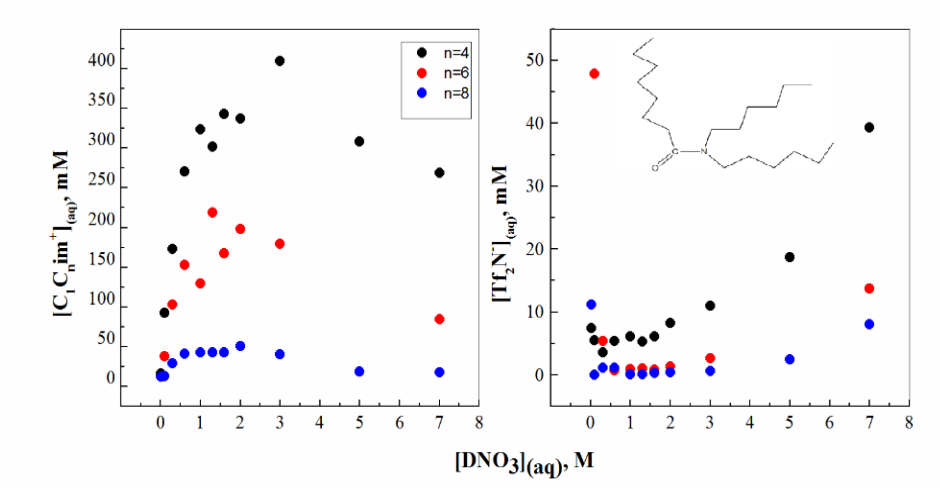


Figure 51. [Tf_2N^-] and [$C_1C_\mathbf{n}im^+$] concentrations in the aqueous upper phase as a function of initial DNO_3 concentration in the presence of DHOA ligand at 1.1 M in the organic media [$C_1C_\mathbf{n}im^+$][Tf_2N^-].The detection limit for both ions is equal to 2 mM for all ILs investigated and over the whole acidic range. For $n = 6$ and 8, [Tf_2N^-] values were below the detection limit for most of the DNO_3 range, anyhow they were inserted for comparison.

The addition of ligands below 1 M concentration seems to have a much lower effect on the solubilities of IL constituents in the aqueous phase, because the calculated values are almost close to those obtained in the absence of extractant molecule. However, a significant difference between the cation and anion solubilities exist, whatever the organic ligand is above the presence of 1 M mineral acid. Up to *ca*. 5 M acidity, all IL anion values are significantly below that obtained in the absence of ligand, while all cation values are above or very close to data in the absence of ligand, as it was schematically summarized in Fig. 52.

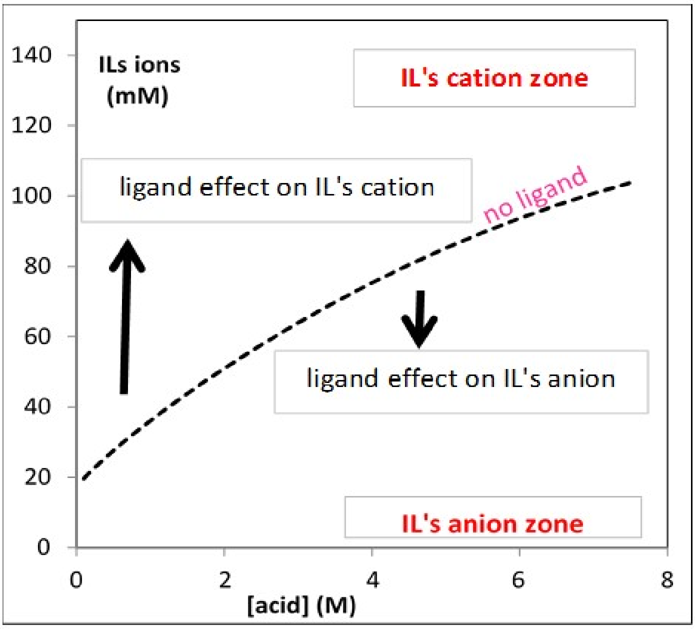


Figure 52. Illustrative representation of IL ions solubility as a function of aqueous acidity induced by addition of ligand in the biphasic system $D_2O/DNO_3/[C_1C_4im^+][Tf_2N^-]$. Adapted from ref. 198.

On the basis of the UV-Vis spectrophotometric data two reaction mechanisms have been proposed for UO_2^{2+} extraction behavior by di-*n*-hexyl octanamide (DHOA), i.e. at low acidity (0.01 M HNO_3) double cation-exchange:[199]

$$UO_2{}^{2+}{}_{(aq)} + 2L_{(o)} + H^+{}_{(o)} + [C_1C_{\mathbf{n}}im^+]_{(o)} \rightleftharpoons$$

$$[UO_2{\cdot}2L]^{2+}{}_{(o)} + H^+{}_{(aq)} + [C_1C_{\mathbf{n}}im^+]_{(aq)} \qquad (31)$$

while at higher nitric acid concentrations (4 M HNO_3) the following solvation mechanism was suggested *op. cit.*, Fig. 53:

$$UO_2{}^{2+}{}_{(aq)} + 2NO_3{}^-{}_{(aq)} + 2L_{(o)} \rightleftharpoons [UO_2(NO_3)_2{\cdot}2L]_{(o)} \qquad (32)$$

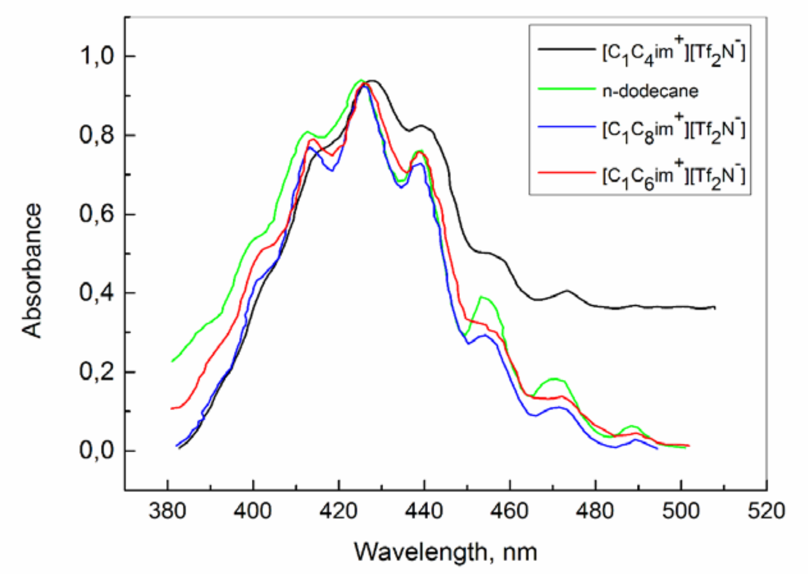


Figure 53. Absorption spectra of U(VI) extracted by 1.1 M DHOA compound using different ILs and one molecular diluent. Aqueous phase: 8 mM U(VI) at 4 M HNO_3. Re-drawn from Ref. 199.

On the other hand, a very interesting reversal extraction trend was reported for the three studied ILs from $[C_1C_4im^+][Tf_2N^-]>[C_1C_6im^+][Tf_2N^-]>[C_1C_8im^+][Tf_2N^-]$ at 0.01 M HNO_3 acidity to the following order $[C_1C_8im^+][Tf_2N^-]>[C_1C_6im^+][Tf_2N^-]>[C_1C_4im^+][Tf_2N^-]$ observed at 4 M HNO_3 concentration. Thus, the cation-exchange mechanism is somehow suppress at higher mineral acid concentration and is less operative in $[C_1C_8im^+][Tf_2N^-]$ environment. Therefore, that is why an increase in *n*, the alkyl chain length of the IL cation, induces a decrease in D_U values. It is clear that the U(VI) extraction is concomitant with the transfer of the IL cation to the aqueous phase, so the $[C_1C_nim^+]$ and $[Tf_2N^-]$ solubilities were estimated in the presence of 1.1 M DHOA ligand in the ionic phase, Fig. 51. As a whole, according to the results the cation and the anion solubility decrease in the order *n*=4>*n*=6>*n*=8 for the entire acidity range 0.1 M to 7 M DNO_3. As an example at 3 M DNO_3 concentration, the reduction of cation solubility is around 10 times changing $[C_1C_4im^+]$ cation with $[C_1C_8im^+]$, at the same time this decrease is 2 times only, if $[C_1C_4im^+]$ cation was exchange with its $[C_1C_6im^+]$ analog. At this point, although the three analyzed ILs involve the same anion $[Tf_2N^-]$, it is good to stress that its solubility is not identical, too. Being negligible for *n*=6 in the pH range 0.6 M to 2 M HNO_3 acidity and from 0.1 M to 3 M acidity for *n*=8 IL sample cases. Conversely, focusing on the effect of mineral acid concentration, Fig. 51 evidences one typical future. For *n*=4 it shows a decrease in [Tf_2N^-] solubility from 0.01 M to 2 M HNO_3 and beyond this acidity increases up to 39 mM [Tf_2N^-] concentration in the aqueous phase at nearly 7 M HNO_3. At this mention so strong acidity, the detected anion concentration for *n*=6 and *n*=8 is 13.6 mM and 8 mM, respectively, so much more less pronounced effect in comparison with the IL cation nature. Unfortunately, the ligand solubility in the aqueous phase was not taken into account in this study especially at 4 M HNO_3 condition proposed as constant value for slope analysis investigation in view of extraction pattern. As illustrated in Fig. 54 after contacting with 0.1 M HNO_3 acid the ligand, solubility is not at all negligible into the aqueous phase. When 1.1 M concentration of DHOA for example was dissolved in [$C_1C_8im^+$][Tf_2N^-] media the maximum absorbance measured at 305 nm is 1.43 for pH equal to 1 and is not affected too much from the ligand concentration concerning the presented picture on Fig. 54. However, the ligand solubility depends strongly from aqueous acidity because (not shown on figire) at pH=4 the 1.1 M DHOA/[$C_1C_8im^+$][Tf_2N^-] organic phase has released the extractant molecule as well in the aqueous layer: at 305 nm the corresponding absorbance is approximately 0.37 and close to nil for 0.04 M DHOA concentration at this low acidity.

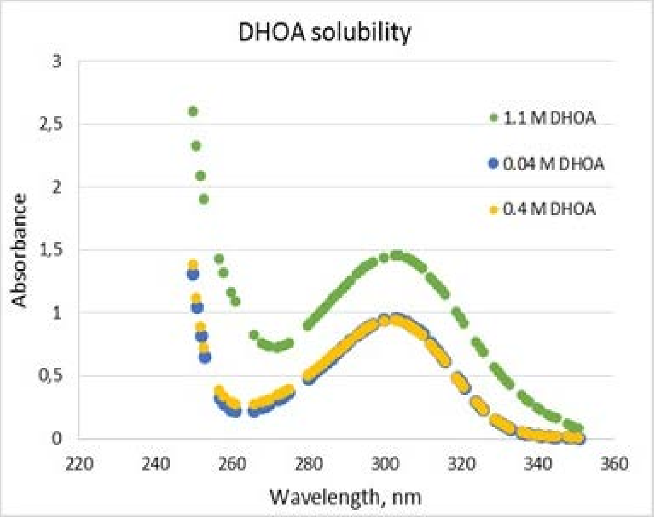


Figure 54. Solubility of the ligand DHOA into the aqueous phase after 2 h mixing of aqueous-biphasic system 0.1 M HNO_3/DHOA/[$C_1C_8im^+$][Tf_2N^-].

Furthermore, DHOA extractant is likely so easily distributed to the aqueous phase and the "free" L concentration in the organic phase is not at all equal to the concentration of L initially added to the liquid–liquid solvent extraction system. Although the studied metal concentration is sufficiently lower (~10^{-5} M ^{233}U) than the initial concentration of ligand (0.05−1.1 M DHOA). If $[L]_{init} \approx [L]_{org,t} \approx [L(free)]_{org}$ in this case, the slope analysis method, to determine the binding number of L molecules, can be very easily applied to the metal distribution data as a function of $[L]_{org,t} \approx [L]_{init}$. Maybe it is necessary to calculate the "free" extractant concentration for such a case, which is usually complicated due to the mathematical complexity and requires supplementary experimental data.[200, 201]

Giridhar et al. have reported the diluent characteristics of imidazolium hexafluorophosphate ILs including their solubility into nitric acid solutions ranging from 0.01 M to 8 M by measuring the absorbance of alkylimidazolium cation. While, for phosphorus analysis the amidol chemical method was applied by authors.[202, 203] The effect of IL alkyl group on the extraction of 5f-series member, uranium, was studied and discussed as well.[202, 203] It appears that both ions distribute to the aqueous phase with no preferential exchange of cation or anion, as demonstrated in Table 20. The solubility of both ILs (n= 4 and 8) increases with increase in the concentration of HNO_3 acid and the presence of TBP molecules in IL medium enhances additionally the ion transfer. However, the solubility of $[C_1C_8im^+][PF_6^-]$ is 2 – 3 times lower, depending upon $[HNO_3]$ added, as compared to its n = 4 analog, as it was discussed in the abovementioned paper. This tendency is also seen for DNO_3/1.1 M DHOA/$[C_1C_nim^+][Tf_2N^-]$ (n = 4, 6 and 8) systems, where at given acidity the difference of cations transfer is approximately 10 times, changing n = 4 with 8, likewise the anion constituent, Fig. 51.

Table 20. Solubility of $[C_1C_nim^+][PF_6^-]$ in aqueous nitric acid medium measured in vol. %.[202]

$[HNO_3]$, M	ligand	$[C_1C_4im^+][PF_6^-]$	$[C_1C_8im^+][PF_6^-]$
1.0	without	3.0	2.1
3.0	without	5.6	3.2
3.0	1.1 M TBP	5.8	4.0
6.0	without	12.8	5.9
6.0	1.1 M TBP	14.1	6.5
8.0	without	16.6	8.3
8.0	1.1 M TBP	18.2	10.0

Supplementary to the cited works, the effect of the salts [$C_1C_4im^+$][$Cl^−$] and [Li^+][$Tf_2N^−$] containing common cationic or anionic parts with the IL, was investigated for two different acidic medium, nitric[75] and hydrochloric.[76] The introduction of these ionic compounds into the aqueous acidic phase was widely used for understanding the extraction mechanism of metallic ions in IL-based biphasic systems. As evidenced in this endeavor, the ion solubilities are highly sensitive to chemical conditions, thus maybe this approach is not so fruitful and perhaps a little obsolete. Nevertheless, it is evident from both reports that the increase of IL aqueous solubility followed the rank order of the studied mineral acids $HClO_4 > HNO_3 > HCl$. The same trend concerning aqueous solubility of betainium and choline bis(trifluorosulfonyl)imide ILs was reported too.[204] Of particular interest is another hydrophobic IL, N,N-dialkylpyrrolidinium−[$Tf_2N^−$], examined as well in strong HCl medium. The following trend was bring to light [$C_1C_2im^+$] > [$C_1C_3pyr^+$] > [$C_1C_4im^+$] > …, concerning water solubility in the reviewed set of [$Tf_2N^−$] – settled ILs plus IL cation components transfer into upper "water rich" layer.[76]

4-Acyl-5-isoxazolones are very interesting class of compounds, analogs to β-diketones, characterized by strong acidity (pK_a=1.23) with potential application at strong acidic media due to the electron delocalization induced by the isoxazolone moiety for developing separation processes and above all metals for f-ions.[23, 118, 190, 205, 206] The pK_a of the acidic molecules containing a protonated functional group dictates the ability to deprotonate, thereby influencing the extracting behaviors.[118,185,190] The distribution behavior of 4-benzoyl-3-phenyl-5-isoxazolone (HPBI, see fig. 42) between the hydrophobic [$C_1C_4im^+$][$Tf_2N^−$] and the aqueous phase was investigated recently as a function of pH. The reader can found the detailed experimental procedure in the corresponding Ref. 207.

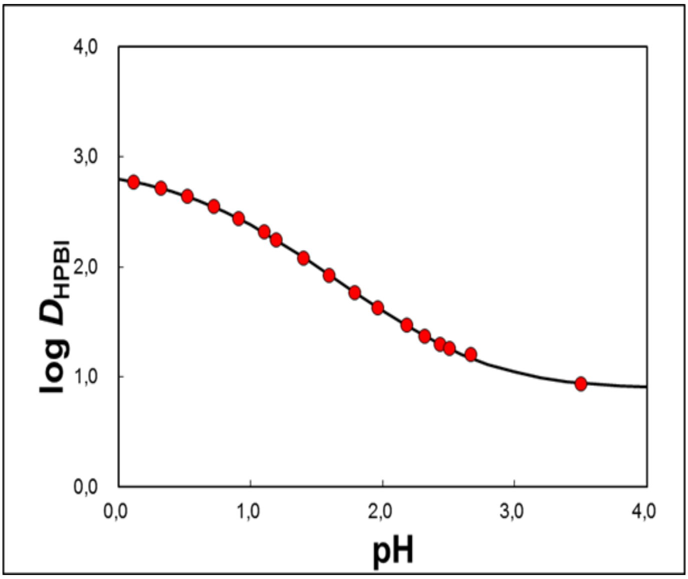


Figure 55. Log D_{HPBI} *vs* pH value of the aqueous phase in the $[C_1C_4im^+][Tf_2N^-]$ system. Initial concentration of HPBI was 10 mM. The solid line was obtained by a non-linear least-squares fitting. Re-drawn from ref. 207.

Fig. 55 shows the obtained relationship between log D_{HPBI} and the measured pHs. It was found that in the lower pH region, the log D_{HPBI} approaches a constant value with decreasing pH in the aqueous phase at the same time the log D_{HPBI} can be assumed to become constant in the higher pH region. It was, therefore, indicated further that the neutral HPBI molecule and its deprotonated anionic PBI^- form can distribute into the IL phase by the following anion-exchange reaction. Firstly, the distribution equilibrium of neutral HPBI is represented as follows:

$$PBI^-_{(aq)} + Tf_2N^-_{(o)} \leftrightarrow PBI^-_{(o)} + Tf_2N^-_{(aq)} \tag{33}$$

Therefore, the distribution ratio of D_{HPBI} between two immiscible liquid phases:

$$D_{HPBI} = \frac{[HPBI]_{(o)} + [PBI^-]_{(o)}}{[HPBI]_{(aq)} + [PBI^-]_{(aq)}} \tag{34}$$

can be rewritten applying $K_{D,HPBI}$, the apparent distribution constant, $K'_{D,PBI-}$, and the corresponding acid dissociation constant (K_a) of the chelating agents can be written as follows:

$$D_{HPBI} = \frac{K_{D,HPBI} + K'_{D,PBI^-}(K_a/[H^+]_{aq})}{1 + (K_a/[H^+]_{aq})} \tag{35}$$

The exact values of $K_{\mathrm{D,HPBI}}$ and $K'_{\mathrm{D,PBI-}}$ were determined by a non-linear least-squares fitting of the plots presented on Fig. 55, based on the last equation in the studied IL system: log $K_{\mathrm{D,HPBI}} = 2.88 \pm 0.01$ and log $K'_{\mathrm{D,PBI-}} = 0.88 \pm 0.01$. The $K_{\mathrm{D,HPBI}}$ value in the $[\mathrm{C_1C_4im^+}][\mathrm{Tf_2N^-}]$ system is higher than $K_{\mathrm{D,HTTA}}$ (log $K_{\mathrm{D,HTTA}} = 1.61 \pm 0.05$; HTTA denotes 2-thenoyltrifluoroacetone, see fig. 42), whereas the $K'_{\mathrm{D,PBI-}}$ value is comparable to $K'_{\mathrm{D,TTA-}}$ (log $K'_{\mathrm{D,TTA-}} = 0.96 \pm 0.10$).[192] In addition, the pK_a value obtained in this study by the fitting was 0.65 ± 0.01, which is in very good agreement with previously reported value (p$K_\mathrm{a} = 0.68$) in the literature.[208] It should be noted, also that the concentration of ligand HPBI in the IL phase after equilibration with the aqueous phase decreases with increasing pH due to the strong acid dissociation of this organic molecule in the aqueous phase. For this reason the HPBI concentration in the IL phase at equilibrium ($[\mathrm{HPBI}]_{\mathrm{IL}}$) could be calculated and as consequence applied in the slope analysis method widely used in solvent extraction of metals using the obtained $K_{\mathrm{D,HPBI}}$, $K'_{\mathrm{D,PBI-}}$, and K_a values as follows:

$$[\mathrm{HPBI}]_{(\mathrm{o})} = \frac{[\mathrm{HPBI}]_{(\mathrm{o}),\mathrm{ini}} K_{D,\mathrm{HPBI}}}{K_{D,\mathrm{HPBI}} + K'_{D,\mathrm{PBI}^-}(K_\mathrm{a}/[\mathrm{H^+}]_{\mathrm{aq}}) + (1 + K_\mathrm{a}/[\mathrm{H^+}]_{\mathrm{aq}})} \qquad (36)$$

where $[\mathrm{HPBI}]_{(\mathrm{o}),\mathrm{ini}}$ is the initial concentration of HPBI in the IL phase.

As an example, slope analysis of lanthanoids extraction with HPBI compound was investigated as a function of HPBI concentration as well as equilibrium pH of the aqueous phase according to the slope analysis method in order to determine the stoichiometry of the $\mathrm{Ln^{3+}}$–HPBI complexes formed in the ionic $[\mathrm{C_1C_4im^+}][\mathrm{Tf_2N^-}]$ phase for all, three chosen 4f-ions by the authors. Taking into account that the stripping was easily achieved using a dilute acidic solution of 1 M $\mathrm{HNO_3}$, D values were calculated as: $D = \frac{[Ln^{3+}]_{aq,back}}{[Ln^{3+}]_{aq,f}}$, where $[\mathrm{Ln^{3+}}]_{\mathrm{aq,f}}$ is the concentration of $\mathrm{Ln^{3+}}$ ion in the aqueous phase after extraction and $[\mathrm{Ln^{3+}}]_{\mathrm{aq,back}}$ is its concentration after back-extraction. The second considerable part of solvent extraction process is the recovery of the desired metal ion from the organic phase in a purified form in a way that the organic diluent can be recycled for the new extraction operation. Most often, various back-extraction protocols have been scrutinized and proposed after that by the scientific groups, depending on metal species and the organic phase. This second, main step is usually called “stripping”. *Per contra*, the problems related to the recycling of organic diluent (molecular or IL) are not too often tackled in the fundamental research investigations. The obtained plots for HPBI concentration were linear with a slope close to 4 suggesting that four chelating molecules were required to extract one 4f ion into the IL in 1:4 metal/ligand ratio. Therefore, two possible complexes could be formed i.e. self-adduct complexes ($LnL_3\cdot HL$) or anionic tetrakis complexes (LnL_4^-) as 1:4 complexes.[11, 99, 100] To elucidate the convincing extraction mechanism, the extraction of La(III), Eu(III) and Lu(III) with HPBI ligand was investigated as a function of log*D* *vs* pH in the aqueous phase. The corresponding slopes obtained for pH dependency were 3.0 for La^{3+}, 4.0 for Eu^{3+}, and 3.9 for Lu^{3+}, respectively, indicating that three protons from the HPBI molecules were exchanged for one La^{3+} ion in the extraction process, and four protons were released to extract Eu^{3+} and Lu^{3+} cations. Thus, in such a case different complex has been established for the first member of the 4f-series in comparison to other two lanthanoid representatives.

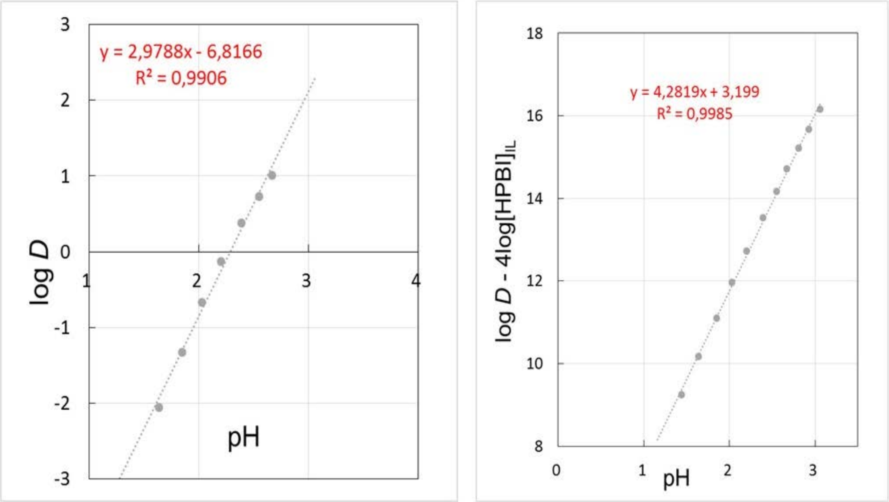


Figure 56. Log *D* *vs*. pH as well as log *D* − 4log $[HPBI]_{(o)}$ *vs*. pH plots for La^{3+} extraction using 1 mM HPBI in $[C_1C_4im^+][Tf_2N^-]$. Adapted from Ref. 207.

Hence, log *D* − 4log [HPBI]IL *vs*. pH plots were collected additionally because the concentration of HPBI in the IL phase at equilibrium strongly varies depending on the pH condition due to its high acidity ($pK_a = 0.65 \pm 0.01$), Fig. 55. As shown on Fig. 56, the slopes obtained for pH dependency were around 4 for all three investigated lanthanoids including La(III) cation. These results indicate now that four protons from the HPBI molecules were released to extract all Ln(III) ions as concluded and published by authors. The extraction of anionic complexes is possible by the exchange of $[Tf_2N^-]$ anions into the aqueous phase, and the extraction of Ln^{3+} with HPBI reagent in this IL system can be expressed by the following equation:

$$Ln^{3+}_{(aq)} + 4HPBI_{(o)} + [Tf_2N^-]_{(o)} \leftrightarrow Ln(PBI)_4{}^-{}_{(o)} + 4H^+_{(aq)} + [Tf_2N^-]_{(aq)} \quad (37)$$

The distribution ratio (D_{HA}) of the β-diketone compound benzoylacetone (Hba) between the same both liquid phases was studied too as a function of pH.[209] At lower pH regions, $\log D_{HA}$ was found to be almost constant due to the distribution of neutral Hba moieties. At medium region of pH, i.e. 8 to 10, the D_{HA} value decreases with increasing pH because of the formation of anionic ba^- species much more stable in the aqueous phase compared with neutral Hba, molecule. While at higher pH values, the D_{HA} was almost constant again, explained with the fact that the formation of mainly anionic ba^- moieties occur that distributes into the IL by an ion-exchange mechanism. The calculated results for $K_{D,HA}$, $K_{D,A}$ and pK_a are 2.67±0.04, -0.84±0.13 and 8.54±0.07, respectively.[209] The last cited value is consistent with the known pK_a of 8.96 for this compound found when molecular diluent benzene was used. This trend unfortunately is not valid for the extractant HPBI where rather remarkable difference was established between molecular and ionic diluents in use. Maybe it is good to mention as well that for 2-thenoyltrifluoroacetove (HTTA) reagent no changes in distribution behavior was caused upon change of benzene with $[C_1C_4im^+][Tf_2N^-]$, $[C_1C_6im^+][Tf_2N^-]$ or $[C_1C_8im^+][Tf_2N^-]$ looking at the calculated pK_a values by Kidani and Imura 6.16, 6.43 and 6.37, respectively applying ILs in comparison to *ca.* 6.23 for C_6H_6.[192]

As it was noted in section introduction, the diluents chosen for organic phase must be suitable as a medium for dissolution of a variety of extracting moieties but in some cases, this is a significant drawback taking into account the structural characteristics of ILs like viscous liquid compounds. The limited solubility of some extractants in short-chain ILs requires the addition of a modifier. A new method employing thermogravimetric analysis (TGA) has been described for the determination of the solubility of various metal ion extractant families including HDEHP, d-tert-butylcyclohaxano-18-crown-ether, CMPO, calix[4]arene-bis(tert-octylbenzo-crown-6) and 2,6-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]tria-zine-3-yl) pyridine in a series of $[C_1C_nim^+][Tf_2N^-]$ ILs.[210] In addition, the precision of the method (1-5%) is comparable to that reported for HPLC and UV-visible spectrophotometry for the determination of extractant solubility in ionic surroundings. On the other hand, this new approach (TGA) is simple and requires little sample (<100 mg). Unfortunately, the proposed technique is not applicable *a* *propos* highly stable molecules like those incorporating multiple aromatic functional groups such as calixarenes. Thus, the solubility determination for ligands in the ILs of interest for liquid-liquid extraction should be imperative and straightforward as a method, at the same time. It is worthwhile to mention that the well-known principle “like-dissolves-like” cannot be fully considered and attributed as well in some extend in these investigations as the IL diluent possesses different chemical nature (i.e. ionic) from the solutes (molecular extracting compounds). On the other hand, mainly the interactions between anionic part of ILs and metal ions are widely studied in respect for their solvation.[211-213] To a large extent the structure and properties of these Coulobm systems are determined by the intermolecular interactions among anions and cations.[214] Moreover, it has been found in the extraction of natural compounds that the interactions between the extracted species and ILs are crucial for efficient processes.[19] The interaction between bifunctional IL $[A336^+][P507^-]$ and acid was considered to be crucial in order to describe the distribution of rare earths in such systems according to detail $^{31}P\{^1H\}$NMR study.[215] As a result, regardless of how the TSIL has been synthesized, once it is exposed to acid containing solutions, the acid-base behavior of IL is undistinguishable from a mixture of two reagents $R_4N^+Cl^-$ + P507. It has been demonstrated that the interactions between ILs and radicals play an important role also in the radical reactions in ionic liquids.[216] A detailed NMR study on the possible interactions between a series of imidazolium based ILs ($[C_1C_nim^+][Tf_2N^-]$, $n = 4, 6, 8, 10$) and some commonly applied in solvent extraction and separation science of 4f and 5f-ions acidic chelating and neutral extractants was undergo.[217] Analytical techniques applied are ^1H, ^{13}C, ^{19}F and ^{31}P NMR spectra and NOESY experiments as well, Figs. 57 and 58.[217] Investigation of the types and strengths of the solvent-solute interactions is necessary for a knowledge-based features concerning chemical solubility, reactivity and selectivity as ILs have a strong influence on the solvent extraction mechanism of metallic species in comparison with traditional molecular solvents used. The goal of the published scientific research is to gain insight on the role of ILs as a perspective efficient “green” medium in the solvent extraction processes with more pro-ecological aspect. The experimental results show that no IL/E interactions occurred in chloroform solution independently on the length of the imidazolium alkyl chain and on the structure and acidity of the investigated organic ligand, whatever the relative proportions of IL and ligand in chloroform are studied.[217]

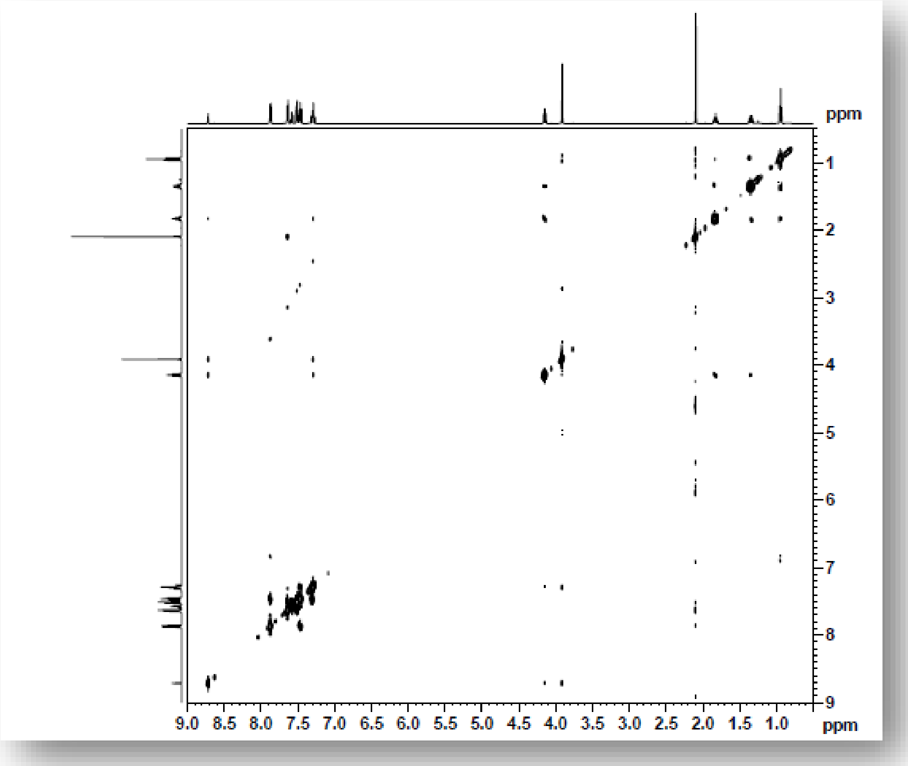


Figure 57. ^{1}H-^{1}H NMR NOESY spectrum of HP:$[C_1C_4im^+][Tf_2N^-]$, 1:1 (HP: 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one). Adapted from Ref. 217.

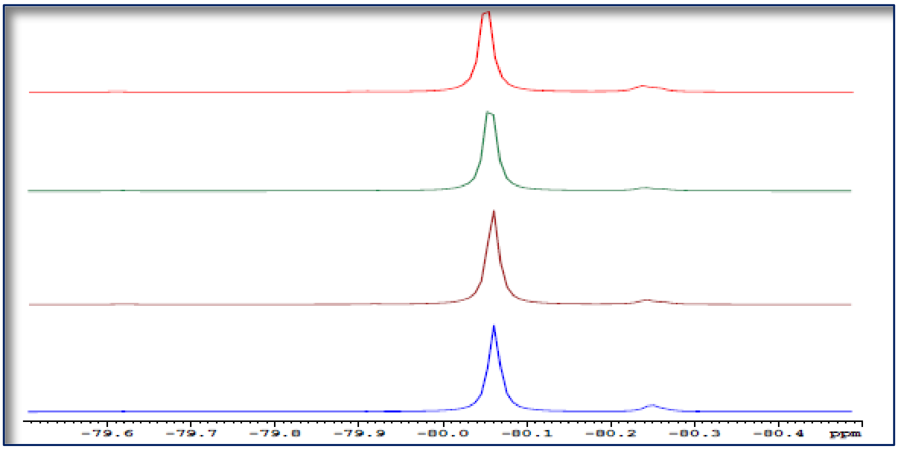


Figure 58. ^{19}F NMR spectra of $[C_1C_4im^+][Tf_2N^-]$ (blue); HP:$[C_1C_4im^+][Tf_2N^-]$, 1:4 (brown); HP:$[C_1C_4im^+][Tf_2N^-]$, 1:2 (green); HP:$[C_1C_4im^+][Tf_2N^-]$, 1:1 (red), (HP: 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one). Adapted from Ref. 217.

All these cited investigations in section 5 have evidenced the great complexity of aqueous-biphasic systems (reservoir of ions) composed of strong acidic aqueous phase put in contact with extracting organic phase (molecular ligand+IL). In particular, a comprehensive understanding of the difference in the IL's cation and anion solubilities would impose a minute analytical examination of phase composition at equilibrium for every case. Although, this is a rather difficult task, probably impossible.[115,116] One should also take into account the differences in IL cation/anion solubilities, depending on the nature of the aqueous phases in which they are prone to dissolve when pH is below 1 and the ligand concentration is above 1 M.

6. Solubility of ILs in the role of second extracting molecules in the aqueous phase when molecular diluents were employed

As a matter of fact, this concept ILs as additives or synergistic agents to traditional extraction systems is in full contradiction with the environmental perspective to discard classical molecular diluents indeed. Of course, this way to use ILs in the field of solvent extraction chemistry is not new because it resembles too much of a synergistic liquid-liquid extraction approach, in accord with what is known *a priori* in molecular diluents. One drawback to remember, a synergism using two extractant molecules simultaneously (organic ligands with different chemical nature), both of which can coordinate with a metal ion to form mixed ligand complexes, generally decreases the metal selectivity.[11, 12, 218] In principle, it could be envisioned that different reaction mechanism will occurring depending on the various possible combinations of compounds designed by authors and on the way ILs are used in the systems.

6.1. Classical ILs as a second compound for metal ions extraction processes in molecular diluents

An imidazolium based IL, $[C_1C_8im^+][Tf_2N^-]$ has been reported by prof. Goto's group to have an extractive selectivity for Pt(IV), because its performance towards Pd was extremely low, see Fig. 28, whereas $[P_{6,6,6,14}{}^+][[Cl^-]$ has a high ability to extract both metallic ions. Applying a mixture of $[C_1C_8im^+][Tf_2N^-]$–$[P_{6,6,6,14}{}^+][[Cl^-]$, the extraction efficiency was improved only for Pt(IV) entities. However, the separation factors between the two metals (Pt/Pd) increased to 1.38×10^2 from the value of 4.07×10^1 obtained for a single system.[219] The extraction percentage has increased as the concentration of ionic salt $[P_{6,6,6,14}^+][[Cl^-]$ increase up to addition of around 10 wt.%, when reaching a constant value 90-100 of E(%). In the case when $[P_{6,6,6,14}^+][Tf_2N^-]$ compound was combined with IL $[C_1C_8im^+][Tf_2N^-]$ no significant influence has been detected, therefore the authors conclusion was that the reaction is due to the anion exchange by release of Cl^- anions. The mechanism was considered to proceed *via* anion exchange of a Pt chloro-complex with IL cation, so the existence of Cl^- in the organic phase facilitated anion exchange model as Cl^- is more hydrophilic than $[Tf_2N^-]$ anion.

For the first time in synergistic solvent extraction an IL was estimated as a modifier in order to evaluate its influence on the supramolecular aggregation in acidic/neutral/$CHCl_3$ systems.[185] In fact, no evidence of enhancement can be revealed from the presented extraction measurements varying the concentration of $[C_1C_4im^+][Tf_2N^-]$ to $2x10^{-3}$ or $1x10^{-3}$ M. However, this is not a guarantee that the addition of IL to the synergistic mixture HBA (benzoylacetone)−CMPO serves as an ineffective modifier. The system with one neutral ligand CMPO/$[C_1C_4im^+][Tf_2N^-]$/$CHCl_3$ provides extraction at higher pH equilibrium values, as $\log D_{max}$ is at pH 7.02 ($\log D$=0.6) compared to pH 6.88 ($\log D$=0.42) for CMPO/$CHCl_3$ case. Analogous dependencies with clear peak formation were obtained by Rout et al. for Nd(III) ion extraction with two IL−based systems 0.01 M $[C_1C_6im^+][DEHP^-]/[C_1C_6im^+][Tf_2N^-]$ and 0.01 M $[C_1C_6pyr^+][DEHP^-]/[C_1C_6pyr^+][Tf_2N^-]$, where DEHP is the anion of bis(2-ethylhexyl)-phosphoric acid.[220]

Other points that should be accounted for are in fact the results published by Turanov and coworkers, which have shown that the efficiency of the extraction of rare earth (III) ions, U(VI), and Th(IV) from nitric acid solutions with CMPO solutions considerably increases in the presence of the ionic liquid 0.1 M $[C_1C_4im^+][Tf_2N^-]$ diluted in dichloroethane.[221] The extraction ability and selectivity of several synthesized CMPOs compounds varies in a wide range depending on substituents at the P and N atoms and on the chemical structure of the fragment linking to the coordinating groups. A considerable synergistic effect was observed in the presence of ILs ($[C_1C_4im^+][Tf_2N^-]$ or $[C_1C_4im^+][PF_6^-]$) in the organic phase containing N,N’-dimethyl-N,N’-diphenyl-3-oxapentanediamide (DMDPhOPDA) molecule diluted in 1,2-dichloroethane for the extraction of microquantities of 15 rare earth elements from aqueous media containing HNO_3 acid.[222] The addition of two compounds HPF_6 and $(CF_3SO_2)_2NH$ or their salts $LiPF_6$ or $LiTf_2N$ to the aqueous HNO_3 or HCl solutions leads to an enchancement of lanthanoids (III) extraction as consequence this effect was connected with the hydrophobic chemical nature of the IL anion. The established extracted species were found to be $EuX_2NO_3L_2$, while in the molecular organic phase $[EuX_3L_3]$ complex has been reported to exist. The extraction efficiency towards Ln(III) is higher for ILs with the $[Tf_2N^-]$ anion than for ILs with the $[PF_6^-]$ anion. Thus, a decrease in D_{Eu} with increasing IL cation hydrophobicity was found too. The data presented in Table 21 suggest that the extractability towards Eu(III) ions increases with DP (diluent parameter proposed by Schmidt[223]) values in the order: chloroform < dichloromethane < 1,2-dichloroethane < nitrobenzene. In spite of the fact that almost similar values of $\log D_{Eu}/[PF_6^-]^2$ calculated for both $[C_1C_4im^+][PF_6^-]$ and $LiPF_6$ studied cases when the same organic diluent is used, the authors have concluded that Eu(III) ion is probably extracted in the same form of metal complex in both investigated systems despite the lack of considerable experimental proofs.

Table 21. Extraction of Eu(III) ion (initial concentration 2×10^{-5} M) by 0.01 M DMDPhOPDA in molecular diluents from 3 M HNO_3 solution.[222]

diluent		0.01 M $LiPF_6$	in the aq phase	0.1 M	$[C_1C_4im^+][PF_6^-]$	in the org phase
	DP	$\log D_{Eu}$	$\log D_{Eu/[PF6-]2}$	$\log D_{Eu}$	$\log D_{[PF6-]}$	$\log D_{Eu/[PF6-]2}$
nitrobenzene	4.48	-0.12	3.88	0.45	0.63	3.89
1,2-dichloroethane	4.00	-0.52	3.48	0.80	0.07	3.47
dichloromethane	3.80	-0.68	3.32	0.75	-0.09	3.27
chloroform	2.87	-1.50	2.50	0.25	-0.59	2.45

A considerable synergistic effect was observed for alkaline earth metal ions (Ca(II), Sr(II), Ba(II)) in the presence of the same two ILs ($[C_1C_4im^+][Tf_2N^-]$ or $[C_1C_4im^+][PF_6^-]$) in the organic phase containing TODGA as a ligand (nitrobenzene, 1,2-dichloroethane, dichloromethane, chloroform and toluene).[224] In view of the obtained stoichiometric ratios, the extraction of **s**-ions from HNO_3 aqueous media into the organic phase containing TODGA−$[C_1C_4im^+][Tf_2N^-]$−molecular diluent could be described by the following equilibrium, when [IL] = < 0.02 M:

$$M^{2+}_{(aq)} + 2[C_1C_4im^+][Tf_2N^-]_{(o)} + 3L_{(o)} \rightleftharpoons$$

$$ML_3(Tf_2N^-)_{2(o)} + 2[C_1C_4im^+]_{(aq)} \qquad (38)$$

The presence of $M(Tf_2N^-)_2L_3$ species in the organic phase was found in the M(II) − $LiTf_2N$ − TODGA examined system as well. It was shown that the transition of the IL anion into the aqueous phase decreases with increasing initial IL concentration in the organic phase, which explains the decrease in the slope of log D_M *vs.* log [IL] curves, when [IL] > 0.02 M. Thus, the possible partition of IL anions between the two liquid phases has been the dominant factor governing the extractability of alkaline earth metal ions in the investigated neutral ligand−IL mixtures by Turanov et al.[224] Extraction of U(VI) (1×10^{-5} M) at 3 M HNO_3 solution with the same mixture of compounds TODGA (0.01-0.25 M)−$[C_1C_4im^+][Tf_2N^-]$(0.1 M) diluted in 1,2-dichloroethane has been investigated by the same research team too. The following equilibrium was established to occur:[225]

$$UO_2^{2+}{}_{(aq)} + 2[C_1C_4im^+][Tf_2N^-]_{(o)} + 2L_{(o)} \rightleftharpoons$$

$$(UO_2^{2+})(L)_2(Tf_2N^-)_{2(o)} + 2[C_1C_4im^+]_{(aq)} \qquad (39)$$

Beside the fact that the concentration of IL cation in the aqueous phase is found to be not at all equal to twice the metal ion concentration in the organic phase at equilibrium. In consequence, again the partition of IL $[Tf_2N^-]$ anions between the two phases is the major factor governing the extractability of metal ions in this case concerning the 5f-series. In addition, the hydration of TODGA molecules has been checked by authors measuring the co-extracted water amount into the pure organic molecular phase and in the presence of 0.1 M ligand as a function of the initial aqueous HNO_3 concentration. The detected small quantity of water ~0.125 M in the whole acidic 0.01-5 M HNO_3 studied range was not a surprise in view of the section 1, while in the presence of organic compound the increase is up to ~0.18 M $[H_2O]_{(o)}$, as well seen for the all acidity range. The monohydrated species of the type $L\cdot H_2O$, $HNO_3\cdot L\cdot H_2O$ and $(HNO_3)_2\cdot L\cdot H_2O$ were described to exist in the extracting phase (1,2-dichloroethane). Aqueous IL anion $[Tf_2N^-]$ transferred concentrations were determined by Turanov et al. using ICP-AES technique for sulfur content measurement. The $[Tf_2N^-]$ anion distribution was examined in two series, when 0.02 M $[C_1C_4im^+][Tf_2N^-]$ applied alone and in combination with 0.02 M TODGA dissolved in 1.2-dichloroethane. The two dependencies are influenced on the aqueous acidity (0.01-5 M HNO_3) in the following way, without TODGA the $D_{[Tf2N-]}$ decreases gradually from 12.6 to 2.5. At 0.02 M concentrations of TODGA−$[C_1C_4im^+][Tf_2N^-]$ in the organic phase, the distribution ratio of $[Tf_2N^-]$ anions increases from 15.8 (0.01 M HNO_3) with maximum value of D equal to 43.7 reached at 0.3 M HNO_3 and further increase of acidity leads to a decrease of $D_{[Tf2N-]}$ again to 15.8 for 5 M HNO_3.

6.2. Application of IL salt Aliquat 336 as a synergistic agent for solvent extraction of 4f-ions in molecular diluents

One ideal representative of ILs is the quaternary ammonium salt, having an industrial nickname Aliquat 336 (trialkyl(C_8-C_{10})methylammonium chloride, m.p.: - 20°C; viscosity: 1500 mPa·s). It is so intensively investigated ionic liquid compound in the academic fundamental research, with essential application for ion-pair complexation in mining industry in the role of extractant.[226] It is not a surprise that numerous scientific articles dealing with evaluation of its coordination ability towards f-elements have appeared also.[117, 227, 228] However, due to high viscosity, this IL is mostly used dissolved in organic molecular diluents. Additionally, the extraction mechanism is based on anion exchange and hence strongly dependents on the composition of the aqueous phase.[118, 229, 230] Synergistic effect in solvent extraction employing combination of two ligands for enhancing metal extraction efficiency has been investigated for more than six decades.[11, 12, 99] The term synergism is used to describe cases, where the extraction capability of a mixture of extractants (in most cases two) is greater than the sum of their individual extractive capabilities. The synergism can be explained by the formation of a mixed metal complex involving the two ligands, which is more hydrophobic than the complexes involving only one of these organic molecules. It was usually suggested when quoting stability constants produced by synergistic mixtures to refer to the diluent in use because so-called “inert” molecular diluents caused an extremely large variation in extraction system ($CHCl_3$<C_6H_6<CCl_4<hexane<cyclohexane). Numerous scientists demonstrated that the synergistic effect depends strongly on the choice of the diluent and it is often higher the lower its polarity. Formation of complex $Q^+[Eu(TTA)_4]^-$ (where TTA^- stands for the thenoyltrifluoroacetone anion) in molecular diluents (C_6H_6, CCl_4, C_6H_{12}) was firstly established in 1977 by Dukov et al. with combination of an acidic chelating compound, β-diketone, and quaternary ammonium salts, Aliquat 336.[231] Later, formation of anionic mixed complexes of the same type $Q^+[M^{n+}L_{n+1}]^-$ (L^- is the anion of the chelating extractant) was confirmed not only for lanthanoids extraction but for other metals too.[232-235] On the basis of the slope analysis data, the synergistic extraction of lanthanoid ions with mixtures of 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one (HL, HP *cf*. Fig. 42) and Aliquat 336 in chloride (QCl) or perchlorate ($QClO_4$) forms in C_6H_6 can be described by the following reaction:[236]

$$Ln^{3+}_{(aq)} + 4HL_{(o)} + Q^+A^-_{(o)} \rightleftharpoons Q^+[LnL_4^-]_{(o)} + 4H^+_{(aq)} + A^-_{(aq)} \qquad (40)$$

where A^- = anion of the IL, Cl^- or ClO_4^-.

The four anions of the chelating extractant (L^-) form the inner coordination sphere of the complex satisfying the coordination abilities of the lanthanoid ion (CN = 8), while the cation of the liquid salt Aliquat 336, Q^+ occupies the outer sphere of the formed anionic metal complex in the organic molecular phase. The variations of calculated equilibrium constants log $K_{L,Q}$ with the atomic number of the lanthanoids are given in Fig. 59.

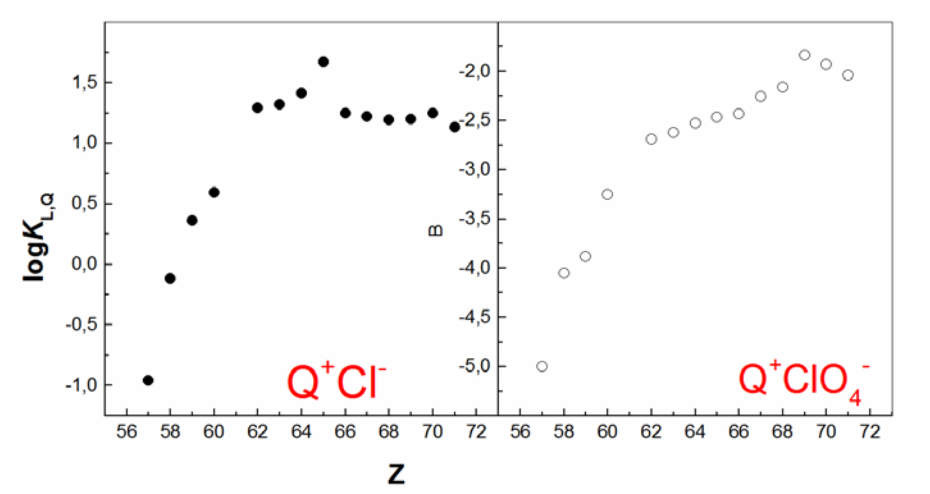


Figure 59. Variation of log$K_{L,Q}$ with atomic number (Z) for synergistic mixtures HP-QCl(ClO_4). Re-drawn from Ref. 236.

It is seen that the log $K_{L,Q}$ values change in almost the same manner with increasing atomic number for both HL–QCl and HL–$QClO_4$ studied combinations. Therefore, the change of the quaternary ammonium salt anion (Cl^- with ClO_4^-) produces only quantitative differences during lanthanoid solvent extraction. As a result, a great decrease of the log $K_{L,Q}$ values (3.5 to 4 orders) caused by the change of the anion of the salt was established. This considerable influence of the anion on the synergistic process can be explained by the fact that the bond in $QClO_4$ is stronger than that in QCl and as consequence the formation of the complexes $Q^+[LnL_4^-]$ is more difficult in the presence of $QClO_4$. The effect of molecular diluents on the metal separation with HTTA−QCl($QClO_4$) mixtures is presented in Fig. 60, showing that the log−log plots describing the role of organic media are in practice parallel to one another.[237] The calculated values of the equilibrium constant $K_{T,Q}$ increase in the order $CHCl_3 < C_6H_6 < CCl_4 < C_6H_{12}$ for both applied extractant combinations. The essential role of the IL anion on the anion exchange mechanism can be seen again with loss of corresponding IL salt anions to the aqueous phase as part of the reaction mechanism, Eq. 40: a decrease of $\log K_{T,Q}$ values more than 3 orders for all metals upon change of Cl^- with ClO_4^-.

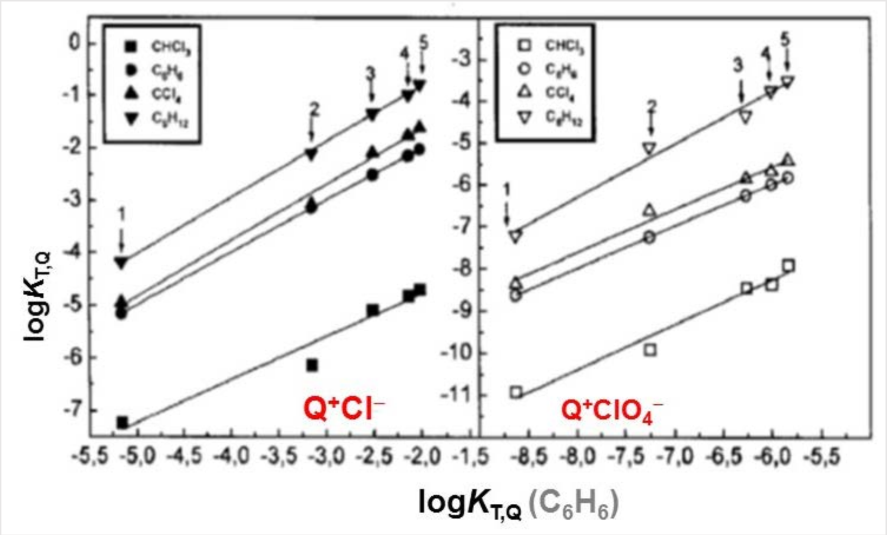


Figure 60. Comparison of $\log K_{T,Q}$ for $CHCl_3$, C_6H_6, CCl_4 and C_6H_{12} to $\log K_{T,Q}$ for C_6H_6 (1–La, 2–Nd, 3–Eu, 4–Ho and 5–Lu). Adapted from Ref. 237.

Taking into account the last consideration, it could be concluded that when metal ions are extracted with mixtures of chelating extractants and alkylammonium salts, two competitive reactions can occur in the organic phase, i.e., formation of mixed metal complexes (no interaction between the two extractants)[106,117] producing a synergism or interaction between the two extractants producing ion-pair formation as a parallel reaction. The possible interaction between the chelating extractant and the quaternary ammonium salt can be represented by the equation:[238, 106]

$$HL_{(o)} + QA_{(o)} \rightleftharpoons Q^{+}\cdot L^{-}_{(o)} + 4H^{+}_{(aq)} + A^{-}_{(aq)} \qquad (41)$$

It could be suggested that when synergism is observed, the bonds in the mixed complex have to be stronger that those in the formed ion-pair $Q^+\cdot L^-$. Then, according to the Le Chatelier's principle the equilibrium connected with the ion-pairs $Q^+\cdot L^-$ formation will be shifted to the left and the ion-pairs (as far as they are formed in the organic molecular phase) will be destroyed. In the opposite case, antagonism will occur.[236-238] The term antisynergism has been used for a destruction of synergism, but some authors have objected to it as a contradiction in terms and have suggested that antagonism be used instead. Such a great influence of the IL salt anion cannot be related with the suggestion of some authors that the synergist is not the ammonium salt but an ion-pair formed by the interaction of the two organic molecules presented in organic phase i.e. the synergistic agent is the ion pair $Q^+{\cdot}L^-$. If such launched entities were synergistic agents, then the synergistic extraction process should be influenced in small extent by the liquid salt anion because in such a case the ion-pair formation (irrespective to the salt anion) should be necessary condition for occurring the synergism as a phenomena. Since the ion-pairs should be spent during the extraction reaction, the equilibrium should be shifted to direction of the ion-pairs formation. So, the extraction process should not depend significantly on the salt anion (Cl^-, ClO_4^-, NO_3^-) as a consequence this suggestion can not be accepted.

In the presence of a ternary mixture of extractants (HP, HTTA and QCl) in molecular diluent C_6H_6 the formation of an anionic mixed complex $Q^+[LnP_3(TTA)]^-$ was established only for lighter lanthanoid(III) ions La−Sm, while an antagonistic effect was found for Eu(III), Gd(III) and the following heavier members of the 4f-series, Table 22.[239]

Table 22. Values of the distribution ratios for the extraction of lanthanoid(III) ions with HP, HTTA, binary mixtures HP−HTTA, HP−QCl, HTTA−QCl and a ternary mixture HP−HTTA−QCl at [HP]=2×10^{-2} M, [HTTA]=2×10^{-2} M, [QCl]=5×10^{-3} M and pH=2.20.[239]

Ln^{3+}	D	D_P	D_T	$D_{P,T}$	$D_{P,Q}$	$D_{T,Q}$	$D_{P,T,Q}$
La	0.37	$> 10^{-6}$	$> 10^{-9}$	$> 10^{-5}$	0.09	$> 10^{-5}$	0.28
Ce	1.10	$> 10^{-5}$	$> 10^{-8}$	$\sim 10^{-5}$	0.63	$> 10^{-4}$	0.47
Pr	2.90	$\sim 10^{-5}$	$\sim 10^{-8}$	$> 10^{-4}$	1.90	$\sim 10^{-4}$	1.00
Nd	4.81	$> 10^{-4}$	$> 10^{-7}$	$\sim 10^{-4}$	3.23	$> 10^{-3}$	1.58
Sm	19.10	$> 10^{-4}$	$> 10^{-6}$	$\sim 10^{-4}$	16.20	$\sim 10^{-3}$	2.90
Eu	14.45	$\sim 10^{-4}$	$> 10^{-6}$	$\sim 10^{-4}$	17.37	$\sim 10^{-3}$	−
Gd	11.57	$\sim 10^{-4}$	$> 10^{-6}$	$> 10^{-3}$	21.37	$> 10^{-2}$	−

Therefore, the synergistic solvent extraction with this ternary mixture involving two chelating agent and the IL, Aliquat 336 can be described as follows:

$$Ln^{3+}_{(aq)} + 3HP_{(o)} + HTTA_{(o)} + QCl_{(o)} \rightleftharpoons$$

$$Q^+[LnP_3(TTA)^-]_{(o)} + 4H^+_{(aq)} + Cl^-_{(aq)} \qquad (42)$$

where Ln^{3+} denotes La, Ce, Pr, Nd and Sm.

Still, some major issues should be taken into account when choosing the better organic media for liquid-liquid equilibrium as in dissolution processes all plausible multiple interactions between solutes and, solutes and "inert diluent" on the other hand may occur.[106, 217] Even thus, the search for more environmentally-benign diluents for extraction purposes is still in its infancy as an alternative choice of extremely high hydrophobic ILs is the only viable approach for now.

6.3.Certain comparison of cationic/anionic exchange in molecular media or ionic environment due to ILs solubility in the aqueous phase

A brief outline of the possible reaction mechanisms that may occurred during solvent extraction of target metal species from an aqueous phase to IL phase by favor of specific type of ligands neutral (L) or acidic (HL) is described in Fig. 61.[240-246] As a whole, the transfer of target metal ions from the aqueous phase to the IL phase with the help of special extracting moieties could be realized with respect to electroneutrality i.e. the net charge of two liquid phases cannot be change. The reaction schemes provided in Fig. 61 have demonstrated clearly that the aqueous solubility of IL cation and/or anion is the main favorable reason for ion exchange when IL media was in use as an organic phase.

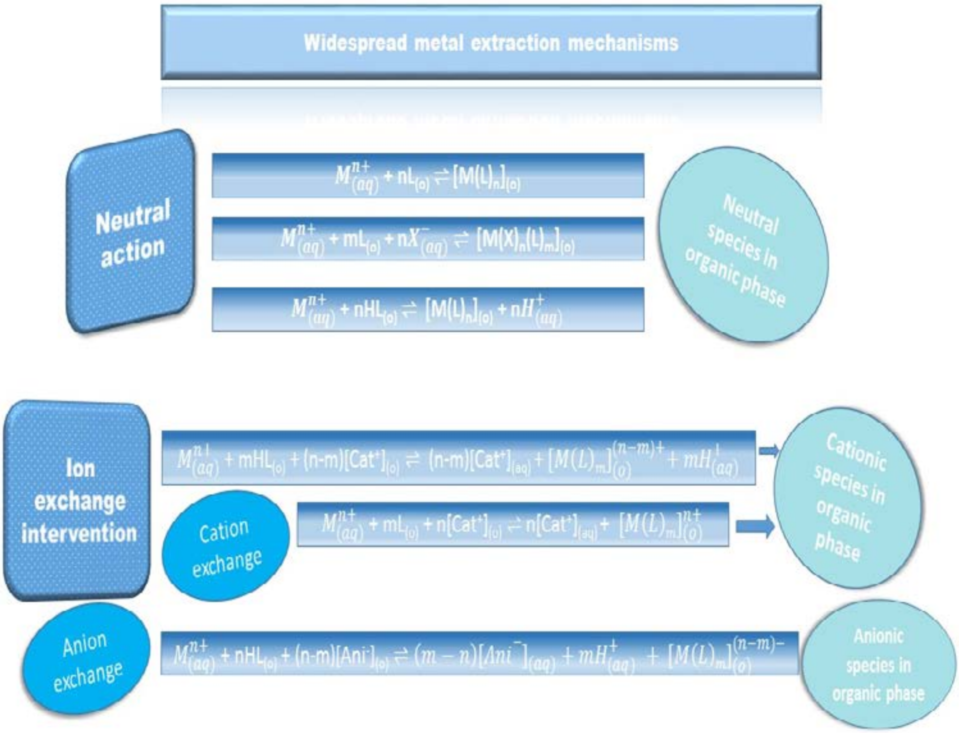


Figure 61. Possible reaction mechanisms in ionic liquid environment ($[Cat^+][Ani^-]$) during solvent metal extraction involving ligands (L or HL).

It was noted in previous sections (e.g. 2.2) that for a given IL anion, D_M falls because of the hydrophobicity of IL cation increase. The magnitude of such a decline generally diminishes when the mineral acid concentration in the aqueous phase increases regardless of the IL's anion nature.[81] The main reason could be the gradual shift from ion-exchange reaction involving cationic constituent of the IL:

$$\mathrm{Na^+\cdot DCH18C6^+_{(aq)} + [C_1C_{\mathbf{n}}im^+]_{(o)} \rightleftharpoons Na\cdot DCH18C6^+_{(o)} + [C_1C_{\mathbf{n}}im^+]_{(aq)}} \tag{43}$$

to an exchange of monovalent sodium ion for a hydronium ion extracted by the crown ether ligand (0.1 M):

$$\mathrm{Na^+_{(aq)} + H_3O\cdot DCH18C6^+_{(o)} \rightleftharpoons Na\cdot DCH18C6^+_{(o)} + H_3O^+_{(aq)}} \tag{44}$$

In particular if the acid HCl concentration exceding 3 M, D_{Na} rises when the IL $[C_1C_5im^+][PF_6^-]$ is employed. At the same time an analogous upturn in D_{Na} has not been observed for the corresponding $[Tf_2N^-]$ IL till 4-5 M HCl, and even *ca.* 8 M HCl concentration for an IL involving more hydrophobic $[BETI^-]$ anion. In contrast to changes observed in view of IL cation hydrophobicity (n=5, 8 and 10) for which the effect of mineral acid dependency of D_{Sr} is more than evident, the influence induced by transformation in IL anion hydrophobicity is less obvious.[81] The D_{Sr} decline observed upon chain length modifications on the imidazole cation from n=5 to n=10 has been consistent considering the greater perplexity encountered for the transfer of a more hydrophobic cation into the aqueous phase:

$$\mathrm{Sr(DCH18C6)^{2+}_{(aq)} + 2[C_1C_{\mathbf{n}}im^+]_{(o)} \rightleftharpoons Sr(DCH18C6)^{2+}_{(o)} + 2[C_1C_{\mathbf{n}}im^+]_{(aq)}} \tag{45}$$

At higher acidity of the aqueous phase (≥ 2 M), the partitioning of a neutral complex is also possible:

$$\mathrm{Sr^{2+}_{(aq)} + 2Cl^-_{(aq)} + DCH18C6_{(o)} \rightleftharpoons SrCl_2\cdot DCH18C6_{(o)}} \tag{46}$$

Notwithstanding, it should be emphasized herein a well-known fact, that lowering the IL hydrophobicity leads to unavoidable decrease of ligand solubility in the organic ionic phase as well, and as a consequence worsening of the extraction efficiency was a commonly distinguished process.

A neutral tridentate ligand incorporating two carbamoyl groups connected by an ether chain, abbreviated as TODGA, is one of the promising extractant for the recovery of actinoids and lanthanoids in the nuclear industry.[247] On the basis of the results of slope analysis in ILs ($[C_1C_n\text{im}^+][Tf_2N^-]$, $n = 2$, 4 and 6), the extraction equilibrium equation of the cation-exchange transfer is represented as follows ([TODGA]=1 mM, $[HNO_3]=0.01$ M, $[Ln^{3+}]_{in}=0.1$ mM):

$$Ln^{3+}_{(aq)} + 3TODGA_{(o)} + 3[C_1C_n\text{im}^+]_{(o)} \rightleftharpoons$$

$$Ln(TODGA)_3{}^{3+}_{(o)} + 3[C_1C_n\text{im}^+]_{(o)} \quad (47)$$

Based on the cation-exchange model, the exchange of 4f-ion Ln^{3+} for $[C_1C_n\text{im}^+]$ becomes difficult when the hydrophobicity of the ILs is high. Indeed, the solubility of ILs in ultrapure water was confirmed to be 47.42 mM ($[C_1C_2\text{im}^+][Tf_2N^-]$), 15.62 mM ($[C_1C_4\text{im}^+][Tf_2N^-]$), and 5.10 mM ($[C_1C_6\text{im}^+][Tf_2N^-]$), respectively.[247]

While, in the isooctane system incorporating molecular diluent, the ion-pair mode of reaction was accompanied by inorganic anions of mineral acid and is represented as follows ([TODGA]=100 mM, $[HNO_3]=1$ M, $[Ln^{3+}]_{in}=0.1$ mM):

$$Ln^{3+}_{(aq)} + (3\text{ or }4)TODGA_{(o)} + 3NO_3{}^-{}_{(aq)} \rightleftharpoons Ln(TODGA)_{(3\text{ or }4)}(NO_3{}^-)_{3(o)} \quad (48)$$

However, the molar ratios of species extracted into isooctane were 1:3 for La^{3+} or 1:4 for Eu^{3+} and Lu^{3+} i.e. depending on the atomic number of 4f-ion.[247]

Higher extraction efficiency of various extractants in ILs as compared to traditional molecular diluents is a common feature and different stoichiometries of the extracted metallic species are usually found by authors, but not always. [99, 100] As a general rule, replacing a molecular diluent by an IL leads to drastic enhancement effects on the distribution ratios (D_M), whatever the type of extracting agent (amine, phosphine oxide, organic acid, etc). Usually, the advantage of IL compared with classical diluents is expressed as a lower concentration of the extracting moiety to be dissolved in the IL in order to obtain an identical D value, with a concentration benefit in the range of a factor 4 to 30 or even 500.[99,247]

Solvent extraction of La^{3+} and Ba^{2+} (could surrogates for radioactive Ac^{3+} and Ra^{2+}) by TODGA from neutral aqueous solutions (H_2O) in twelve imidazolium-based ILs ($[C_1C_n\text{im}^+][Tf_2N^-]/[BETI^-]$, $n = 2$, 3, 4, 6, 8 and 10) was investigated by Bell and co-researchers.[246] The use of $[C_1C_n\text{im}^+][BETI^-]$ ILs for organic diluents generally have resulted in larger

D_{La} and smaller D_{Ba} values than the implementation of $[C_1C_n\text{im}^+][Tf_2N^-]$ ILs. The $[BETI^-]$ anion gaves as much as an order of magnitude higher separation factors than the $[Tf_2N^-]$ anion in the short chain (n = 2, 3 till 4) ILs. The maximum monovalent/divalent cation extraction selectivity occurs at $[C_1C_3\text{im}^+][BETI^-]$ medium: SF for La^{3+}/Ba^{2+} pair is equal to 3000 in comparison to *ca.* 53 calculated for $[C_1C_3\text{im}^+][Tf_2N^-]$ liquid phase.[246] It has been clearly demonstrated that a cation exchange mechanism is dominant in the more hydrophilic ILs. Thus, shorter alkyl chain lengths give greater extraction efficiencies, and at or above n = 6, the mode of reaction might switch to formation of neutral metal complexes, much like in molecular organic diluents.[246]

The solvent extraction of UO_2^{2+} and Th^{4+} from a nitric acid solution into an imidazolium-type ILs $[C_1C_n\text{im}^+][PF_6^-]$, n = 6 or 8 was carried out using TODGA as an extractant.[248] It was found that the extraction efficiency of metallic species is higher in comparison with that done in n-dodecane diluent, being standard observation IL *vs.* molecular diluents. Transfer of both ions is assumed to proceed predominantly through the neutral solvation mechanism: The UO_2^{2+} ion forms a 1:2 complex with TODGA in ILs at lower aqueous acidity and a 1:1 complex in ILs and in n-dodecane organic phase at higher acidity. The more hydrophobic IL favors the partition of a neutral complex. While, the Th^{4+} ion forms a 1:2 complex with TODGA in $[C_1C_6\text{im}^+][PF_6^-]$ organic media or a 1:1 complex in $[C_1C_8\text{im}^+][PF_6^-]$ at lower aqueous acidity. At the same time, a 1:1 complex was established in both ILs, and molecular diluent n-dodecane at higher acidity. The extraction processes of UO_2^{2+} can be illustrated with the following two reactions ($[M^{n+}]_{in}=1\times10^{-3}$ M, [TODGA]=0.04 M, $[HNO_3]$=3 M or $[HNO_3]$=0.01 M):

$$UO^{2+}_{2(aq)} + TODGA_{(o)} + 2NO_3^-{}_{(aq)} \rightleftharpoons UO_2\cdot TODGA(NO_3^-)_{2(o)} \tag{49}$$

$$UO^{2+}_{2(aq)} + 2\ TODGA_{(o)} + 2\ [C_1C_n\text{im}^+]_{(o)} \rightleftharpoons$$
$$UO_2\cdot(TODGA)_2{}^{2+}{}_{(o)} + 2\ [C_1C_n\text{im}^+]_{(aq)} \tag{50}$$

Mechanism of Pu(IV) extraction from nitric acid medium using TBP as a ligand (1.1 M) was found to be cation exchange at lower acidity which changes to formation of neutral complexes at higher aqueous acidity greater than 1 M concentration of the mineral acid HNO_3 for $[C_1C_n\text{im}^+][Tf_2N^-]$, n = 4, 6, 8:[241]

$$Pu(TBP)_2{}^{4+}{}_{(o)} + 4[C_1C_n\text{im}^+][Tf_2N^-]_{(o)} \rightleftharpoons$$
$$Pu(TBP)_2\cdot(Tf_2N^-)_{4(o)} + [C_1C_n\text{im}^+]_{(aq)} \tag{51}$$

The $D_{P(IV)}$ value decreases with increasing alkyl chain length as a result of a decrese in IL solubility into the aqueous phase disfavoring the cation mode of exchange up to 1 M HNO_3. However, it has been repoted that there are two TBP molecules involved in the neutral extracted complexes at 3 M HNO_3 acidity irrespective of the diluent used IL or n-dodecane:

$$Pu^{4+}_{(aq)} + 4NO_3^{-}{}_{(aq)} + nTBP_{(o)} \rightleftharpoons Pu(NO_3)_4{\cdot}TBP_{(o)},$$

$$n = 2 \text{ or } 1 \text{ depending on the feed acidity} \qquad (52)$$

Because it was found that at 7.3 M HNO_3 the plot of $D_{Pu(IV)}$ *vs*. [TBP] concentration gives a slope dependency of 2 for the molecular diluent n-dodecane at the same time it is close to 1 in $[C_1C_4im^+][Tf_2N^-]$ case.[241] Unfortunately, the poor solubility of the attractive calixarene ligands in ILs is a serious barrier for their application. In almost the majority of cases, nitrophenyl alkyl ethers were used as molecular diluents for the metal ion extraction tests, because they are able to dissolve calixarene molecules at relatively high concentrations.[94] Needless to say, it would be interesting to determine the stoichiometry of the formed 4f-complexes and to validate their probable coordination number when calix[4]arene ligand was applied. In line with several previously published results for different lanthanoid extraction systems in ILs, the extraction stoichiometry proceeds probably through cationic exchange with this specially synthesized reagent (containing four P=O ligating groups on the lower rim) and can be expressed as:

$$Ln^{3+}_{(aq)} + \mathbf{2}\ C4_{(o)} + 3[C_1C_{\mathbf{n}}im^+]_{(o)} \rightleftharpoons [Ln(C4)_{\mathbf{2}}]^{3+}_{(o)} + 3[C_1C_{\mathbf{n}}im^+]_{(aq)} \qquad (53)$$

Increasing the length of the alkyl chain in IL's cation leads to a decrease of extracting ability of the inspected neutral ligand towards Eu(III) ion: n=4 > n=6 > n=8 > n=10, Fig. 62. The liquid-liquid extraction of trivalent rare earth ions by neutral calix[n]arenes usually proceeds *via* formation of a complex ion pair of stoichiometry 1:1, metal:ligand in molecular diluents: ($CHCl_3$, 1,2-dichloroethane, nitrobenzene).[99]

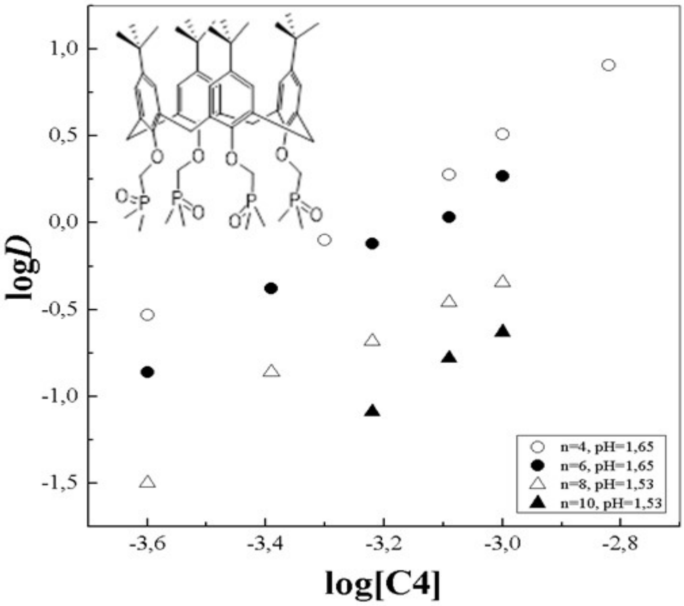


Figure 62. Log*D* of Eu(III) *vs*. log[C4]. Adapted from Ref. 94.

Selection of an appropriate extractant agent often determines the success of a chemical process.[157] In particular, a cyclic ligand such as calixarenes, which consists of phenol rings connected by methylene bridges, has attracted much attention of separation chemists because the cyclic molecule can recognize the size of metal ions with its cavity and consequently, this unique property often leads to an extremely high selectivity for a target metal ion.[11,94,96,99,100] The pyridinocalix[4]arene ($^tBu[4]CH_2Py$) was found to form a stable 1:1 complex with silver ions applying both slope analysis and Job's method.[96] The solvent extraction equilibriums in IL and in chloroform were determined to be as follows:

$$Ag^+_{(aq)} + {}^tBu[4]CH_2Py_{(o)} + NO_3^-{}_{(aq)} \rightleftharpoons Ag{\cdot}{}^tBu[4]CH_2Py{\cdot}NO_{3(o)} \text{ in } CHCl_3 \tag{54}$$

$$Ag^+_{(aq)} + {}^tBu[4]CH_2Py_{(o)} + [C_1C_8im^+]_{(o)} \rightleftharpoons Ag{\cdot}{}^tBu[4]CH_2Py^+_{(o)} + [C_1C_8im^+]_{(aq)} \text{ in } [C_1C_8im^+][PF_6^-] \tag{55}$$

In comparison to the molecular diluent system, a 0.1 M HNO_3 acid solution ensures the recovery of 90% of the Ag^+ extracted into the ionic $[C_1C_8im^+][PF_6^-]$ phase, whereas in chloroform, only 10% of the Ag^+ could be recovered under the same conditions. A 5 M HNO_3 solution has required to completely recovering Ag^+ from the molecular organic phase according to the published results by Shimojo and Goto. In addition, it was found that Ag^+ recovery could be achieved using a stripping solution containing 1 M concentration of the thiourea compound. A recycling test for the ILs phase ($[C_1C_n\mathrm{im}^+][PF_6^-]$, $n = 4, 6, 8$) was also carried out in this study, following the same procedure. A 0.5 M HNO_3 solution was employed as the receiving phase, and the ionic phase was then recycled. Even though five cycles of forward and back extraction were carried out, the $^t\mathrm{Bu}[4]\mathrm{CH_2Py}$−ILs extraction system maintained its high extraction ability (the average degree of extraction was approximately 99.5%). Thus, the proposed solvent extraction system including IL diluent was found to be very reproducible.[96]

Chelate ligands acting as weak organic acid reagents, especially β-diketones, were widely used essentially in the role of efficient extractants in order to study the metal behavior at solvent extraction equilibrium.[99,100,188,190] In this way, the centered metal ion could be coordinated with two carbonyl groups more strongly than a monodentate neutral ligand. When considering the mechanism of lanthanoid(III) ions extraction towards IL or molecular liquid phases by use of β-diketone chelating compounds as an example, 2-thenoytrifluoroacetone, two very different situations can happen obviously. In traditional organic molecular diluents, the extracted metallic species formed in the organic molecular phase are always neutral:[188]

$$\mathrm{Ln^{3+}}_{(aq)} + 3\ \mathrm{HTTA}_{(o)} \rightleftharpoons \mathrm{Ln(TTA)_3(H_2O)}_{n(o)} + 3\mathrm{H^+}_{(aq)} \quad n = 2, 3 \tag{56}$$

$$\mathrm{Ln^{3+}}_{(aq)} + 4\ \mathrm{HTTA}_{(o)} \rightleftharpoons \mathrm{Ln(TTA)_3(HTTA)}_{(o)} + 3\mathrm{H^+}_{(aq)} \tag{57}$$

Coordination numbers of mononuclear β-dicarbonyl lanthanoid complexes are genrally high, varying from 6 to 12, with 8 or 9 being rather common.[99] Three main types of lanthanoid complexes in organic solution can be considered:[99, 100, 249] i) tris complexes containing three chelating ligands (HL) for an ion LnL_3. However, the coordination sphere of the trivalent ion is unsaturated in this six-coordinate chelate. So, the lanthanoid ion can expand its coordination sphere by adduct formation, depending on the experimental protocol, with water for example $LnL_3{\cdot}(H_2O)_x$, x = 2 or 3; ii) formation of self-adduct species $LnL_3{\cdot}HL$ including one unprotonated acidic ligand; iii) it is also possible to arrange four bidentate ligands around a single metal ion; in this way, tetrakis anionic complexes with general formula $[Ln^{3+}L_4]^-$ are formed and the electroneutrality is achieved by a counter cation.

While in ILs, the established extracted metal species are in most cases predominantly charged, owing to the ionic nature of the applied diluent, of course, leading to ion exchange mechanism, that is not possible reaction for molecular organic phases, Eqs. 56 or 57. Only neutral metal complexes can be formed that can enter into the molecular hydrophobic liquid phase. In particular, the extraction of anionic metal complexes by HTTA molecule has been shown to proceed to the greatest extent by the exchange of the IL [Tf_2N^-] anions into the aqueous phase:

$$Ln^{3+}_{(aq)} + 4\ HTTA_{(o)} + [C_1C_4im^+][Tf_2N^-]_{(o)} \rightleftharpoons$$
$$[C_1C_4im^+][Ln(TTA)_4^-]_{(o)} + 4H^+_{(aq)} + [Tf_2N^-]_{(aq)} \qquad (58)$$

However, other reaction mechanisms are also possible, such as cationic/anionic exchange or extraction of neutral species, in a way rather similar to that occurring in molecular diluents (Eqs. 56 and 57):[188, 250, 251]

i) anionic species, n > Z^+ :

$$M^{Z+}_{(aq)} + n\ HTTA_{(o)} + (n\text{-}z)[Tf_2N^-]_{(o)} \rightleftharpoons$$
$$M^{Z+}(TTA)_n{}^{(n-z)-}{}_{(o)} + nH^+_{(aq)} + (n\text{-}z)[Tf_2N^-]_{(aq)} \qquad (59)$$

ii) cationic species, n < Z^+:

$$M^{Z+}_{(aq)} + n\ HTTA_{(o)} + (z\text{-}n)[C_1C_nim^+]_{(o)} \rightleftharpoons$$
$$M^{Z+}(TTA)_n{}^{(z-n)+}{}_{(o)} + nH^+_{(aq)} + (z\text{-}n)[C_1C_nim^+]_{(aq)} \qquad (60)$$

In principle, the anionic exchange mechanism could be assessed quantitatively by following the amount of [Tf_2N^-] anions transferred to the aqueous phase during the extraction process. But such a determination is rather laborious.[101,129] Under other conditions as seen in section 3, even in the absence of metallic species i.e. aqueous-biphasic systems, some [Tf_2N^-] anions could be transferred to the aqueous phase in amounts that are in the range of 2-70 mM depending on IL nature and aqueous phase composition (Cl^-, NO_3^-, ClO_4^-). While the transfer amount of [Tf_2N^-] anion is due exactly to the extraction mechanism itself and is in the order of the metallic ion concentration in agreement with Eqs. 58 and 59, which, most of the time, is very low as compared to the above- mentioned mM range.

The extraction behavior of Am(III) ion from nitric acid medium was studied in a solution of benzoylpyrazolone ligand (HP, see fig. 42) in [$C_1C_4pyr^+$][Tf_2N^-] or in conventional diluent n-dodecane under similar experimental condition applied.[245] The slope analysis of the extraction data was carried out to evaluate the mechanistic aspects of the chemical process. Different reaction modes was revealing in the two type of organic liquid phases. The most plausible equilibrium can be given by the following expression:[245]

$$Am^{3+}_{(aq)} + 3HP_{(o)} + x[C_1C_4pyr^+][Tf_2N^-]_{(o)} \rightleftharpoons$$
$$Am(P)_{3-x}\cdot(HP)_x\cdot(Tf_2N^-)_{x(o)} + (3\text{-}x)H^+_{(aq)} + x[C_1C_4pyr^+]_{(aq)} \quad (61)$$

Since NO_3^- anion does not participate in it, it is quite likely that IL anion $[Tf_2N^-]$ could compensate the charge of Am(III) ion for maintaining the neutrality as a whole. Another good example was proposed by Kumar et al., who have established the complex $[UO_2(TTA)_2^{2+}(Tf_2N^-)_2]$ in the organic oil phase.[103]

A neutral complex extraction mechanism of $Th(TTA)_4$ was reported in all four ILs, $[C_1C_n im^+][Tf_2N^-]$, $n = 2, 4, 6, 8$ without direct participation of ILs cation or anion in the chemical process.[194] The solvent extraction behavior of two trivalent lanthanoids Nd^{3+} and Dy^{3+} was investigated with the organic phase benzoyltrifluoroacetone(Hbfa)/triethyl-pentyl bis(trifluoromethyl-sylfonyl)amide $([P_{2225}^+][TFSA^-])$ in 3:1 volume ratio (a/o).[252] The different pH values of aqueous phase were adjusted by adding HTFSA or HNO_3 acid, or NaOH solutions. The reaction mechanism in this system could be described in typical chelate extraction mode as follows:

$$Ln^{3+}_{(aq)} + 3\ Hbfa_{(o)} \rightleftharpoons Ln(bfa)_{3(o)} + 3H^+_{(aq)} \quad (62)$$

To such a degree, the anion component of the aqueous acid media ($[TFSA^-]$ or $[NO_3^-]$) did not participate in the equilibrium equation. Furthermore, the optimized structure of these two formed metal complexes $Nd(bfa)_3(H_2O)_3$ and $Dy(bfa)_3(H_2O)_2$ were evaluated additionally by the density functional theory (DFT) calculation.[252] The two ILs $[C_1C_6im^+][Tf_2N^-]$ and $[C_1C_6pyr^+][Tf_2N^-]$ act solely as diluents during solvent extraction of Nd^{3+} ions from aqueous HNO_3 medium by bis(2-ethylhexyl)-phosphoric acid (DEHPA) and are not involved in the reaction equilibrium: formation of the chelate NdL_3 was also established.[245]

IL $[C_1C_4im^+][NfO^-]$ was used as an organic media for europium and neodymium extraction from 1 $mol\cdot dm^{-3}$ $NaClO_4/HClO_4$ aqueous solutions when metal:HTTA stoichiometries of 1:0 ($Eu(H_2O)_9^{3+}$), 1:2 and 1:3 were detected with different numbers of inner sphere water molecules (2 or 0) depending on the ligand concentration and pH.[253] Additional complexation of these three IL phase species by either ClO_4^- or NfO^- is required to complete the coordination spheres and ensuring the neutrality. Radiotracer distribution, absorption spectroscopy, time-resolved laser-induced fluorescence spectroscopy, and X-ray absorption fine structure measurements point to the solvent extraction of multiple lanthanoid species i.e. all these analyses detect the presence of three distinct metallic species at equilibrium in the $[C_1C_4im^+][NfO^-]$ liquid phase. Fully dehydrated

$[Ln(TTA)_4]^-$ species appear unable to be formed in the presence of 9-10 moles/L of water, Eq. 58. The underlying reason by Jensen et al. is the greatly increased solubility of water in $[C_1C_4im^+][NfO^-]$, the $[NfO^-]$ IL anion is significantly more hydrophilic than the $[Tf_2N^-]$ anion. The water content of 0.5 M HTTA dissolved into $[C_1C_4im^+][NfO^-]$ in equilibrium with water was measured to be 14.2±0.1wt.% (9.4 moles H_2O/L). While, the water in neat $[C_1C_4im^+][NfO^-]$ without the precense of ligand molecules was found to be 20.7±0.1wt.% (10.9 moles H_2O/L).[253] Hatakeyama and co-workers have established the metal species $Ln(ba)_2^+$ formed at lower $[ba^-]$ concentration in the IL phase and $Ln(ba)_3$ chelate at higher available amount of $[ba^-]$, when the β-diketone benzoylacetone was applied for trivalent lanthanoid extraction (La^{3+}, Nd^{3+}, Eu^{3+}, Dy^{3+} and Lu^{3+}) in $[C_1C_4im^+][Tf_2N^-]$ medium.[209] The corresponding extraction constant for each Ln(III) ion was determined indicating that $Ln(ba)_3$ chelates have higher affinities for IL. The last one is more polar than benzene (e.g. ε_r=14.0 for $[C_1C_4im^+][Tf_2N^-]$ and 2.27 for C_6H_6) in spite of the lower $K_{D,HA}$ value: $K_{D,HA}(IL) < K_{D,HA}(C_6H_6)$.[209] However, the presence of multiple extraction equilibria that vary when the extraction parameters were changed over a wide range (ex. chemical composition of the biphasic system, acid concentration in the aqueous phase, ionic strength, ligand concentration in the organic phase, solubility of ionic liquid ions into the aqueous phase) are not commonly adopted extraction model in ionic medium.[104,188]

The mechanism of the hydrophobic anion effect has been clarified by Naganawa et al.[201], that clearly have shown the definitive difference in the hydration between the picrate ion pairs and the NO_3^- ones. The Ln(III) ions seem to be dehydrated to a great extent by the influence of the hydrophobic pic^- anions. The dehydration of the metals can cause the great enhancement of the extractability. It is concluded that extraction of only a single ion pair, $[LnL_3]^{3+}(pic)_3^-$, governs the cooperative effect of CMPO ligand (0.1 M) and picric acid (0.01 M) on Ln(III) ions extraction from aqueous nitric acid solutions (0.1 M) into th molecular diluent benzene. Accordingly, the water hydrating Ln(III) ions seems to disturb the coordination of the neutral CMPO ligand, which occurs in the inner-sphere of the metals. Furthermore, the metal dehydration could produce a better separation for various Ln(III) ion pairs. Additionally, as the CMPO coordination can be performed more effectively with much less water molecules that was hydrating the 4f-ions. The reported magnitude of $K_{ex(\text{L-pic})}$ is indeed $3{-}11\times10^{11}$ times larger than that of $K_{\text{ex,(L-NO3)}}$. However, the presence of pic^- anions itself does not seem to work to destroy the metal hydration shell too aggressively, because this anion is not capable of coordinating with metal ions and so cannot push the hydrating water molecules out of their shell. Consequently, CMPO molecules could substituted the water hydrating molecules much more easily in the presence of highly hydrophobic, weak in electrostatic interaction due to its bulkiness pic^- ions than in the case of the hydrophilic NO_3^- anions, which can shield additionally the metal hydration from the CMPO ligand coordination.

The investigations of lanthanoid ions solvent extraction with chelating extractants HTTA or HPBI into $[C_1C_4im^+][Tf_2N^-]$ media have shown a great similarity with their extraction with mixture of HTTA combined with quaternary ammonium salts (Aliquat 336) in conventional organic diluents, Eq. 40.[91,93,101] It has been reported that in the presence of IL cations $[C_1C_4im^+]$ and HTTA ligand concentration higher than 1×10^{-6} M anionic metal complexes of the type $[C_1C_4im^+][Ln(TTA)_4]^-$ are extracted, Eq. 58. Therefore, the extraction of $[Ln(TTA)_4]^-$ or $[Ln(PBI)_4]^-$ metal complexes is somehow comparable to that observed into conventional molecular diluents.[117,118,207] These results suggest that using a more hydrophobic quaternary ammonium cation or methylimidazolium cation with longer alkyl groups could increase the possibility of observing the anion exchange mechanism for a given IL. [91,93,101]

Hyrayama et al. have studied the extraction of several divalent transition metals with β-diketones containing trifluoromethyl group (benzoyltrifluoroacetone, 2-naphtoyltrifluoroacetone, trifluoroacetylacetone) into $[C_1C_4im^+][Tf_2N^-]$ and $[C_1C_4im^+][PF_6^-]$ ILs environment.[102,250,254] Formation of anionic complexes $[M^{II}(\beta\text{-diketone})_3]^-$ has been established again for Zn(II), Cd(II), Pb(II), Mn(II) and Co(II). The change of the anion of the IL from $[PF_6^-]$ to more hydrophobic one $[Tf_2N^-]$ resulted in changing the extracted species for Ni(II) ion from hydrated neutral chelate $Ni(TTA)_2\cdot nH_2O$ (n = 1 or 2) to a hydrophobic anionic complex $[Ni(TTA)_3]^-$. Therefore, the selection of a suitable IL seems to be an important factor for enhancement of the extraction selectivity as well. The extraction selectivity order was found to be $Cu^{2+}>>Ni^{2+}>Co^{2+}>Zn^{2+}>Mn^{2+}>Cd^{2+}$ for all $[C_1C_nim^+][Tf_2N^-]$ studied ILs. As far as 43 years ago Noriki has concluded that chelates like $M(TTA)_2\cdot2H_2O$ for Ni(II) and Co(II) ions are hardly extracted directly into inactive organic molecular diluents because of the water molecules involved.[255]

On the other hand, the $[Eu(tta)_3(H_2O)_3]$ complex was found to be almost completely dehydrated in the series of $[C_1C_nim^+][Tf_2N^-]$ ILs saturated with water. Whereas, hydrated chelate complexes were usually established in molecular diluents.[106] The special role of the $[Tf_2N^-]$ anions in the IL−water distribution of Eu(tta)−chelates was elucidated in the paper of

Okamura et al.[187] Assuming that three water molecules of $[Eu(tta)_3(H_2O)_3]$ complex were released by the coordination of **m** entities of $[Tf_2N^-]$ in the mixed organic liquid medium (1,2-dichloroethane containing 1.0–3.0 vol.% $[C_1C_4im^+][Tf_2N^-]$). The following equation was derived, Fig. 63:

$$[Eu(tta)_3(H_2O)_3]_{(mix)} + m[Tf_2N^-]_{(mix)} \rightleftharpoons [Eu(tta)_3(Tf_2N^-)_m]_{(mix)} + 3H_2O_{(mix)} \quad (63)$$

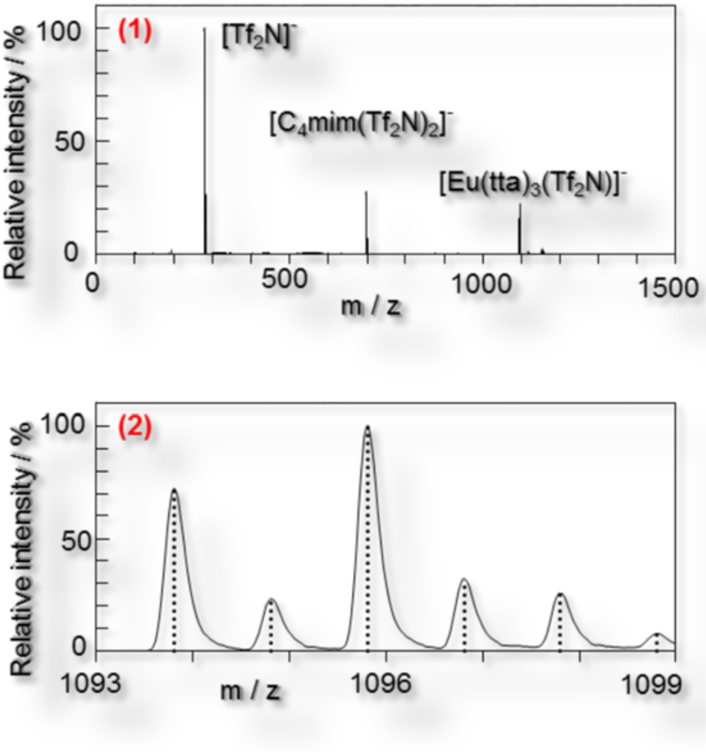


Figure 63. Negative ion electrospray ionization mass spectrum of 3.0×10^{-4} M $[Eu(tta)_3(H_2O)_3]$ complex dissolved in 1,2-dichloroethane containing 3.4×10^{-4} M $[C_1C_4im^+][Tf_2N^-]$ (1) and the high resolution mass spectrum (solid line) and the calculated mass spectrum (dotted line) for $[Eu(tta)_3(Tf_2N^-)]$ (2). Re-drawn from 187.

The dissociated $[Tf_2N^-]$ anions in solutions effectively coordinates to $[Eu(tta)_3(H_2O)_3]$ and displaces the coordinated water molecules. The distribution ratio of Eu(III) ion as a function of the $[TTA^-]$ concentration in the aqueous phase (pH 2.5 –5.4) at different concentration of HTTA

1×10^{-3} to 1.6×10^{-2} mol/dm^3 in $[C_1C_n\text{im}^+][Tf_2N^-]$, n=4, 6 and 8 has shown that the 4f-ion was extracted as neutral and anionic chelates at lower and higher $[TTA^-]$ concentration, respectively. The D values in the pH region of 3-5 were found to decrease in the following order $n=8 \approx n=6 >> n=4$. Thus, the mutual solubility with water is an important factor.[187] HTTA molecule shows better extraction ability towards Eu^{3+} ion in the $[C_1C_{10}\text{im}^+][Tf_2N^-]$ system.[188] The two equilibrium constants for the distribution of the chelate compound $Eu(tta)_3$ and $[Eu(tta)_4^-]$ anion complex depend actually on the hydrophobicities of ILs in use. If the former attributes only to the distribution constant of tris-chelate, the latter was so affected by the solubility product of the IL in the aqueous phase. The distribution of the anionic $[Eu(tta)_4^-]$ chelate increased with a decrease in $[Tf_2N^-]$ concentration in the aqueous phase ($K_{sp} = [C_1C_n\text{im}^+]\times[Tf_2N^-]$) in accord with the equilibrium shift (Le Chatelier's principle):

$$Eu^{3+}_{(aq)} + 4\,HTTA_{(o)} + [Tf_2N^-]_{(o)} \rightleftharpoons [Eu(TTA)_4^-]_{(o)} + 4H^+_{(aq)} + [Tf_2N^-]_{(aq)} \qquad (64)$$

The complementary physicochemical methods have been used by Jensen and co-workers such as equilibrium thermodynamics, optical absorption and luminescence spectroscopies, high-energy X-ray scattering, EXAFS and molecular dynamics simulations to support the formation of anionic $[Nd(TTA)_4^-]$ or $[Eu(TTA)_4^-]$ complexes without coordinated water molecules to the metal center into $[C_1C_4\text{im}^+][Tf_2N^-]$ organic medium.[101] So, the significant amount of water present in the IL extracting phase does not favor the coordination of water molecules indeed.[256] The reason for the formation of differently charged complexes under different conditions is due to the considerable ion exchange in conjunction with the strong relationship among coordination chemistry and metal partitioning, which is remarkably common situation produced in ionic liquid phase in comparison with the properties of classical molecular diluents.[27, 104, 257-262] Extended X-ray absorption fine structure (EXAFS) measurement was used to study the Sr coordination environment with a neutral complexing agent (DCH18C6) in $[C_1C_5\text{im}^+][Tf_2N^-]$ ($Sr(DCH18C6)(H_2O)_2^{2+}$ and in a conventional organic diluent 1-octanol, $Sr(NO_3)_2(DCH18C6)$.[263] Consequently, the insignificant coextraction of counterions (9% $[NO_3^-]_{(o)}$, 0% $[Cl^-]_{(o)}$ and 16% $[SO_4^{2-}]_{(o)}$, with an uncertainty ±7%, measurement by ion chromatography) clearly indicates that the phase-transfer reaction proceeds mainly through the cation-exchange mechanism described by Eq. 45, with its positive charge being balanced by two noncoordinated $[Tf_2N^-]$ anions. The behavior of different solutes in biphasic systems with ILs varies and seems to be very complex. Combining analytical measurements of the H_2O, Na^+, H^+, ClO_4^-, $[C_1C_4im^+]$, $[Tf_2N^-]$, HTTA and $[TTA^-]$ concentrations (moles/L) with the requirements of charge neutrality within each phase (a/o) and the mass balance in the system, the equilibrium concentration of each of the solutes was determined in the absence of lanthanoid cation (Eu^{3+} or Nd^{3+}): pH=2, 1 M $NaClO_4$, 0.5 M HTTA in $[C_1C_4im^+][Tf_2N^-]$.[264] Combining all obtained information Jensen and co-workers have concluded that the two lanthanoid partitioning equilibrium operation in IL media can be identified with Eq. 56 for $[TTA^-] < 1\times10^{-6}$ M and with Eq. 58 when $[TTA^-] > 1\times10^{-6}$ M.

Some of the reported works attempt to address some of the questions that would arise during practical application of the hydrophobic ILs as synergistic additives in a separation process rather than bulk “inert” diluents.[185,224,236] The new proof-of-principle for the separation of metals (Co and Ni) by liquid-liquid extraction implementing two mutually immiscible ILs was administered by Binnemans’s group for the first time.[46] Relatively costly but so elegant, advancing and knowledgeable way of water replacement with 1-ethyl-3-methylimidazolium chloride was demonstrated by authors. Cobalt was extracted by trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate with *D* value of *ca*. 44 and the announced separation factor for the Co/Ni pair was calculated to be approximately 207. Undoubtedly, this research topic is a great scientific challenge that opens the door for “ionometallurgy” as a new alternative to hydrometallurgy.

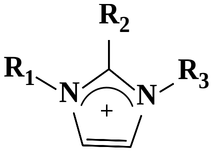
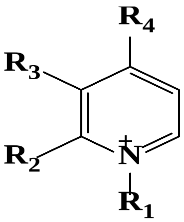
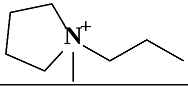
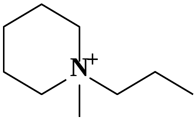
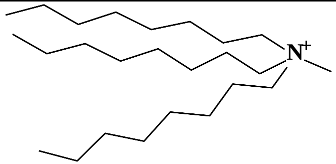
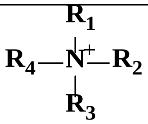
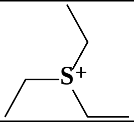
7. Conclusions and outlook

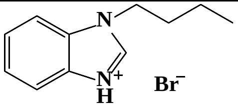
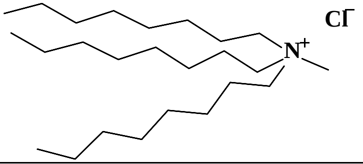
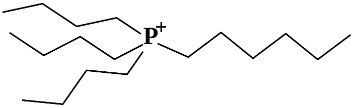
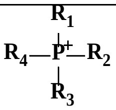
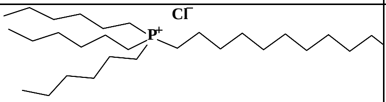
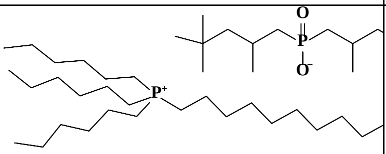
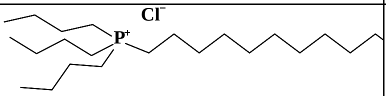
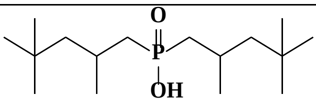
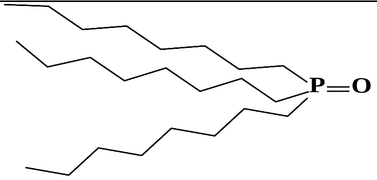
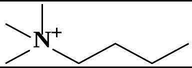
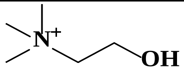
A significant number of scientific articles on synthesis of various types of ILs have been reported up to date, either on their characterization or on exploring their viability on the separation of target metal compounds. These new fluids have been claimed long time as representatives of an innovative approach to green chemistry, although the existence of a large controversy. The most meaningful thing is the ionicity of ILs which high ionic strength media is rather unlike than typical molecular organic solutions. In view of this, the ILs are discussed according to their application as a second hydrophobic phase in liquid-liquid metal extraction processes. One of the major disadvantages of ILs conveys on the limited number of possible reagents able to induce phase separation with water regarding the subject of solvent extraction chemistry. Attention must be paid to the chemical nature, toxicity and biodegradation of ILs apropos their solubility in water, which poses serious concern regarding their possible enter into the ecosystems. With a plethora of ILs available now (end of 2018) and the established physico-chemical properties it is not so difficult to generalize or to predict the behavior of future newcomers. Furthermore, the set-up of a well-defined guideline with respect to some typical classes would be in practical use, too. Both the chemical nature of cation and anion could affect the mutual solubilities between water and ILs, but the anion plays the major role on their phase behavior. In light of the cited information available, the following order of increasing hydrophobicity of common species has been established: Br^-, Cl^- < $[TfO^-]$ < $[BF_4^-]$ < $[PF_6^-]$ < $[Tf_2N^-]$ < $[BETI^-]$. Meanwhile, the solubility of water in ILs generally is several orders of magnitude higher than the solubility of ILs in water. Furthermore, the finding that the ILs solubility in water decreases with the alkyl chain length increase due to the increased hydrophobicity is in good agreement with certain toxicity studies now. This is certainly a valid concern when one is focusing on the lengthened of the 1-alkyl group on the cationic $[C_1C_nim^+]$ species. On an environmental perspective, it is thus not enough to conclude that increasing the length of the alkyl chains of 1-alkyl-3-methylimidazolium cations for example; the undesirable IL's component solubilities can be successfully reduced considering the established differences between ILs' cation and anion solubility in some experimental cases. In the context of green and sustainable chemistry especially in order to develop a broader platform of cost-effective and sustainable ILs with potential to be applied at an industrial technological scale, there might be a vision of apt molecular design. The structure should combined convenient technical advantages with a set of favorable chemical properties with low risk for environment, beneficial to ameliorate their fair legitimacy in the green chemistry portfolio. It is expected as a challenging goal, that IL reagents with greener features will be synthesized and tested in the future. We know today for certain that there is no a "universal" IL compound like no single "multifunctional" diluent exist, that can be perfect for every chemical process. At this stage $[C_1C_nim^+][Tf_2N^-]$ type of IL pretends to be more supportive in the field of solvent extraction of metal ions employed as pure diluents despite the existence of some unignorably issues relating to the environment. In any case, it must be taken into account that these biphasic systems necessarily require a hydrophobic IL, which is somehow disadvantageous from an environmental point of view. Thus, the search for safer and cheaper ILs with tailored extraction efficiencies and selectivities for ABS in solvent extraction chemistry as well as taking advantage of their benefits is still an impressive scientific issue. Organic losses due to the extractant or diluent molecules can occur through a number of physical and chemical mechanism during solvent extraction circuit implementing VOCs too and thus always presents engineering challenges in ensuring minimize solubility losses. It would be so accurate to say, regarding the revealed herein nuanced picture, that the zenith of the so-called "gold-rush" of ILs is already reached. However, significant barriers remain even now to commercial exploitation of ILs for metal recovery to name a few, from natural ores or recycling of precious metals found in secondary sources, the so called urban mine, in turn of spent nuclear fuel, but also in the light of polluted either industrial or communal waste water. The high costs of ILs will rest one of the major drawbacks *vs* traditional molecular diluents when envisaging their large-scale application in chemical industry. Thus, the recycling or reutilization of ILs is an essential step to guarantee the economic viability. Despite the numerous contributions including the mutual solubilities among water and hydrophobic ILs, there are still many gaps in what concerns the understanding of the equilibrium metal extraction mechanism in aqueous−IL biphasic systems. A mechanistic modeling approach still seems to be far off. It is quite likely that all diversity of unique chemistry provided by ILs is somehow builds on their unique ionic solvation environment and the ion-exchange capabilities. The solvent extraction mechanism of metallic species incorporating ligand(s) dissolved in an IL could be achievable in two ways *via* formation of neutral complexes or ion-exchange scheme, cation or anion, which seems to be more favorable reaction mode realizable in ionic environment. It is essential to underline that the aqueous solubility of IL's constituents is the crucial factor leading to ion exchange mode of solvent metal extraction.

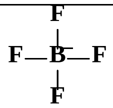
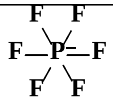
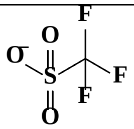
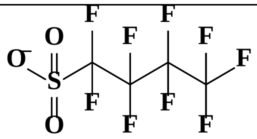
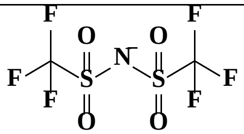
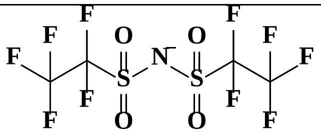
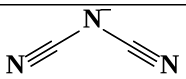
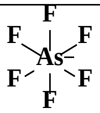
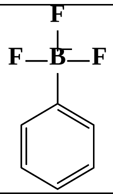
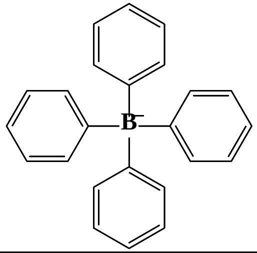
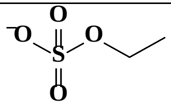
Although, some equilibrium liquid-liquid processes have already been established in traditional molecular diluents like formation of anionic complexes of the type $[M^{n+}L_{n+1}]^{-}$, where L^{-} is the anion of chelating ligand. The essential factors determining the chemical process are the hydrophobicity of IL cation and anion including their surroundings, the presence or not of organic species in this ionic medium, and from other side the hydration energy of the metal aqueous complex and the chemical composition of the aqueous phase. From a theoretical point of view, the influence of extraction mechanism on the mutual solubility is so marginal, especially in the cases when lower metal concentration were employed in the process in the range of traces up to *ca.* 10^{-4} M. There are still a lot of open questions and many unrevealed aspects about the role of ILs, but this is a good part of the excitement of scientific work not only in the field of separation chemistry, without doubt, there is still plenty of room for surprises in future research investigations. As a final word to the wise, Mendeleev’s words written in the preface of his book entitled *The Principles of Chemistry* (1891): “Knowing how contented, free and joyful is life in the realms of science; one fervently wishes that many would enter their portals.”

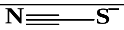
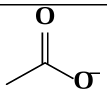
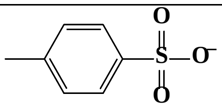
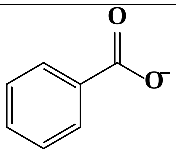
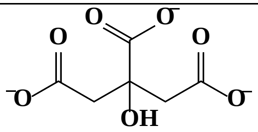
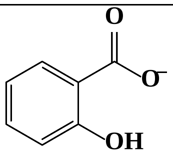
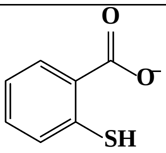
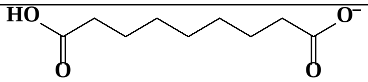
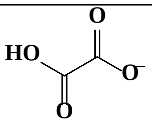
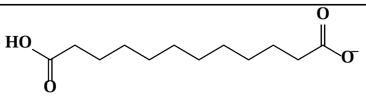
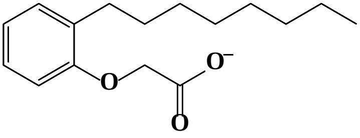
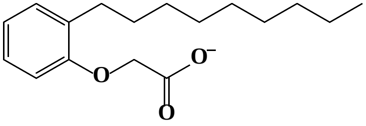
8. Abbreviations

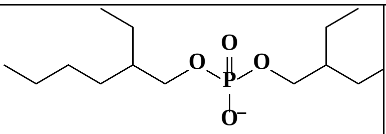
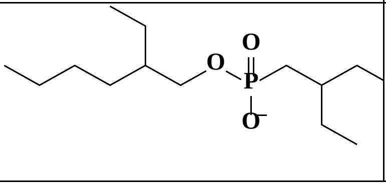
Table 23. Ionic structure and respective abbreviations for the presented ILs herein: cations, popular ligands and anions.

Cations	Imidazolium−based cations	Abbreviatios
R_1: methyl R_2: hydrogen, methyl R_3: ethyl, butyl, pentyl, hexyl, heptyl, octyl, decyl,…		[C_1C_nim$^+$]
	Pyridinium−based cations	
R_1: butyl, hexyl, octyl, propyl,… R_2: hydrogen R_3: hydrogen, methyl R_4: hydrogen, methyl		[C_1C_npy$^+$] [1-C4-3-mpy$^+$] N-octylpyridinium:[Opy$^+$] 4-methyl-N-octylpyridinium: [4Mopy$^+$] 2-methyl-N-octylpyridinium: [2-Mopy$^+$]
	Pyrrolidinium−based cations	
R_1: methyl R_1: propyl, butyl,…		[C_1C_npyr$^+$]
	Piperidinium−based cations	
R_1: methyl R_1: propyl, butyl,….		[C_1C_npip$^+$]
trioctylmethyl-ammonium		[$N_{8,8,8,1}^+$], [TOMA$^+$] [$N_{R,222}^+$]: N-alkyl-triethyl-ammonium
tetraalkyl ammonium, tetrabutyl-ammonium, methyltrioctyl-ammonium		[N_{nnnn}^+], [TBA$^+$], [MTOA$^+$]
triethylsulfonium		[S_{222}^+]

1-butyl-3-benzimidazolium bromate		[HBBIm$^+$][Br$^-$]
trialkyl(C$_8$-C$_{10}$)methyl-ammonium chloride		Aliquat 336, [A336]
tributylhexyl-phosphonium		[P$_{4,4,4,6}^+$]
tetraalkyl phosphonium, trihexyl(tetradecyl) phosphonium	 $R_4{-}P^+(R_1)(R_3){-}R_2$	[P$_{nnnn}^+$], [THTP$^+$]
trihexyl(tetradecyl) phosphonium chloride		Cyphos IL 101
trihexyl(tetradecyl) phosphonium *bis*(2,4,4-trimethylpentyl) phosphinate		Cyphos IL 104
tributyl(tetradecyl) phosphonium chloride		Cyphos IL 167
Cyanex 272		
Cyanex 923		
trimethylbutyl-ammonium		[Me$_3$BuN$^+$]
choline		[N$_{1112(OH)}^+$]
Anions	ILs–anions	abbreviations
chloride	**Cl$^-$**	[Cl$^-$]
bromide	**Br$^-$**	[Br$^-$]

tetrafluoroborate		$[BF_4^-]$
hexafluorophosphate		$[PF_6^-]$
trifluoromethanesulfonate		$[CF_3SO_3^-][TfO^-]$
nonafluoromethylsulfonate		$[NfO^-]$
bis[(trifluoromethyl)sulfonyl]imide		$[N(CF_3SO_2)_2^-]$,$[Tf_2N^-]$
bis(pentafluoroethylsulfonyl)imide		$[BETI^-]$
dicyanadmide		$[N(CN)_2^-]$
hexafluoroarsenate		$[AsF_6^-]$
trifluorophenyl borate		$[BF_3Ph^-]$
tetraphenyl borate		$[BPh_4^-]$
ethylsulfate		$[EtSO_4^-]$

thiocyanate		[SCN$^-$]
acetate		[CH_3COO^-]
tosylate		[TOS$^-$]
benzoate		[$C_7H_5O_2^-$]
citrate		[$C_6H_5O_7^{3-}$]
salicylate		
thiosalicylate		
azelate		
oxalate		
dodecanedioate		
sec-octylphenoxy acetic acid		[CA-12$^-$]
sec-nonylphenoxy acetic acid		[CA-100$^-$]

di-(2-ethylhexyl)phosphate		[P204^{-}]
2-ethylhexyl phosphoric acid mono(2-ethylhexyl) ester		[P507^{-}]

9. Acknowledgements

No funding was received for this work. Sincere appreciation is expressed to all colleagues of Dr. Atanassova who assisted in various ways during the preparation of this book, and to all co-researchers who contributed to the results, which names are mentioned in the respective references. The author wish to thank the PhD student Dessislava Gerginova (BAS, IOOCP) for her valuable help in preparing the Q-NMR figures and the table in the Abbreviations section.

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11. Author biography

Maria Atanassova Petrova obtained her MSc degree (1998) and PhD in Inorganic Chemistry (2003) with a thesis entitled “Synergistic extraction of lanthanoids with chelating extractants and the quaternary ammonium salt Aliquat 336“ (under the direction of Prof. Dukov, DSc) at University of Chemical Technology and Metallurgy-Sofia. Since 1999 till-now she works as an Assistant Professor at the Department of General and Inorganic Chemistry. List of diverse teaching chemical courses: Introduction to General chemistry, Chemical calculations, Coordination chemistry for MSc students, Practical laboratory works in General, Inorganic and Coordination chemistry. Lecturer courses, seminars and practical work in French language for Bulgarian and international students of Filière francophone: “General and Inorganic chemistry” and “Inorganic chemistry. Chemistry of elements.” Dr. Atanassova was an affiliate member of IUPAC (2005-2011), a national representative in Division Committee VIII of IUPAC: Chemical Nomenclature and Structural Representation for biennium 2018-2019 and 2020-2021 as well as a voluntury member of the Subcommittee on Solubility and Equilibrium Data of Analytical Division V from 2015 year. She has published over 60 peer-reviewed scientific journal papers and several university manuals. Her current research interests include synergistic solvent extraction and coordination chemistry of lanthanoids, separation chemistry and interfacial field chemistry with ionic liquids.