



HAL
open science

Malonamide, phosphine oxide and calix[4]arene functionalized ionic liquids: synthesis and extraction of actinides and lanthanides

Dariia Ternova

► **To cite this version:**

Dariia Ternova. Malonamide, phosphine oxide and calix[4]arene functionalized ionic liquids: synthesis and extraction of actinides and lanthanides. Chemical Physics [physics.chem-ph]. Université de Strasbourg; Kiiivs kij nacionalnij univërsitet imeni Tarasa Ševčëнка (Ukraine), 2014. English. NNT: 2014STRAE041 . tel-01157804

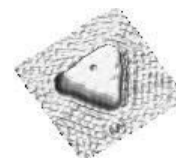
HAL Id: tel-01157804

<https://theses.hal.science/tel-01157804>

Submitted on 28 May 2015

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



THÈSE en co-tutelle présentée par :

Dariia TERNOVA

soutenue le : **25 septembre 2014**

pour obtenir le grade de : **Docteur de l'université de Strasbourg**

Discipline/ Spécialité : chimie et chimie physique

Malonamide, phosphine oxide and calix[4]arene functionalized ionic liquids. Synthesis and extraction of actinides and lanthanides

THÈSE dirigée par :

Mme BILLARD Isabelle
M. KALCHENKO Vitaly

Dr., IPHC, CNRS, Strasbourg, France
Prof. Dr., Institut de chimie organique, Académie des Sciences Ukraine, Kiev

RAPPORTEURS :

M. KOSTYUK O.

Dr., Institut de chimie organique, Académie des Sciences d'Ukraine, Kiev

M. PADUA A.

Prof., Institut de chimie de Clermont-Ferrand, France

AUTRES MEMBRES DU JURY :

Mme HUBSCHER V.
M. CHAINET E.

Dr., Université de Strasbourg, France
Dr., Laboratoire d'Electrochimie et de Physicochimie des Matériaux et des Interfaces, Grenoble, France

GENERAL INTRODUCTION

Nuclear energy provides about 12% of the world's electricity. In the world there are some proponents (World Nuclear Association, IAEA¹) and opponents (Greenpeace International, NIRS²) of nuclear energy production, however today 31 countries use nuclear energy to generate up to three quarters of their electricity, thereby there are 435 nuclear power reactors in operation and 75 new reactors are under construction [1, 2]. The advantages of nuclear power are relatively small amount of radioactive wastes and almost no greenhouse gas emissions. Moreover it is the only large-scale energy-producing technology which takes the full responsibility for all its wastes.

Among all radioactive wastes high-level waste (HLW) is of highest concern. The HLW arises from spent nuclear fuel and consists mostly of uranium (95%), plutonium (1%), other actinides (0.1%) and fission products (3–4%). Two different management strategies are used for spent nuclear fuel. In one the fuel is reprocessed to extract usable material (uranium and plutonium) for new fuel. In the other, spent fuel is simply considered a waste and is stored pending disposal.

The first strategy is applied in France, Russia, China, India and Japan, where spent nuclear fuel undergoes reprocessing before storage. The primary goal of reprocessing is a separation of uranium and plutonium for reusing in next fuel cycle. The separation is implemented by the PUREX process (plutonium uranium extraction), which is based on liquid-liquid extraction. PUREX uses tributylphosphate diluted in kerosene, and ensures 99% of U and Pu recovery, but the waste still contains other hazardous metal cations: Np, Am, Cm, I-129, Tc-99, Cs-135, Sr-90. Their partitioning and transmutation (P&T) is an important step in the reduction of the waste radiotoxicity, and according to the IAEA report the P&T can help to reduce the time during which nuclear waste should be isolated from the biosphere from 130 000 years to between 500 and 1500 years [3].

Hereby nowadays the search of new efficient and selective extractants is of high scientific and industrial importance. **This thesis is thus a contribution to the development of new extracting systems, involving the synthesis of new ligands, based on an ionic liquid frame together with the use of ionic liquids as diluents.**

The choice of these two components for the extraction system (ionic liquids as new extractants and ionic liquids as new solvents) has been made considering the following arguments:

- Modern processes of liquid-liquid extraction involve the use of organic solvents, which are explosive, volatile and toxic. There is a strong impulse toward “greener” industrial processes through the REACH³ regulation (entered into force in 2007), which will limit the future use of volatile organic compounds in nowadays liquid–liquid extraction systems. One possible alternative to these detrimental chemicals is the use of a new class of solvents, called ionic liquids (ILs). These solvents are usually presented as nonvolatile and nonflammable. Some of them are claimed to be nontoxic, biodegradable, and even edible. Moreover due to their chemical nature ILs display fantastic physicochemical

1 International Atomic Energy Agency

2 Nuclear Information and Resource Service

3 Registration, Evaluation, Authorization and Restriction of Chemicals is a European Union Regulation

properties allowing unusual chemistry to occur. Consequently ILs were chosen as a solvent for the extraction experiments in this work.

- Another very promising concept is the creation of so-called task specific ionic liquids (TSILs). TSILs are ionic liquids, which besides their ionic and liquid properties are provided with certain functionality. In the case of extraction it is complexing properties. Most of the times TSILs are synthesized on the basis of common ionic liquids by functionalization of their cations or anions with extracting patterns. Thus TSILs for extraction are liquid extractants of ionic nature, which can be used as a pure phase or diluted in similar non-functionalized IL. Together with ILs as diluents these are the ionic analogs of the molecular extractant/molecular solvent.

This manuscript is thus organized as follows:

- **Chapter I** is devoted to literature review as it provides the qualitative and quantitative basics of liquid-liquid extraction, as well as general information about ionic liquids, the peculiarity of their structure along with their physicochemical properties, and how they are used for the liquid-liquid extraction. For this part, archetypal experimental data are presented and then modelling of extraction data is presented. Finally a specific section is dedicated to the presentation of literature review on various task-specific ionic liquids, because the main objective of the research presented in this thesis is the synthesis and investigation of new TSILs with phosphine oxide, carbamoyl phosphine oxide, malonamide and calix[4]arene platforms.
- **Chapter II** reports the synthetic methods for the new TSILs that have been synthesized. First, the general routes for the syntheses are depicted and then detailed experimental information is given.
- **Chapter III** first presents the extracting properties of the compounds that have been tested. Then, a qualitative discussion is presented along with proposed mechanisms of extraction. For some of the compounds, a quantitative approach is also presented, in term of equilibrium sets of equations, turned into a mathematical fitting of the extraction data.
- **General Conclusions** makes an overview of the work before presenting open questions.
- **Supplementary data** contain synthetic information (if needed) together with the extraction protocol.

1 <http://www.world-nuclear.org>

2 <http://www.iaea.org/pris/>

3 Technical report of IAEA series no.435 Implications of Partitioning and Transmutation in Radioactive Waste Management, 2004, INTERNATIONAL ATOMIC ENERGY AGENCY VIENNA, 2004

CONTENTS

General Introduction	3
I. Chapter: Literature review	7
<i>I.1 Introduction</i>	7
<i>I.2 Liquid-liquid extraction</i>	7
I.2.1 General information about liquid-liquid extraction	7
I.2.2 Evaluation of liquid-liquid extraction	8
I.2.3 Mechanisms of liquid-liquid extraction: classic cases	9
<i>I.3 Ionic Liquids</i>	11
I.3.1 What are ILs?	11
I.3.2 ILs physicochemical properties of interest for liquid-liquid extraction	11
I.3.3 Terms “task-specific ionic liquid” and “functionalized ionic liquid”	15
<i>I.4 Extraction in Ionic Liquids</i>	16
I.4.1 Experimental facts	16
I.4.2 Modelling of extraction data in IL.....	18
<i>I.5 Review of TSILs</i>	21
I.5.1 Carboxylate TSILs.....	22
I.5.2 β -Diketonate TSILs.....	23
I.5.3 Hexafluoroacetylacetonate TSILs	23
I.5.4 Trifluoroacetylacetonate TSILs	24
I.5.5 Thenoyltrifluoroacetylacetonate TSILs	25
I.5.6 Organophosphorus TSILs	26
I.5.6.1 Phosphate and phosphonate TSILs	26
I.5.6.2 Carbamoylphosphine oxide TSILs	28
I.5.7 Urea-, thiourea-, and thioether-TSILs	29
I.5.8 Terpyridine TSILs	30
I.5.9 2-Hydroxybenzylamine TSILs	31
I.5.10 Diglycolamide TSILs	31
I.5.11 Iminodiacetic TSILs	32
I.5.12 TSILs with bis-sulfide and nitrile functional groups	34
I.5.13 Crown ether TSILs	35
I.5.14 Calixarene-TSILs	36
<i>I.6 Conclusions</i>	37
II. CHAPTER: Synthesis of Functionalized Ionic Liquids and their Precursors	40
<i>II.1 Introduction</i>	40
<i>II.2 Synthetic results and discussion</i>	41
II.2.1 Synthesis of Functionalized Ionic Liquids	41
II.2.1.1 Malonamide Functionalized Ionic Liquid	41
II.2.2 Functionalized Ionic Liquids with phosphine oxide groups	42
II.2.2.1 Cationic FILs with phosphine oxide groups	42
II.2.2.2 Anionic FILs with phosphine oxide groups	43
II.2.2.3 TSIL with CMPO fragment	45
II.2.3 Calixarene phosphine oxide FILs	46
II.2.3.1 Cationic FILs on the basis of calix[4]arene phosphine oxides	47
II.2.3.2 Precursors of anionic calix[4]arene phosphine oxide FILs	50
<i>II.3 Conclusions</i>	57
<i>II.4 Experimental part. Synthesis</i>	58
II.4.1 Synthesis of malonamide-IL (FIL-MA)	58
II.4.2 Synthesis of phosphine oxide FILs	59
II.4.2.1 Synthesis of cationic phosphine oxide FIL.....	59

II.4.2.2	Synthesis of anionic phosphine oxide FILs	60
II.4.3	Synthesis of CMPO-IL.....	64
II.4.4	Synthesis of calix[4]arenes	65
III.	CHAPTER: EXTRACTION. RESULTS AND DISCUSSION.....	73
III.1	<i>Introduction</i>	73
III.2	<i>Extraction experiments</i>	74
III.2.1	Experimental results for neutral compound - tributyl phosphine oxide (TBPO)	75
III.2.2	Experimental results for cationic phosphine oxide FIL (SM1006)	78
III.2.3	Experimental results for anionic phosphine oxide FIL (DM01).....	83
III.2.4	Experimental results for cationic carbamoyl phosphine oxide FIL (CMPO-IL).....	89
III.2.5	Experimental results for cationic calixarene-based phosphine oxide FIL (calix-IL)	92
III.3	<i>Discussions</i>	93
III.3.1	Qualitative analysis for TBPO and SM1006	95
III.3.2	Quantitative discussion for TBPO and SM1006: Mathematical treatment, basic chemical considerations and fitting procedure	96
III.3.3	Qualitative analysis for CMPO-IL	105
III.3.4	Quantitative discussion for CMPO-IL.....	107
III.4	<i>Conclusions</i>	110
	General Conclusions	112
	Supplementary Data	114
	Acknowledgments.....	117

I. CHAPTER: LITERATURE REVIEW

1.1 Introduction

This Chapter deals with two key topics of this research – liquid-liquid extraction and ionic liquids (ILs). First these concepts will be considered separately in order to provide the background for the complex idea of this work. Thus definitions, main abbreviations, physicochemical parameters, and “classical” examples will be given.

Then the concepts of liquid-liquid extraction and ionic liquids will be brought together to the idea of task-specific ionic liquid, which is the central idea of the present research.

The literature data about task-specific ionic liquids for the liquid-liquid extraction of metal cations have been collected; they were classified according to the complexing patterns. Particular attention is given to the task-specific ionic liquids on the basis of macrocyclic molecules – calix[4]arenes, which in many cases ameliorate the properties of the functional groups placed on them. Moreover calix[4]arenes were chosen as scaffolds for the synthesis of some of the new task-specific ionic liquids obtained during this work.

1.2 Liquid-liquid extraction

1.2.1 General information about liquid-liquid extraction

Liquid-liquid extraction (also called solvent extraction) is a separation process, which is based on the distribution of a solute between two immiscible solvents, one of which is usually an aqueous phase, and the other one – an organic solvent. Due to the different solubilities of the solute in the aqueous and the organic phases, the solvent extraction can be used for purposes of purification, enrichment and separation.

Liquid-liquid extraction was known since the 19th century, but attracted much attention in the middle of previous century along with the development of nuclear technology, when the problem of radionuclides recovery and separation appeared. Nowadays solvent extraction is the basis of the industrial PUREX process – the standard aqueous nuclear reprocessing method for the recovery of uranium and plutonium from spent nuclear fuel. In this work liquid-liquid extraction was applied to study the complexation of the synthesized compounds with radionuclides in ionic liquid media.

In general, metallic cations do not spontaneously transfer from an aqueous phase to an organic phase, because of difference of solvation energy between the two solvents. In order to favour solubilisation of the metal into the organic solvent, complexing ligands, *L*, dissolved in organic phase, are to be used. Complexing ligands are also called *extractants*, *chelating agents* or *complexants*. Furthermore, to avoid hydrolysis and precipitation, aqueous phases are usually acidified by mineral acids such as HCl or HNO₃. Thus, the aqueous phase also contains many other species (H⁺, NO₃⁻, etc.), sometimes in large excess as compared to the species to be extracted, therefore the efficiency of extraction should be characterized by yields and separation factors.

There are several measures of extraction effectiveness:

In the following, subscripts *aq*, *org*, and *IL* in the notation $[X]_{i,j}$ correspond to the aqueous, molecular organic, and IL phase concentrations, respectively, while subscripts *init* and *eq* designate the initial and equilibrium concentrations, respectively.

1) **Distribution ratio**, $D(M)$, of species M , is equal to the total amount of M in the organic phase divided by its total amount in the aqueous phase.

$$D(M) = \frac{[M]_{org,eq}}{[M]_{aq,eq}} \frac{V_{aq}}{V_{org}} \quad (I-1)$$

Where V_{aq} and V_{org} are the volumes of the aqueous and organic phase, respectively. Most of the time, extraction experiments are performed with $V_{org} = V_{aq}$, leading to the usual equation:

$$D(M) = \frac{[M]_{org,eq}}{[M]_{aq,eq}} \quad (I-2)$$

2) An alternative parameter is the **extraction efficiency** of a species M , $E(M)$, for equal volumes:

$$E(M) = \frac{100 [M]_{org,eq}}{[M]_{aq,init}}, \% \quad (I-3)$$

$D(M)$ and $E(M)$ are related according to simple equations. In the case volumes are equal, these turn to be:

$$E(M) = \frac{100 D(M)}{1 + D(M)}, \% \quad (I-4)$$

An extraction process is considered efficient, when obtained D values are above 10 ($E > 90.91\%$) and can be above 10^4 ($E > 99.99\%$) in some cases, while “inefficient” extraction corresponds to D values below 1. $D = 1$ ($E = 50\%$) means the equal distribution 50/50 of the solute between aqueous and organic phases.

3) The **separation factor**, $SF_{M_1M_2}$, characterizes the selectivity of extraction, as a measure of the ability of the system to separate two solutes. The separation factor, $SF_{M_1M_2}$, of M_1 towards M_2 is defined as:

$$SF_{M_1M_2} = \frac{D(M_1)}{D(M_2)} \quad (I-5)$$

1.2.2 Evaluation of liquid-liquid extraction

Nowadays analytic facilities allow determining metals even at very low concentrations. In this respect atomic emission spectroscopy, atomic absorption spectroscopy, spectrophotometry, and radiometric measurements are useful techniques.

The choice of facilities depends on the physical aspects of the sample: nature of metal (radioactive, nonradioactive), nature of aqueous or organic phase, concentration limits, etc.

The most widely used techniques are next:

For nonradioactive samples

Inductively coupled plasma–mass spectrometry (ICP-MS). This is a type of mass spectrometry which is capable of detecting metals and several non-metals at very low concentrations. This is achieved by ionizing the sample with inductively coupled plasma and then using a mass spectrometer to separate and quantify those ions. This method is characterized by very low detection limits (even below the ppt range) and a high level of productivity.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample.

Spectrophotometry method is based on the Beer–Lambert–Bouguer law, and can be applied for substances which absorb from 200 to 800 nm. For quantitative determination of metal cations the chromogenic reagents are used, for example, Arsenazo III for lanthanides or 1-(2-pyridylazo)-2-naphthol for Zn, [4, 5]. The metal concentration can be determined by measuring the absorbance of these metal complexes in relation to the absorbance of reference solution. This method is considered as accessible, but quite time-consuming and less sensitive.

For radioactive samples

Radiometric measurements are performed with *γ -scintillation counter*. Scintillation counters are the detectors of ionizing radiation, based on the luminescence phenomenon. Luminescent materials (e.g., NaI(Tl) crystal for γ -rays), used in these counters, when struck by an incoming particle emit light. Then the light is reemitted in the form of electrons via the photoelectric effect. The subsequent multiplication of those electrons results in an electrical pulse which can then be analysed and yields meaningful information about the particle that originally struck the scintillator.

This technique is widely used because it can be made inexpensively yet with good quantum efficiency and can measure both the intensity and the energy of incident radiation.

1.2.3 Mechanisms of liquid-liquid extraction: classic cases

Extraction in molecular solvents has been studied for years, therefore the mechanisms occurring are now quite well understood. The understanding of that is based on the simple fact – ion pairing occurs, which means that any entity transferring through the phase interface is always neutral.

The essential symbols for the extraction mechanisms are next:

M^{m+} – metal cation

X^- – for anion of mineral acid ($HX \rightleftharpoons H^+ + X^-$)

Cat^+ is a cation of IL, A^- is an anion of IL

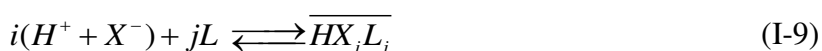
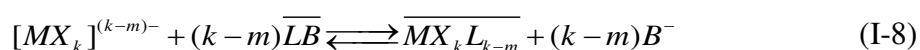
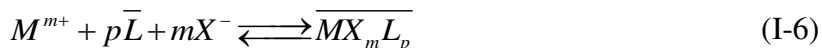
Mol is a molecular solvent

L – ligand (syn. extractant, complexant)

Bars over species will denote they are dissolved in the organic (IL) phase. Extraction systems will be denoted by indicating first (left hand side) the major components of the starting (aqueous) phase, that are the metallic ion and the type of mineral acid. For the sake of simplicity, the water solvent will be omitted. The biphasic nature of the system will be noted by a double bar and on the right hand side, the ligand and the solvent (molecular or IL) will be noted. This corresponds to the general notation: $M^{m+} / HX // L / IL$.

The exact description of the extraction process can be divided into three categories, depending on the ligand nature. Non protonable ligands, L , extract a metallic neutral entity under the form $\overline{MX}_m pL$ (see Equation I-6), while protonated ligands, here denoted as HL , form

the neutral species \overline{ML}_n , nH^+ cations being transferred to the aqueous phase to insure electrical neutrality of both phases (Equation I-7). The third possibility, which is not as common as the previous two, arises from quaternary ammonium salts, denoted LB , that may extract negatively charged metallic ions of the form $[MX_k]^{(k-m)-}$ (Equation I-8). Apart from these extraction equilibria, ligands are usually also extracting part of the acid dissolved in the aqueous phase, under various stoichiometries (Equation I-9). Acid extraction is competing to the extraction of metal cations. This phenomenon may have different impact at extraction process and depends on the ligand nature, range of acid concentration, complexing abilities of counteranion X^- .



Finally ligand can be protonated at high acidities (Equation I-10). This is well known and corresponds to the case of decreasing of extraction ability of phosphine oxides at high acid concentrations, for example.

Taking all these aspects into account, the typical extraction systems of the form $M^{m+} / HX // L / Mol$ display a so called *bell shape* for the plot D vs $[HX]$, as illustrated for several elements in Figure I-1.

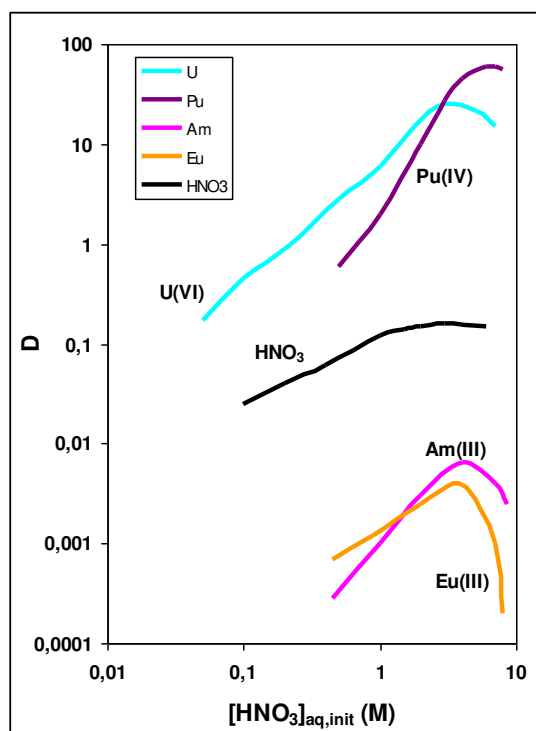


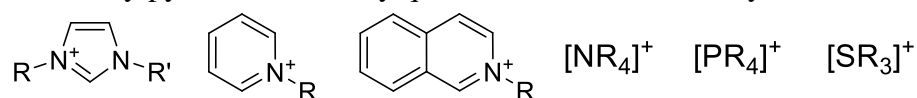
Figure I-1. Typical D variation as a function of $[HNO_3]_{aq,init}$ for some radionuclides and HNO_3 by use of a malonamide dissolved in a molecular solvent

1.3 Ionic Liquids

1.3.1 What are ILs?

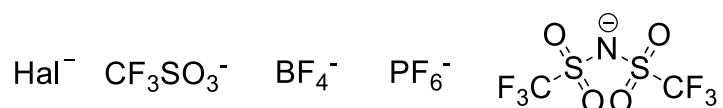
The most common definition of ILs is next: ILs are compounds made of cation and anion with melting temperature below 100 °C, even though this temperature limit is rather subjective, and may be extended depending on experimental content. Such a definition was given in order to differentiate these salts from high-temperature molten salt. “Molten salt” is a very general term applied for ionic compounds in liquid state (for example: *NaCl mp* = 801 °C). Therefore ILs are often called “low temperature molten salt”, “ambient temperature molten salt”. In this manuscript I will adhere to the aforementioned definition: an IL is a salt with *mp* < 100 °C.

The most common salts in use are those with alkylammonium, alkylphosphonium, alkylsulfonium, *N*-alkylpyridinium, *N*-alkylquinolinium and *N,N*-dialkylimidazolium cations:



Scheme I-1. Chemical structures of the most classical IL cations

The most widely used anions are halide, triflate, tetrafluoroborate, hexafluorophosphate, bis(trifluorosulfonyl)imide anions:



Scheme I-2. Chemical structures of the most classical IL anions

The number of cations and anions for ILs is growing, it means that the number of ILs which can be synthesized by combining of these ionic components is huge.

The most common ILs for extraction consist of *N,N*-dialkylimidazolium, so they will appear quite often in this work, that's why I chose an abbreviation C_mC_nimA to note them, where *n* and *m* are the alkyl chain lengths and A is the counteranion.

Another big family of ILs are halogenoaluminate(III) ionic liquids, which were obtained by mixing of aluminum(III) halide with imidazolium or pyridinium halide salts [6, 7]. These ILs are extremely sensitive toward moisture and corrosive to many materials. So they should be handled at special conditions, what make them inapplicable in certain domains, as extraction in our case. Therefore they will not be considered in this work.

1.3.2 ILs physicochemical properties of interest for liquid-liquid extraction

In the following, I will briefly summarize what is known from literature concerning several physicochemical properties of ILs that all are of relevance to liquid-liquid extraction as performed in this work. ILs may possess different physicochemical properties due to their chemical versatility. Any of these properties is strongly dependent on both chemical structures of the cation and the anion, so it is difficult, if not impossible to present a clear picture. Furthermore, these properties are strongly affected by the presence of impurities, a point that

will be discussed in one dedicated section below. In general, many papers have been attempting classification and have derived empirical rules, giving tendencies that apply either to a family of ILs (imidazolium type, for example) or to a very limited series of new compounds. As a consequence, I will limit myself to few citations of general impact, mostly arising from review books to which the reader is referred for a deeper insight.

1) melting points

According to the definition chosen for ILs, *mp* is below 100 °C but can span in a very wide range. Striking examples can be found for C₁C₂imCl (*mp* = 87 °C) and C₁C₂imN(CN)₂ (*mp* = -21 °C) [8]. Slight changes on the chemical structure can affect *mp* in a large range, as illustrated in Figure I-2 [8]: It is important to note that many ILs do not present a clear melting point but a glass transition instead. Supercooling is also quite a common phenomenon with these compounds, in ranges that can reach over 200 °C. Various studies on melting points have been performed, and some limited trends can be derived:

- The more asymmetric are the cation and anion, the lower the melting point
- Alkyl substituent length (imidazolium pattern) has a complex effect:

The variation in melting points as a function of length of alkyl substitutes was studied for the series of C₁C_nimBF₄ ionic liquids. Such dependence is explained by two competing effects: initial lengthening of alkyl chain leads to a reduction in the melting points because of destabilization of Coulombic packing, and a trend toward glass formation. However, further increases in substitution lead to increase of van der Waals forces between the hydrocarbon chains and increased structural ordering, what is reflected on higher melting points [8]. The lowest melting points were observed for ILs C₁C_nimBF₄ with *n* = 4 – 9.

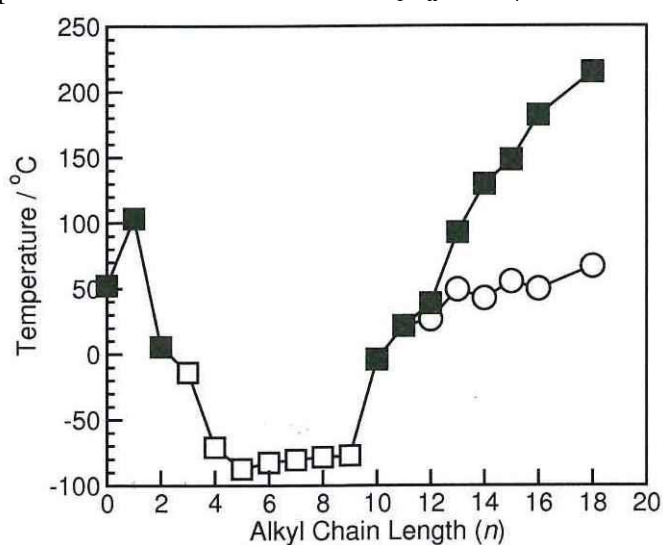


Fig. 3.1-4 Changes in melting points for 1-alkyl-3-methylimidazolium tetrafluoroborate [26] ionic liquids as a function of chain length, showing true melting points (■) and glass transitions (□) with the general trends for decreasing melting points with *n* = 1 to *n* = 8, followed by an increase in melting point and formation of a smectic liquid crystal phase (○) with increasing *n* clearly visible.

Figure I-2. Figure and caption taken from reference [8]

However this rule does not work all the time, thus for terpyridine-functionalized ionic liquids, the compounds with C₄-substituents have their melting points > 100 °C, while those with C₁₂- and C₁₆- melt below 10 °C [9].

2) viscosity

As a general rule, ILs are much more viscous than molecular solvents, with viscosities usually above 40 cP and some very viscous compounds reach values above 10⁶ cP. It has been repeatedly observed that ILs composed on Tf₂N⁻ anions are less viscous than any of their homologues containing for examples BF₄⁻ or PF₆⁻. In the last ten years, some new anionic moieties have been developed that induce lower viscosities (down to 3 cP at 25°C) but these anions, all based on fluorinated backbones, are not commercial at the moment and quite expensive. Furthermore, their synthesis cannot be qualified green [10, 11, 12].

3) miscibility/immiscibility to other solvents

Although of importance, this aspect is not so studied in the literature and rules of thumb have been derived mostly from a wide scope of individual experiments. ILs based on the Tf₂N⁻ anions are not miscible to water and acidic aqueous phases. This is true also for PF₆⁻ based ILs, while BF₄⁻ lead to water miscible compounds. In the case of triflate based ILs, the chain length on the imidazolium cation is known to dictate the water solubility, with compounds being water soluble for chain lengths below $n = 14$ and non-miscible above that value.

However, this clear distinction between miscible and non-miscible compounds (to the water phase or any other solvents) needs more precise information to be really exploited. First, the amount of ILs which is contacted with the aqueous phase is an obvious important parameter, which is in fact not mentioned, most of the time, as most data are obtained for equal volumes of the IL and aqueous phases. However, it has to be kept in mind that ILs, as being composed of ions, strongly interact with the polar molecules of water so that some solubility of the IL phase cannot be avoided. It means, in turn, that ‘small’ quantities of ILs may dissolve fully in aqueous phases, although large amounts used for equilibration experiments will act as a biphasic system. Another important parameter is temperature, as it influences solubility. Such phenomenon is used in the so called cloud point extraction, where a system is turned at will from biphasic to monophasic by simply changing temperature [13, 14].

Conversely, aqueous phases dissolve in IL phases, to amounts that strongly depend on the IL nature but also on the acidic nature and quantity [15, 16]. In the Strasbourg group recent experiments for several biphasic systems $HNO_3 // C_1C_4imTf_2N$ can be summarized as follows [17]:

It was found that water does transfer to ionic liquid phase (up to *ca.* 30 000 ppm), and the higher acid concentration of aqueous phase, the more H₂O goes to IL-phase. Similarly, H⁺ ions dissolve in IL phases, depending on IL and acid nature and concentration. In case of $HNO_3 // C_1C_4imTf_2N$, it has been shown that the amount dissolved in the IL phase equals *ca.* 94% of the initial nitric amount in the range 10⁻² – 7 M.

ILs in their turn transfer to aqueous phase and this transfer is also increasing with increase of nitric acid concentration.

As regard pure aqueous phase, in order to comply with the charge balance, should the IL dissolve in water, its cationic and anionic component dissolve in identical amounts (*ca.* 20 mM). Therefore, a solubility product can be defined as:

$$k_s = Cat^+ \cdot A^- \quad (I-11)$$

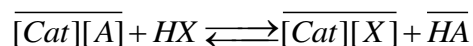
But in the presence of nitric acid, the electroneutrality principle allows Tf_2N^- to be exchanged with NO_3^- and H^+ to be exchanged with the IL's cation. The difference in solubilities of HTf_2N and $CatNO_3$ results in $[Tf_2N]_{aq} \neq [Cat^+]_{aq}$.

Another interesting phenomenon was observed for the systems, where aqueous phase contains the salts of a cation or an anion of the ionic liquid, which is used as the second phase: enhancing the concentration of $[C_1C_4im^+]_{aq}$ causes the decrease of $[Tf_2N^-]_{aq}$ and vice versa. These facts were used for explanation of mechanisms of extraction in Chapter III.

These results have been obtained by means of quantitative NMR experiments and Fischer method which I also used in my work.

4) Radiolysis and acid resistance

Regarding ILs as potential solvents in nuclear cycle separations the stability to acids and radiation are crucial factors used to evaluate their potential application, as this involves contact of the ILs with aqueous solutions, many of which are oxidizing and highly acidic (for example, 1 - 5 M nitric acid). It has to be recalled here that both the IL's cations and anion dissolve in the aqueous phase. Under these conditions many of the constituent anions are protonated:



Therefore it's desirable that the constituent IL anion A^- is a superacid ion, and cannot be protonated even at high acidity.

According to the treatment of spent nuclear fuel, the extraction systems receive ionizing radiation between 0.1 and 1.0 MGy. Usually the common ILs do not suffer significant changes under 0.5 MGy, despite the slight changes of color, viscosity and conductivity [18].

Common families of ILs C_1C_nimA and $NAlk_4A$ have been studied under gamma irradiation at doses of 1.2 – 2 MGy. Chromatography, NMR, and mass spectrometry studies report the fragmentation in the constituent cations and anions such as BF_4^- , PF_6^- , TfO^- , and Tf_2N^- [19, 20, 21]. The degradation order for anions is $Tf_2N^- < TfO^- < PF_6^- < BF_4^-$ and leads to the radicals $\bullet CF_3$, $\bullet F$, $CF_3SO_2N\bullet$. Both imidazolium and tetraalkylammonium cations degrade with loss of hydrogen, this homolytic cleavage leads to the formation of gaseous H_2 from direct recombination of $H\bullet$. C-H bond in imidazolium cation also releases H^+ which influences the extraction efficiency by changing pH. Yuan et al. observed a decrease in D values for $Sr(II) / HNO_3 // DCH18C6 / C_1C_4imPF_6$ and $Sr(II) / HNO_3 // DCH18C6 / C_1C_4imTf_2N$ [22]. It is explained by occurring of competitive reaction of DCH18C6 with $Sr(II)$ and radiation-generated H^+ from the ILs.

On the other hand, quantitative studies show that the radiochemical stability of ionic liquids is in the same range as systems envisioned for nuclear fuel reprocessing with relatively low hydrogen yields.

5) Solubility of organic compounds, metal complexes, ions in ILs

First of all it should be taken into account that the only general property of ILs is ionic nature, all other may vary depending on the chemical composition. For example, solubility of water in IL changes dramatically from $CatCl$ to $CatTf_2N$ (inversely to their lipophilicity). ILs are considered as highly polar, thus do not mix with alkanes and other non-polar solvents, while the ionic liquids containing docusate (dioctylsulfosuccinate) anion are miscible with hydrocarbon solvents [8]. There are several trends which are common for classic ionic liquids: ILs are generally considered to be highly polar, though weakly coordinating solvents, ionic compounds are poorly soluble in ILs, ionic complexes are more soluble than neutral ones, solubilization in ILs occurs due to complexation.

6) *Green properties*

The ecological situation is of high concern nowadays. In this respect ionic liquids are considered green solvents. Due to their ionic nature they possess very low vapour pressure, which makes them non-volatile unlike organic solvents, non-flammable and in many cases non-toxic. They have high thermal stability and low combustibility. Therefore ILs have attracted much attention as green alternatives to traditional organic solvents used in industrial processes of liquid-liquid extraction, after which they are turned into toxic and flammable wastes.

However, the term “green” should be used carefully, since very often the synthesis of ILs requires the use of harmful reagents.

7) *Effect of impurities*

Since ionic liquids are different from traditional organic solvent, and cannot be purified by distillation, the impurities are of high concern. The most of commercially available ionic liquids have purities 95% or greater 99%.

The nature of impurities mainly depends on starting materials left in ionic liquid and methods of preparation. Among the most common impurities are starting organic compounds (as haloalkanes, which are used to form the IL's cation or, for example, unreacted 1-methylimidazole), halide anions (left from anion exchange), protic impurities (from the exchange reaction with a strong acid), metal cations (from alkali salt used in metathesis reaction), and water. The significance of impurities may depend on the ionic liquid application. In respect to liquid-liquid extraction, several ions can interfere in metal cation extraction (as can be seen in Chapter III); presence of water affects the volume of “pure” ionic liquid, and, therefore, D appears to be slightly inaccurate (see Equation I-1), also water may have the influence on stability of some ILs, for instance, PF_4^- and PF_6^- containing ionic liquids will undergo hydrolysis with formation of protic impurities. In the present work we used ILs with very hydrophobic and stable toward water Tf_2N^- anion, however they were dehydrated directly before use by heating to 60 °C under vacuum. Other impurities were neglected due to their minor concentrations.

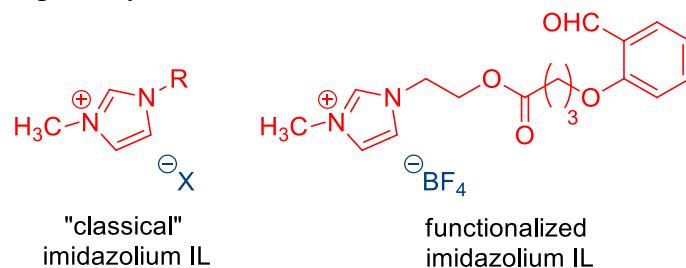
1.3.3 Terms “task-specific ionic liquid” and “functionalized ionic liquid”

The above section gives a global view of what is an IL, in terms of general physicochemical properties, such as the liquidus characteristics of ILs, and these allow us to consider them as alternative solvents and ionic media.

Many authors also consider other qualities, for instance catalytic or chiral properties. These properties that are linked to the chemical structure are however of a different nature than the basic physicochemical properties. Viscosity of an IL is measured as such, while its catalytic activity needs to be tested by interactions with other chemicals. This is also true for extractant capabilities or chiral induction. As a consequence, numerous authors use the term ‘task specific ILs’, especially because it needs the creation of new ILs. Another term often found in the literature is “functionalized ionic liquids”. What is the difference?

From the title “task-specific” it's clear that an IL was made to match a certain task. For example, in the synthesis of indolyldinecyclic-1,3- and -1,4-diketones an ionic liquid - tetrabutylammonium acetate apart of being a reaction medium acts as a catalyst. So its specific task is to catalyze the reaction [23]. In the term “functionalized ionic liquid” the word

“functionalized” points that a “classical” IL was functionalized according to a certain need, which does not exclude the fact of its special task. For example, Bazurea et al. synthesized imidazolium ILs with appended benzaldehyde fragments, which have been used as replacements for solid polymer supports in the heterogeneous phase synthesis of small organic molecules via Knoevenagel and 1,3-dipolar cycloaddition reactions (Scheme I-3) [24].



Scheme I-3. Examples of “classical” and functionalized ionic liquids

But the use of the term functionalized implies the existence of a starting “classical” IL which is to be modified. Many authors use the terms “classical” or “typical” IL, it is explained by the historical fact, as some families of ILs are used so often that they become “classical”, even though in fact they are just widely used, because there is no essential difference between imidazolium IL or a brand new one. Consequently, I would say that all functionalized ILs can be called task-specific and vice versa.

In my work I deal with the imidazolium family of ILs, therefore I will apply the names “functionalized IL” (FILs) and “classical IL” indifferently to point that the goal of my work was a creation of new ILs by chemical modification of well-known imidazolium fragments.

1.4 Extraction in Ionic Liquids

1.4.1 Experimental facts

In recent years ILs have attracted much attention due to their unique properties, also have applied as replacements for traditional organic solvents. In a large variety of ILs it is possible to find those which satisfy the requirements of liquid-liquid extraction. Moreover it was discovered that due to their ionic nature they allow unusual chemistry to occur.

In Section I.2.3 the classical mechanisms (i.e. in molecular solvents) of extraction were discussed, it was shown that the main principle of extraction in molecular solvents is neutralization of the charge of entities transferring through the phase interface. The fundamental difference of ILs as media is their ionic nature, thus they welcome ionic exchange and transfer of charged entities. Furthermore, it is known from the literature that some ILs can cause the extraction in the systems without any ligand added, just due to the exchange of ions, schematically: $M^{m+} / HX // IL$.

This is seen for example in the experiments of Rout et al., who investigated the extraction behaviour of $Pu(IV) / HNO_3 // C_1C_nimTf_2N$ [25]. The authors observed the gradual increase in Pu(IV) distribution ratio above 3M nitric acid. The extraction of Pu(IV) in $C_1C_nimTf_2N$ was attributed to the anion exchange of $[Pu(NO_3)_5(H_2O)]^-$ or $[Pu(NO_3)_6]^{2-}$ species

present in the aqueous phase with the Tf_2N^- ion of ionic liquid phase. Other examples of this phenomenon can be found in the review paper by Billard [27].

However in most cases an extractant is required; such IL-systems for liquid-liquid extraction can be presented schematically as: $M^{m+} / \text{HX} // L / \text{IL}$.

The different character of IL-media is well shown in the work of Shimojo et al., where the picture of extraction of some Ln(III) by the extractant - tetraoctyl-1,5-diglycolamide (hereafter TODGA) is right opposite to that in isooctane [26]. In isooctane the extraction efficiency for Lu(III), Eu(III), La(III) increases with the increase of acidity, by contrast, in $\text{C}_1\text{C}_2\text{imTf}_2\text{N}$, the extraction is more efficient at low concentration of nitric acid (Figure I-3).

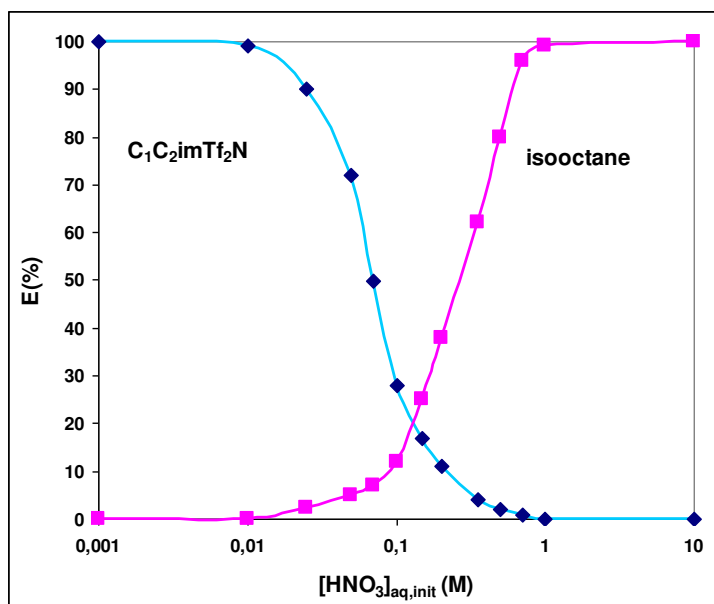


Figure I-3. Schematic variation of E(%) for Ln(III) as a function of $[\text{HNO}_3]_{\text{aq,init}}$ in $\text{C}_1\text{C}_2\text{imTf}_2\text{N}$ and isooctane. Adapted from Shimojo et al. [26]

Another characteristic example displaying different influence of ILs on the process of liquid-liquid extraction is *boomerang shape* of the $D(M)$ variation as a function of $[\text{HX}]_{\text{aq,init}}$. This is quite common in the literature. The visual illustration can be found in Figure I-4 (the data are taken from [27]). Such shape is an indication of two different mechanisms of extraction in the ILs systems described.

Another concept “available” for ionic liquids is “2 in 1” when an ionic liquid (namely a task-specific ionic liquid) can play two roles, acting as a solvent and as an extractant the same time. The concept of TSILs is explained in Sections I.3.3 and I.5.

The metal extraction by TSILs occurs according to the similar mechanisms of ion exchange observed in ionic liquids as diluents, with dissolved molecular extractant [28]. Although few studies have focused on quantitative investigation of this problem, boomerang shapes have been obtained [29].

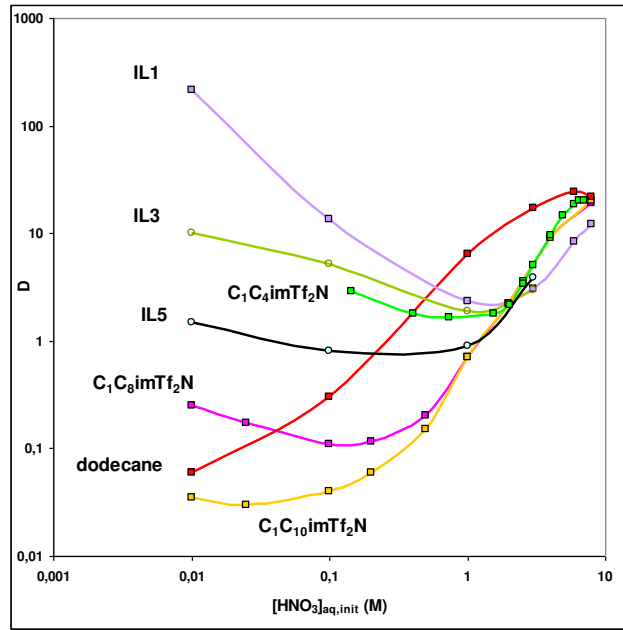
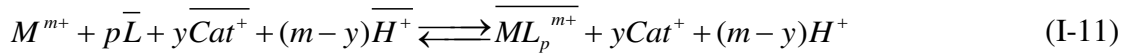


Figure I-4. Comparison of the distribution ratio of UO_2^{2+} as a function of $[\text{HNO}_3]_{\text{aq,init}}$ in various ILs of the $\text{C}_1\text{C}_n\text{imTf}_2\text{N}$ family, and in dodecane, by use of TBP. IL1, IL3, IL5 and dodecane data are from [30], $\text{C}_1\text{C}_n\text{imTf}_2\text{N}$ data ($n = 5, 8, 10$) are from [31] and $\text{C}_1\text{C}_4\text{imTf}_2\text{N}$ data are from [32]. IL1: $(\text{CH}_3)_3(\text{CH}_2\text{CH}_2\text{OMe})\text{NTf}_2\text{N}$. IL3: $(\text{CH}_3)_3(\text{CH}_2\text{CH}_2\text{Cl})\text{NTf}_2\text{N}$. IL5: $(\text{CH}_3)_3(\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2)\text{NTf}_2\text{N}$

I.4.2 Modelling of extraction data in IL

It is not surprising that ILs obviously impact the $D(M)$ variation features as a consequence of their ionic nature (boomerang shape of D vs. $[\text{HNO}_3]$ is a vivid example of this). However for the extracting systems investigated in my work most of the times coefficients D are continuously decreasing as a function of HNO_3 . The main principle of the extraction in ionic liquids is ion exchange, and there are two possibilities of it, which can be explained with the help of two general equilibria:

cationic exchange occurs due to exchange of cations between two phases adhering the electroneutrality principle:



constant of the cationic exchange is defined as:

$$K = \frac{(\overline{ML_p^{m+}})(\overline{Cat^+})^y (\overline{H^+})^{(m-y)}}{(M^{m+})(\bar{L})^p (\overline{H^+})^{(m-y)}} \quad (\text{I-12})$$

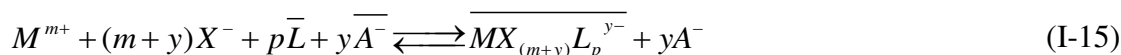
coefficient of extraction via cation exchange:

$$D(M) = K \frac{(\bar{L})^p (\overline{H^+})^{(m-y)}}{(\overline{Cat^+})^y (\overline{H^+})^{(m-y)}} \quad (\text{I-13})$$

in logarithmic form:

$$\log D(M) = \log K + p \log(\bar{L}) - y \log(\overline{Cat^+}) + (m-y) \log\left(\frac{\overline{H^+}}{\overline{H^+}}\right) \quad (\text{I-14})$$

anionic exchange occurs due to exchange of anionic species between two phases following the electroneutrality principle:



constant of the cationic exchange is defined as:

$$K = \frac{\left(\overline{MX_{(m+y)}L_p^{y-}}\right)(A^-)^y}{(M^{m+})(\bar{L})^p(X^-)^{(m+y)}} \quad (\text{I-16})$$

coefficient of extraction via cation exchange:

$$D(M) = K \frac{(\bar{L})^p(X^-)^{(m+y)}}{(A^-)^y} \quad (\text{I-17})$$

in logarithmic form:

$$\log D(M) = \log K + p \log(\bar{L}) + (m+y) \log(X^-) - y \log(A^-) \quad (\text{I-18})$$

Another case which should be mentioned is extraction of neutral species – its equilibrium is similar to that in molecular solvents, even though usually is not favorable in ionic liquids (Equation I-6).

constant for neutral extraction:

$$K = \frac{\left(\overline{MX_m L_p}\right)}{(M^{m+})(\bar{L})^p(X)^m} \quad (\text{I-19})$$

On the assumption of the Equation I-14 and I-18: K is a constant of extraction, as well as distribution of protons between two phases $\frac{\overline{H^+}}{H^+} = \text{const}$, therefore D can be affected only by changes in ligand or ions concentrations. Thus, when acid concentration is increasing the factors of negative influence on extraction are:

- metal is locked up in a nonextractable form
- extracting efficiency of a ligand is decreasing
- concentration of Cat^+ in aqueous phase is increasing (cationic exchange case)
- concentration of A^- in aqueous phase is increasing (anionic exchange case)

The influence of Cat^+ and A^- can be verified experimentally by addition of corresponding salt, as in case of $C_1C_n\text{imTf}_2\text{N}$: $C_1C_n\text{imCl}$ and LiTf_2N (see Section I.3.2 – miscibility and Chapter III).

A decrease of extractant efficiency is often due to its protonation. This phenomenon is not studied in ionic liquids yet, therefore some additional experiments have been carried out for the IL systems used in this work (see Chapter III).



$$K = \frac{\left(\overline{LH^+}\right)}{(\bar{L})(\overline{H^+})} \quad (\text{I-21})$$

The chemical equations of extraction mechanisms have been presented by many groups (see reviews [27], [33]). However the mathematical calculations for computer modeling have been performed only by Strasbourg group.

All the phenomena, described in this section, were taken into account for the mathematical modeling of extraction in ILs.

The set of chemical equilibria describing the phenomena occurring in the systems under study is turned to its corresponding set of mathematical equations on the basis of mass action law and mass balance. Some basic assumptions have been done and listed below.

The activity coefficients were fixed to a constant value, thus the extraction constants for the all possible extraction equilibria, K , become conditional constants.

The aqueous complexation constants, K_i , are fixed to their thermodynamic values, as found in literature: $K_1 = 1.99$ and $K_2 = 0.07$ for U(VI)/NO₃⁻; $K_1 = 1.86$ and $K_2 = 0.43$ for Eu(III)/NO₃⁻; $K_1 = 21.38$ for Am(III)/NO₃⁻ [34, 35, 36, 37, 38].

All the species: X , Cat^+ , H^+ , A^- , L are considered in large excess as compared to metal, therefore they are constant quantities. Their values have been taken from the experimental data.

Ligand protonation in the IL phase (Equation I-20, I-21) is also taken into consideration. In case of large protonation, free ligand can become close to metal concentration, therefore a warning is inserted in program, when the free ligand concentration is only a factor of 10 above that of initial concentration of metal. Moreover, we assume that ligand does not dissolve in aqueous phase.

An expression relating D to all initial concentrations (H^+ , ligand etc...) can always be derived. In this expression, the parameters as extraction constants, ligand stoichiometry, number of H^+ , X and Cat^+ , A^- exchanged are also found. This expression is implemented in a Fortran routine, which aims to adjust the parameters to fit the data (least square adjustment). Formula for which is:

$$\chi^2 = \left(\sum \frac{(D_{calc} - D_{exp})^2}{D_{exp}} \right) / N \quad (I-22)$$

where N corresponds to the number of D_{exp} values.

Such a method is also used for protonation studies and is detailed in Chapter III as an example.

All programs were already written at the beginning of my work and were used as received.

1.5 Review of TSILs

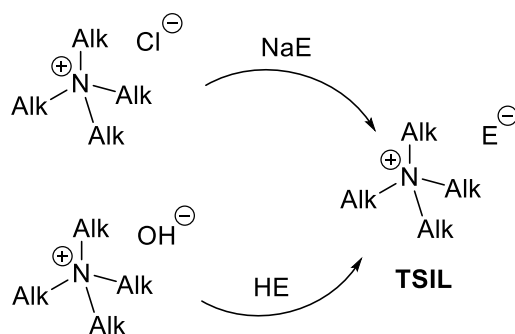
The present review concerns task-specific ionic liquids, whose task is an extraction of different metal cations in biphasic systems.

This section is organized as follows: the TSILs reviewed were classified according to their extracting patterns. Therefore, first, the general information about an extracting pattern (E) and its complexing properties is provided, the synthetic route of the TSILs containing the E is described, and then the information about metal extraction in liquid-liquid systems is given. The emphasis was put on the ILs systems.

There are two different approaches for functionalization of ionic liquids: first - is covalent tethering of an extracting pattern to the cation or anion of IL, second - is formation of FILs by ionic exchange with extracting ions. If we present an ionic liquid as $[Cat]^+[A]^-$, then ionic liquids functionalized by covalent tethering of E will look like $[Cat-E]^+[A]^-$ or $[Cat]^+[A-E]^-$. This concept has been applied for the synthesis of my FILs. The second approach is applied for onium compounds (ammonium, phosphonium cations) and heterocyclic compounds, bearing positive charge (pyridinium, pyrrolidinium). They are combined with certain anions which possess complexing properties, yielding functionalized ILs. Schematically it can be presented as $[Cat]^+[E]^-$.

In present literature review the ionic liquids modified with extracting moieties are called task-specific in order to highlight their application. Thus they are denoted as $TSIL_x$, where x is a consecutive number.

One of the most numerous families of TSILs has been synthesized on the basis of quaternary ammonium salts. The TSILs on their basis can be easily prepared by replacement of the chloride anion to any other “task-specific” one by anion exchange or acid-base neutralization methods (Scheme I-4).



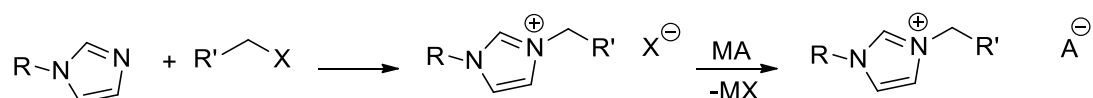
where Alk = Oct, Dec (or their mixture
in case of A336),
E = anion-extractant

Scheme I-4. General synthesis of TSILs with anions-complexants

Most of the times Aliquat 336 (A336) was chosen as a starting material for synthesis, because it is a commercially available reagent. A336 is composed of a 2:1 mixture of methyl trioctylammonium and methyl tridecylammonium chloride [39].

Another very widely used family of ionic liquids is based on imidazolium cation. The starting material for its synthesis is 1-alkylimidazole, which is also a commercially available

reagent, can be easily quaternized with functionalized alkyl halides to afford the corresponding functionalized imidazolium halides.



Scheme I-5. General synthesis of FILs with functionalized cations

I.5.1 Carboxylate TSILs

Many carboxylates are known to strongly bind metal ions [40]. Thus in 2008 the new ammonium TSILs with aliphatic and aromatic carboxylate anions have been obtained by Kogelnig et al. [41]. The equimolar amounts of A336 and corresponding Bronsted acids were stirred in a sodium hydroxide solution. Deprotonation of the acid followed by anion metathesis led to the desired ionic liquids (Figure I-5).

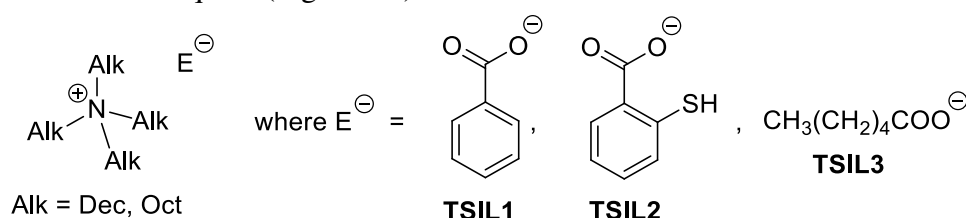


Figure I-5. Tetraalkylammonium TSILs with benzoate and thiosalicylate anions

Compounds **TSIL1-3** appeared to be liquids at room temperature and immiscible with water but miscible with common organic solvents such as ethyl acetate, acetone, ethanol, methanol and acetonitrile. These carboxylate TSILs were evaluated as potential extracting agents for Cd(II). The extraction was performed from ultrapure and natural river water, in both cases the efficiency increases in the row **TSIL1** < **TSIL3** << **TSIL2**. Using **TSIL2** the efficiency of extraction reached *ca.* 99.9%.

A similar carboxylate **TSIL4** has been synthesized by Egorov et al. by mixing A336 and sodium salicylate in chloroform [42].

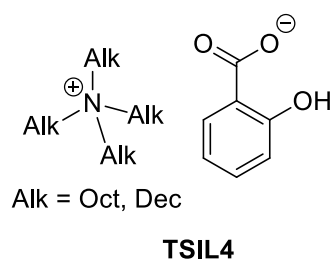
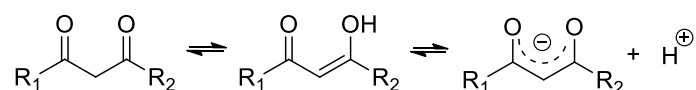


Figure I-6. Tetraalkylammonium TSIL with salicylate anion

Salicylates are known to form the most stable complexes with iron and copper, and in contrary much less stable complexes with Ni(II) and Mn(II). Thus, Fe(III), Cu(II), Ni(II), Mn(II) have been chosen to study the extraction by trioctylmethylammonium salicylate (**TSIL4**). The maximal distribution ratio was observed for Fe(III) and Cu(II) (99% and 89% for 1×10^{-3} M, respectively), and lower distribution ratio for Ni(II), Mn(II) which is in agreement with stability constants of salicylate complexes.

1.5.2 β -Diketonate TSILs

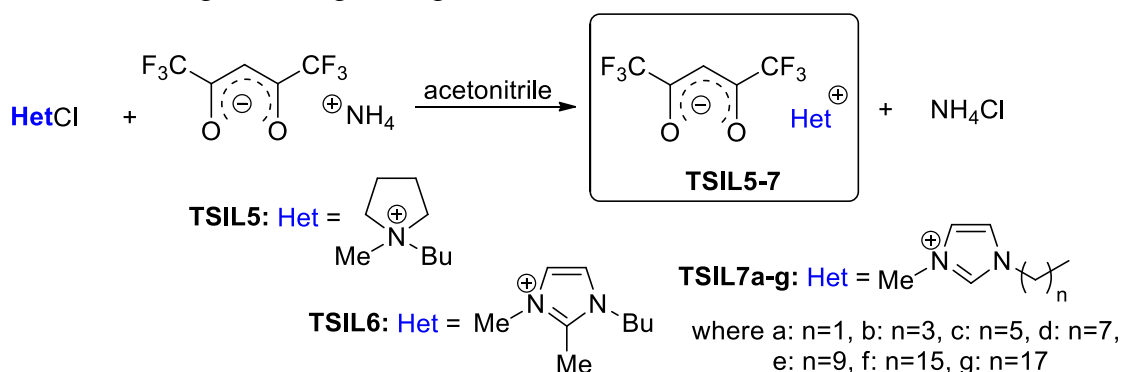
β -diketonates are well known as potent ligands usually after deprotonation to the mono-anion for a wide variety of metal ions. 1,3-Diketones have several advantages over phosphine or oligopyridine ligands due to their relative ease of synthesis, their ready deprotonation under mildly basic conditions and easy formation of both their transition metal and lanthanide complexes. β -diketonates react with metal ions to form neutral chelates through the enolate anions shown by the following equilibria (Scheme I-6):



Scheme I-6. Tautomerization of β -diketonates

1.5.3 Hexafluoroacetylacetonate TSILs

Usually ILs consist of big asymmetric organic cations and weakly coordinating anions (such as PF_6^- , BF_4^- , Tf_2N^- , etc) to prevent the packing into crystals and hereby disfavor the coulombic interactions between the cations and the anions. However the ILs with weakly coordinating anions poorly dissolve metal salts. The weakly coordinating anions can be replaced by strongly coordinating anions (as chloride anion), but in this case the melting points and viscosities are increasing, moreover ILs become more hydrophilic, what makes them inapplicable for liquid-liquid extraction. The solution of this problem was found by Mehdi et al., who obtained ILs with hexafluoroacetylacetonate (hfac) anion [43]. These TSILs (**TSIL5-7**) were prepared by a metathesis reaction between an organic chloride salt and ammonium hexafluoroacetylacetonate in acetonitrile (Scheme I-7). The precipitate of ammonium chloride was filtered off and the acetonitrile solvent was removed under reduced pressure. The residue was redissolved in dichloromethane and washed with water to remove impurities of ammonium chloride until the AgNO_3 test gave negative results for chloride ions.



Scheme I-7. Synthesis of TSILs with hexafluoroacetylacetonate

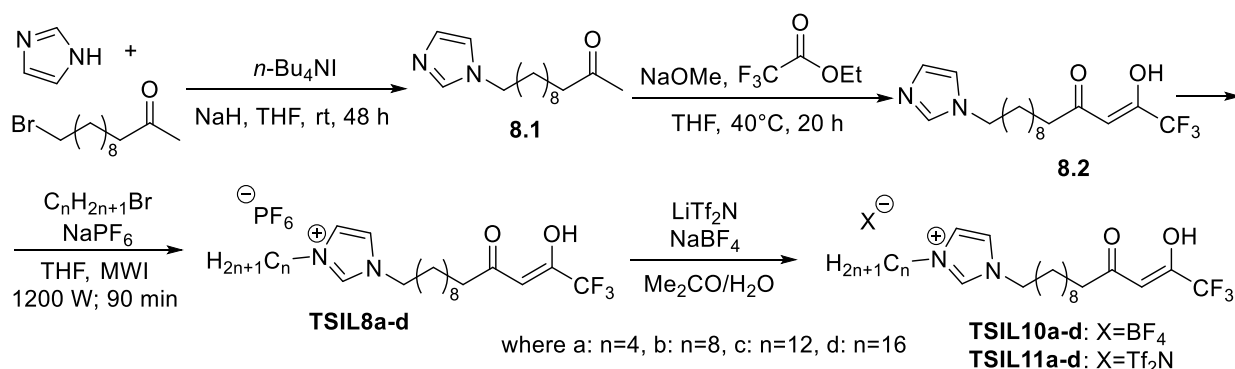
All ILs, with the exception of **TSIL7a**, appeared to be immiscible with water. The hydrophobic ionic liquid **TSIL7b** exhibited a relatively low viscosity ($\eta = 65$ cP at 20°C) and has a low melting point, therefore it was chosen to study complex formation with metal ions (Nd(III), Co(II) and Cu(II)). Metal complexes were formed by bringing the ionic liquid in contact with an aqueous solution of a corresponding salt ($\text{Co}(\text{Tf}_2\text{N})_2$, $\text{Nd}(\text{Tf}_2\text{N})_3$, $\text{Cu}(\text{Tf}_2\text{N})_2$). Metal ions were extracted into the IL phase with formation of corresponding complexes in each

case ($[\text{C}_1\text{C}_4\text{im}][\text{Nd}(\text{hfac})_4]$, ($[\text{C}_1\text{C}_4\text{im}][\text{Co}(\text{hfac})_3]$, ($[\text{C}_1\text{C}_4\text{im}][\text{Cu}(\text{hfac})_3]$), at high metal loading, the complexes precipitate out of the solutions. Their structures have been investigated by means of X-ray spectroscopy.

I.5.4 Trifluoroacetylacetonate TSILs

Olivier et al. have obtained a series of β -diketonate-functionalized ionic liquids on the basis of imidazolium cation [44]. Trifluoroacetylacetonate function (facac) was connected to imidazolium ring via flexible alkane chain from the one side, and from another it has a paraffin chain of various lengths ($n = 4, 8, 12$). Moreover, these functionalized ILs were provided with different anions (PF_6^- , BF_4^- , Tf_2N^-).

The trifluoroacetate **TSIL8a-d**, **TSIL9a-d**, and **TSIL10a-d** were synthesized as shown in Scheme I-8. Imidazolyldodecanone was synthesized by alkylation of imidazole with bromododecanone. Trifluoroacetate group was attached by reaction of imidazolyldodecanone with ethyl trifluoroacetate. The target compounds **TSIL8a-d** were prepared by treating imidazole **8.2** with the corresponding bromoalkane in THF under microwave irradiation (1200 W, 130 °C, 90 min, 4–5 bar). After evaporation of the solvent, the crude product was precipitated as its hexafluorophosphate salt with KPF_6 in THF/water (5:1). Other salts **TSIL9a-d** and **TSIL10a-d** were obtained from THF or water/acetone by using excess NaBF_4 or LiTf_2N as precipitants.



Scheme I-8. Synthesis of trifluoroacetylacetonate TSILs

By means of microscopy observations, DSC analysis and rheological measurements, it was found that all compounds **TSIL8-10a-c** are room temperature ionic liquids, with the exception of C_{16} -compounds (**TSIL8-10d**), which have the longest alkane chains. It's in agreement with literature data, which say that lengthening of substituent leads to increase of van der Waals forces between the hydrocarbon chains and increase structural ordering.

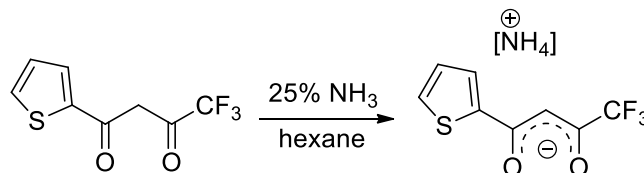
Also it was confirmed that the ILs with Tf_2N^- ions have lower viscosity compared to those ones with PF_6^- , BF_4^- . Moreover, viscosity depends on chain length and decreases in the order $\text{C}_{12} > \text{C}_8 > \text{C}_4$.

TSIL10a ionic liquid as the best fluid and, thus, least viscous one was chosen to study the extraction. **TSIL10a** forms a luminescent complex with $\text{Eu}(\text{III})$ in biphasic system, but the extraction efficiency was rather low in view of absence of stirring/shaking and amounted to 29%. Better results were obtained for solid-liquid extraction of $\text{Eu}(\text{III})$ with **TSIL8a**, $E = 99.8\%$.

I.5.5 Thenoyltrifluoroacetate TSILs

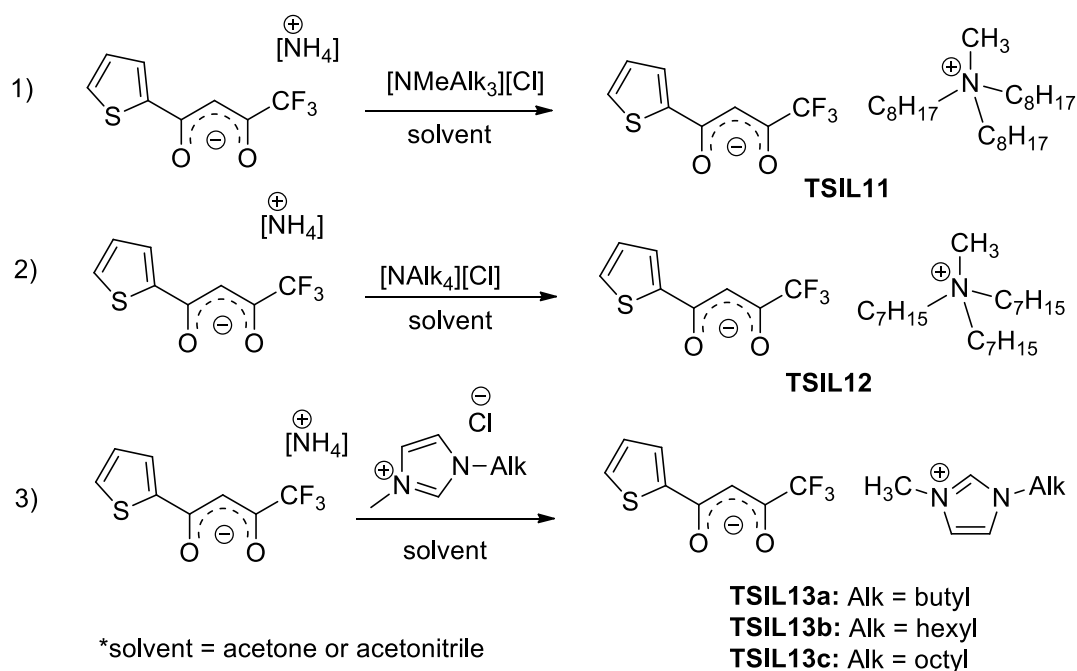
Thenoyltrifluoroacetate (TTA) is a sort of β -diketonates containing thiophene ring. They are known as π -conjugated ligands for lanthanides (and actinides) [45]. Therefore Rout et al. have synthesized TSILs containing thenoyltrifluoroacetate anion and traditional tetraalkyl ammonium and alkylimidazolium cations [46].

Target pattern - ammonium thenoyltrifluoroacetate was prepared by addition of 25% ammonia solution to the solution of thenoyltrifluoroacetone in hexane (Scheme I-9).



Scheme I-9. Synthesis of ammonium thenoyltrifluoroacetate

All TTA ionic liquids were obtained through the general procedure which involves the addition of ammonium thenoyltrifluoroacetate dissolved in acetonitrile (or acetone) to the solutions of corresponding salts as alkylammonium chlorides or methylalkylimidazolium chlorides in similar solvent.



Scheme I-10. Synthesis of TTA ionic liquids.

The TTA ionic liquids synthesized have been studied for the extraction of $^{239}\text{Pu(IV)}$, $^{233}\text{U(VI)}$, and $^{241}\text{Am(III)}$ from nitric acid medium. First of all it should be mentioned that the distribution ratio of U was always lower than *ca.* 3, while Am extraction was negligible.

Concerning Pu extraction, in the case of trioctylammonium thenoyltrifluoroacetate **TSIL11** dissolved in corresponding IL, the distribution coefficients *D* are increasing together with increase of acid concentration and reaches *ca.* 160 at 5M HNO_3 . The authors assume the anion exchange of $[\text{Pu}(\text{NO}_3)_{5+x}]^{-(1+x)}$ species from the aqueous phase with Tf_2N^- from the IL-phase, as it was mentioned in Section I.4.

A very different picture is observed for the imidazolium ionic liquids: **TSIL13**. The curves of extraction have the boomerang shape: initial decrease of distribution ratio $D(Pu)$ is followed by its increase along with rise of acid concentrations. Such an increase was explained by the anion exchange of $[Pu(NO_3)_{5+x}]^{-(1+x)}$ species with $[Tf_2N]^-$. At low acid concentrations the extraction is governed by HTTA (protonated TTA⁻).

1.5.6 Organophosphorus TSILs

Organophosphorus compounds play an important role in nuclear reprocessing. Thus PUREX (plutonium uranium extraction), which is the one of key-processes in nuclear industry, is based on liquid-liquid extraction using tributyl phosphate (TBP) diluted in a kerosene. It provides recovery of more than 99% of both uranium and plutonium as well as ensures excellent decontamination of both elements from fission products.

TBP remains a main extractant for recovery of uranium and plutonium from spent nuclear fuel, that is why many of potential complexants have been synthesized on the basis of TBP or its analogs.

1.5.6.1 Phosphate and phosphonate TSILs

Phosphate, phosphonate and phosphinate TSILs were synthesized using both approaches described in the beginning of Section I.5.

The series of TSILs with anions-complexants has been acquired by the group of Sun. First of all they pointed that A336 was widely used as extractant in solvent extraction [47, 48], and to further enhance the extraction capacity of A336 they developed the TSILs by combining ammonium or phosphonium cation with anions of traditional extractants as di-(2-ethylhexyl)-phosphate (**a**), 2-ethylhexyl phosphoric acid mono(2-ethylhexyl) ester (**b**), and bis(2,4,4-trimethylpentyl)phosphinic acid (**c**).

It was discovered that the TSILs have so-called “inner synergistic” effect, the distribution coefficients of these TSILs are higher than those of the mixed precursors.

The TSILs have been synthesized using acid/base neutralization method, where E^- comes from the traditional extractants mentioned above [49, 50, 51]:

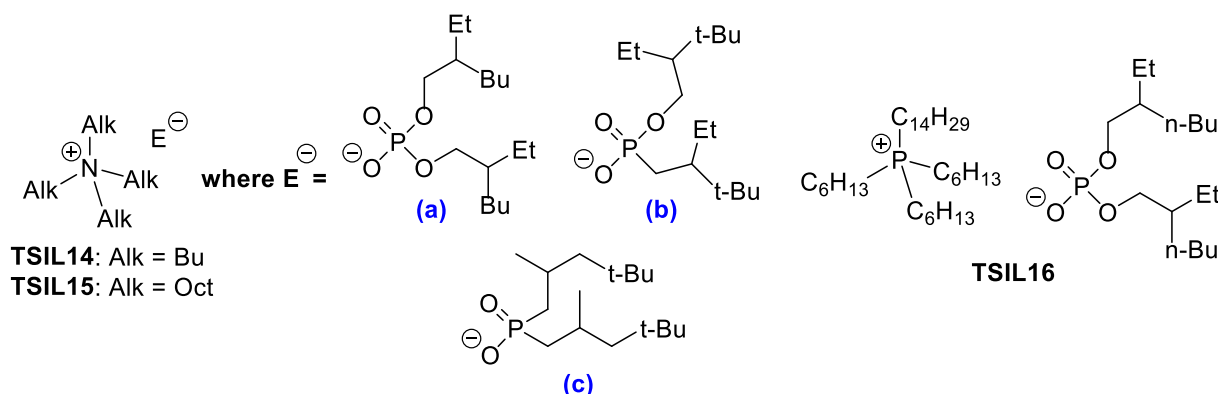


Figure I-7. TSILs on the basis of traditional extractants

First the TSILs synthesized were checked for extraction of Eu(III) in molecular solvents [49]. The next approach of Sun and coworkers was the investigation of the extraction by ammonium TSILs in ionic liquid media. Task-specific ILs with deprotonated di-(2-ethylhexyl)-

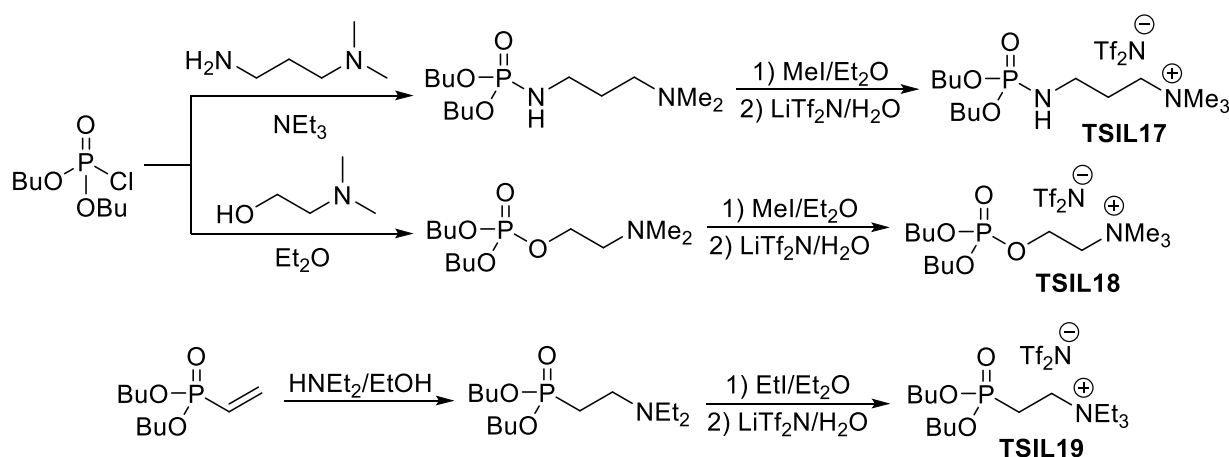
phosphate anion have been evaluated as extractants for rare earth elements in imidazolium ILs $C_1C_n\text{imTf}_2\text{N}$ ($n = 4, 6, 8, 10$) and 1-alkyl-3-methylimidazolium bis(perfluoroethane-sulfonyl)-imide ($C_1C_n\text{imBETI}$, $n = 4, 6, 8, 10$). The results were compared with those of protonated di-(2-ethylhexyl)phosphate in 1,4-diisopropylbenzene. The distribution coefficients of **TSIL14a**, **TSIL15a**, and **TSIL16** are much higher than those for di(2-ethylhexyl)phosphoric acid. The authors attribute it to well-known principle “like dissolves like”.

A novel class of hydrophobic TSILs based on quaternary ammonium cation with covalently tethered phosphoryl groups was obtained by Ouadi et al. [52].

The precursor dibutylchlorophosphate was reacted with *N,N*-dimethyl-1,3-diaminopropane and 2-dimethyl-aminoethanol resulting in the formation of phosphoramidate ester and phosphate, which were converted into corresponding TSILs by quaternization with alkyl iodide and metathesis reaction with LiTf_2N (Scheme I-11).

Phosphonate TSIL5 was obtained from dibutyl vinylphosphonate which was treated with diethylamine, then was subjected to quaternization with ethyl iodide and metathesis with LiTf_2N . All TSILs synthesized appeared to be liquid at room temperature.

TSIL17 and **TSIL19** were rather viscous but **TSIL18** showed a sufficiently low viscosity to be directly employed in liquid-liquid extraction experiments.



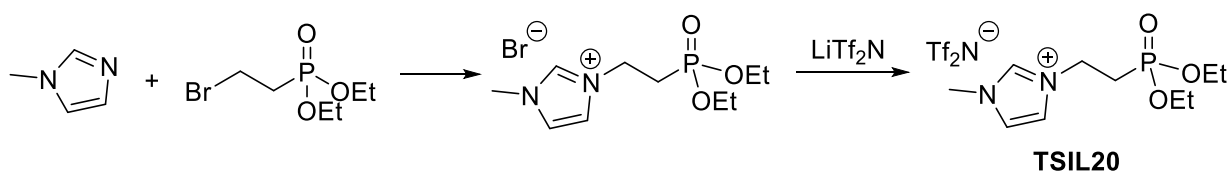
Scheme I-11. Synthesis of phosphoramidate-, phosphate-, and phosphonate-TSILs

The TSILs synthesized have been tested under conditions similar to those of PUREX process: RTILs and TBP for comparison were diluted in the $[\text{Me}_3\text{NBu}][\text{Tf}_2\text{N}]$ up to a 1.1 M solution, and the concentration of nitric acid in the aqueous phase was 3 M.

The extracting properties of the phosphate-TSIL and the phosphonate-TSIL are rather low, in contrast to the phosphoramidate-TSIL with distribution coefficient D ca. 170 (for TBP $D = 4.70$).

Then the method of phosphorylation was applied to imidazolium entities by Rout et al. [25, 53]. It should be mentioned that a similar concept of phosphorylated ionic liquids was also realized in my work, which will be presented in Chapter II.

Methylimidazole was alkylated by bromoethylphosphate at $100\text{ }^\circ\text{C}$ yielding phosphorylated imidazolium bromide. This bromide was treated with LiTf_2N , and **TSIL20** was obtained (Scheme I-12).



Scheme I-12. Synthesis of phosphonate TSIL

TSIL20 appeared to be liquid at ambient temperature and its viscosity was 42 cP at 30 °C.

Extraction of Pu(IV), U(VI), and Am(III) has been investigated using the solutions of ImpNTf₂ in two common ILs C₁C₄Tf₂N and C₁C₈Tf₂N at various concentrations of nitric acid.

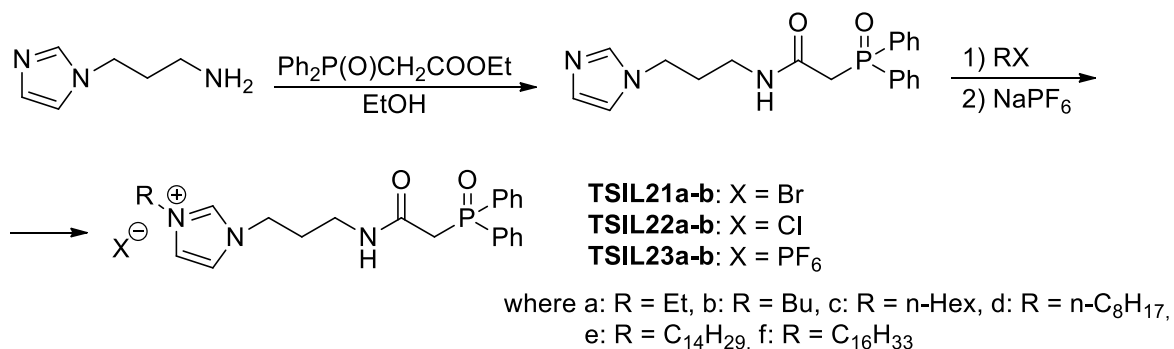
It was observed that distribution ratios of Pu(IV) in C₁C_nTf₂N (*n* = 4, 8) are significant, while the values observed for U(VI) and Am(III) are much less. The distribution ratio in C₁C₈Tf₂N is nearly an order higher than the values observed for C₁C₄Tf₂N, which implies the ion exchange with Tf₂N⁻ (as it was already mentioned for the extraction of Pu(IV) in ILs).

An interesting peculiarity of **TSIL20** is that separation factors $SF_{Pu,U}$ reach values of *ca.* 520 depending of acidity and IL used, while generally, neutral extractants containing phosphoryl group, when used for extraction, exhibit a comparable distribution ratio for U(VI) and Pu(IV). That is why in PUREX process Pu(IV) is separated from U(VI) by changing its redox state to Pu(III).

I.5.6.2 Carbamoylphosphine oxide TSILs

In industry after the separation of uranium and plutonium the next goal is recovery of minor actinides, which constitute the source of the long term radiotoxicity. For the extraction of actinides (and lanthanides) the TRUEX process was developed. It is based on the use of the CMPO (carbamoyl-methyl-phosphine oxide), which is capable of actinide and lanthanide extraction.

First the TSILs with CMPO-moieties were synthesized by Odinet et al. [54]. Functionalized imidazole was obtained via direct amidation of diphenylphosphorylacetic acid ethyl ester with 3-aminopropylimidazole in ethanol solution. The next step was the general procedure of quaternization of (phosphorylmethylcarbamoyl)propylsubstituted imidazole by alkyl halides yielding corresponding imidazolium halides (**TSIL21a-b**, **TSIL22a-b**). The subsequent anion exchange (metathesis) under the treatment with NaPF₆ afforded **TSIL23a-b** with the hexafluorophosphate anion (Scheme I-13).

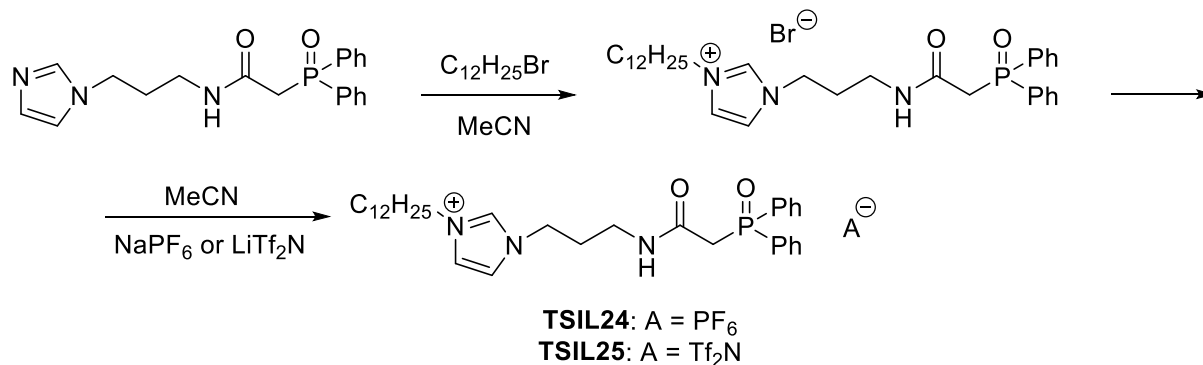


Scheme I-13. Synthesis of CMPO-TSILs

TSIL23a-b were isolated as white hygroscopic solids with melting points in the range of 57–161 °C.

Their extracting properties have been examined via solid extraction, by preparing solid extractants with the TSILs inside. The best extraction results ($E > 90\%$) have been observed for the TSIL with $C_{16}H_{33}$ -alkyl substituent, impregnated into carbon nanotubes matrix.

Liquid-liquid extraction by CMPO-TSILs has been investigated by Mohapatra et al. [28]. For this purpose two task-specific ionic liquids: **TSIL24** and **TSIL25** were synthesized as shown in Scheme I-14 (the chemical route is alike to the previously shown one).



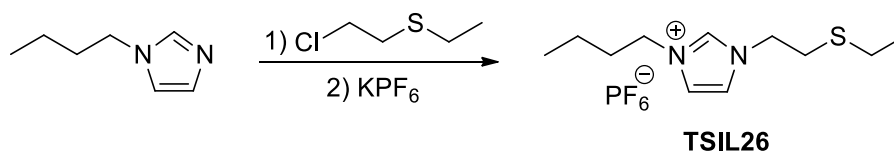
Scheme I-14. Synthesis of CMPO-TSILs

Both TSILs **24**, **25** were tested for the extraction of Am(III), Pu(IV), U(VI), Eu(III) from 3M HNO₃ aqueous phases, using the solutions of these TSILs in C₁C_nimTf₂N ($n = 4, 6, 8$). The data concerning the extraction by **TSIL24** are very few, while for **TSIL25** a detailed study has been performed. The extraction by **TSIL25** is increasing in the series $Eu(III) > Am(III) > U(VI) > Pu(IV)$. The best kinetics and extraction efficiency were observed for the systems with C₁C₄imTf₂N. Moreover the authors have performed the comparison of extraction abilities of the CMPO-TSILs dissolved in ILs with those of CMPO dissolved. However the values obtained for CMPO appeared to be either comparable with CMPO-TSILs ones or even higher.

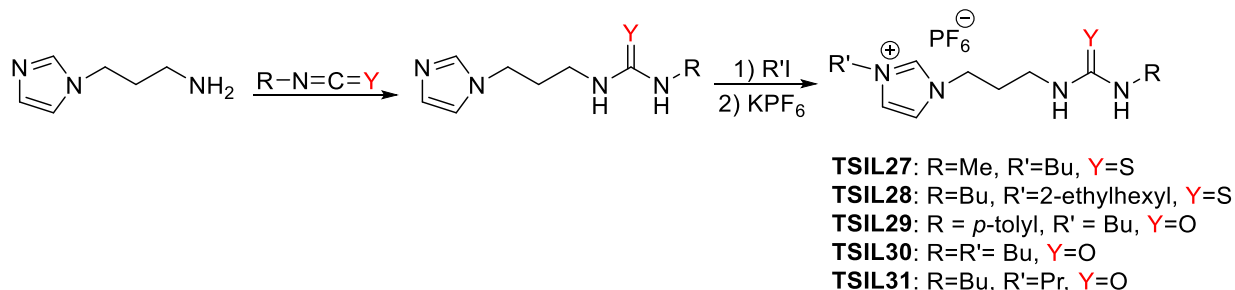
1.5.7 Urea-, thiourea-, and thioether-TSILs

Organic compounds containing chalcogens (in particular S and O) are known to form complexes with heavy metals. For example, thiourea binds such metals as Cr, Zn, Cd, Hg, Pb, Ni, and Co, urea forms inclusion complexes (clathrates) with many molecules. Therefore Visser et al. have chosen these compounds as complexing fragments for the functionalization of the common ionic liquid - C₁C₄imPF₆ [55], [56].

The thioether-**TSIL26** was synthesized as follows: 1-butylimidazole was alkylated with 1-chloro-2-(ethylsulfanyl)ethane, yielding functionalized imidazolium chloride. Chloride anion was exchanged by metathesis reaction with KPF₆ (Scheme I-15). The series of (thio)urea-TSILs (**TSIL27-31**) has been synthesized starting from aminopropyl-imidazole, which was reacted with alkyl isocyanates, resulting in the formation of (thio)urea-imidazoles. Then the imidazole derivatives were treated with a corresponding iodide, giving imidazolium salts, which in turn were subjected to metathesis reaction with KPF₆ (Scheme I-16).



Scheme I-15. Synthesis of thioether-TSILs



Scheme I-16. The synthesis of urea- and thiourea-TSILs

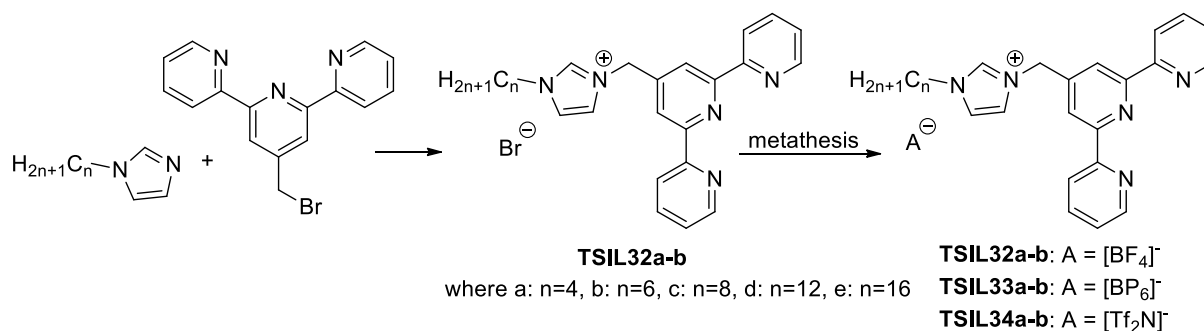
These ionic liquids have been designed to extract Hg(II) and Cd(II) from water phases by means of liquid-liquid extraction. The extraction study has been performed using them as pure phases, or as their 50:50 mixtures in C₁C₄imPF₆ at pH = 1 or 7. In all cases, the distribution ratios of Cd were lower than those of Hg, which can be explained by HSAB theory. It was also found that both the appended functional group and the alkyl substituent on the *N* imidazolium atom affect the extraction. The authors reported that *D* values for Hg(II) are the highest with *urea* > *thiourea with the "tail"* > *thiourea*, while those for Cd(II) decrease from thiourea with the "tail" > *thioether* > *urea* > *thiourea*.

I.5.8 Terpyridine TSILs

Terpyridines are capable of forming complexes with various metal ions, which have found applications in molecular electronics, chemistry of sensors, supramolecular chemistry, and extraction [57].

The imidazolium TSILs containing terpyridine fragments have been obtained and explored by [58].

The terpyridine-imidazolium salts with various alkyl substituents at *N* atom ($n = 4, 6, 8, 12, 16$) and different counterions were synthesized by reaction of terpyridine with corresponding alkylimidazoles under microwave irradiation (Scheme I-17). The salts were purified by precipitation from a CH₂Cl₂-Et₂O mixture. Anion exchange was performed by metathesis reaction with NaBF₄, KPF₆ or LiTf₂N.

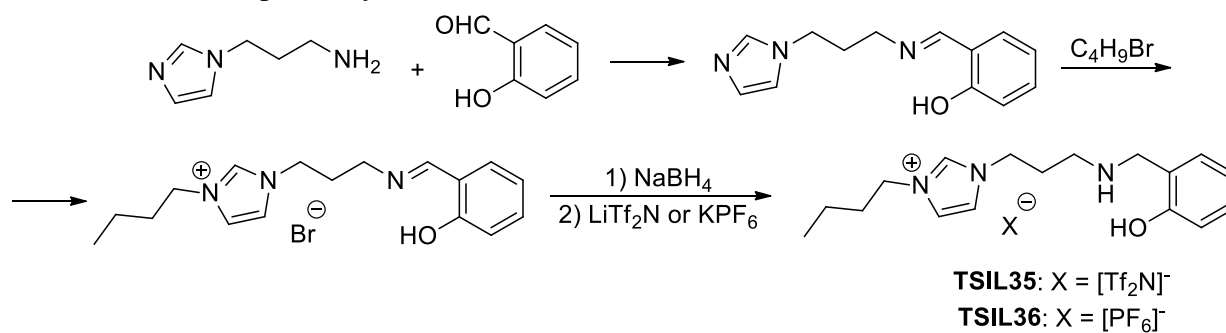


Scheme I-17. Synthesis of terpyridine-imidazolium ionic liquids

The complexing abilities of terpyridine **TSIL34d** have been examined. The ionic liquid used as a pure phase formed a colored complex with Fe(II), which further was isolated by extraction with CH₂Cl₂. The efficiency of extraction reached 99%, but the procedure of phase separation (including CH₂Cl₂) was quite complicated, which causes difficulties in use.

I.5.9 2-Hydroxybenzylamine TSILs

2-Hydroxybenzylamine forms complexes with Co(II), Fe(III), etc. Ouadi et al. obtained the imidazolium TSILs, which contain the 2-hydroxybenzylamine moieties and Tf₂N⁻ or PF₆⁻ as counterions [59]. These compounds have been synthesized via three-step synthesis starting from salicylaldehyde and 3-aminopropylimidazole (Scheme I-18). The imine formed at first stage was alkylated with 1-bromobutane, and the resulting ionic imine was reduced with sodium borohydride. The water-soluble imidazolium bromide was finally transformed into the bis(trifluoromethanesulfonylimide) **TSIL35** and the hexafluorophosphate **TSIL36** by using LiTf₂N or KPF₆, respectively.



Scheme I-18. Synthesis of 2-hydroxybenzylamine-TSILs

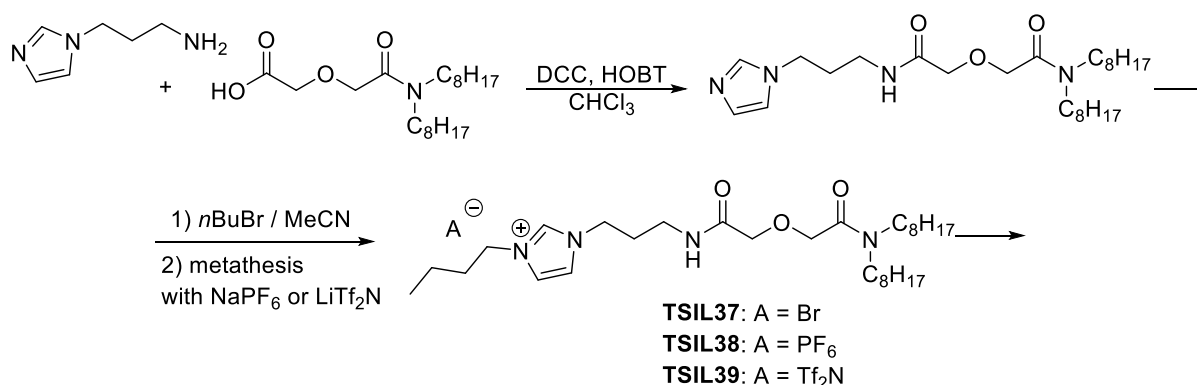
The TSILs synthesized appeared to be viscous oils at room temperature. Further they have been tested for the liquid-liquid extraction of Am(III), and their extracting abilities were compared with those of molecular counterpart – 2-propylaminomethyl-phenol. At identical concentrations, the TSILs extract americium more effectively than the aminophenol. According to the authors the high extracting ability was attributed to the higher hydrophobicity of Tf₂N.

I.5.10 Diglycolamide TSILs

Diglycolamide ligands (DGA) with an ether bridge between the two carbonyl groups were discovered by Sasaki et al. [60]. In the extraction field they are mostly known because of TODGA extractant - *N,N,N',N'*-tetraoctyl-1,5-diglycolamide, which is traditionally used for the extraction of trivalent lanthanides, actinides and other fission products from high-level radioactive waste [61].

TSILs with the DGA patterns have been synthesized by Mohapatra, Sengupta et al. [62, 63]. Commercially available imidazole propanamine was treated with dioctylcarbamoyl-methoxyacetic acid in chloroform by using *N,N'*-dicyclohexylcarbodiimide and 1-hydroxybenzotriazole as coupling agents to afford imidazolidiglycolamide. The functionalized imidazole was further reacted with *n*-butyl bromide in acetonitrile to give ionic liquid **TSIL37** with bromide as the counteranion. The bromide counteranion of compound **TSIL37** was

exchanged with either hexafluorophosphate or bis(trifluoromethane)sulfonamide by treating with NaPF_6 or LiTf_2N , to give DGA-TSILs **TSIL38** and **TSIL39**, respectively.



Scheme I-19. Scheme of synthesis of DGA-TSILs

The DGA-TSILs (**TSIL38**, **TSIL39**) were tested for the extraction of actinides and fission products. In the extraction experiments these TSILs were used as pure phases: $M^{m+} / \text{HNO}_3 // \text{TSIL}$ and were compared with a traditional extractant TODGA, diluted in ILs and dodecane. The D values for Am(III) and Eu(III) by using DGA-TSILs were very high – of the order 10^3 and 10^4 respectively, and exceeded those of TODGA by several orders of magnitude. The extraction abilities of the TSILs are decreasing in the series:

$\text{Eu(III)} > \text{Am(III)} \gg \text{Pu(IV)} > \text{Np(IV)} \gg \text{U(VI)} \gg \text{Sr(II)} \approx \text{Cs(I)}$,

which makes them very promising extractants for trivalent actinides.

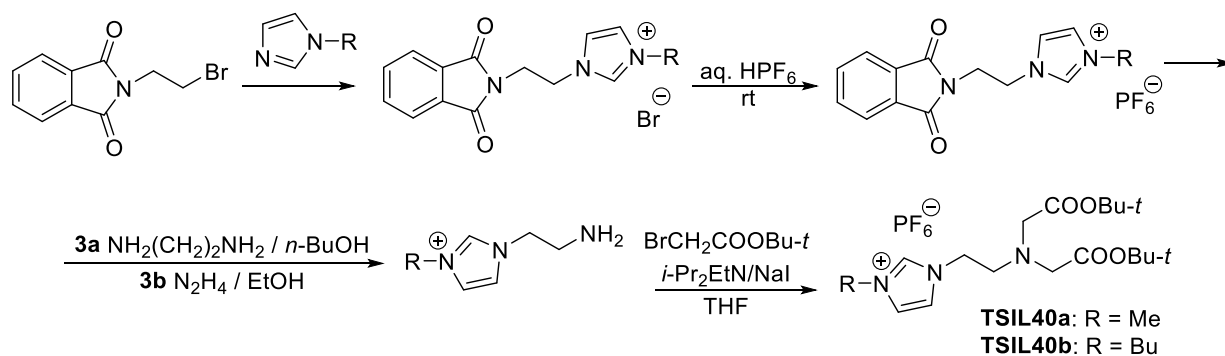
The separation factors were: $\text{SF}_{\text{Eu/Am}} = 8.88$ for **TSIL38** and $\text{SF}_{\text{Eu/Am}} = 4.89$ for **TSIL39**.

I.5.11 Iminodiacetic TSILs

Iminodiacetic acid is a dicarboxylic acid amine, which in its anion form can act as a tridentate ligand to form metal complexes.

Thus a new class of imidazolium ionic liquids with appended iminodiacetic acid moieties has been synthesized and investigated by Harjani et al. [64].

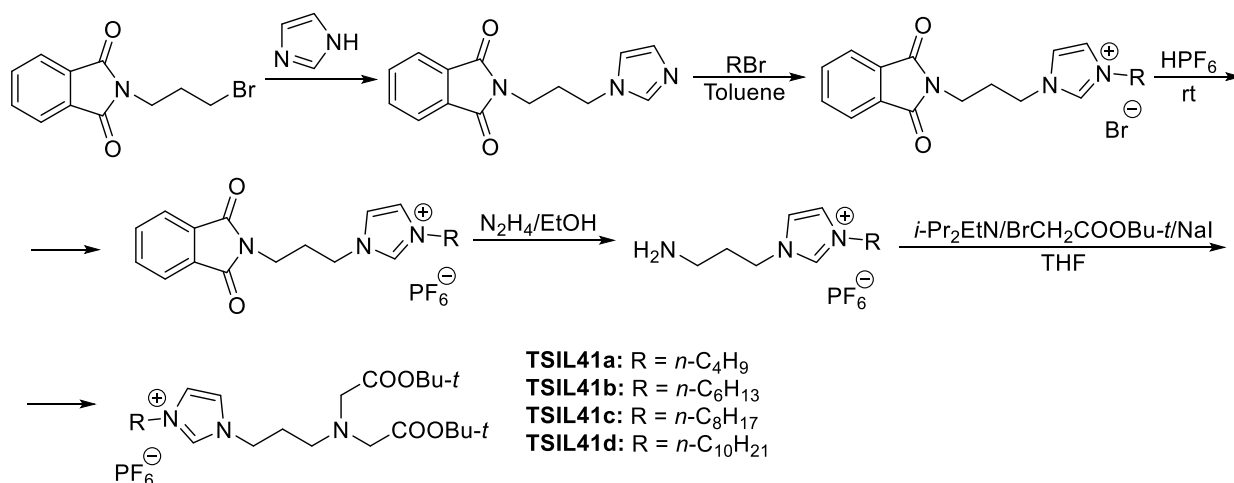
The synthesis is presented in Scheme I-20. 1-Alkylimidazole was quarternized with *N*-(2-bromoethyl)phthalimide, resulting in the formation of the quaternary bromide salt. The water-soluble quaternary bromide was subjected to an anion-exchange reaction with an aqueous solution of HPF_6 , resulting in the formation of an imidazolium salt with a phthaloyl group on the side chain and PF_6^- as the counteranion. This hexafluorophosphate salt was then subjected to deprotection of the phthaloyl group with ethylenediamine in 1-butanol (or with hydrazine in ethanol), to result in the formation of the imidazolium salt carrying an amino group in the side chain, namely, alkylimidazolium hexafluorophosphate. The amino-functionalized imidazolium salt was then subjected to base-promoted *N,N*-dialkylation using 2 equiv of *tert*-butylbromoacetate so as to afford the diester of aminodiacetic acid.



Scheme I-20. Synthesis of ethylaminodiacetic task-specific ionic liquids

It was found that the increase in alkyl chain length from *C1* to *C4* (**TSIL40a**, **TSIL40b**) decreases the melting point from 91 °C to 69 °C.

Moreover the synthetic route was changed in order to generate the imidazole derivative with phthaloyl group on the side chain which is solid, and therefore easy to handle and purify. This imidazole derivative was used for the synthesis of the imidazolium ILs with appended propylaminodiacetic moiety and *C4*, *C6*, *C8*, and *C10* side chains. The synthetic procedures used for quaternization, metathesis, dephthaloylation and *N,N*-dialkylation are essentially the same as used earlier in Scheme I-21.



Scheme I-21. Synthesis propylaminodiacetic task-specific ionic liquids

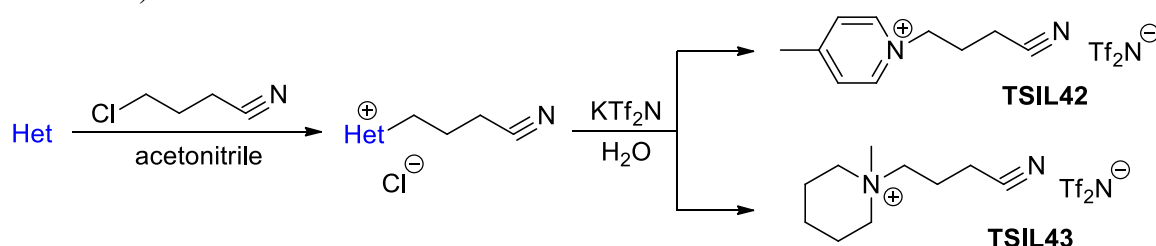
The TSILs synthesized (**TSIL40a-b** and **TSIL41a-d**) have been tested for their complexing properties by the formation of metal chelates with Cu(II), Ni(II) and Co(II) in aqueous solutions.

First the aminodiacetic moieties in the compounds **TSIL40a-b** and **TSIL41a-b** were detertbutylated by reacting with trifluoroacetic acid. The addition of metal halide salt followed by adjustment of the pH with aqueous ammonia resulted in the formation of octahedral complexes of 2:1 ratio of the complexing TSIL-based ligand to the metal cation. It appeared that the ligand used to chelate metal is zwitterionic imidazolium alkylaminodiacarboxylate ligand with a (-1) overall charge, therefore the resulting complex is neutral. According to the authors the composing hexafluorophosphate ion is not required anymore, and probably was removed as NH₄PF₆(aq) during the formation of the complex. Thus the concept of ionic liquid disappears, moreover the use of such IL in liquid-liquid extraction will lead to its losses.

1.5.12 TSILs with bis-sulfide and nitrile functional groups

It is known that ionic liquids composed of pyridinium with appended nitrile group are able to form stable complexes with Pd(II) [65]. Papaiconomou et al. investigated the role of a pyridinium cation and nitrile function group on the extraction properties of corresponding TSILs [66].

For this purpose the ionic liquids with grafted nitrile group to either a pyridinium or a piperidinium cation have been synthesized. A heterocyclic compound (**Het** = 4-methylpyridine or 1-methylpiperidine) was alkylated with 4-chlorobutyronitrile resulting in the formation of corresponding chloride. Then chloride anion was exchanged with bistriflimide anion by metathesis reaction, resulting in the formation of pyridinium **TSIL42** and piperidinium **TSIL43** (Scheme I-22).



Scheme I-22. General features of synthesis of nitrile TSILs

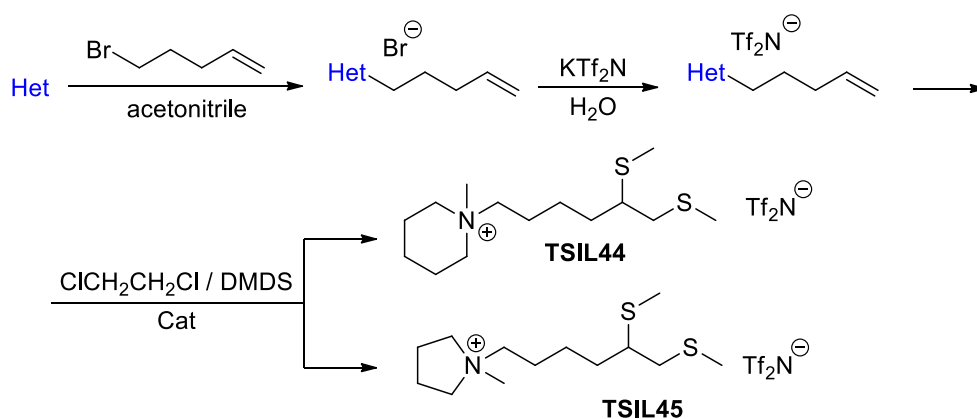
The extracting properties of the nitrile TSILs were tested by means of liquid-liquid extraction. It was found that both nitrile TSILs fully extract Pd(II) from aqueous phases, while Ag(I) and some other metals are better extracted by the pyridinium TSIL compared to the piperidinium one. Thus the authors conclude that results significantly depend on the cation, but that supplementary data is needed.

The effect of nitrile group was estimated by comparison of extracting properties of the TSILs with their non-modified analogues for several metals (except Ag and Pd). The authors claim that the metal distribution coefficients in the case of the TSILs are one order of magnitude higher than those of non-modified ILs, however all the D values obtained are rather low (e.g. 0.22 vs 1.35 for Hg(II)).

Another aspect of interest was the study of extracting abilities of sulfur-containing TSILs, since mercury and sulfur are known to interact strongly.

The TSILs with bis-sulfide functional groups on the basis of piperidinium and pyrrolidinium (**TSIL44**, **TSIL45**) have been synthesized via a similar procedure as describe above. The disulfide group was introduced by the catalyzed reaction with dimethyl disulfide (Scheme I-23).

As expected, Hg(I) was completely extracted by the piperidinium and pyrrolidinium disulfide TSILs, even though similar distribution coefficients were also observed for non-functionalized pyridinium ILs. Therefore the data obtained are not enough to make a conclusion about effect of a cation or a function group. Apart of that, both disulfide TSILs demonstrated high capability of Cu(II) extraction ($D > 1000$), while Sn(IV) was extracted only by pyrrolidinium TSIL, which can be related to the nature of the cationic part.



Scheme I-23. The general synthesis of disulfide TSILs

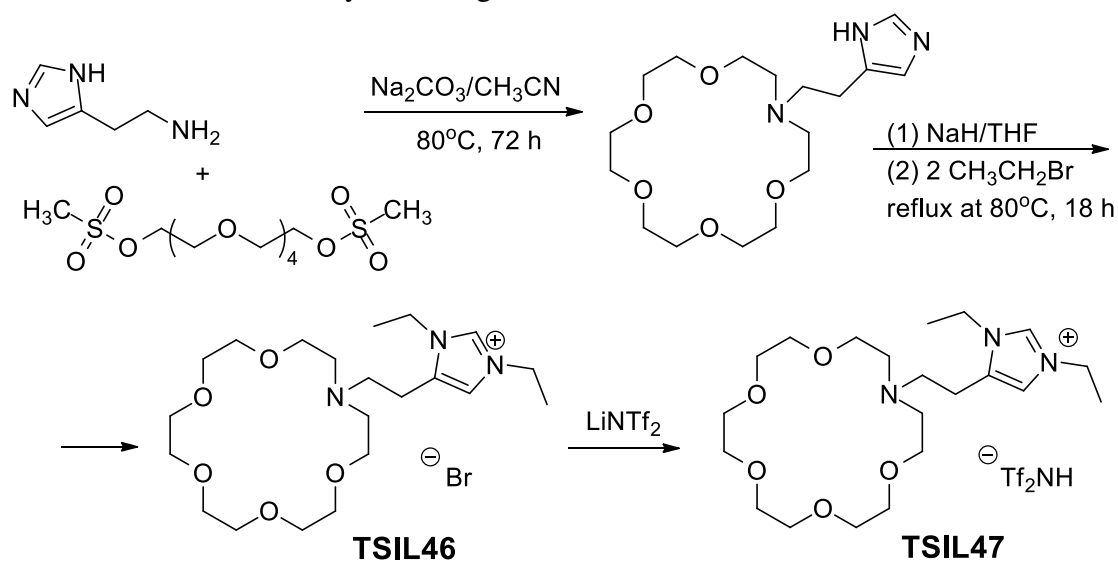
I.5.13 Crown ether TSILs

Crown ethers are cyclic compounds that consist of several ether groups [67]. They appeared to be very strong “guest-host” complexants for metal cations: 18-crown-6 has high affinity for potassium cation, 15-crown-5 for sodium cation, and 12-crown-4 for lithium cation. The oxygen atoms of crown ethers are well situated to coordinate with a cation located at the interior of the ring, whereas the exterior of the ring is hydrophobic. The complex formed becomes soluble in organic solvent, which favors phase transfer.

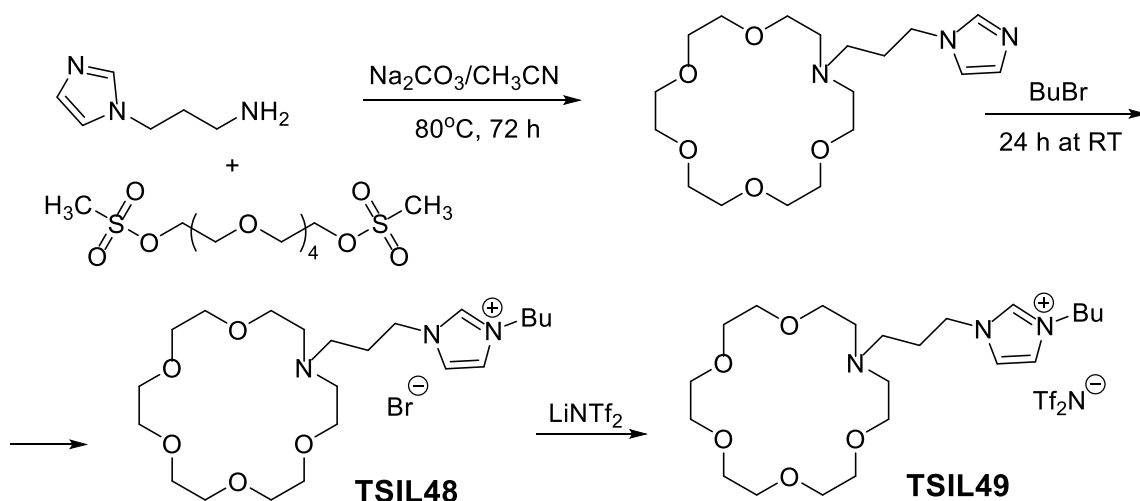
In extraction application dicyclohexyl-18-crown-6 is known to form a strong complex with Sr(II). Moreover, Dai et al. reported that dicyclohexyl-18-crown-6 dissolved in ILs extracts Sr(II) several orders of magnitude better in comparison to the extraction in organic solvents [68].

Thus the idea of TSILs with crown ether moieties has been realized by Luo and coworkers [69]. These new TSILs can be considered as derivatives of the imidazolium family $\text{C}_1\text{C}_n\text{imTf}_2\text{N}$.

The reactions used for synthesizing these TSILs are illustrated in Schemes I-24 and I-25.



Scheme I-24. Synthesis of monoaza-crown ether TSIL



Scheme I-25. Synthesis of monoaza-crown ether TSIL

By treating histamine dihydrochloride or 1-(3-aminopropyl)-imidazole with pentaethylene glycol dimethylate two imidazole derivatives with monoaza-18-crown-6 fragments were obtained. Further alkylation and metathesis reaction led to four new **TSILs46-48**. These compounds differ in the structure of the imidazolium cation and conjugated anions.

The task-specific ionic liquids containing the aza-crown ether fragment were synthesized in order to investigate their potential applications in liquid-liquid extraction of Cs(I) and Sr(II). Thus the extraction experiments have been performed for **TSIL47** and **TSIL49** (since they are more hydrophobic), dicyclohexyl-18-crown-6 and *N*-octylaza18-crown-6 for comparison. Both substances extract Cs and Sr, but their efficiency is lower than the efficiency of the above mentioned crown ethers. Authors claim that the reduction of the extraction capabilities of **TSIL47** and **TSIL49** in comparison with those of crown ethers can be attributed to the cationic imidazolium groups in both compounds, which repel the binding of cationic species, such as Cs(I) and Sr(II) (Coulombic repulsion from the covalently attached imidazolium cation). This is closely related to my work and will be discussed in Chapter III.

I.5.14 Calixarene-TSILs

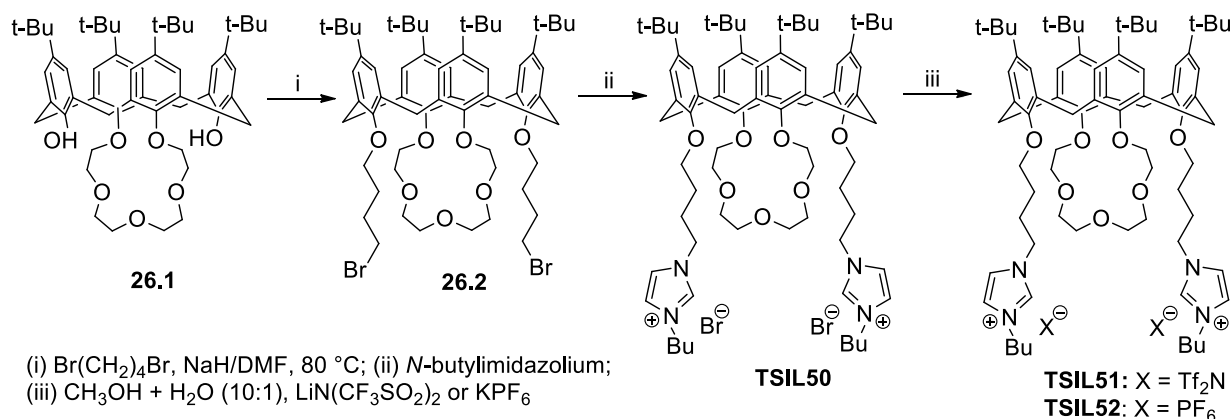
Another very promising idea was to synthesize TSILs on the basis of calixarenes.

Calix[*n*]arenes are a class of macrocyclic compounds, obtained by cyclocondensation of *para*-substituted phenols with formaldehydes, where *n* is the number of phenolic rings [70] (see Chapter II). They have received much attention due to their three-dimensional structure, which can be modified with different functional groups. Therefore calixarenes are used as building blocks for the synthesis of different complexants, and their derivatives are widely applied for binding and recognition of metal ions, neutral molecules and ions. Such interest can be explained by so called preorganization effect of calixarene platform, when the functional groups placed on the calixarene platform act more efficiently than a sum of them.

Concerning liquid-liquid extraction there is large amount of data about calixarenes as extractants, bearing different functional groups like crown ether, carbamoyl phosphine oxide, carboxylate, amide, etc. Recently some functionalized calixarenes have been checked in ionic liquid extracting systems toward different metal cations [71, 72, 73, 74]. Also there are very few examples of calixarenes containing the fragments of ionic liquids [75, 76].

The idea of the TSIL on the calixarene platform has been realized by Jin et al. [75]. They synthesized the tetra-*tert*-butylcalixarene containing the crown-5 extracting pattern along with imidazolium fragment at its lower rim.

Starting calix[4]arene-crown-5 was alkylated with dibromobutane at basic conditions giving the dibromobutoxycalixarene (Scheme I-26). The calix[4]arene **TSIL50** was prepared by the reaction of the dibromobutoxycalixarene and *N*-butylimidazole under neat conditions at 80 °C. Metathesis of **TSIL50** with two metal salts (Tf₂N or KPF₆) led to the formation of two quaternary salts **TSIL51** and **TSIL52** respectively, which exist in cone conformations.



Scheme I-26. Synthesis of a calix[4]arene-crown-5 with fragments of imidazolium salts.

The melting points of the calixarenes **TSIL51** and **TSIL52** are 38 °C and 56 °C respectively. Thus these compounds can be regarded as ionic liquids according to their general definition.

To learn about the extractive interactions of **TSIL52** with alkali metal salts, ¹H NMR titration experiments were carried out. The changes in the proton spectra evidence the complexation of cations K. While ¹H NMR titration experiments using NaSCN caused no change in the proton spectra, which clearly indicated that **TSIL52** has a higher selectivity and stronger binding ability with K than with Na.

1.6 Conclusions

The aim of this Chapter was providing the information background about ionic liquids in respect to liquid-liquid extraction. It was shown that ILs are very versatile, thus may possess different physicochemical properties. Liquid-liquid extraction requires the ILs which, of course, are liquid at ambient temperatures, have low viscosity, are stable under acidic conditions and radiolysis, nontoxic.

The last section of the literature review was dedicated to task-specific ionic liquids. It was shown that almost any complexing pattern can be appended on the ionic liquid frame, making them capable of metal cation extraction. However the majority of the FILs synthesized today have been obtained by modification of cation, while anionic FILs remain very few. Therefore the aim of present work was to develop the new functionalized ionic liquids, bearing the extracting moieties grafted on cation and on anion parts for further comparison of their extracting abilities.

-
- 4 S.B. Savvin, *Arsenazo III*, Atomizdat: Moskva, **1966**, 172 (in Russian)
 - 5 G. Ackerman, J. Kothe, *Talanta* **1979**, *26*, 693-703
 - 6 J. S.Wilkes, J. A. Levisky, R. A.Wilson, C. L. Hussey, *Inorg. Chem.* **1982**, *21*, 1263-1264
 - 7 A. A. Fannin, D. A. Floreani,; L. A. King, J. S. Landers, B. J. Piersma, D. J. Stech, R. L. Vaughn, J. S. Wilkes, J. L. Williams, *J. Phys. Chem.* **1984**, *88*, 2614-2621
 - 8 T. Welton, P. Wasserscheid, *Ionic Liquids in Synthesis*, Vol. 1, Wiley VCH, Weinheim, **2003**, Chapter 3
 - 9 J.-H. Olivier, F. Camerel, J. Selb, P. Retailleau, R. Ziessel, *Chem. Commun. (Camb)*. **2009**, 1133–1135
 - 10 Zh.-B. Zhou, H. Matsumoto, K. Tatsumi, *Chem. Eur. J.* **2004**, *10*, 6581-6591
 - 11 Zh.-B. Zhou, H. Matsumoto, K. Tatsumi, *Chem. Eur. J.* **2005**, *11*, 752-766
 - 12 O. D. Gupta, B. Twamley, J. M. Shreeve, *Tetrahedron Lett.* **2004**, *45*, 1733-1736
 - 13 G. Zhou, H. Bai, G. Xie, J. Xiao, *J. Chromatogr. A* **2008**, 1177, 43-49
 - 14 T. V. Hoogerstraete, B. Onghema, K. Binnemans, *J. Phys. Chem. Lett.* **2013**, *4*, 1659-1663
 - 15 M. G. Freire, C. M. S. S. Neves, P. J. Carvalho, R. L. Gardas, A. M. Fernandes, I. M. Marrucho, L. M. N. B. F. Santos, J. a P. Coutinho, *J. Phys. Chem. B* **2007**, *111*, 13082–13089
 - 16 K. Rehak, P. Moravek, M. Strejc, *Fluid Phase Equilibr.* **2012**, *316*, 17-25
 - 17 V. Mazan, I. Billard, N. Papaiconomou, *RSC Adv.* **2014**, *4*, 13371-13384
 - 18 L. Berthon, S. I. Nikitenko, I. Bisel, C. Berthon, M. Faucon, B.Saucerotte, N. Zorz and P. Moisy, *Dalton Trans.*, **2006**, *21*, 2526–2534
 - 19 L. Berthon, S. I. Nikitenko, I. Bisel, C. Berthon, M. Faucon, B. Saucerotte, N. Zorz, P. Moisy, *Dalton Trans.* **2006**, *21*, 2526–2534
 - 20 E. Bosse, L. Berthon, N. Zorz, J. Monget, C. Berthon, I. Bisel, S. Legand, P. Moisy, *Dalton Trans.* **2008**, *7*, 924–931
 - 21 G. Le Rouzo, C. Lamouroux, V. Dauvois, A. Dannoux, S. Legand, D. Durand, P. Moisy, G. Moutiers, *Dalton Trans.* **2009**, *31*, 6175–6184
 - 22 L. Yuan, J. Peng, L. Xu, M. Zhai, J. Li, G. Wei, *Dalton Trans.* **2008**, *48*, 6358–6360
 - 23 S. Riyaz, a. Indrasena, a. Naidu, P. Dubey, *Synth. Commun.* **2014**, *44*, 368–373
 - 24 J. Fraga-Dubreuil, J. P. Bazureau, *Tetrahedron Lett.* **2001**, *42*, 6097–6100
 - 25 A. Rout, K. A. Venkatesan, T. G. Srinivasan, P. R. Vasudeva Rao, *Radiochim. Acta* **2010**, *98*, 459–466
 - 26 K. Shimojo, K. Kurahashi, H. Naganawa, *Dalton Trans.* **2008**, *37*, 5083–5088
 - 27 I. Billard, *Handbook on the Physics and Chemistry of Rare Earth*, Vol. 43, Chapter 256, Elsevier, Amsterdam, **2013**
 - 28 P. K. Mohapatra, P. Kandwal, M. Iqbal, J. Huskens, M. S. Murali, W. Verboom, *Dalton Trans.* **2013**, *42*, 4343–4347
 - 29 M. Bonnaffé-Moity, A. Ouadi, S. Miroshnichenko, V. Mazan, D. Ternova, M. Sypula, C. Gaillard, I. Billard, S. Georg, *Dalton Trans.* **2012**, *41*, 7526-7536
 - 30 T. J. Bel, Y. Ikeda, *Dalton Trans.* **2011**, *40*, 10125-10130
 - 31 M.L. Dietz, S. Jakab, K. Yamato, R.A. Bartsch, *Green Chem.* **2008**, *10*, 174-176
 - 32 I. Billard, A. Ouadi, E. Jobin, J. Champion, C. Gaillard, S. Georg, *Solv. Extr. Ion Exchange* **2011**, *29*, 577-601
 - 33 X. Sun, H. Luo, S. Dai, *Chem. Rev.* **2012**, 2100–2128
 - 34 A. Ruas, O. Bernard, B. Caniffi, J. P. Simonin, P. Turq, L. Blum and P. Moisy, *J. Phys. Chem. B* **2006**, *110*, 3435-3440
 - 35 L. Sémon, C. Boehme, I. Billard, C. Hennig, K. Lützenkirchen, T. Reich, A. Roßberg, I. Rossini, G. Wipff, *J. Chem. Phys. Chem.* **2001**, *2*, 591–598
 - 36 S. Andersson, K. Eberhardt, C. Ekberg, J. O. Lijenzin, M. Nilsson, G. Skarnemark, *Radiochim. Acta* **2006**, *94*, 469-474
 - 37 A. Nehlig, M. Elhabiri, I. Billard, A. M. Albrecht-Gary, K. Lützenkirchen, *Radiochim. Acta* **2003**, *91*, 37-43
 - 38 R. Guillaumont, T. Fanghanel, J. Fuger, I. Grenthe, V. Neck, D. A. Palmer, M. H. Rand, *Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium*, Elsevier, Amsterdam, **2003**
 - 39 J.-P. Mikkola, P. Virtanen, R. Sjöholm, *Green Chem.* **2006**, *8*, 197–250

-
- 40 G. Wilkinson, *Comprehensive coordination chemistry: The synthesis, reactions, properties and applications of coordination compounds, Vol. 2, Chapter 15.6*, Pergamon Press, Oxford, **1987**
- 41 D. Kogelnig, A. Stojanovic, M. Galanski, M. Groessel, F. Jirsa, R. Krachler, B. K. Keppler, *Tetrahedron Lett.* **2008**, *49*, 2782–2785
- 42 V. M. Egorov, D. I. Djigailo, D. S. Momotenko, D. V Chernyshov, I. I. Torocheshnikova, S. V Smirnova, I. V. Pletnev, *Talanta* **2010**, *80*, 1177–1182
- 43 H. Mehdi, K. Binnemans, K. Van Hecke, L. Van Meervelt, P. Nockemann, *Chem. Commun. (Camb)*. **2010**, *46*, 234–236
- 44 J.-H. Olivier, F. Camerel, R. Ziessel, *Chemistry* **2011**, *17*, 9113–9122
- 45 J. Alstad, J. H. Augustson, I. Farbu, *J. Inorg. Nucl. Chem.* **1974**, *36*, 899–903
- 46 A. Rout, K. a. Venkatesan, T. G. Srinivasan, P. R. Vasudeva Rao, *Solv. Extr. Ion Exch.* **2011**, *29*, 602–618
- 47 C. J. Fowler, T. J. Haverlock, B. A. Moyer, J. A. Shriver, D. E. Gross, M. Marquez, J. L. Sessler, M. A. Hossain, K. Bowman-James, *J. Am. Chem. Soc.* **2008**, *130*, 14386–14387
- 48 E. Marguá, C. Fontàs, K. Van Meel, R. Van Grieken, I. Queral, M. Hidalgo, *Anal. Chem.* **2008**, *80*, 2357–2364
- 49 X. Sun, Y. Ji, F. Hu, B. He, J. Chen, D. Li, *Talanta* **2010**, *81*, 1877–1883
- 50 X. Sun, H. Luo, S. Dai, *Talanta* **2012**, *90*, 132–137
- 51 X. Sun, H. Luo, S. Dai, *Dalton Trans.* **2013**, *42*, 8270–8275
- 52 A. Ouadi, O. Klimchuk, C. Gaillard, I. Billard, *Green Chem.* **2007**, *9*, 1160–1162
- 53 A. Rout, K. A. Venkatesan, T. G. Srinivasan, P. R. V. Rao, *Desalin. Water Treat.* **2012**, *38*, 179–183
- 54 I. L. Odinets, E. V Sharova, O. I. Artyshin, K. A. Lyssenko, Y. V Nelyubina, G. V. Myasoedova, N. P. Molochnikova, E. A. Zakharchenko, *Dalton Trans.* **2010**, *39*, 4170–4178.
- 55 A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis, R. D. Rogers, *Environ. Sci. Technol.* **2002**, *36*, 2523–2529.
- 56 A. E. Visser, R. P. Swatloski, W. M. Reichert, J. H. Davis Jr., R. D. Rogers, R. Mayton, S. Sheff, A. Wierzbicki, *Chem. Commun.* **2001**, *1*, 135–136.
- 57 U. S. Schubert, H. Hofmeier, G. R. Newkome, *Modern Terpyridine Chemistry*, Wiley-VCH, Weinheim, **2006**
- 58 J.-H. Olivier, F. Camerel, J. Selb, P. Retailleau, R. Ziessel, *Chem. Commun.* **2009**, *9*, 1133–1135
- 59 A. Ouadi, B. Gadenne, P. Hesemann, J. J. E. Moreau, I. Billard, C. Gaillard, S. Mekki, G. Moutiers, *Chem. Eur. J.* **2006**, *12*, 3074–3081
- 60 Y. Sasaki, G. R. Choppin, *Anal. Sci.* **1996**, *12*, 225–230
- 61 G. Modolo, H. Asp, C. Schreinemachers, H. Vijgen, *Solvent Extr. Ion Exch.* **2007**, *25*, 703–721
- 62 A. Sengupta, P. K. Mohapatra, M. Iqbal, J. Huskens, W. Verboom, *Sep. Purif. Technol.* **2013**, *118*, 264–270
- 63 P. K. Mohapatra, A. Sengupta, M. Iqbal, J. Huskens, W. Verboom, *Chemistry* **2013**, *19*, 3230–3238
- 64 J. R. Harjani, T. Frišćić, L. R. MacGillivray, R. D. Singer, *Dalt. Trans.* **2008**, *34*, 4595–4601
- 65 D. Zhao, Z. Fei, T. J. Geldbach, R. Scopelliti, P. J. Dyson, *J. Am. Chem. Soc.* **2004**, *126*, 15876–15882
- 66 N. Papaiconomou, J.-M. Lee, J. Salminen, M. von Stosch, J. M. Prausnitz, *Ind. Eng. Chem. Res* **2008**, *47*, 5080–5086
- 67 M. Hiraoka, *Crown Compounds: Their Characteristics and Applications*, Elsevier, Amsterdam, **1982**
- 68 S. Dai, Y. H. Ju, C. E. Barnes, *J. Chem. Soc., Dalton Trans.* **1999**, *8*, 1201–1202
- 69 H. Luo, S. Dai, P. V. Bonnesen, A. C. Buchanan, *J. Alloys Compd.* **2006**, *418*, 195–199
- 70 C. D. Gutsche, *Calixarenes*, Cambridge: Royal Society of Chemistry, **1989**
- 71 K. Shimojo, M. Goto, *Anal. Chem.* **2004**, *76*, 5039–5044
- 72 C. Xu, L. Yuan, X. Shen, M. Zhai, *Dalton Trans.* **2010**, *39*, 3897–3902
- 73 A. Sengupta, P. K. Mohapatra, M. Iqbal, J. Huskens, W. Verboom, *Dalton Trans.* **2012**, *41*, 6970–6979
- 74 L. Ma, X. Zhu, W. Wang, *J. Mol. Liq.* **2013**, *178*, 20–24
- 75 C. Jin, J. M. Shreeve, **2004**, *43*, 1215–1221
- 76 F. Yang, H. Guo, Z. Jiao, C. Li, J. Ye, *J. Iran. Chem. Soc.* **2012**, *9*, 327–332

II. CHAPTER: SYNTHESIS OF FUNCTIONALIZED IONIC LIQUIDS AND THEIR PRECURSORS

II.1 Introduction

Liquid-liquid extraction is the most used technique for the recovery of radionuclides from spent nuclear fuels (see Chapter I). The search of new effective and selective extractants is of high scientific and industrial concern. Thus synthesis of such extractants and new extracting systems was the aim of this work.

In this work different types of extractants have been synthesized. Foremost we were interested in the development of new extracting media – functionalized ionic liquids, which can be solvent and extractant the same time (see Chapter I). The FILs were obtained by covalent tethering of extracting fragment to the “classic” ionic liquids, and since ionic liquids consist of ions, there are two ways for their chemical modifications – functionalization of cation or anion.

Nowadays the majority of FILs synthesized are cationic ionic liquids, based on imidazolium or ammonium cations. This is due to the accessible methods for their chemical modifications. In this work both types of FILs have been synthesized in order to investigate better the complexing properties of the functional groups in terms of the extraction in ionic liquid media.

The next level of the IL modification is the introduction of those to the rigid platforms, such as calixarenes, which allow preorganization of functional groups, enhancing their properties.

Originally calixarenes are macrocyclic platforms, derived from *p*-substituted phenols and formaldehyde, and can be modified with different functional groups. Therefore, another goal of this work was to synthesize the calixarenes with phosphine oxide groups, and provide them with properties of ionic liquids.

Thus, the general idea of this work was to synthesize cationic, anionic and containing calix[4]arene scaffold ionic liquids with the same extracting pattern (phosphine oxide) in order to compare their extracting properties and to conclude about the influence of charged part and calixarene platform on the mechanisms of extraction.

The synthesis of cationic FILs and anionic FILs is presented in section “Functionalized Ionic Liquids with phosphine oxide groups”. The synthesis of calix[4]arene phosphine oxide IL can be found in “Functionalization of the calix[4]arene phosphine oxides”.

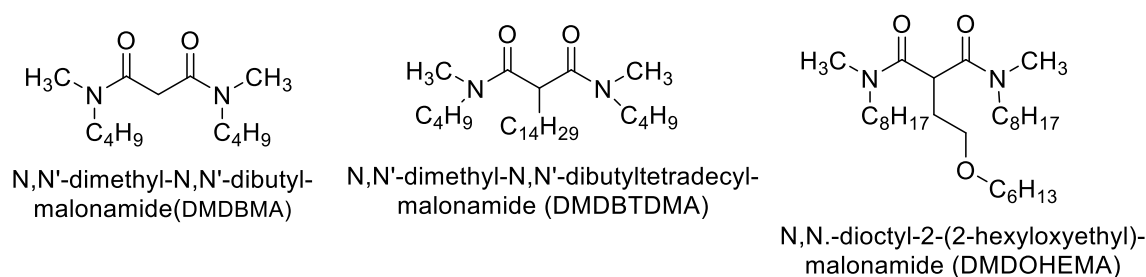
This chapter is organized as follows: each part contains the general information about the extracting pattern used for functionalization, and then the synthetic details. The section about calixarenes starts with general information about calixarenes, then followed by two sections – Cationic FILs on the basis of calix[4]arene phosphine oxides and Precursors of anionic calixarene phosphine oxides.

II.2 Synthetic results and discussion

II.2.1 Synthesis of Functionalized Ionic Liquids

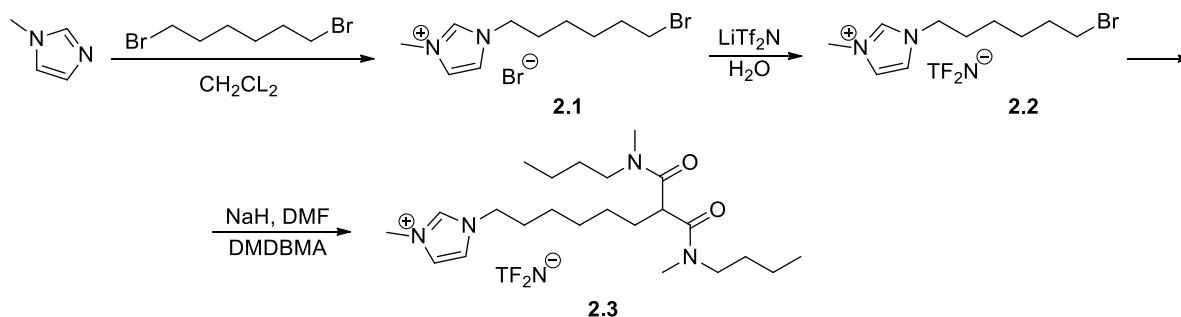
II.2.1.1 Malonamide Functionalized Ionic Liquid⁴

Malonamides are bidentate oxygen donor extractants, which are used for the extraction of An(III) and Ln(III) in DIAMEX process [77]. They belong to the category of the CHNO extractants (consist only of carbon, nitrogen, oxygen and hydrogen), thus can be fully incinerated.



Scheme II-1. Malonamide extractants for DIAMEX process

Considering extracting and ecological (“green”) properties of malonamides, they appeared to be a basis for the development of the new TSILs. *N,N'*-dimethyl-*N,N'*-dibutylmalonamide (DMDBMA) was chemically modified by the imidazolium fragments. The synthesis of the FIL-MA is shown in Scheme II-2.



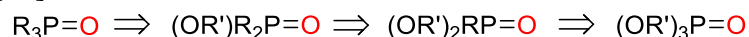
Scheme II-2. Synthesis of malonamide-FIL

By reaction of 1-methylimidazole with 1,6-dibromohexane 1-(6-bromohexyl)-3-methylimidazolium bromide **2.1** was obtained. 1,1'-(Hexane-1,6-diyl)bis(3-methyl-1*H*-imidazolium-1-yl) dibromide is formed as a minor product and was removed by silica column chromatography. The metathesis with LiTf_2N exchanged the Br^- anion into bis(trifluoromethanesulfonyl)amide anion. Treatment of DMDBMA with NaH followed by the addition of 1-(6-bromohexyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide **2.2** provided FIL-MA **2.3**.

⁴ This section is based on the article: M. Bonnaffé-Moity, A. Ouadi, S. Miroshnichenko, V. Mazan, D. Ternova, M. Sypula, C. Gaillard, I. Billard, S. Georg, *Dalt. Trans.* **2012**, 41, 7526.

II.2.2 Functionalized Ionic Liquids with phosphine oxide groups

Organophosphorus compounds play the key role in reprocessing of radioactive wastes. Since the 50s of XX century tributylphosphate (TBP) remains the principal component for uranium, plutonium separation from spent nuclear fuel. However TBP has relatively low extraction ability. The most efficient extractants among monodentate organophosphorous compounds are trialkylphosphine oxides (TAPO). First, the high efficiency of TAPO-extractants is explained by high donor properties of oxygen [78]. Schurhammer et al. analyzed the lanthanide cation binding to phosphoryl ligands by quantum mechanical calculations in the series [79]:



It was concluded that the steric effects play a more important role in coordination with metal than basicity effects of oxygen in P=O groups.

Therefore it was decided to synthesize the FILs functionalized with efficient dialkylphosphine oxide groups. In order to investigate the role of the charge on the complexing properties of tethered phosphine oxide group, the FILs of both types (cationic and anionic) were synthesized.

II.2.2.1 Cationic FILs with phosphine oxide groups

Nowadays $C_nC_mimTf_2N$ family of ILs is the most widely used in the processes of liquid-liquid extraction due to its physicochemical properties: relatively low viscosity, “stability” under acidic conditions, radiolysis resistance, etc.

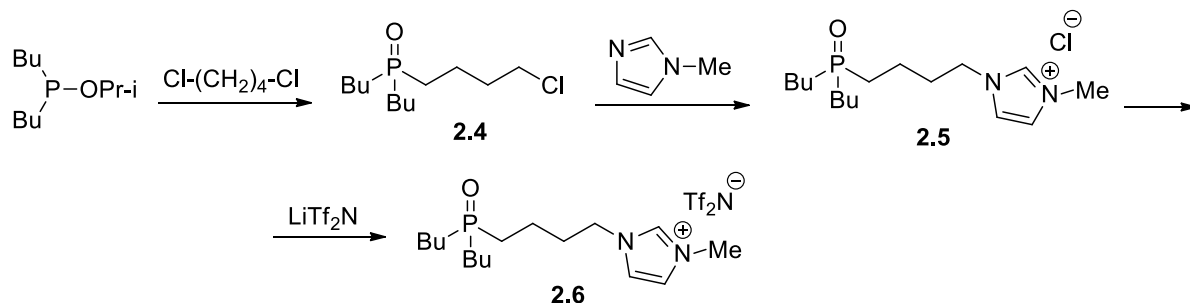
It was already shown that imidazole ring can be easily transformed to imidazolium cation via quaternization reaction with haloalkanes, affording corresponding imidazolium halides. These halides are useful materials in following anion metathesis reactions, and can be exchanged to PF_6^- , BF_4^- , Tf_2N^- , $CF_3SO_3^-$, resulting in the ionic liquids formation. Therefore imidazole was chosen for the creation of cationic TSILs modified by phosphine oxide fragments.

Tf_2N^- was chosen as counterion for the cationic FILs synthesized in this work because of its high lipophilicity and stability in acidic media, which are the necessary conditions in radionuclides extraction processes.

In the synthesis of cationic IL bearing phosphine oxide groups dibutyl-(4-chlorobutyl) phosphine oxide **2.4** was a key substance (Scheme II-3). Substance **2.4** was synthesized via the Arbuzov reaction of isopropyl-dibutylphosphinite with 20-excess of 1,4-dichlorobutane at 100 °C during 4 h with a yield 87 %. An attempt to use more reactive 1,4-bromobutane in place of 1,4-chlorobutane failed, because under the reaction conditions (Arbuzov reaction followed by vacuum distillations at 100 °C, 0.01 mm Hg) the formed dibutyl-(4-bromobutyl) phosphine oxide underwent dehydrobromination. Thus, the reaction mixture cannot be purified from by-product dibutyl-(1-buten-4-yl)phosphine oxide by vacuum distillation.

An alternative method to obtain compound **2.4** is alkylation of dibutylphosphine oxide with 1,4-dichlorobutane in a media of DMSO / NaOH (50% aqueous solution), but the yield of the product is less than 30% [80]. At the next stage, 3-methylimidazole was alkylated with dibutyl-(4-chlorobutyl)phosphine oxide (ratio of reagents 1:1, 120 °C, 72 g, vacuum sealed ampoule), and dibutyl-4-(3-methylimidazolium)butylphosphine oxide chloride **2.5** was formed.

Substance **2.5** was used for preparation of salt without further purification: it was dissolved in water, and the equivalent of lithium bis(trifluoromethanesulfonyl)imide (LiTf₂N) was added to this solution. After the reaction, the more lipophilic bis-trifluoromethanesulfonimidate **2.6** was extracted with chloroform and purified with charcoal in ethanol mixture. Compound **2.6** (yield 72%) is a yellow fluid liquid, well soluble in most organic solvents.



Scheme II-3

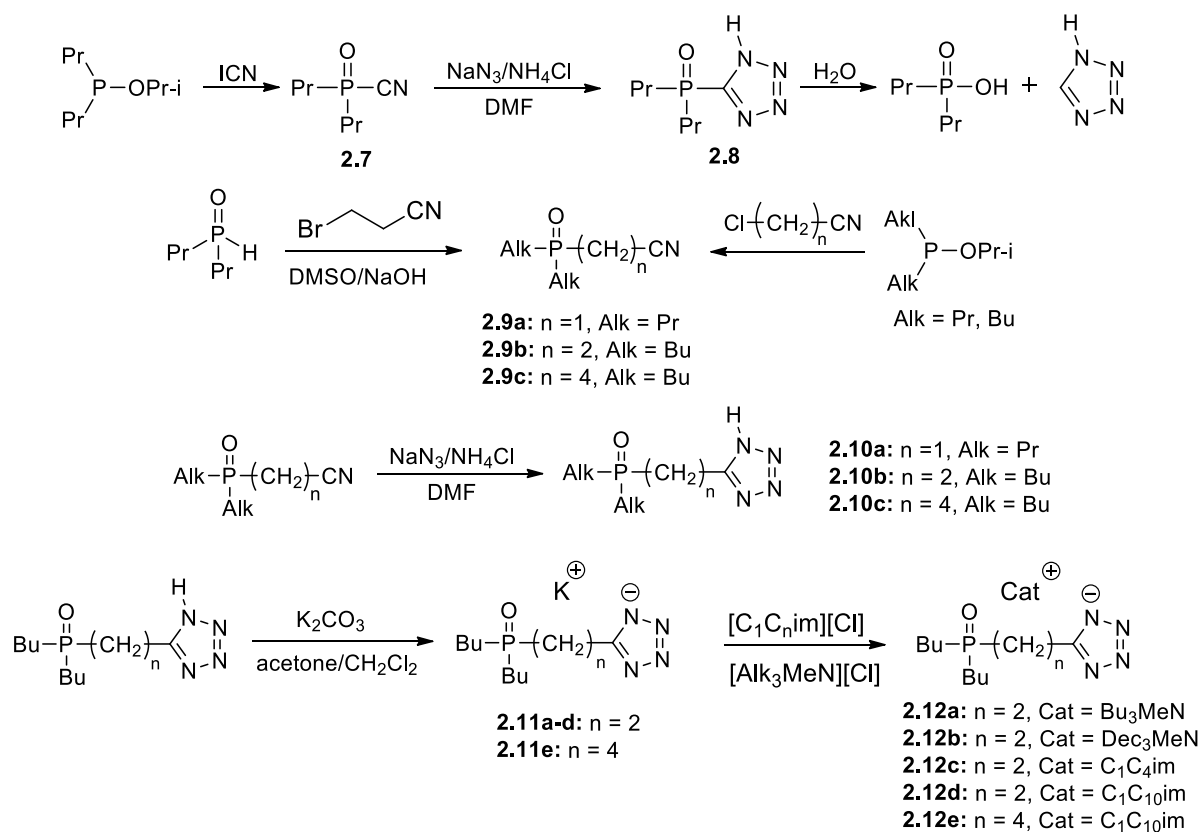
The understanding of extracting mechanisms occurring in ionic liquids is a very challenging task. These extraction processes are characterized by ion exchange, which is apparently the main difference with extraction in molecular solvents.

For a better understanding of the mechanisms of extraction the TSILs with extracting patterns grafted to the anionic part have been synthesized.

II.2.2.2 Anionic FILs with phosphine oxide groups

Despite a quite large variety of cationic functionalized TSILs, the anionic ones remain very few, and in all cases the anionic FILs were obtained from available materials by combination of imidazolium or ammonium cation with negatively charged patterns as deprotonated acids, acetylacetonate [81, 82].

Tetrazole was chosen as a scaffold for anionic phosphine oxide ionic liquids. Firstly, NH proton is rather acidic (pK_a equal 5.63, 5.73 for 5-methyl- and 5-(*n*-octyl)tetrazoles respectively; 4.90 for tetrazole [83]) and dissociates in neutral or slightly acidic aqueous solutions. Secondly, tetrazolate-anion can be a multicentral *N*-ligand, and along with the oxygen atom of the grafted P=O group can bind cations of actinides and lanthanides [84]. Thus, at the certain distances between oxygen and nitrogen, strong chelation of metal cation may occur. In order to study this aspect we decided to synthesize the series of tetrazolate ionic liquids with phosphine oxide groups covalently tethered directly to the heterocycle or through the alkyl spacers of different lengths (Scheme II-4). Moreover for the further investigation of the extracting properties of tetrazolate anion in ionic liquids, a model compounds without phosphine oxide group has been synthesized.



Scheme II-4. Synthesis of anionic FILs

The key compounds for the synthesis of tetrazolate FILs are phosphine oxides **2.7** and **2.9**, containing C≡N reactive group at different distances to P atom, were obtained via two synthetic methods. Thus, cyanodipropylphosphine oxide **2.7** has been synthesized by the Arbuzov reaction of isopropylidipropylphosphinite with iodine cyanide (Yields 44%). The relatively low yield can be increased if iodine cyanide is replaced by dicyane. The nitriles **2.9a** and **2.9c** were obtained via the Arbuzov reaction of the corresponding phosphinites with chloronitriles with good yields (95% and 68% respectively). The alternative method was realized for the synthesis of dibutyl-(2-cyanoethyl)phosphine oxide: dibutylphosphine oxide was alkylated with 3-bromopropionitril under the conditions of the Michaelis-Becker reaction [85].

Cyanophosphine oxides **2.7**, **2.9** were transformed to the corresponding tetrazole derivatives **2.8**, **2.10** by treatment with sodium azide and ammonium chloride in DMF solution. It should be mentioned, that P-C bond of dipropyl(1*H*-tetrazol-5-yl)phosphine oxide **2.8** appeared to be hydrolytically unstable, which caused its decomposition to dipropylphosphinic acid and tetrazole while contacting with water. All other tetrazoles **2.10** were successfully isolated as crystal compounds (Yields 37-78%). The molecular structure of (dibutylphosphinoyl)butyl-1*H*-tetrazole **2.10c** was examined by X-ray diffraction analysis (Figure II-1).

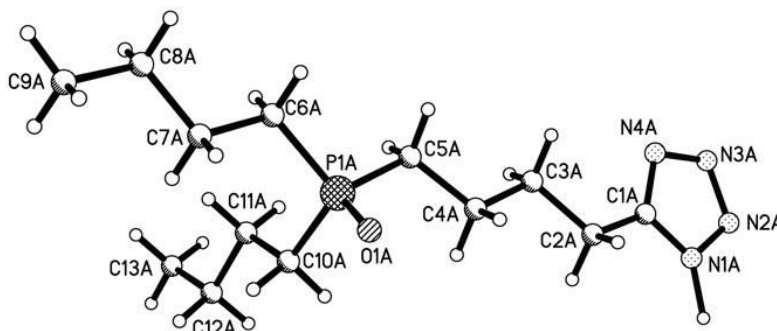


Figure II-1. Structure of compound **2.10c** according to X-ray diffraction data

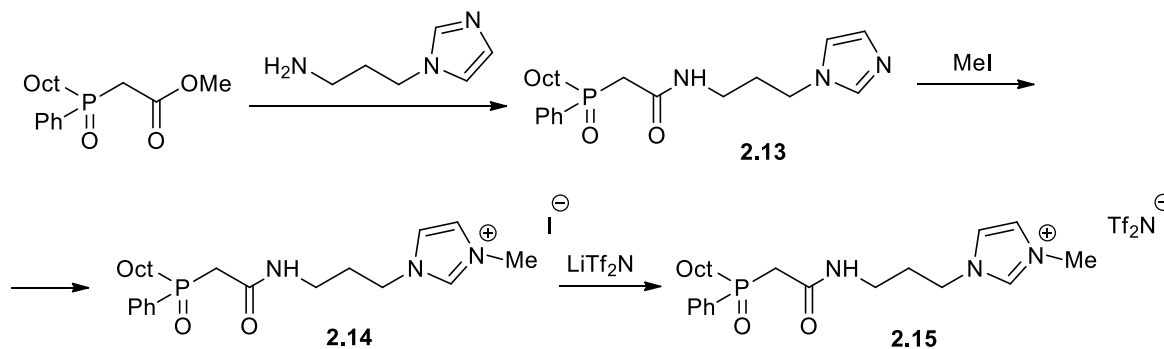
Tetrazoles **2.10** when treated with anhydrous potassium carbonate in acetone form potassium salts **2.11**. By reaction of salts **2.11** with tetraalkyl ammonium chlorides or alkylmethylimidazolium chlorides the corresponding derivatives of dibutyl- ω -(5-tetrazolate)-alkylphosphine oxides **2.12** were obtained as oils.

II.2.2.3 TSIL with CMPO fragment

CMPO (carbamoylphosphine oxide, octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide) is a bidentate complexant, which was synthesized in 1981 by two independent research groups [86, 87]. CMPO found its application in TRUEX (transuranic extraction) as a second extracting agent along with TBP, and allows to extract transuranic elements (Np, Am, Pu, Cm, etc) [88].

Moreover in papers of Rout and Visser it was reported that CMPO demonstrates much larger *D* values for An in $C_1C_4\text{imTf}_2\text{N}$ and $C_1C_4\text{imPF}_6$ ionic liquids compared to *n*-dodecane extracting systems [89, 90].

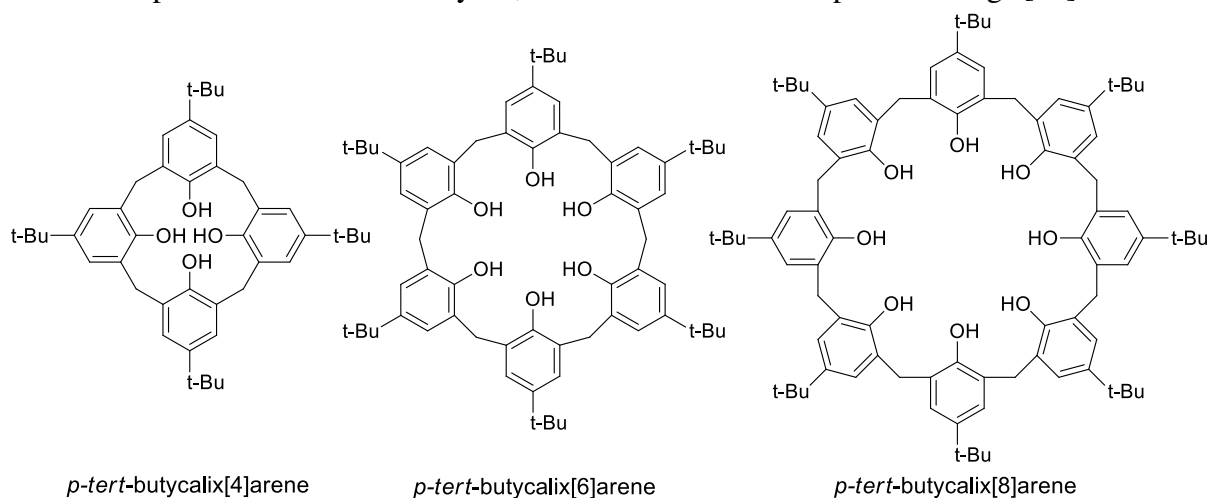
The procedure for the synthesis of CMPO ionic liquid, (further denoted as CMPO-IL) and the structures of the precursors are summarized in Scheme II-5. The key substance CMPO-imidazole **2.13** was obtained through the acylation of 3-aminopropylimidazole with methyl (octylphenylphosphinyl)acetate (ratio of reagents 1:2, 105 °C, 72 h, sealed ampoule). Then CMPO-imidazole **2.13** was alkylated with iodomethane (reagents ratio 1:1.5 in dichloromethane solution, rt, 12h) to give imidazolium iodide **2.14** in quantitative yield. CMPO-IL **2.15** was obtained by the metathesis reaction of **2.14** with LiTf_2N in aqueous solution (Yield 70%).



Scheme II-5. Synthesis of CMPO-IL

II.2.3 Calixarene phosphine oxide FILs

Calix[*n*]arenes is a class of macrocyclic compounds, obtained by cyclocondensation of *para*-substituted phenols with formaldehydes, where *n* is a number of phenolic rings [91].



Scheme II-6. *p*-tert-butylcalix[*n*]arenes

There are two obvious places to modify a calixarene, namely the phenolic hydroxyl groups at narrow rim (formation of ethers and esters) and the *p*-positions at wide rim (electrophilic substitution, ipso-substitution). Due to the possibility for their different chemical modifications, a large diversity of new compounds on the calixarenes basis were synthesized: catalysts [92], sensors [93], enzyme mimetics [94], selective membranes [95].

Calix[4]arenes are the most widespread because they can exist in *cone*-conformation, which results in a hydrophobic cavity and ensures so-called pre-organisation of functional groups. Therefore calix[4]arenes appeared to be the most favorable scaffold for the complexants synthesis, their *cone*-structure along with certain functionality allows strong binding of different molecules and ions.

Due to this calixarene effect the tetraphosphorylated calixarenes are more efficient extractants for the metal cations than their acyclic analogs or some industrial extractants such as trialkylphosphinoxides, carbamoylphosphin oxide, bis-2-diethylhexyl phosphoric acid.

It has been shown that the cone shaped calix[4]arenes possessing trialkylphosphine oxide binding groups at the lower rim or the upper rim of the calixarene platform due to so called *macrocyclic cooperative effect* up to three orders of magnitude superior monodentate trialkylphosphine oxides in extraction of actinides, lanthanides, noble metals existing in spent nuclear fuels [96, 97, 98, 99, 100, 101, 102].

The complexation of metal cations by calix[4]arenes bearing phosphine oxide groups at narrow and upper rim is shown in Figure II-2. The simulations have been performed by Monte Carlo conformational search followed by molecular mechanics energy minimization of the most stable structures. This gives a vivid picture of the most probable complexation by the calix[4]arene phosphine oxides.

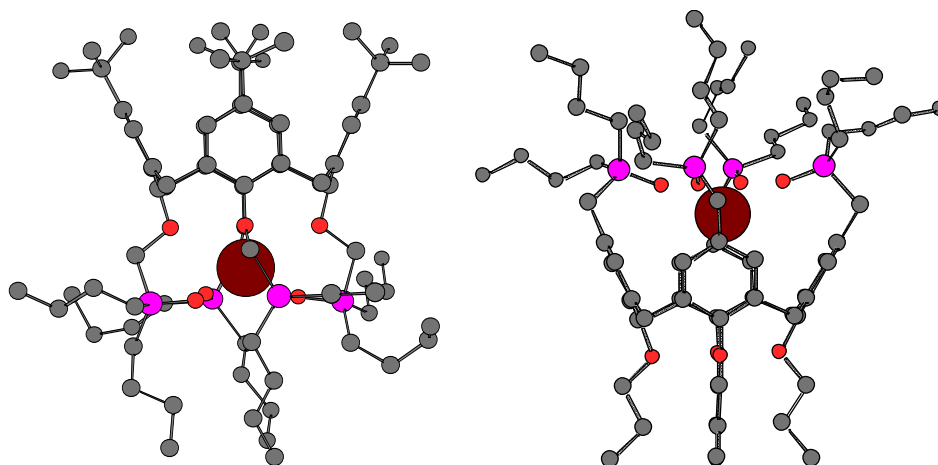
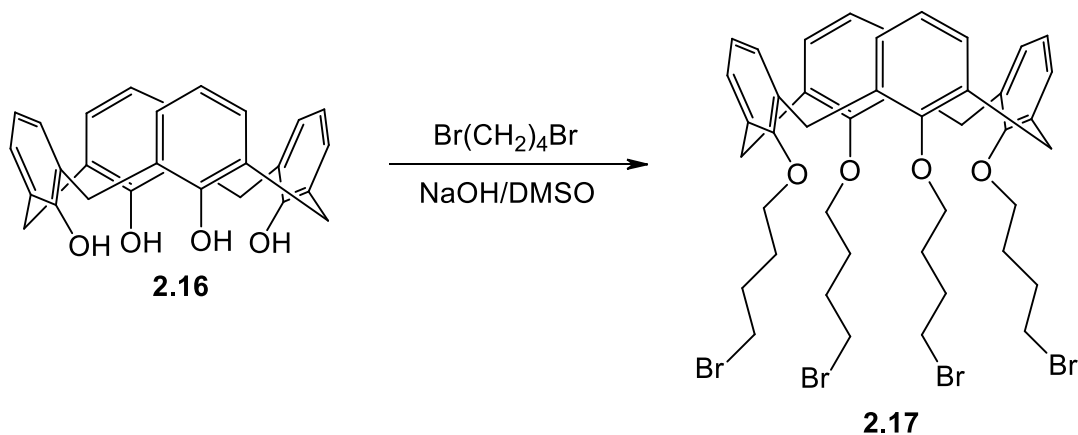


Figure II-2. The structures of the Ca^{2+} complexes with calixarene phosphine oxides obtained from Monte–Carlo conformational search [103]

II.2.3.1 Cationic FILs on the basis of calix[4]arene phosphine oxides

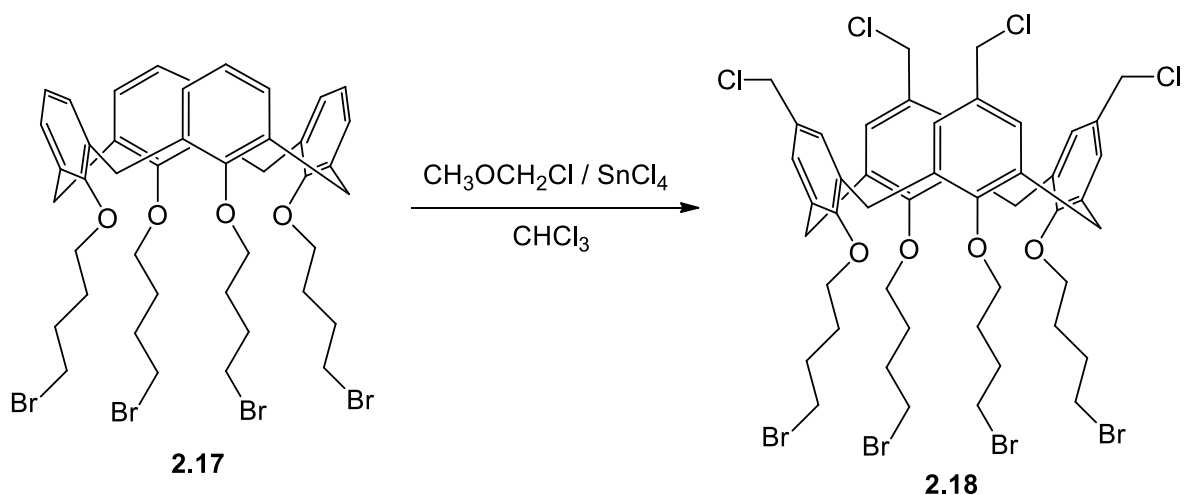
Calixarenes **2.19** bearing four trialkylphosphine oxide binding groups at the upper rim and four methylimidazolium groups at the lower rim were synthesized in several steps starting from tetrahydroxycalix[4]arene **2.16**.

The first stage (Scheme II-7) is synthesis of tetrabromobutoxycalix[4]arene **2.17**. The synthesis has been performed following the procedure described in the work [104]. Tetrahydroxycalix[4]arene **2.16** was alkylated with 1,4-dibromobutane in the solution of DMSO/NaOH at the mole ratio of **2.16** : NaOH : 1,4-dibromobutane = 1 : 7.5 : 20 at 55 °C.



Scheme II-7

The next stage was chloromethylation of tetrabromobutoxycalix[4]arene **2.17** with methyl chloromethyl ether in the presence of SnCl_4 affording chloromethylcalix[4]arene **2.18** (Scheme II-8) [104].



Scheme II-8

The structure of the chloromethylcalix[4]arene **2.18** has been investigated by the X-ray diffraction studies of a single-crystal, obtained from the mixture heptane/acetone (Figure II-3). The macrocycle scaffold of **2.18** possesses *pinched cone* conformation.

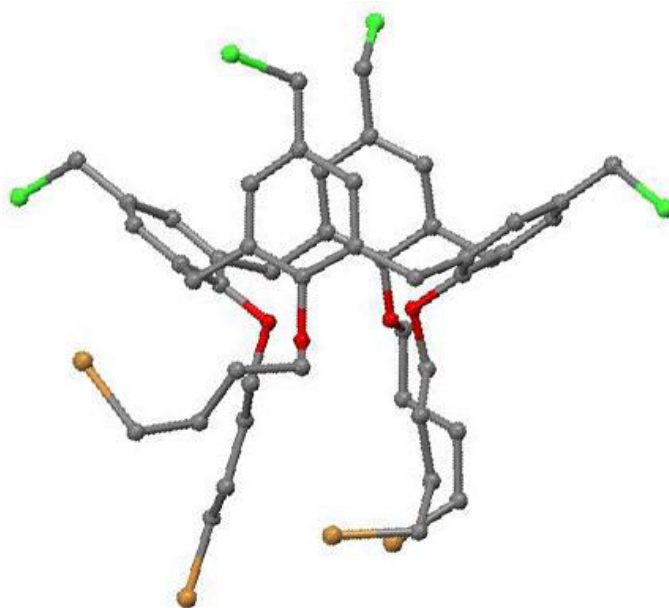
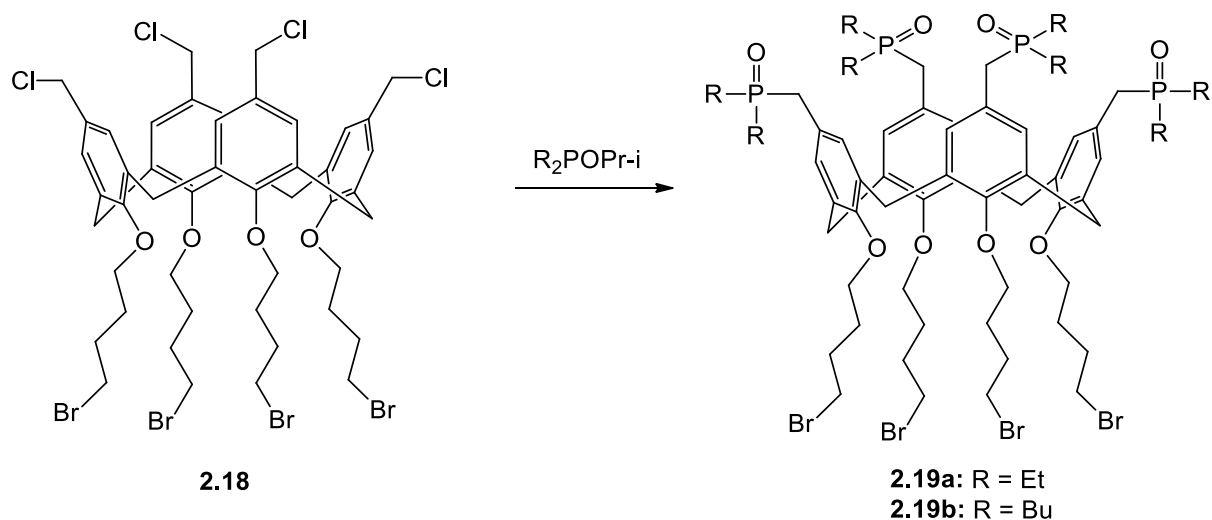


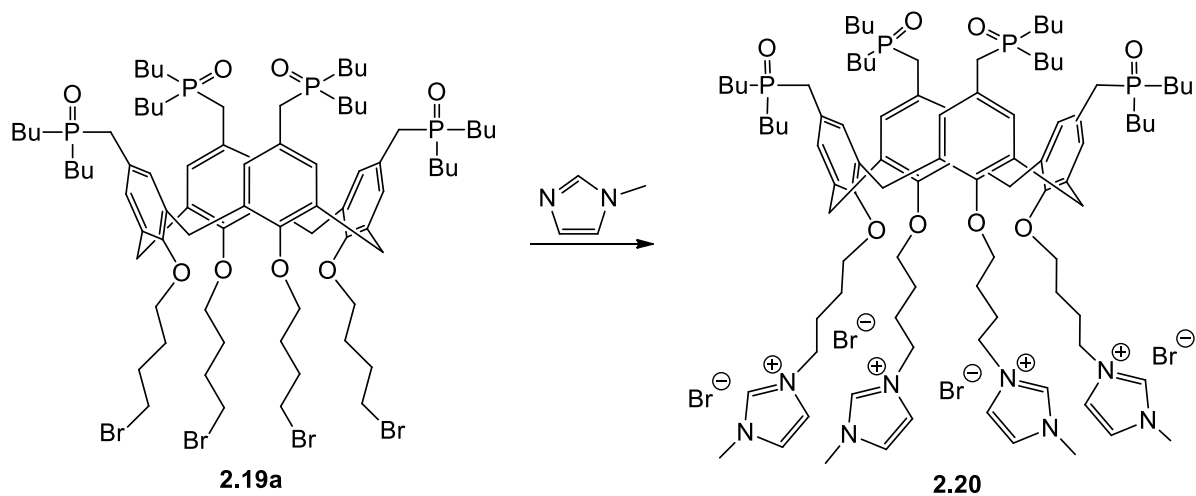
Figure II-3. Structure of compound **2.18** according to X-ray diffraction data

Calix[4]arene **2.18** has two types of reactive centers available for phosphorylation under the conditions of Arbuzov reaction. Following the approach described in the work [104], the selective phosphorylation of the wide rim was performed. The reaction proceeds selectively when 4 equivalents of a phosphinite are added gradually (during 10-15 min) to the cold solution of calix[4]arene **2.18** (0-5 °C) in chloroform. After 24h of stirring at rt, the yield of the product was 90-94%. Calix[4]arene phosphine oxides **2.19** were purified by charcoal treatment of their aqueous solutions.



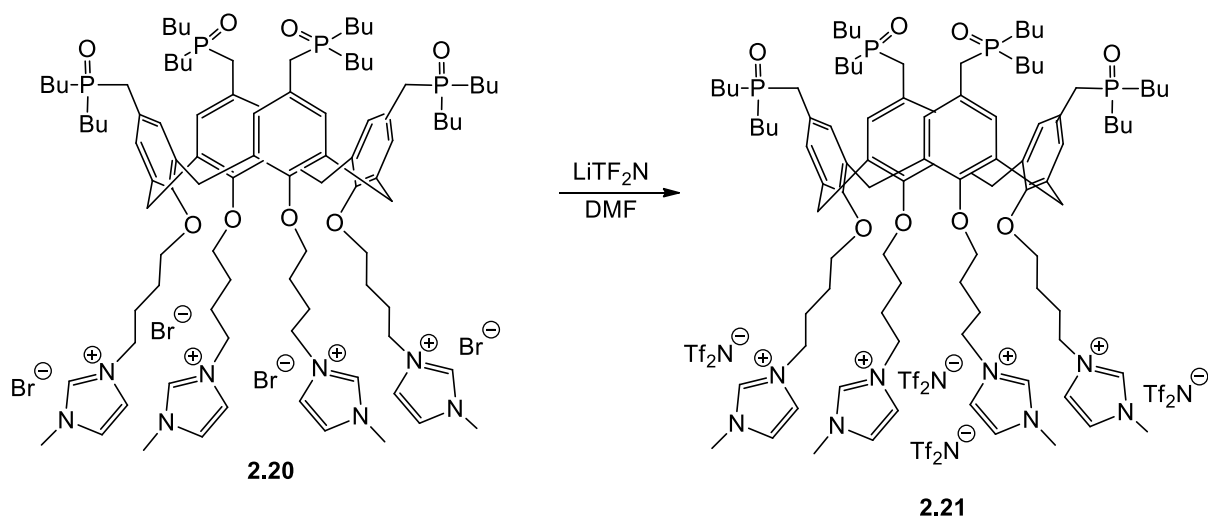
Scheme II-9

Introduction of imidazolium fragments to the lower rim of calixarene phosphine oxide **2.19a** was performed by reaction with an excess of 1-methylimidazole at 70 °C yielding imidazolium-functionalized calixarene phosphine oxide **2.20** (Scheme II-10). Obtained calixarene **2.20** is a colorless hygroscopic compound, which melts in a wide temperature range (50-90 °C).



Scheme II-10

The substitution of bromide anions in **2.20** on *bis*(trifluoromethylsulfonyl)imide anions in DMF solution leads to calixarene **2.21** (Scheme II-11):



Scheme II-11

Surprisingly calixarene **2.21** melts at 120 °C that is higher compared with its bromide analogue **2.20**.

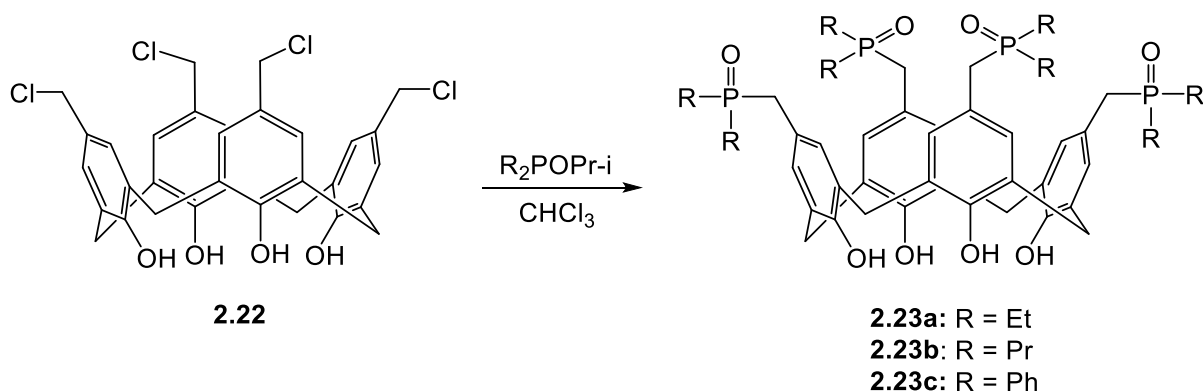
However, bromobutoxycalix[4]arenes **2.19** can be used as synthons for quarterisation of various alkylimidazoles, pyridines, trialkylamines, and along with the metathesis of bromide anion, may give a large series of the cationic FILs based on the calixarene phosphine oxide.

II.2.3.2 Precursors of anionic calix[4]arene phosphine oxide FILs

As it was discussed in the literature review (Section I.5), anionic FILs can be easily obtained via exchange reactions of corresponding salts of phosphoric, phosphonic, phosphinic acids (as well as carboxylic acids) with quaternary ammonium or phosphonium basis.

This approach can be also applied for the synthesis of anionic FILs on the basis of the calixarene phosphine oxides. Rich synthetic chemistry of calixarenes allows to obtain the calixarenes possessing phosphine oxide groups at one rim and mentioned acidic groups at another rim, which can be used as precursors for the anionic FILs.

Calix[4]arene phosphine oxide **2.25** bearing two fragments of phosphoric acid at the narrow rim has been synthesized involving three stages starting from chloromethyl tetrahydroxy calixarene **2.22**. In the first stage **2.22** was treated with isopropyl dialkyl phosphinite in the chloroform solution under the conditions of Arbuzov reaction, giving calixarene phosphine oxides **2.23** (Scheme II-12). These calixarene phosphine oxides have reactive phenolic OH-groups on the narrow rim of the macrocyclic platform. These compounds are the interesting synthons for the further functionalization.



Scheme II-12

It is known from the literature that the Arbuzov reaction between chloromethyl calixarene and trialkylphosphite is successfully used for the synthesis of analogous calixarene phosphonates [105, 106]. Usually the reaction is performed by refluxing a chloromethyl calixarene in the excess of phosphorylating agent.

This method was failed for the synthesis of calixarene phosphine oxides **2.23**. After the reaction mixture was heated the insoluble polymer mass was formed, which appeared to be a product of the selfalkylation of calixarene **2.23**. The competitive reaction can be explained by the high basicity of phosphinite, which effectively accepts hydrogen chloride forming not stable polymerizable calixarene quinonmethide.

In order to solve this problem the series of experiments for optimization of phosphorylation of tetrachloromethyl tetrahydroxycalixarene has been performed. By the variation of the reactants mole ratio, the nature of the solvent and the reaction mixture temperature, it was found that the unwanted processes of dehydrochlorination can be avoided if the reaction is performed at stoichiometric proportions of reagents in dry chloroform solution at 50 °C.

The ^{31}P NMR analysis showed that the full conversion of phosphinite proceeds within 96h. After the solvent evaporation tetraphosphine oxides **2.23** were obtained with 90-95% yield. Calixarenes **2.23a,b** were purified by charcoal treatment of their aqueous solutions, compound **2.23c** – by crystallisation from acetonitrile. Calixarenes **2.23a** and **2.23b** appeared to be hygroscopic colorless compounds, well soluble in water and polar organic solvents, almost insoluble in nonpolar solvents. Calixarene **2.23c** is a crystalline compound, insoluble in water.

The ^1H NMR spectra of **2.23** correspond to the C_{2v} symmetry, which is characteristic for the *pinched cone* conformation. In the ^{31}P NMR the chemical shifts of phosphorus are δ 49.29 ppm, 46.40 ppm for dialkyl derivatives **2.23a,b** and δ 29.40 ppm for diphenyl derivative **2.23c**.

The *pinched cone* structure of calixarene **2.23c** was also confirmed by X-ray diffraction studies of a single-crystal, obtained from toluene (Figure II-4). All the phosphine oxide groups of calixarene **2.23c** are oriented to the periphery of the macrocycle.

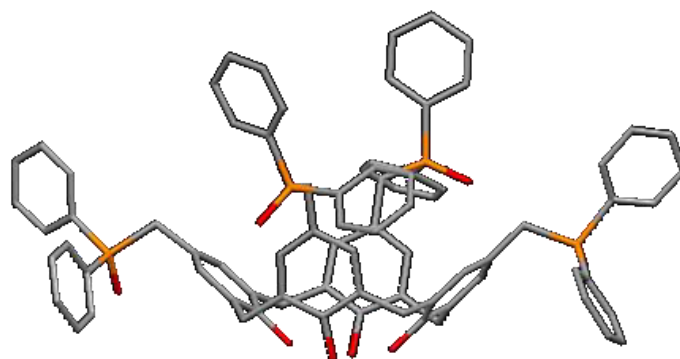
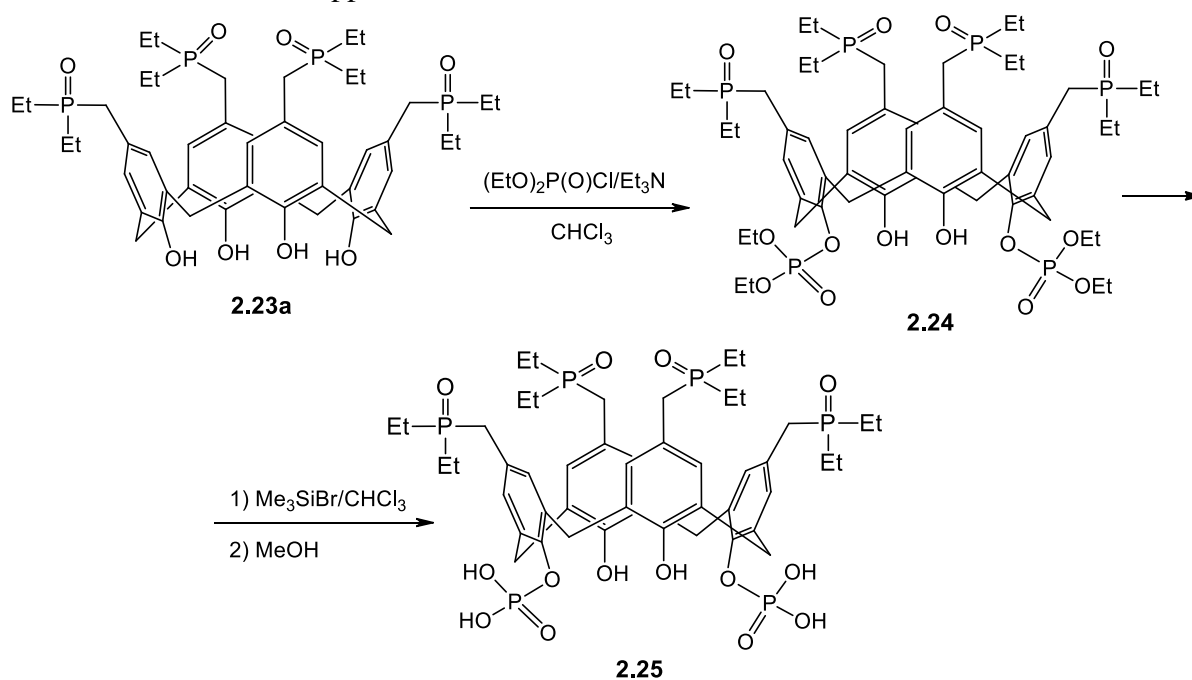


Figure II-4. General view of **2.23c** molecule according to X-ray analysis

In the second stage the phosphorylation of the narrow rim of calix[4]arene phosphine oxide **2.23a** has been performed by diethylchlorophosphate in the presence of triethylamine in the chloroform solution (Scheme II-13). It was discovered that the reaction occurs regioselectively with quantitative formation of 1,3-diphosphate **2.24** in *pinched cone* conformation. The ^1H NMR of **2.25** shows two characteristic doublets of the axial and equatorial protons of *AB* spin system $\text{Ar-CH}_2\text{-Ar}$ $J = 13$ Hz. The difference between the chemical shifts $\Delta\delta$ is 0.98 ppm.



Scheme II-13

The third stage is dealkylation of **2.24**. The interaction between diethoxycalixarene **2.24** and the excess of bromotrimethylsilane in the dry chloroform solution (24h, 20 °C) leads to the formation of the intermediate silyl ester. The subsequent methanolysis of the silyl ester breaks the labile bond P-O-Si resulting in the formation of bis-dihydroxyphosphoryloxy-calix[4]arene tetraphosphine tetraoxide **2.25** (Scheme II-13).

Acid **2.25** is a colorless crystal compound, easily soluble in polar solvents. The structure and composition of the compound obtained were determined by ^1H and ^{31}P NMR as well as by element analysis. The distal type of substitution was unambiguously confirmed by ^1H NMR. In

the spectrum ^1H NMR (DMSO, 300 MHz) of 1,3-disubstituted calixarene **2.25** (Figure II-5) we can observe two singlets of the aromatic protons δ 6.71 and 7.10 ppm, the singlet of hydroxyl groups δ 4.78 ppm, two doublets of AB system for the axial and equatorial protons of methylene spacers Ar-CH₂-Ar at δ 3.35 and 4.20 ppm with the constant $J = 13.80$ Hz, two doublets of the methylene spacers next to the P atom δ 2.82 and 3.15 ppm with the constant $J = 13.50$ Hz, the signals of the methyl protons P(CH₂-CH₃)₂ appear as multiplets δ 1.37 ppm, the signals of the methylene protons P(CH₂-CH₃)₂ have the shape of multiplets because of diastereotopic character of P atom.

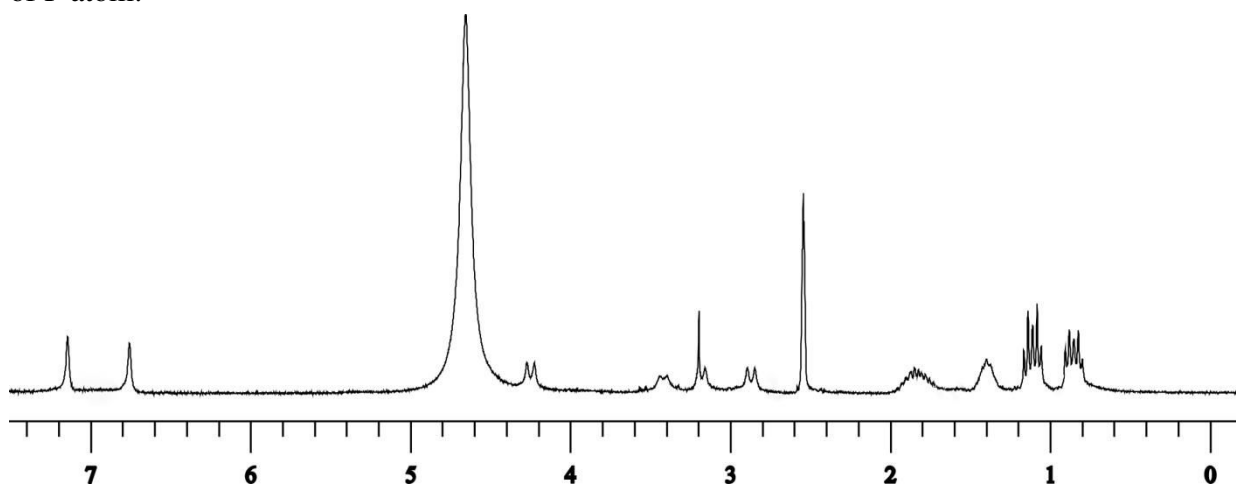
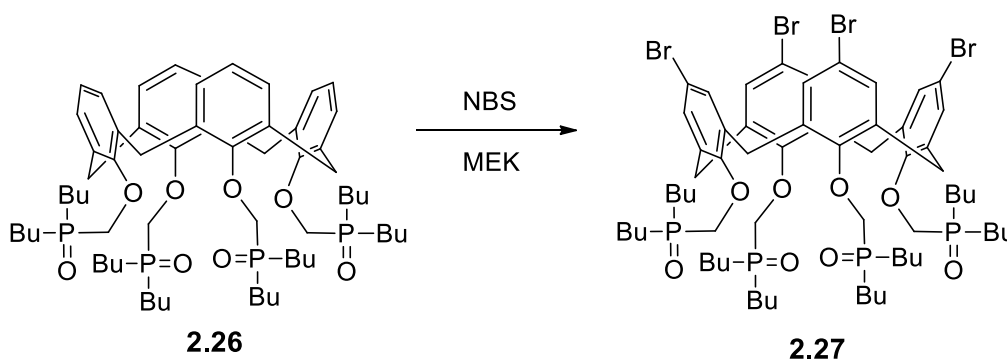


Figure II-5. ^1H NMR spectrum (300 MHz, CDCl_3) of calixarene **2.25**

It is known that calixarene phosphine oxide **2.26** synthesized earlier in our research group by alkylation of tetrahydroxycalix[4]arene by dibutylphosphinoylmethyl tosylate can extract metal cations from aqueous solutions [100]. In order to transform **2.26** to a synthon for anionic calixarene phosphine oxide FILs, the synthetic route described below has been applied.

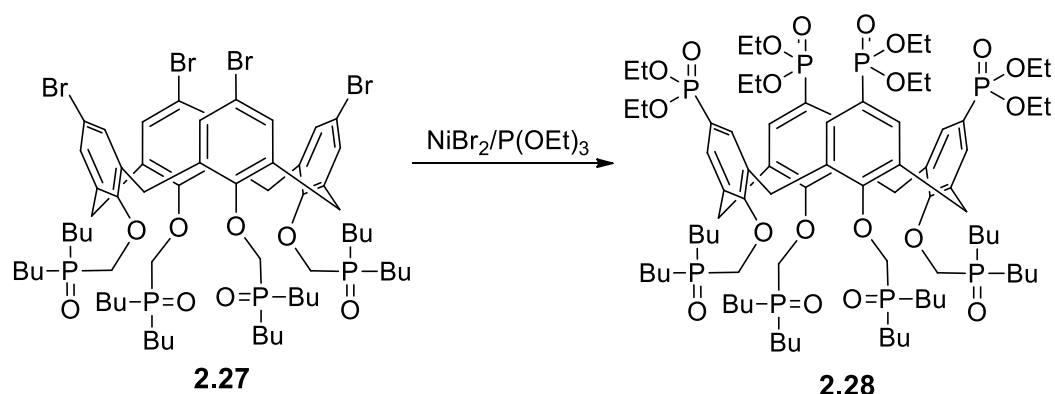
The bromination of the wide rim of **2.26** was performed with *N*-bromosuccinimide in the solution of methyl ethyl ketone during 72h at rt, giving tetrabromide **2.27** with yield 55%. (Scheme II-14).



Scheme II-14

The direct introduction of phosphonate groups to the wide rim of calix[4]arenes phosphine oxides was realized through the nickel-catalysed reaction of Arbuzov-Tavs [107] with an excess of triethylphosphite in the presence of catalytic amount of NiBr_2 at 180°C

(Scheme II-15). Thus calix[4]arene diethylphosphonate **2.28** was obtained with almost quantitative yield.



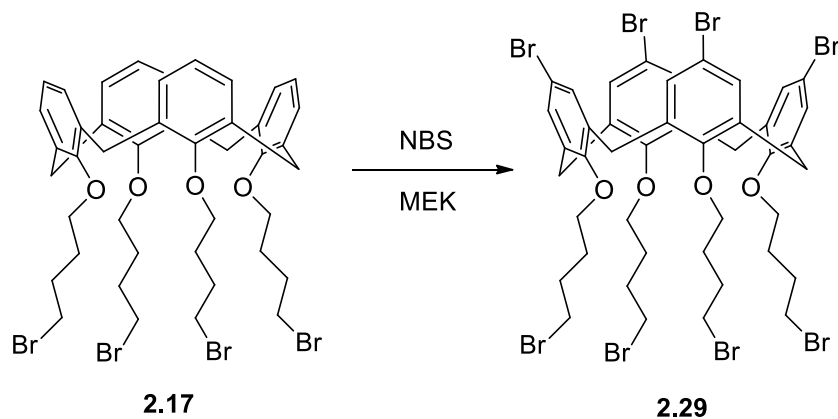
Scheme II-15

The structure and the composition of the compound obtained were determined by ^1H , ^{31}P NMR and elemental analysis. Calixarene **2.28** adopts the *cone* conformation, as evidenced by the two characteristic doublets of AB spin system of axial and equatorial protons of Ar-CH₂-Ar methylene groups in ^1H NMR spectra. The constants of spin-spin axial-equatorial spin interaction are 13.2 Hz, the difference in the chemical shifts $\Delta\delta = 1.83$ ppm, which corresponds to the C_{4v} symmetry. In the ^{31}P NMR spectrum two singlet signals are observed, which corresponds to the phosphine oxide groups of narrow rim (δ 44.28 ppm) and phosphonate groups of wide rim (δ 18.7 ppm) of the macrocycle.

The FILs on the basis of calixarene **2.28** synthon can be obtained via two methods: by direct reaction with appropriate alkylimidazole, trialkylamine, trialkylphosphine using alkylation property of the upper rim diisopropylphosphonous groups or by the method described above – dealkylation of the diethyl phosphonate group to the phosphonous acid group.

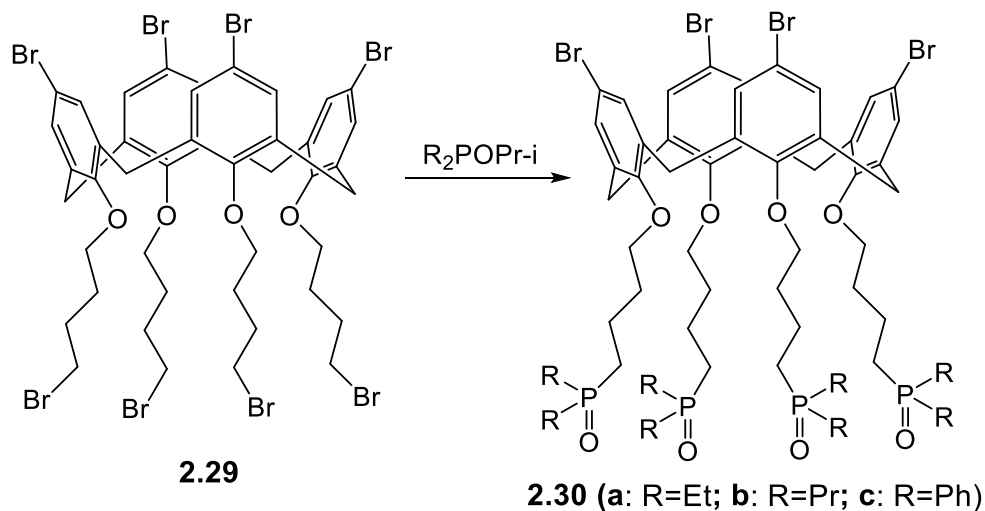
The similar synthetic strategy has been used for the synthesis of calixarene **2.32**, which differs from **2.28** in that its phosphine oxide groups linked to the narrow rim through butylene spacers.

The bromination of wide rim of the tetrabromobutoxycalix[4]arene **2.17** was performed with *N*-bromosuccinimide in the solution of methyl ethyl ketone at rt during 24 h, giving octabromocalixarene **2.29** with yield 94% (Scheme II-16). Octabromocalix[4]arene **2.29** is well soluble in the most organic solvents, and almost insoluble in alcohols.



Scheme II-16

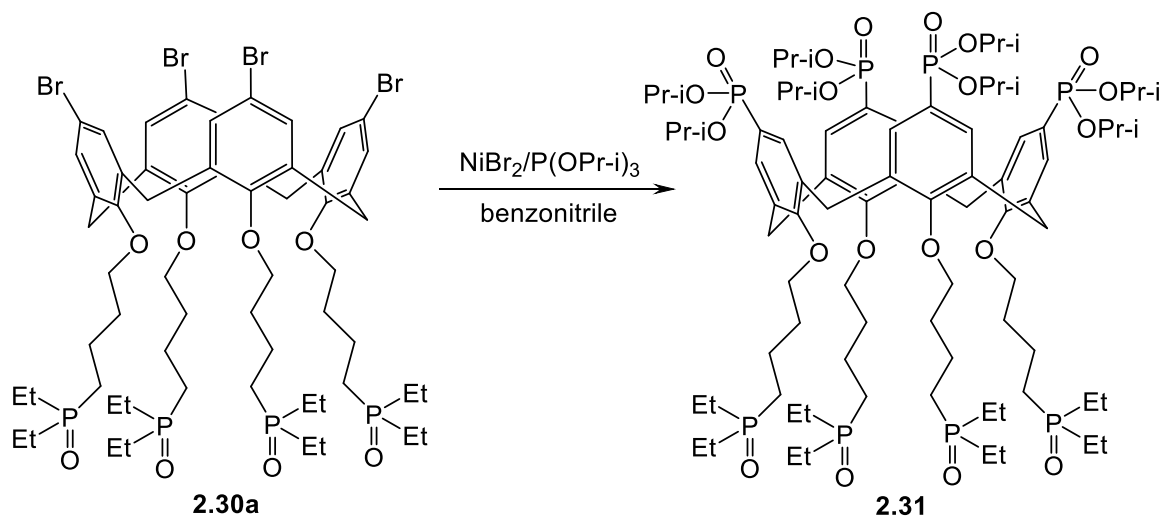
Due to the difference in the reactivities of $Br-C_{Ar}$ and $Br-C_{Alk}$ functions, the phosphorylation of octabromide **2.29** under the Arbuzov reaction conditions (150 - 180 °C) occurs only at lower rim and leads to the quantitative formation of calixarene phosphine oxides **2.30** (Scheme II-17).



Scheme II-17

The composition and the structure of the compounds obtained were determined by 1H and ^{31}P NMR spectroscopy and elemental analysis. Calix[4]arene **2.30** exists in the *cone* conformation. It is confirmed by the presence of two characteristic doublets AB spin system of axial and equatorial protons Ar-CH₂-Ar methylene groups in the 1H NMR spectra. The constants of spin-spin interaction of the axial and the equatorial protons are 13.8 Hz, the difference in chemical shifts $\Delta\delta$ is 1.18 ppm (Figure II-6), which corresponds to the C_{4v} symmetry of the scaffold.

The wide rim of calixarene **2.30a** was phosphorylated with triisopropylphosphite in the presence of a catalytic quantity NiBr₂ in the benzonitrile solution at 180 °C during 1 h (Scheme II-18).



Scheme II-18

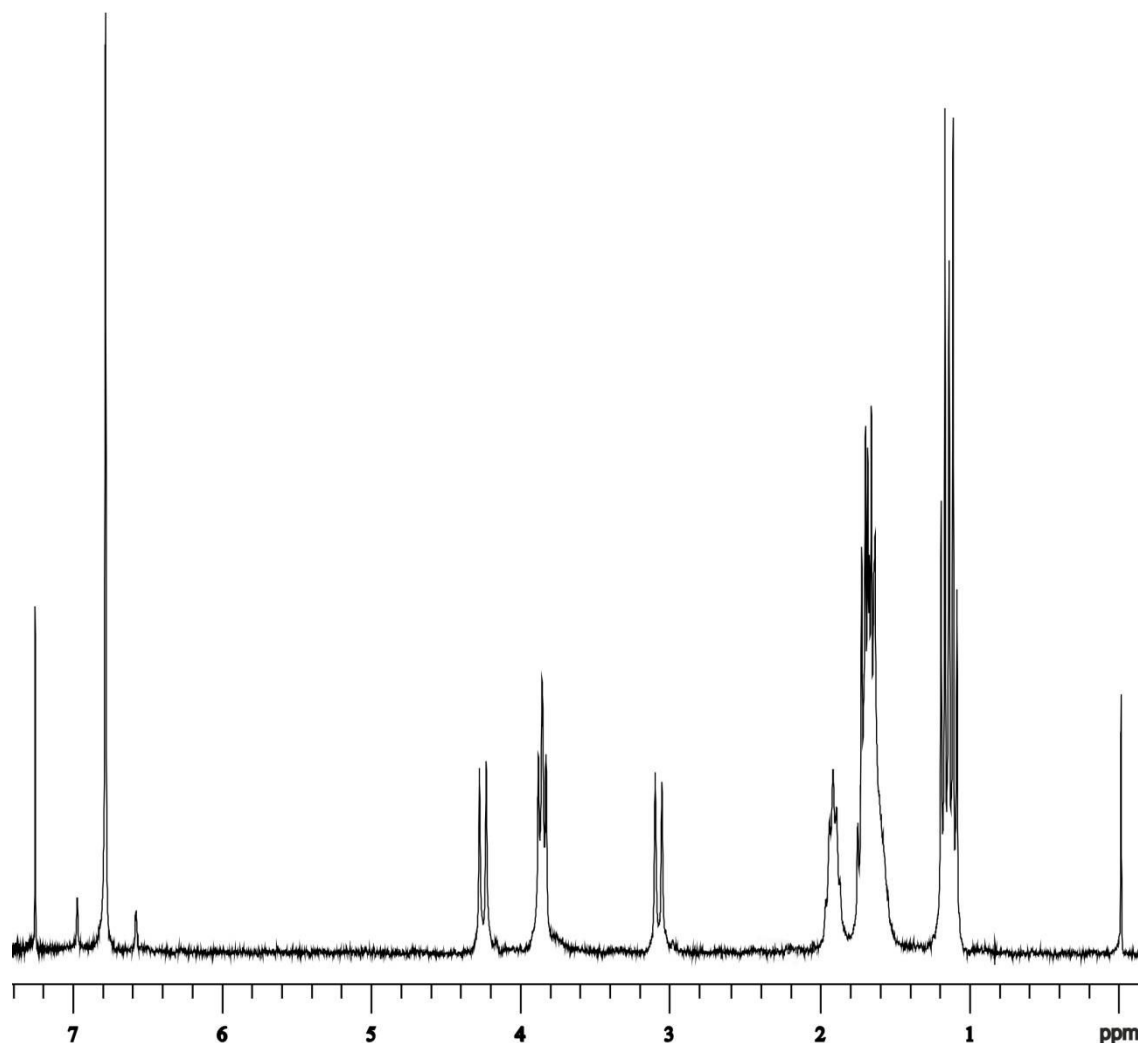
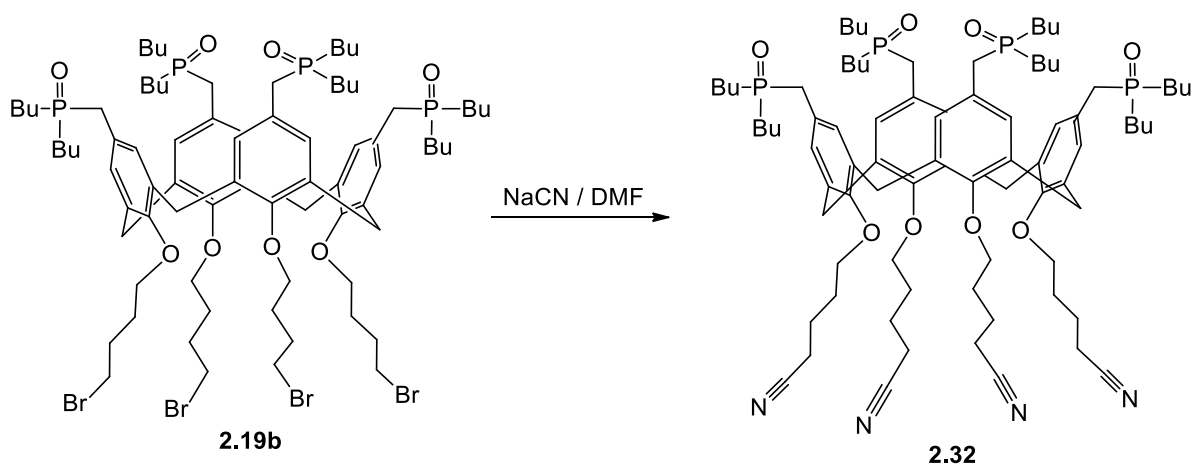


Figure II-6. ^1H NMR spectrum (300 MHz, CDCl_3) of calixarene **2.30a**

Calixarene **2.31** exists in the *cone* conformation, which is confirmed by presence of two doublets AB spin system of axial and equatorial protons $\text{Ar-CH}_2\text{-Ar}$ of methylene groups with $J = 13.5$ Hz and chemical shifts difference of $\Delta\delta$ 1.12 ppm. In the ^{31}P NMR spectrum two singlet signals are observed - δ 52.396 ppm, 18.174 ppm of phosphine oxide and phosphonate groups respectively.

Calixarene phosphine oxide **2.32** containing cyanobutyl substituents at the narrow rim is a promising synthon for the synthesis of FILs. Cyano groups can be quantitatively hydrolysed to carboxylic groups, which in their turn - transformed to ammonium, imidazolium, phosphonium salts, providing substances with properties of ionic liquids (Chapter I).

Cyanobutoxy calixarene phosphine oxide **2.30** was obtained with almost quantitative yield by the reaction of calixarene phosphine oxide **2.19b** with fivefold excess of sodium cyanide in DMF solution (Scheme II-19).



Scheme II-19

Tetracyanocalixarene phosphine oxide **2.32** is a glass substance of light-yellow color. ^1H NMR spectrum of **2.32** corresponds to the C_{4v} symmetry of the scaffold, which is characteristic of the *cone* conformation.

II.3 Conclusions

In this work the preparative methods of synthesis of functionalized ionic liquids and their synthons were developed. Imidazolium cation, which is the fragment of the most common IL used in processes of liquid-liquid extraction, has been functionalized with malonamide pattern, phosphine oxide and carbamoyl phosphine oxide groups, yielding the cationic FILs. For the comparison purposes the series of anionic FILs on the basis of tetrazolate anion functionalized with phosphine oxide groups has been synthesized. The structure of FILs was varied by different counterions – imidazolium and tetraalkylammonium cations, as well as by the lengths of alkyl spacers between the heterocycle and phosphine oxide group.

Furthermore imidazolium fragments were covalently tethered to calix[4]arene phosphine oxide, affording the functionalized cationic ionic liquid. The upper rim or the lower rim calix[4]arene phosphine oxides containing dihydroxyphosphoryl, dialkoxyposphonyl and nitrile functional groups at the opposite rim of macrocycle were obtained as synthons for preparation of anionic FILs.

The structures of compounds were confirmed by ^1H , ^{31}P NMR, element analysis, and X-ray. All compounds synthesized have $mp < 100\text{ }^\circ\text{C}$, thus according to the general definition are ionic liquids.

II.4 Experimental part. Synthesis

Melting temperatures were determined on a Boetius apparatus and were not corrected. The column chromatography was performed with silica gel “Merck” (L 40/100). NMR spectra (^1H , ^{31}P) were recorded at 25 °C on Varian-VXR300 and Gemini-200 spectrometers (unless otherwise specified).

X-ray studies were performed by Dr. S.V.Shishkin and Prof. O.V.Shishkin in State Scientific Institution “Institute for Single Crystals”, National Academy of Sciences of Ukraine.

X-Ray diffraction studies were performed on an automatic «Xcalibur 3» diffractometer (graphite monochromated MoK_α radiation, CCD-detector, ω -scanning). The structures were solved by direct method using SHELXTL package.

All the solvents were distilled prior the synthesis. Acetone and chloroform were used right after distillation over P_2O_5 . Ether, hexane, benzene after the same purification were stored over sodium wire.

Starting phosphorylating reagents $\text{R}_2\text{POPr-i}$, RP(OPr-i)_2 та P(OPr-i)_3 were synthesized according to the methods [108].

Starting calix[4]arenes **2.16**, **2.17**, **2.18**, **2.19a**, **2.26**, **2.29**, **2.30a,b** were obtained as described in literature [109, 104].

All calixarenes are named according to the nomenclature proposed in the work of Gutsche et al [110].

Abbreviations for multiplicities and descriptors in NMR spectra:

- s = singlet
- dd = doublet of doublets
- d = doublet
- dt = doublet of triplets
- t = triplet
- td = triplet of doublets
- q = quartet
- br s = broad singlet
- m = multiplet (denotes complex pattern)

II.4.1 Synthesis of malonamide-IL (FIL-MA)

1-(6-Bromohexyl)-3-methylimidazolium bromide 2.1

A solution of 1-methylimidazole (5 g, 62 mmol) in methylene chloride (50 ml) was added to a solution of 1,6-dibromohexane (60 g, 240 mmol) at room temperature. The reaction mixture was refluxed for 10 h. After evaporation of the solvent, the unreacted 1,6-dibromohexane was washed out thoroughly with hexane. The resulting solid was purified by silica column chromatography (acetone : MeOH = 3 : 1) to give the product (16.8 g, 84%) and 1,1'-(hexane-1,6-diyl) bis(3-methyl-1*H*-imidazolium-1-yl) dibromide as the second product (1.26 g, 5%).

^1H NMR (300.130 MHz, D_2O): δ 1.25–1.78 (m, 8H; $\text{NCH}_2(\text{CH}_2)_4\text{CH}_2\text{Br}$), 3.45 (t, 2H, CH_2Br), 3.84 (s, 3H; NCH_3), 4.14 (t, 2H; im- CH_2), 7.38 (s, 1H, NCHCHN), 7.42 (s, 1H, NCHCHN), 8.66 (s, 1H, NCHN).

1-(6-Bromohexyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide 2.2

To a solution of 1-(6-bromohexyl)-3-methylimidazolium bromide (3 g, 9.2 mmol) in deionized water (50 ml) LiTf_2N (2.9 g, 10 mmol) was added in water (15 ml). The mixture was stirred at

room temperature for 35 h. The solid was filtered off through Celite, and the filtrate was evaporated to remove the solvent. The product was extracted with dichloromethane (30 ml) and washed several times with aliquots of water (20 ml) until bromide anion was no longer detected by the AgNO_3 test. Evaporation of the solvent yielded the compound as a yellow viscous liquid (4.6 g, 95%).

^1H NMR (300.130 MHz, CDCl_3): δ 1.39–1.97 (m, 8H; $\text{NCH}_2(\text{CH}_2)_4\text{CH}_2\text{Br}$), 3.42 (t, 2H, CH_2Br), 3.97 (s, 3H; NCH_3), 4.20 (t, 2H; im- CH_2), 7.28 (s, 1H, NCHCHN), 7.32 (s, 1H, NCHCHN), 8.80 (s, 1H, NCHN).

3-Bis(butyl(methyl)carbamoyl)butyl-1-methyl-1*H*-imidazolium bis(trifluoromethylsulfonyl)imide 2.3

Sodium hydride (0.16 g of a 60 % dispersion in mineral oil, 4.1 mmol) was washed with dry hexane and suspended in dry DMF (10 ml). Compound DMDDBMA (1 g, 4.1 mmol) was added, the solution was cooled to 0 °C in an ice bath and the reaction was allowed to stir at room temperature until hydrogen evolution had ceased. 1-(6-bromohexyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (2.17 g, 4.1 mmol) in DMF (10 ml) was added and the mixture was stirred at 80 °C for 24 h. DMF was removed under vacuum and then water was added to the reaction product and the aqueous phase was extracted into chloroform. The organic phase was then washed with dilute HCl and NaCl, dried over Na_2SO_4 , filtered, and evaporated from chloroform to give 2 g of crude product. The yellow oil was then dissolved in acetone (30 ml), charcoal (0.2 g) was added to the solution and the resulting mixture was stirred at room temperature for 12 h. The solution was then passed through a gravity column (diameter 1 cm) containing approximately 4 cm of activated neutral alumina to remove any residual mineral oil and charcoal. Solvent was removed by rotary evaporation at room temperature and the ionic liquid was finally dried under reduced pressure for three days at 100 °C to give FIL-MA as a highly viscous liquid (1.83 g, 64 %).

^1H NMR (300.130 MHz, CDCl_3): δ 0.93 (6H, t, C- CH_3), 1.39–1.82 (m, 18H; C- CH_2 -C), 2.91 (m, 6H; N- CH_3), 3.31 (m, 4H, N- CH_2), 3.52 (t, 1H, CH), 3.90 (s, 3H; im- CH_3), 4.13 (t, 2H; im- CH_2), 7.21 (s, 1H, NCHCHN), 7.31 (s, 1H, NCHCHN), 8.99 (s, 1H, NCHN);

^{13}C NMR (75.47 MHz, CDCl_3): δ 13.8, 20.0, 23.54, 25.3, 27.2, 28.3, 28.5, 28.9, 29.5, 30.3, 30.8, 33.8, 35.5, 36.4, 47.8, 48.64, 49.6, 117.7, 121.9, 122.5, 123.6, 136.5, 169.9, 170.7.

II.4.2 Synthesis of phosphine oxide FILs

II.4.2.1 Synthesis of cationic phosphine oxide FIL

4-Chlorobutyl-dibutylphosphine oxide 2.4

The mixture of 1,4-dichlorobutane (40 ml, 0.365 mol) and isopropyl-dibutylphosphinite (5 g, 0.024 mol) was heated and stirred at 100 °C for 4 h. After the vacuum evaporation of the excess of dichlorobutane the residual liquid was distilled fractionally under reduced pressure (0.01 mm Hg). The fraction with boiling point 120–124 °C was collected. (Yield 5.28 g, 87 %).

^1H NMR (300.130 MHz, CDCl_3): δ 0.78 (t, 6H, J 7.5 Hz, - CH_2 - CH_3), 1.24–1.34 (m, 4H, - CH_2 - CH_2 - CH_3), 1.34–1.46 (m, 4H, - CH_2 - CH_2 - CH_3), 1.52–1.62 (m, 8H, P- CH_2 - CH_2 & - CH_2 - CH_2 - CH_2 -Cl), 1.69–1.79 (m, 2H, - CH_2 - CH_2 - CH_2 -Cl), 3.43 (t, 2H, J 6.3 Hz, - CH_2 - CH_2 -Cl);

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

1-Methyl-3-[4-(dibutylphosphinoyl)butyl]-3H-imidazol-1-ium bis-trifluoromethyl-sulphonylimidate (SM1006) 2.6

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

¹H NMR (300.130 MHz, CDCl₃): δ 0.93 (t, 6H, J 7.5 Hz, -CH₂-CH₃), 1.38-1.55 (m, 8H, -CH₂-CH₂-CH₂-CH₃), 1.67-1.77 (m, 8H, P-CH₂-CH₂- & -CH₂-CH₂-CH₂-N), 2.04-2.15 (m, 2H, -CH₂-CH₂-CH₂-N), 3.93 (s, 3H, N-CH₃), 4.24 (t, 2H, J 7.2 Hz, -CH₂-N), 7.30 (s, 1H, C5H in Im); 7.44 (s, 1H, C4H in Im); 8.93 (s, 1H, N=CH-N);

³¹P NMR (121.421 MHz, CDCl₃): δ 50.0.

II.4.2.2 Synthesis of anionic phosphine oxide FILs

***n*-Dipropyl-cyanophosphine oxide 2.7**

The solution of cyanogen iodide (20.5 g, 0.134 mol) in 100 ml of diethyl ether was added dropwise to the stirring solution of the isopropyl-di-*n*-propylphosphinite (23.6 g, 0.134 mol) in 250 ml of diethyl ether at the room temperature. The reaction mixture was left at room temperature for 1 hour and then the volatile compounds were removed under reduced pressure (10 mm Hg). The heavy brown residual liquid was distilled fractionally under the vacuum (0.01 mm Hg). Two fractions were collected. The first one is *n*-dipropyl-cyanophosphine oxide (dipropylphosphinyl cyanide) *mp* 36-37 °C, *bp* 70-72 °C, (Yield 9.81 g, 46%). The second fraction is iodine anhydride of *n*-dipropylphosphinous acid *mp* ~ 50 °C, *bp* 122-124 °C (Yield 10.02 g, 44 %).

¹H NMR (299.943 MHz, CDCl₃): δ 1.096 (t, 6H, CH₃), 1.66-1.88 (m, 4H, -CH₂-CH₂-CH₃), 1.88-2.09 (m, 4H, -CH₂-CH₂-CH₃);

³¹P NMR (121.421 MHz, CDCl₃): 30.6.

Dipropyl-cyanomethylphosphine oxide 2.9a

The mixture of chloroacetonitrile (5 ml, 79 mmol) and isopropyl-dipropylphosphinite (9.83 g, 55.8 mmol) was stirred for 3 h at 45 °C in the bath. After vacuum evaporation of the excess of chloroacetonitrile the residual white solid mass was recrystallized (*pentane:isopropanol* = 10:1). The colorless crystals of the phosphine oxide were obtained *mp* 78 °C. (Yield 8.56 g, 95.5 %).

¹H NMR (299.943 MHz, CDCl₃): δ 1.054 (t, 6H, CH₃), 1.58-1.78 (m, 4H, -CH₂-CH₂-CH₃), 1.78-1.91 (m, 4H, -CH₂-CH₂-CH₃), 2.80-2.86 (d, 2H, -CH₂-P);

³¹P NMR (121.421 MHz, CDCl₃): 44.5.

Dibutyl-(2-cyanoethyl)phosphine oxide 2.9b

The 3-bromopropionitrile (5.78 g, 0.04 mol) was added to a solution of dibutylphosphine oxide (7 g, 0.04 mol) in the DMSO (50 ml). Then the solution of sodium hydroxyde (1.72 g, 0.04 mol) in 1.8 g of water was added dropwise at room temperature with magnetic stirring. After 12 hours of stirring the reaction mixture was poured into ice water (300 ml) and extracted with dichlorometnane (2×100 ml). The combined organic layers were dried with sodium sulfate and evaporated in vacuum. The resulting liquid was dried in vacuum and use for next stage without purification. (Yield 7 g, 76.25 %).

¹H NMR (300.130 MHz, CDCl₃): δ 0.835 (t, 6H, J 7.5 Hz, -CH₂-CH₃), 1.14-1.34 (m, 8H, -CH₂-CH₂-CH₂-CH₃), 1.62 (m, 4H, P-CH₂-CH₂-CH₂-CH₃), 1.81 (m, 2H, -CH₂-CH₂-CN), 3.35 (m, 2H, -CH₂-CH₂-CN);

³¹P NMR (121.421 MHz, CDCl₃): δ 34.9.

5-(Dibutylphosphinoyl)-pentanenitrile 2.9c

The mixture of freshly distilled 5-chloropentanenitrile (50g, 0.425 mol) and isopropyl dibutylphosphinite (25g, 0.122 mol) was stirred at 80 °C under vacuum (12 mm Hg) for 8 hours. After the evaporation of the excess of 5-chloropentanenitrile, the viscous residue was distilled twice in a high vacuum to give the product as colorless viscous liquid (Yield 19.9 g, 68%) (*bp* 141 (0.01 mm Hg)).

¹H NMR (400 MHz, CDCl₃): δ 0.904-0.941 (m, 6H, -CH₂-CH₃), 1.275-1.469 (m, 4H, P-CH₂-CH₂-CH₂-CH₃), 1.469-1.601 (m, 4H, P-CH₂-CH₂-CH₂-CH₃), 1.601-1.731 (m, 6H, P-CH₂-CH₂-CH₂-CH₃, P-CH₂-CH₂-CH₂-CH₂-CN), 1.731-1.850 (m, 4H, P-CH₂-CH₂-CH₂-CH₂-CN), 2.386(m, 4H, P-CH₂-CH₂-CH₂-CH₂-CN);

³¹P NMR (121.421 MHz, CDCl₃): δ 45.8.

Dipropylphosphinoyl-1,2,3,4-tetraazole 2.8

6.93 g (0.044 mol) of dipropyl-cyanophosphine oxide, 4.34 g (0.067 mol) of sodium azide, 4.55 g (0.085 mol) of ammonium chloride and 35 ml of DMF were mixed and heated to 125 °C in the bath. The reaction mixture was stirred at this temperature within 24 h. Then the solvent was evaporated under reduced pressure (100 mm Hg). The residue was dissolved in 25 ml of H₂O. The product was extracted with CH₃Cl (2×50 ml). The extracted fractions were dried over Na₂SO₄ with further evaporation of the solvent. The residue was triturated in pentane and filtrated. White powder was obtained (Yield 3.62, 42%).

³¹P NMR (121.421 MHz, CDCl₃): δ 60.3.

5-(2-(Dibutylphosphinoyl)methyl)-1H-tetrazole 2.10a

The reaction mixture containing cyanomethyl-dipropylphosphine oxide (5.0 g, 0.029 mol), sodium azide (2.85 g, 0.044 mol), and ammonium chloride (3.0 g, 0.056 mol) in 25 ml of dry DMF was stirred for 24h at 120 °C. The solvent was removed in vacuum. To the residue 30 ml of H₂O were added. The product was isolated by extraction with chloroform. The combined organic layers were dried over Na₂SO₄, then filtered and dried in high vacuum (0.01 mm Hg). The viscous product was triturated in 30 ml of hexane +1 ml of methanol, and then filtered. Colorless powder was obtained *mp* 178-180 °C (Yield 3.75 g, 59.6%).

^1H NMR (299.943 MHz, CDCl_3): δ 1.054 (t, 6H, $-\text{CH}_2-\text{CH}_3$), 1.58-1.75 (m, 4H, $-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 1.76-1.94 (m, 4H, P- $\text{CH}_2-\text{CH}_2-\text{CH}_3$), 2.805-2.853 (d, J 14.4 Hz, 4H, $\text{CH}_2-\text{CN}_4\text{H}$);
 ^{31}P NMR (121.421 MHz, CDCl_3): δ 43.8.

5-(2-(Dibutylphosphinoyl)ethyl)-1H-tetrazole 2.10b

The mixture of 2-cyanoethyl-dibutylphosphine oxide (5 g, 0.023 mol), sodium azide (1.95 g, 0.034 mol), and ammonium chloride (2.5 g, 0.046 mol) in dry DMF (20 ml) was stirred for 24 h at 120 °C. After evaporation of the solvent, the residue was poured into a glass with cold water (100 ml). The product was isolated by extraction of dichloromethane ($2 \times 100\text{ml}$). The combined organic phases were dried over sodium sulphate and evaporated under the vacuum to dryness. The crude tetrazole was recrystallized (hexane). Light cream crystals were obtained *mp* 121-122 °C (Yield 2.2g, 37.28 %).

^1H NMR (300.130 MHz, CDCl_3): δ 0.86 (t, 6H, J 7.25 Hz, $-\text{CH}_2-\text{CH}_3$), 1.31-1.42 (m, 4H, $-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 1.45-1.55 (m, 4H, P- $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 1.66-1.76 (m, 4H, P- $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 2.19-2.28 (m, 2H, $-\text{CH}_2-\text{CH}_2-\text{CN}_4\text{H}$), 3.20-3.29 (m, 2H, $-\text{CH}_2-\text{CH}_2-\text{CN}_4\text{H}$);
 ^{31}P NMR (121.421 MHz, CDCl_3): δ 52.6.

(Dibutylphosphinoyl)butyl-1H-1,2,3,4-tetrazole 2.10c

The mixture of 4-cyanobutyl-dibutylphosphine oxide (25 g, 0.102 mol), sodium azide (12 g, 0.17 mol), and ammonium chloride (11 g, 0.2 mol) in dry DMF (100 ml) was stirred at 120 °C for 24 h. After evaporation of the solvent, the residue was poured into a glass with cold water (250 ml). The precipitate formed was filtered and washed twice with ice-cold water and dried on air to constant weight (Yield 22.7 g, 78 %).

^1H NMR (400 MHz, CDCl_3): δ 0.878-0.8914 (m, 9H, $-\text{CH}_2-\text{CH}_3$), 1.325-1.443 (m, 4H, P- $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 1.443-1.555 (m, 4H, P- $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 1.455-1.651 (m, 2H, P- $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}$), 1.651-1.800 (m, 6H, P- $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$, P- $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}$), 1.935 (m, 2H, P- $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}$), 2.958 (P- $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}$);
 ^{31}P NMR (80.950 MHz, CDCl_3): δ 56.7.

X-ray diffraction study: There are two molecules (A and B) of compound **2.10c** in the asymmetric part of unit cell. The C2-C3-C4-C5-P1-C6-C7-C8-C9 fragment in both molecules has all-trans conformation (the corresponding torsion angles are C1-C2-C3-C4 178.1(2)° A -178.0(2)° B; C2-C3-C4-C5 178.3(2)° A -178.5(2)° B; C3-C4-C5-P1 178.9(2)° A -176.9(2)° B; C4-C5-P1-C6 168.2(2)° A -168.9(2)° B; C5-P1-C6-C7 179.8(2)° A -179.7(2)° B; P1-C6-C7-C8 -179.9(2)° A -179.1(2)° B; C6-C7-C8-C9 -176.3(2)° A 177.8(2)° B). N-Butyl substituent C10-C11-C12-C13 also has all-trans conformation (the P1-C10-C11-C12 and C10-C11-C12-C13 torsion angles are 179.3(2)° A -177.7(2)° B and 177.6(3)° A -172.7(3)° B, respectively). It is located in +*sc* (molecule A) or -*sc* (molecule B) conformation relatively the C4-C5 bond (the C10-P1-C5-C4 torsion angle is -75.9(2)° A 75.8(2)° B) and is turned essentially relatively the C5-P1 bond (the C5-P1-C10-C11 torsion angle is -68.0(2)° A 68.8(2)° B).

In the crystal phase the molecules of compound **13c** form the centrosymmetric dimers (A-A and B-B) by the N1A-H...O1A' (-*x*, -*y*, 1-*z*) (H...O 1.45 Å N-H...O 172°) and N1B-H...O1B' (2-*x*, 1-*y*, 1-*z*) (H...O 1.78 Å N-H...O 173°) intermolecular hydrogen bonds.

General procedure for the preparation of tetraazolates (2.11a-e)

Anhydrous potassium carbonate (0.16 g, 1.1 mmol) was added to a solution of the (dibutylphosphinoyl)ethyl-tetraazole (0.2 g, 0.77 mmol) in dry acetone (5 ml) and the mixture was stirred for 10 min at 20-25 °C. Then the solution of the appropriate tetraalkylammonium or imidazolium halide (0.77 mmol) in dichloromethane was added and the reaction mixture was stirred for 24h at rt. The mixture was filtered and concentrated under vacuum to give the product as viscous oil.

Tributyl-methylammonium dibutylphosphinoylethyl-1,2,3,4-tetraazolate 2.12a

(Yield 97 %)

¹H NMR (300.130 MHz, CDCl₃): δ 0.84-0.97 (m, 15H, -CH₂-CH₃), 1.31-1.43 (m, 10H, P-CH₂-CH₂-CH₂-CH₃ & -CH₂-CH₂-CH₂-N), 1.45-1.70 (m, 14H, P-CH₂-CH₂-CH₂-CH₃ & -CH₂-CH₂-N-CH₃), 2.18-2.26 (2 H, P-CH₂-CH₂-N), 3.06-3.15 (m, 2H, P-CH₂-CH₂-N), 3.13 (s, 3H, N-CH₃), 3.23-3.29 (m, 6H, -CH₂-N-CH₃);

³¹P NMR (121.421 MHz, CDCl₃): δ 49.0.

Trioctyl-methylammonium (dibutylphosphinoyl)ethyl-1,2,3,4-tetraazolate 2.12b

(Yield 89 %)

¹H NMR (300.130 MHz, CDCl₃): δ 0.77-0.87 (m, 15H, -CH₂-CH₃), 1.14-1.38 (m, 38H, P-CH₂-CH₂-CH₂-CH₃ & -(CH₂)₅-CH₂-CH₂-N), 1.42-1.67 (m, 10H, P-CH₂-CH₂-CH₂-CH₃ & -CH₂-CH₂-N), 2.16-2.26 (2 H, P-CH₂-CH₂-N), 3.05-3.15 (m, 2H, P-CH₂-CH₂-N), 3.11 (s, 3H, N-CH₃), 3.20-3.27 (m, 6H, -CH₂-N-CH₃);

³¹P NMR (121.421 MHz, CDCl₃): δ 49.0.

1-Butyl-3-methylimidazolium (dibutylphosphinoyl)ethyl-1,2,3,4-tetraazolate 2.12c

(Yield 96 %)

¹H NMR (300.130 MHz, CDCl₃): δ 0.83 (t, 9H, J 7.5 Hz, -CH₂-CH₃), 1.20-1.81 (m, 16H, P-CH₂-CH₂-CH₂-CH₃ & -CH₂-CH₂-CH₂-N), 2.16-2.26 (m, 2H, P-CH₂-CH₂-N), 3.03-3.14 (m, 2H, P-CH₂-CH₂-N), 3.92 (s, 3H, N-CH₃), 4.17 (t, 2H, J 7.5 Hz, -CH₂-N=CH-N), 7.32 (s, 1H, C5H in Im); 7.41 (s, 1H, C4H in Im); 9.95 (s, 1H, N=CH-N);

³¹P NMR (121.421 MHz, CDCl₃): δ 49.5.

1-Decyl-3-methylimidazolium dibutylphosphinoylethyl-1,2,3,4-tetraazolate 2.12d

(Yield 78 %)

¹H NMR (300.130 MHz, CDCl₃): δ 0.86-0.96 (m, 9H, -CH₂-CH₃), 1.16-1.76 (m, 24H, P-CH₂-CH₂-CH₂-CH₃ & -CH₃-(CH₂)₈-CH₂-N), 1.86-1.92 (m, 4H, P-CH₂-CH₂-CH₂-CH₃), 2.24-2.34 (m, 2H, P-CH₂-CH₂-N), 3.11-3.22 (m, 2H, P-CH₂-CH₂-N), 4.00 (s, 3H, N-CH₃), 4.24 (t, 2H, J 7.8 Hz, -CH₂-N=CH-N), 7.23 (s, 1H, C5H in Im); 7.31 (s, 1H, C4H in Im); 10.16 (s, 1H, N=CH-N);

³¹P NMR (121.421 MHz, CDCl₃): δ 49.0.

1-Decyl-3-methylimidazolium dibutylphosphinoylbutyl-1,2,3,4-tetraazolate (DM01) 2.12e

Anhydrous potassium carbonate (10.46 g, 0.076 mol) was added to a solution of the (dibutylphosphinoyl)butyl-tetraazole (15.08 g, 0.053 mol) in dry acetone (400 ml) and the

mixture was stirred for 1 hour at 20-25 °C. Then imidazolium bromide (15.97 g, 0.053 mol) was added and the reaction mixture was stirred for 24h at rt. The mixture was filtered off and concentrated under vacuum, to give product as viscous oil. (Yield, 83 %)

¹H NMR (400 MHz, CDCl₃): δ 0.755-0.865 (m, 9H, -CH₂-CH₃), 1.110-1.233 (m, 14H, CH₃-(CH₂)₇-CH₂-CH₂-N), 1.255-1.370 (m, 4H, P-CH₂-CH₂-CH₂-CH₃), 1.370-1.491 (m, 4H, P-CH₂-CH₂-CH₂-CH₃), 1.491-1.681 (m, 6H, P-CH₂-CH₂-CH₂-CH₃, P-CH₂-CH₂-CH₂-CH₂-C), 1.681-1.777 (m, 2H, P-CH₂-CH₂-CH₂-CH₂-C), 1.777-1.861 (m, 2H, N-CH₂-CH₂-(CH₂)₇-CH₃), 2.822 (m, 2H, P-CH₂-CH₂-CH₂-CH₂-C), 3.652 (P-CH₂-CH₂-CH₂-CH₂-C), 3.875 (s, 3H, N-CH₃ in Im), 4.105 (m, 2H, N-CH₂-CH₂-(CH₂)₇-CH₃), 7.238 (s, 1H, C5H in Im), 7.341 (s, 1H, C4H in Im), 9.907 (s, 1H, N=CH-N);

³¹P NMR (80.950 MHz, CDCl₃): δ 46.3.

II.4.3 Synthesis of CMPO-IL

3-(Octylphenylphosphinoylacetyl amino)propyl-3H-imidazole 2.13 (imidazole-CMPO)

A mixture of methyl(phenyloctyl)phosphinoyl acetate (10 g, 0.0322 mol) and 1-(3-aminopropyl)-imidazole (7.7ml, 0.0644 mol) was heated in a sealed ampoule at 105 °C for 72 h. The ampoule was opened and the solvent was removed in vacuum. The viscous yellow residue was recrystallized from hexane to give amide as a white solid. *Mp* 47-49 °C. (Yield 10 g, 77.5%).

¹H NMR (300.130 MHz, CDCl₃): δ 0.84 (t, 3H, J 7.0 Hz, CH₃), 1.21-1.61 (m, 14H, CH₂), 1.83 (q, 2H, J 6.6 Hz, CH₂-CH₂-NHC(O)), 1.87-2.18 (m, 2H, P-CH₂-CH₂), 3.29 (qv, 2H, J 6.4 Hz, CH₂-NH-C(O)), 3.84 (t, 2H, J 7.15 Hz, CH₂-CH₂-CH₂-NHC(O)), 6.87 (s, 1H, C5H in Im); 6.91 (s, 1H, C4H in Im); 7.03 (s, 1H, NH); 7.45 (s, 1H, N=CH-N); 7.47-7.77 (m, 5H, *m*- & *p*-C₆H₅-P & *o*-C₆H₅-P);

³¹P NMR (121.421 MHz, CDCl₃): δ 38.2.

1-Methyl-3-(octylphenylphosphinoylacetyl amino)propyl-3H-imidazol-1-ium bis-trifluoromethanesulfonimide (CMPO-IL) 2.15

To a solution of phenyloctyl-*N*-(1-imidazolylpropyl)carbamoylmethylphosphine oxide **2.13** (3.5 g, 8.67 mmol) in dichloromethane (20 ml) iodomethane (1.85 g, 13 mmol) was added at rt. The mixture was stirred for 12h at rt. Then the volatile compounds were evaporated under vacuum and the resulting oil was washed with dry Et₂O (2×15 ml). The residual ether was removed under reduced pressure. The viscous compound **2.14** (yield 4.73 g, 100%) was used for the next stage without purification.

To a solution of imidazolium iodide **2.14** (4.73g, 8.67 mmol) in water (50 ml) the lithium bis(trifluoromethane)sulfonimide (3.75 g, 13 mmol) was added at rt. The mixture was stirred for 12 h at rt. The product was extracted with dichloromethane (2×100ml), and then washed with water (72×50 ml), combined organic layers were dried over sodium sulphate and concentrated under reduced pressure. Resulting ionic liquid **2.15** (oil) was dried in high vacuum to afford 4.36 g (Yield 72%).

¹H NMR (300.130 MHz, CDCl₃): δ 0.79 (t, 3H, J 7.0 Hz, CH₃), 1.07 - 1.40 (m, 14H, CH₂), 1.40-1.51 (m, 2H, P-CH₂-CH₂), 1.91 (m, 2H, CH₂-CH₂-NHC(O), J 6.6 Hz), 3.06 (m, 2H, J 6.4 Hz, CH₂-NH-C(O)), 3.78 (s, 3H, CH₃-N), 4.04 (m, 2H, CH₂-CH₂-CH₂-NHC(O)), 7.21 (s, 1H, C5H

in Im); 7.35 (s, 1H, C4H in Im); 7.42 (s, 1H, NH); 7.33-7.53 (m, 3H, *m*- & *p*-C₆H₅-P); 7.56-7.68 (m, 2H, *o*-C₆H₅-P), 8.92 (s, 1H, N=CH-N);
³¹P NMR (121.421 MHz, CDCl₃): δ 39.2.

II.4.4 Synthesis of calix[4]arenes

25,26,27,28-Tetrabromobutoxycalix[4]arene 2.17

5.4 ml of a NaOH solution (25M in H₂O) were added to a solution of tetrahydroxycalixarene 2.7 (7.7 g, 0.018 mol) in 160 ml of DMSO at 50 °C. At this temperature 1,4-dibromobutane (43.3 ml, 0.362 mol) was added and the mixture was stirred for 2 h. After cooling to rt, the mixture was poured on 400 ml of ice-cold water. The oil layer formed was separated, the aqueous phase was subjected to extraction with chloroform (300 ml). The combined organic layers were washed with water (2×150 ml) and dried over Na₂SO₄. Chloroform was evaporated under reduced pressure. The excess of dibromobutane was evaporated in high vacuum (0.01 mm Hg). The oil residue was triturated in methanol, filtered off and dried in the open air to afford **2.8** as white solid. Yield 77.58%, *mp* 80-82 °C.

¹H NMR (300 MHz, CDCl₃): δ 2.04 (m, 16H, O-CH₂-CH₂-CH₂-CH₂-Br), 3.19 and 4.39 (two d, 8H, J 13.50 Hz, Ar-CH₂-Ar), 3.51 (t, 8H, O-CH₂-CH₂-CH₂-CH₂-Br), 3.93 (t, 8H, O-CH₂-CH₂-CH₂-CH₂-Br), 6.61 (m, 12H, ArH);

Calculated for C₄₄H₅₂Br₄O₄, %: C 54.79, H 5.43, Br 33.14, O 6.64;

Found, %: C 54.83, H 5.36.

5,11,17,23-Tetrachloromethyl-25,26,27,28-tetrabromobutoxycalix[4]arene 2.18

Methyl chloromethyl ether (5.5 ml, 72 mmol) was added to the solution of calixarene **2.17** (1.4 g, 1.45 mmol) in 100 ml of chloroform. The reaction mixture was cooled down to -55 °C and tin tetrachloride (1.44 ml, 12.3 mmol) was added while stirring. After 1h of stirring at this temperature 100 ml of hot water were added, the mixture was stirred 15 minutes. The organic layer was separated, washed with distilled water, and dried over Na₂SO₄. The solvent was removed under reduced pressure, and after the crystallization from the mixture heptane/acetone **2.18** was obtained as white powder. Yield 78%, *mp* 129-30 °C.

¹H NMR (300 MHz, CDCl₃): δ 2.00 (m, 16H, O-CH₂-CH₂-CH₂-CH₂-Br), 3.18 and 4.36 (two d, 8H, J 13.20 Hz, Ar-CH₂-Ar), 3.49 (t, 8H, O-CH₂-CH₂-CH₂-CH₂-Br), 3.93 (t, 8H, O-CH₂-CH₂-CH₂-CH₂-Br), 4.30 (s, 8H, Ar-CH₂-Cl), 6.67 (m, 8H, ArH);

Calculated for C₄₈H₅₆Br₄Cl₄O₄, %: C 49.77, H 4.87, Br 27.59, Cl 12.24, O 5.52;

Found, %: C 49.82, H 4.91.

5,11,17,23-Tetrakis(diethylphosphinoylmethyl)-25,26,27,28-tetrabromobutoxycalix[4]arene 2.19a

To the solution of calixarene **2.18** (1 g, 0.86 mmol) in chloroform (3 ml) at 0-5 °C the solution of isopropylphosphinite (0.68 ml, 3.8 mmol) in chloroform (0.6 ml) was added dropwise. The reaction mixture was stirred for 1h at 0-5 °C, and 24h at rt. The volatile compounds were removed under reduced pressure. The oil obtained was dissolved in water (50 ml) and stirred with charcoal (0.5 g) at 25 °C for 30 min, then filtered. The filtrate was acidified with HCl (pH

3-4) and extracted with chloroform (2×50 ml). The organic layers were combined, and the solvent was evaporated under reduced pressure. The residue was treated with hexane to give a powder, which was filtered and dried in vacuum (0.01 mm Hg, 40 °C) to afford **2.19a** as a colorless crystal compound. Yield 73%, *mp* 86-88 °C.

¹H NMR (300 MHz, CDCl₃): δ 1.08 (m, 24H, CH₃), 1.49 (m, 16H, P-CH₂-CH₃), 2.01 (m, 16H, O-CH₂-CH₂-CH₂-CH₂-Br), 2.74 (d, 8H, J 13.8 Hz, Ar-CH₂-P), 3.13 and 4.30 (two d, 8H, J 13.35 Hz, Ar-CH₂-Ar), 3.47 (t, 8H, O-CH₂-CH₂-CH₂-CH₂-Br), 3.87 (t, 8H, O-CH₂-CH₂-CH₂-CH₂-Br), 6.56 (s, 8H, ArH);

³¹P NMR (80.95 MHz, CDCl₃): δ 49.7;

Calculated for C₇₂H₁₁₂Br₄O₈P₄, %: C 55.82, H 7.29, P 8.00;

Found, % C 55.66, H 7.11, P 8.07.

5,11,17,23-Tetrakis(dibutylphosphinoylmethyl)-25,26,27,28-tetrabromobutoxy-calix[4]arene 2.19b

Isopropyl dibutyl phosphinite was added to the solution of calixarene **2.18** (4.253 g, 3.761 mmol) in benzene (20 ml) at 5 °C. The reaction mixture was stirred during 1h at rt, and 96h at 60 °C. The volatile compounds were removed under reduced pressure. Compound **2.19b** was obtained as light-yellow powder. Yield 82%, *mp* 75-79 °C.

¹H NMR (300 MHz, CDCl₃): δ 0.865 (m, 24H, CH₃), 1.343 - 1.455 (m, 40H, P-CH₂-CH₂-CH₂-CH₃, O-CH₂-CH₂-CH₂-CH₂-Br), 1.829 (m, 16H, P-CH₂-CH₂-CH₂-CH₃), 1.956 (m, 8H, O-CH₂-CH₂-CH₂-CH₂-Br), 2.727 (d, 8H, Ar-CH₂-P), 3.079 and 4.273 (two d, 8H, J 13.2 Hz, Ar-CH₂-Ar), 3.574 (t, 8H, O-CH₂-CH₂-CH₂-CH₂-Br), 3.832 (t, 8H, O-CH₂-CH₂-CH₂-CH₂-Br), 6.435 (s, 8H, ArH);

³¹P NMR (80.95 MHz, CDCl₃): δ 41.3;

Calculated for C₈₀H₁₂₈Br₄O₈P₄, %: C 57.84, H 7.77, Br 19.24, O 7.70, P 7.46%;

Found, % C 57.66, H 7.92, P 7.04.

5,11,17,23-Tetrakis(dibutylphosphinoylmethyl)-25,26,27,28-tetra(4-(1-methylimidazolium)butoxy)calix[4]arene tetra bromide 2.20

The mixture of calixarene **2.19b** (0.69 g, 0.418 mmol) and 1-methyl-imidazole (1 ml, 12.54 mmol) was stirred at 70 °C for 3 h. The excess of 1-methyl-imidazole was evaporated under reduced pressure (10 mmHg, 100 °C). The solid residue was washed with dry diethyl ether (3×15 ml) and dried under high vacuum to constant weight. Yielded colorless compound **2.20** (0.69 g, 96%), *mp*= 50-90 °C.

¹H NMR (300 MHz, CDCl₃): δ 0.914 (t, 24H, CH₃), 0.902 (m, 16 H, O-CH₂-CH₂-CH₂-CH₂-N), 1.352 (m, 16H, P-CH₂-CH₂-CH₂-CH₃), 1.49 (m, 16H, P-CH₂-CH₂-CH₂-CH₃), 1.894 (m, 16H, P-CH₂-CH₂-CH₂-CH₃), 2.727 (d, 8H, Ar-CH₂-P), 2.895-3.025 (m, 12H, O-CH₂-CH₂-CH₂-CH₂-N and Ar-CH₂-Ar_{eq}), 3.21 (s, 12 H, N-CH₃), 3.301-3.526 (m, 12 H, O-CH₂-CH₂ and Ar-CH₂-Ar_{ax}), 5.842 (s, 8H, Ar), 6.435 and 6.485 (two d, 8H, J = 15Hz, N-CH=CH-N), 6.713 (s, 4H, N-CH=N);

³¹P NMR (80.95 MHz, CDCl₃): δ 42.7;

5,11,17,23-Tetrakis(dibutylphosphinoylmethyl)-25,26,27,28-tetra(4-(1-methyl-imidazolium)butoxy)calix[4]arene tetra(bis(trifluoromethanesulfonyl)amide) 2.21 (Calix-II)

Lithium bis(trifluoromethylsulfonyl)imide (0.56 g, 1.95 mmol) was added to the solution of calix[4]arene **2.20** (0.69 g, 0.39 mmol) in DMF, the mixture was stirred during 4h in a 40 °C bath. The solvent was evaporated under reduced pressure (10 mm Hg). The residue was dissolved in CH₂Cl₂ and carefully washed with deionized water (10×150 ml). The compound is crystal solid with *mp* = 120 °C.

¹H NMR (300 MHz, CDCl₃): δ 0.796 (m, 24H, CH₃), 1.200-1.766 (m, 48H, O-CH₂-CH₂-CH₂-CH₂-N, P-CH₂-CH₂-CH₂-CH₃), 1.845 (m, 16H, P-CH₂-CH₂-CH₂-CH₃), 2.742-2.784 (d, 8H, Ar-CH₂-P), 3.104-3.147 (d, 4H, Ar-CH₂-Ar_{eq}), 3.909-3.923 (m, 20H, N-CH₃ and O-CH₂-CH₂), 4.114-4.394 (m, 12H, -CH₂-CH₂-N and Ar-CH₂-Ar_{ax}), 6.560 (s, 8 H, Ar), 7.781 and 7.738 (two d, 8 H, *J* = 12.1 Hz, N-CH=CH-N), 9.141 (s, 4 H, N-CH=N);

³¹P NMR (80.95 MHz, DMSO-d₆): δ 44.5.

General procedure for the preparation of tetrahydroxycalixarene tetrphosphine oxides 2.23

The solution of R₂POPr-i (10.25mmol) was added to the solution of tetrahydroxycalixarene **2.22** (2.5 mmol) in chloroform (5 ml). The reaction flask was closed tight and left with magnetic stirring at 65 °C for 24h (**2.23a**, **2.23b**) or 96h (**2.23c**). The volatile compounds were evaporated under reduced pressure. Each crystal residue was purified as described further.

5,11,17,23-Tetrakis-diethylphosphinylmethyl-25,26,27,28-tetrahydroxycalix[4]arene 2.23a

Calixarene phosphine oxide **2.23a** was dissolved in water (30 ml) and treated with charcoal (0.5 g) at 50 °C (30 minutes). The filtrate was acidified with HCl (pH 3-4) and extracted with chloroform (2×50 ml). The organic layers were combined, and the solvent was evaporated under reduced pressure. The residue was treated with hexane to give a powder, which was filtered and dried in vacuum (0.01 mm Hg, 40 °C) to afford **2.23a** as a colorless crystal compound. Yield 86%, *mp* 145-147 °C.

¹H NMR (300 MHz, CDCl₃): δ 1.08 (m, 24H, CH₃), 1.61 (m, 16H, P-CH₂-CH₃), 3.49 (d, 8H, *J* = 14.10 Hz, Ar-CH₂-P), 3.49 and 4.13 (two d, 8H, *J* = 13.70 Ar-CH₂-Ar), 6.95 (s, 8H, ArH), 10.02 (m, 4H, Ar-OH);

³¹P NMR (80.95 MHz, CDCl₃): δ 49.3;

Calculated for C₄₈H₆₈O₈P₄, %: C 64.28, H 7.64; P 13.81;

Found, %: C 64.02, H 7.56, P 13.94.

5,11,17,23-Tetrakis-dipropylphosphinylmethyl-25,26,27,28-tetrahydroxycalix[4]arene 2.23b

Phosphine oxide **2.23b** was purified similarly to **2.23a**. Compound **2.23b** was obtained as colorless white crystalline solid. Yield 97%, *mp* 138-140 °C.

¹H NMR (300 MHz, CDCl₃): δ 0.95 (m, 24H, CH₃), 1.52 (m, 32H, P-CH₂-CH₂-CH₃), 2.81 (d, 8H, *J* = 13.97 Hz, Ar-CH₂-P), 3.45 and 4.13 (two d, 8H, *J* = 13.79 Hz, Ar-CH₂-Ar), 6.93 (s, 8H, ArH), 10.05 (s, 4H, Ar-OH);

^{31}P NMR (80.95 MHz, CDCl_3): δ 46.4;

Calculated for $\text{C}_{56}\text{H}_{84}\text{O}_8\text{P}_4$, %: C 66.65, H 8.39, P 12.28

Found, %: C 66.54, H 8.42, P 12.25

5,11,17,23-Tetrakis-diphenylphosphinylmethyl-25,26,27,28-tetrahydroxycalix[4]arene 2.23c

The crystallization of crude calixarene phosphine oxide from acetonitrile afforded compound **2.23c** as colorless crystalline solid. Yield 87%, *mp* 253-256 °C.

^1H NMR (300 MHz, CDCl_3): δ 3.21 and 3.95 (two d, 8H, $J = 14.69$ Hz, Ar- CH_2 -Ar), 3.37 (8H, $J = 13.16$ Hz, Ar- CH_2 -P), 6.75 (s, 8H, ArH), 7.33 and 7.59 (40H, PPh), 9.86 (c, 4H, Ar-OH);

^{31}P NMR (80.95 MHz, CDCl_3): δ 30.0;

Calculated for $\text{C}_{80}\text{H}_{68}\text{O}_8\text{P}_4$, %: C 74.99, H 5.35, P 9.67;

Found, %: C 74.86, H 5.01, P 9.53.

5,11,17,23-Tetrakis-diethylphosphinoylmethyl-25,27-dihydroxy-26,28-bis(diethoxyphosphoryloxy)calix[4]arene 2.24

Diethylchlorophosphate (1.73 g, 10.1 mmol) was added to the solution of tetrahydroxycalixarene **2.22** (4.48 g, 5 mmol) in 100 ml of chloroform and 20 ml of triethylamine. The reaction mixture was refluxed during 4h, then the solvent was evaporated under reduced pressure. The obtained oil was dissolved in water (50 ml) and treated with charcoal (0.8 g) at 50 °C (30 min). After filtration the aqueous solution was acidified with HCl (pH 3-4) and extracted with chloroform (3×50 ml). The combined organic layers were concentrated in vacuo and then triturated with hexane to yield a powder product. Filtration and drying under high vacuum (0.01 mm Hg, 40 °C) provided compound **2.24** as light-yellow solid. Yield 74%, *mp* 95-97 °C.

^1H NMR (300 MHz, CDCl_3): δ 0.78 and 1.09 (two m, 24H, P- CH_2 - CH_3), 1.34 (m, 8H, P- CH_2 - CH_3 and 12H, P-O- CH_2 - CH_3), 1.64 (m, 8H, P- CH_2 - CH_3), 2.67 and 2.98 (two d, 8H, $J = 15.00$ Hz, Ar- CH_2 -P), 3.40 and 4.37 (two d, 8H, $J = 14.40$ Hz, Ar- CH_2 -Ar), 5.69 (s, 2H, Ar-OH), 6.66 and 7.01 (two s, 8H, ArH);

^{31}P NMR (80.95 MHz, CHCl_3): δ -4.3 (s, 2P, P(OEt) $_2$), 50.4 (s, 4P, PEt $_2$);

Calculated for $\text{C}_{56}\text{H}_{86}\text{O}_{14}\text{P}_6$, %: C 57.53, H 7.41, P 15.90;

Found, %: C 57.62, H 7.41, P 15.84.

5,11,17,23-Tetrakis(diethylphosphinylmethyl)-25,27-dihydroxy-26,28-bis(dihydroxyphosphoryloxy)calix[4]arene 2.25

Bromotrimethylsilane was added to the solution of calixarene **2.24** (2 mmol) in chloroform on the basis of 3 mol per one diethylphosphate group. The mixture was left for 24h at 20 °C. The volatile components were evaporated under reduced pressure. The solid residue was dried in vacuum (0.01 mm Hg) within 1h at 20 °C. Then methanol (20 ml) was added and the mixture was refluxed for 6h. The reaction mixture was concentrated under reduced pressure and dried in high vacuum (0.01 mm Hg, 50 °C). After crystallization from isopropanol the product was dried in vacuum (0.01 mm Hg) for 4h. Yield 79%, *mp* 138-140 °C.

^1H NMR (300 MHz, DMSO-*d*6): δ 0.81 and 1.11 (two m, 24H, P- CH_2 - CH_3), 1.37 and 1.81 (two m, 16H, P- CH_2 - CH_3), 2.82 and 3.15 (two d, 8H, $J = 13.50$ Hz, Ar- CH_2 -P), 3.35 and 4.20 (two d, 8H, $J = 13.80$ Hz, Ar- CH_2 -Ar), 4.78 (br s, 2H, Ar-OH), 6.71 and 7.10 (two s, 8H, ArH);

^{31}P NMR (80.95 MHz, DMSO-*d*6): δ -4.3 (br s, 2P, POH), 62.2 (s, 4P, PEt);
Calculated for $\text{C}_{48}\text{H}_{70}\text{O}_{14}\text{P}_6$, %: C 54.55, H 6.68, P 17.58;
Found, %: C 54.12, H 6.39, P 17.13.

5,11,17,23-Tetrabromo-25,26,27,28-tetra(dibutylphosphinoylmethoxy)calix[4]arene 2.27

A portion of *N*-bromosuccinimide was added to a solution of calixarene phosphine oxide **2.26** (2.5 g, 2.23 mmol) in methylethylketone (100 ml). The reaction mixture was stirred during 72h at rt, and then the solvent was evaporated. The residue was mixed with 50 ml of water and refluxed with stirring for 2h. Aqueous solution was decanted; the residue was washed with water and dissolved in 50 ml of benzene. The solvent was evaporated under reduced pressure and dried in high vacuum (0.01 mm Hg). Crystallization from acetonitrile afforded white solid. Yield 55%, *mp* 187 °C.

^1H NMR (300 MHz, CDCl_3): δ 0.87 (t, 24H, CH_3), 1.12-2.00 (m, 48H, P- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$), 3.30 and 4.82 (two d, 8H, J 13.25 Hz, Ar- $\text{CH}_2\text{-Ar}$), 4.45 (s, 8H, O- $\text{CH}_2\text{-P}$), 6.76 (s, 8H, ArH)

^{31}P NMR (80.95 MHz, CDCl_3): δ 45.4;

Calculated for $\text{C}_{64}\text{H}_{96}\text{Br}_4\text{O}_8\text{P}_4$, %: C 53.49, H 6.73, Br 22.24, O 8.91, P 8.62;

Found, %: C 53.54, H 6.59, P 8.23.

5,11,17,23-Tetrakis(diethylphosphonyl)-25,26,27,28-tetra(dibutylphosphinoylmethoxy)-calix[4]arene 2.28

The mixture of calixarene **2.27** (0.5 g, 0.348 mmol) and triethylphosphite (1.16 g, 7 mmol) was heated to 180 °C. Under argon atmosphere NiBr_2 (0.3 g, 1.4 mmol) was added, the reaction mixture was stirred for 1h, then cooled down under argon atmosphere. The excess of phosphorylating agent was removed in vacuum (0.01 mm Hg). The reaction mixture was dissolved in CH_2Cl_2 , washed with ammonia solution (6 \times 100 ml), with Trilon B (3 \times 50 ml), and with water. The organic layer was dried over CaCl_2 . The solvent was removed in vacuum. The residue was purified by silica column chromatography (CH_2Cl_2 : CH_3OH = 10 : 1), giving **2.28** as white powder. Yield 40%, *mp* 187 °C.

^1H NMR (300 MHz, CDCl_3): δ 0.845 (t, 24 H, P- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$), 1.155 (t, 24 H, P-O- $\text{CH}_2\text{-CH}_3$), 1.297 (m, 32 H, P- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$), 1.412 (m, 16 H, P- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$), 1.571 (m, 16 H, P- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$), 3.355 and 5.182 (two d, J 13.2 Hz, Ar- $\text{CH}_2\text{-Ar}$), 3.925 (m, 16 H, P(O)-O- $\text{CH}_2\text{-CH}_3$), 4.786 (s, 8H, O- $\text{CH}_2\text{-P(O)Bu}_2$), 7.26 (d, 8H, ArH);

^{31}P NMR (80.95 MHz, CDCl_3): δ 44.3, 18.7;

Calculated for $\text{C}_{80}\text{H}_{136}\text{O}_{20}\text{P}_8$, %: C 57.68, H 8.23, O 19.2, P 14.87.

Found, %: C 57.73, H 8.17, P 14.62.

5,11,17,23-Tetrabromo-25,26,27,28-tetrabromobutoxycalix[4]arene 2.29

N-bromosuccinimide (9 g, 0.051 mmol) was added to a solution of calixarene **2.8** (5 g, 5.184 mmol) in methylethylketone (80 ml). The reaction mixture was stirred within 24h at rt. The solvent was evaporated under reduced pressure. The solid residue was consequently washed with water (100 ml) and methanol (150 ml). Calixarene **2.9** was obtained as colorless crystal compound. Yield 94%, *mp* 139-141 °C.

^1H NMR (300 MHz, CDCl_3): δ 1.97 (m, 16H, O- CH_2 - CH_2 - CH_2 - CH_2 -Br), 3.11 and 4.28 (two d, 8H, J 12.90 Hz, Ar- CH_2 -Ar), 3.49 (t, 8H, O- CH_2 - CH_2 - CH_2 - CH_2 -Br), 3.88 (t, 8H, O- CH_2 - CH_2 - CH_2 - CH_2 -Br), 6.81 (m, 12H, ArH);

Calculated for $\text{C}_{44}\text{H}_{48}\text{Br}_8\text{O}_4$, %: C 41.29, H 3.78, Br 49.94, O 5.00;

Found, %: C 41.31, H 3.96.

The general procedure of synthesis of calixarenes 2.30a-c

The mixture of octobromocalixarene **2.29** (2 mol) and corresponding phosphinite (30 mmol) was heated to boiling and left for 3h. The excess of phosphorylated agent was removed under reduced pressure. The solid residue was triturated with pentane, filtered off and rinsed with dry pentane (3 \times 25 ml), then dried in high vacuum (0.01 mm Hg).

5,11,17,23-Tetrabromo-25,26,27,28-tetra(diethylphosphinoylbutoxy)calix[4]arene 2.30a

Colorless powder. Yield 96%, *mp* 118-120 $^\circ\text{C}$

^1H NMR (300 MHz, CDCl_3): δ 1.15 (m, 24H, CH_3), 1.73 (m, 32H, P- CH_2 - CH_3 and O- CH_2 - CH_2 - CH_2 - CH_2 -P), 1.95 (m, 8H, O- CH_2 - CH_2 - CH_2 - CH_2 -P), 3.11 and 4.32 (two d, 8H, J 13.50 Hz, Ar- CH_2 -Ar), 3.87 (t, 8H, O- CH_2 - CH_2 - CH_2 - CH_2 -P), 6.56 (s, 12H, ArH);

^{31}P NMR (80.95 MHz, CDCl_3): δ 52.8;

Calculated for $\text{C}_{60}\text{H}_{88}\text{Br}_4\text{O}_8\text{P}_4$, %: C 52.19, H 6.42, P 8.97;

Found, % C 52.30, H 6.38, P 9.01.

5,11,17,23-Tetrabromo-25,26,27,28-tetra(dipropylphosphinoylbutoxy)calix[4]arene 2.30b

Light-yellow glassy compound. Yield 98%, *mp* 90-92 $^\circ\text{C}$.

^1H NMR (300 MHz, CDCl_3): δ 1.02 (t, 24H, CH_3), 1.61 (m, 48H, P- CH_2 - CH_2 - CH_3 and O- CH_2 - CH_2 - CH_2 - CH_2 -P), 1.89 (m, 8H, O- CH_2 - CH_2 - CH_2 - CH_2 -P), 3.06 and 4.24 (two d, 8H, J 13.50 Hz, Ar- CH_2 -Ar), 3.84 (t, 8H, O- CH_2 - CH_2 - CH_2 - CH_2 -P), 6.77 (s, 8H, ArH);

^{31}P NMR (80.95 MHz, CDCl_3): δ 62.5;

Calculated for $\text{C}_{68}\text{H}_{104}\text{O}_8\text{P}_4$, %: C 54.70, H 7.02, Br 21.41, P 8.30;

Found, % C 54.83, H 7.20, P 8.24.

5,11,17,23-Tetrabromo-25,26,27,28-tetra(diphenylphosphinoylbutoxy)calix[4]arene 2.30c

Colorless powder. Yield 98%, *mp* 190 $^\circ\text{C}$

^1H NMR (300 MHz, CDCl_3): δ 1.56 (d, 8 H, O- CH_2 - CH_2 - CH_2 - CH_2 -P), 1.81 (d, 8 H, O- CH_2 - CH_2 - CH_2 - CH_2 -P), 1.56 (m, 8 H, O- CH_2 - CH_2 - CH_2 - CH_2 -P), 2.89 and 4.06 (two d, 8H, J 13.50 Hz, Ar- CH_2 -Ar), 3.71 (t, 8H, O- CH_2 - CH_2 - CH_2 - CH_2 -P), 6.68 (s, 8H, ArH), 7.40 and 7.70 (two m, 40H, PPh);

^{31}P NMR (80.95 MHz, CDCl_3): δ 105.9;

Calculated for $\text{C}_{92}\text{H}_{88}\text{Br}_4\text{O}_8\text{P}_4$, %: C 62.60, H 5.02, Br 18.11, O 7.25, P 7.02;

Found, % C 62.43, H 5.1, P 6.99.

5,11,17,23-Tetrakis(diisopropylphosphonyl)-25,26,27,28-tetra(dibutylphosphinoylbutoxy)calix[4]arene 2.31

The mixture of calixarene **2.30a** (0.5 g, 0.362 mmol) and triisopropylphosphite (0.603 g, 2.896 mmol) was heated to 180 °C. Under argon atmosphere NiBr₂ (0.316 g, 1.448 mmol) was added, the reaction mixture was stirred for 1h at this temperature, then cooled down under argon atmosphere. The excess of phosphorylating agent was removed in vacuum (0.01 mm Hg). The reaction mixture was dissolved in CH₂Cl₂, washed with ammonia solution (6×100 ml), with Trilon B (3×50 ml), and with water. The organic layer was dried over CaCl₂. The solvent was removed in vacuum to afford **2.31** as yellowish glass. Yield 55.5%, *mp* 82 °C.

¹H NMR (300 MHz, CDCl₃): δ 1.07 – 1.19 (m, 72H, CH₃), 1.59 (m, 32H, P-CH₂-CH₃ and O-CH₂-CH₂-CH₂-CH₂-P), 1.87 (m, 8H, O-CH₂-CH₂-CH₂-CH₂-P), 3.20 and 4.32 (two d, 8H, J 13.50 Hz, Ar-CH₂-Ar), 3.90 (t, 8H, O-CH₂-CH₂-CH₂-CH₂-P), 4.27 (m, 8H, O-CH), 7.16 (s, 8H, ArH);

³¹P NMR (80.95 MHz, CDCl₃): δ 52.4, 18.2;

Calculated for C₈₄H₁₄₄O₂₀P₈, %: C 58.60, H 8.43, O 18.58, P 14.39;

Found, %: C 58.62, H 8.5, P 14.492.

5,11,17,23-Tetrakis(dibutylphosphinoylmethyl)-25,26,27,28-tetracyanobutoxycalix[4]arene 2.32

Tetrabromobutoxycalixarene **2.19b** (6.2 g, 3.671 mmol) was dissolved in 100 ml of DMF, NaCN was added (1 g, 20.4 mmol). The reaction mixture was heated up to 60 °C and stirred for 48h. After cooling the reaction mixture was poured on 200 ml of water, acidified with HCl (pH≈ 7), and extracted with chloroform (2×100 ml). The extract was washed with water (2×100 ml) and dried over Na₂SO₄. The solvent was removed under reduced pressure; the residue was dried in high vacuum (0.01 mm Hg) to give light-yellow compound **2.30**. Yield 92%, *mp* 102 °C.

¹H NMR (300 MHz, CDCl₃): δ 0.866 (m, 24H, CH₃), 1.369 - 1.457 (m, 40 H, P-CH₂-CH₂-CH₂-CH₃, O-CH₂-CH₂-CH₂-CH₂-CN), 1.697 (m, 16H, P-CH₂-CH₂-CH₂-CH₃), 2.06 (m, 8H, O-CH₂-CH₂-CH₂-CH₂-CN), 2.449 (m, 8H, O-CH₂-CH₂-CH₂-CH₂-CN), 2.727 (d, 8H, J 14.7 Hz, Ar-CH₂-P), 3.092 and 4.256 (two d, 8H, J 12.9 Hz, Ar-CH₂-Ar), 3.841 (t, 8H, O-CH₂-CH₂-CH₂-CH₂-CN), 6.435 (s, 8H, ArH);

³¹P NMR (80.95 MHz, CDCl₃): δ 41.3;

Calculated for C₈₄H₁₂₈N₄O₈P₄, %: C 69.78, H 8.92, N 3.87, O 8.85, P 8.57;

Found, % C 69.60, H 9.11, P 8.36.

77 C. Madic et al., Actinide partitioning from high level waste using the Diamex process, Nuclear Fuel Reprocessing and Waste Management, *Rep. CEA-CONF-12297*, **1994**, Marcoule

78 Korobets, *Russian Journal of Coordination Chemistry* **1987**, *13*, 85-97

79 R. Schurhammer, V. Erhart, L. Troxler, G. Wipff, *Chem Soc., Perkin Trans.* **1999**, *2*, 2423-2431

80 E. N. Tsvetkov, N. A. Bondarenko, I. G. Malakhova, M. I. Kabachnick, *Synthesis* **1986**, *3*, 198-208

81 X. Sun, Y. Ji, F. Hu, B. He, J. Chen, D. Li, *Talanta* **2010**, *81*, 1877–1883

82 H. Mehdi, K. Binnemans, K. Van Hecke, L. Van Meervelt, P. Nockemann, *Chem. Commun. (Camb)* **2010**, *46*, 234–236

83 a) G. I. Koldobskii, V. A. Ostrovskii, B. V. Gidasov, *Chem. Heterocycl. Compd.* **1980**, *16*, 665-674

b) L. D. Hansen, E. J. Baca, P. Scheiner, *J. Heterocycl. Chem.* **1970**, *7*, 991-996

84 L. G. Lavrenova, S. V. Larionov, V. N. Ikorskii, Z. A. Grankina, *Zhurnal Neorganicheskoi Khimii* **1985**, *30*, 964 (in Russian)

-
- 85 I. L.Odinets, E. V.Sharova, O. I. Artyshin, K. A. Lyssenko, Y. V. Nelyubina, G. V. Myasoedova, N. P. Molochnikova, E. A. Zakharchenro, *Dalton Trans.* **2010**, *39*, 4170
- 86 T. Ya. Medved, M. K. Chumatova, N. P. Nesterova, *Izvestia Akademii Nauk SSSR, Khimia*, 1981, *9*, 2121 (in Russian)
- 87 D.G. Kalina, E.P. Horwitz, L. Kaplan, *Sep. Sci. Technol.* **1981**, *16*, 1127-1145
- 88 G.F. Vandegrift, D. B. Chamberlain, C. Conner, J M. Copple, J. A. Dow, L. Everson, J. C. Hutter, R. A. Leonard, L. Nufiez, M. C. Regalbuto, J. Sedlet, B. Srinivasan, S. Weber, D. G. Wygmans, Development and demonstration of the TRUEX solvent extraction process, Argonne, p.1045
- 89 A. Rout, K. A. Venkatesan, T. G. Srinivasan, P. R. Vasudeva Rao, *Radiochim. Acta* **2009**, *97*, 719-725
- 90 A. E. Visser, R. D. Rogers, *Solid State Chem.* **2003**, *171*, 109-113
- 91 C. D Gutsche, *Calixarenes*. Cambridge: Royal Society of Chemistry, **1989**
- 92 R. A. Kemp, D. S. Brown, M. Lattman, J. Li, *J. Molec. Cat. A: Chem.* **1999**, *149*, 125-133
- 93 R. Grigg, J. M. Holmes, S. K. Jones, W. D. J. Amilaprasadh Norbert, *J. Chem. Soc., Chem.Commun.* **1994**, 185-187
- 94 A. Casnati, E. Di Modugno, M. Fabbi, N. Pelizzi, A. Pochini, F. Sansone, G. Tarzia, R. Ungaro, *Bioorg. Med. Chem. Lett.* **1996**, *6*, 2699–2704
- 95 T. Jin, M. Kinjo, Y. Kobayashi, H. Hirata, *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 3135–3140
- 96 L. Atamas, O. Klimchuk, V. Rudzevich, V. Pirozhenko, V. Kalchenko, I. Smirnov, V. Babain, T. Efremova, a Varnek, G. Wipff, et al., *J. Supramol. Chem.* **2002**, *2*, 421–427
- 97 I. V. Smirnov, M. D. Karavan, T. I. Yefremova, V. A. Babain, S. I. Miroshnichenko, S. A. Cherenok, V. I. Kalchenko, *Radiochemistry* **2007**, *49*, 482-492
- 98 V. G.Torgov, T. V. Us, T. M. Korda, G. A. Kostin, S. I. Miroshnichenko, O. V. Klimchuk, V. I. Kalchenko, *J Incl. Phenom. Macrocycl. Chem.* **2008**, *62*, 51-58.
- 99 F. Arnaud-Neu, M.Karavan, V. Hubscher-Bruder, I. Smirnov, V. Kalchenko, *J. Incl. Phenom. Macrocycl. Chem.* **2010**, *66*, 113-123
- 100 G. A. Kostin, T. V. Us, T. M. Korda, V. G. Torgov, N. V. Kuratieva, S. I. Miroshnichenko, V.I.Kalchenko, *J. Incl. Phenom. Macrocycl. Chem.* **2010**, *68*, 131-137
- 101 V. G. Torgov, G. A. Kostin, T. V. Us, T. M. Korda, O. V. Klimchuk, S. I. Miroshnichenko, K. Suwinska, A. A. Varnek, V. I. Kalchenko, *J. Incl. Phenom. Macrocycl. Chem.* **2011**, *71*, 67-77
- 102 S. G. Kharchenko, A. B. Drapailo, S. V. Shishkina, O. V. Shishkin, M. D. Karavan, I. V. Smirnov, A. B. Ryabitskii, V. I. Kalchenko, *Supramolecular Chemistry* **2014**
<http://dx.doi.org/10.1080/10610278.2014.890198>
- 103 O. Klimchuk, L. Atamas, S. Miroshnichenko, V. Kalchenko, I. Smirnov, V. Babain, A. Varnek, G. Wipff, *J. Incl. Phenom.* **2004**, *49*, 47–56
- 104 S. I. Miroshnychenko, Dissertation, Kyiv, **2009** (in Ukrainian)
- 105 M. Almi, A. Arduini, A. Casnati., A. Pochini, R. Ungaro, *Tetrahedron* **1989**, *45*, 2177-2182
- 106 T. Arimura, T. Nagasaki, S. Shinkai, T. Matsuda, T. Arimura, *J. Org. Chem.* **1989**, *54*, 3766-3768
- 107 P. Tavs, *Chem. Ber.* **1970**, *103*, 2428-2436
- 108 V. V. Kormachev, M. S. Fedoseev, *Preparativnaya khimiya fosfora (Preparative Chemistry of Phosphorus)*, Russian academy of sciences, Perm, **1992** (in Russian)
- 109 Macrocyclic synthesis. A practical approach. Ed. D. Parker. Oxford University Press, **1996**, 145-172
- 110 C. D. Gutsche, B. Dhawan, K. H. No, R. Muthukrishnan, *J.Am. Chem. Soc.* **1981**, *103*, 3782-3791

III. CHAPTER: EXTRACTION. RESULTS AND DISCUSSION

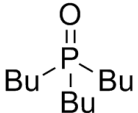
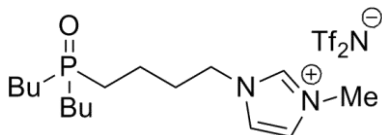
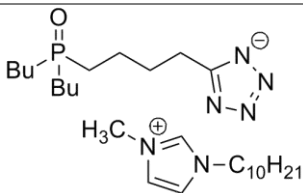
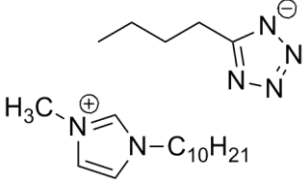
III.1 Introduction

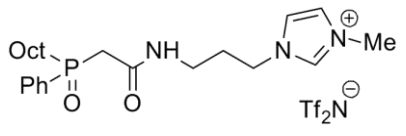
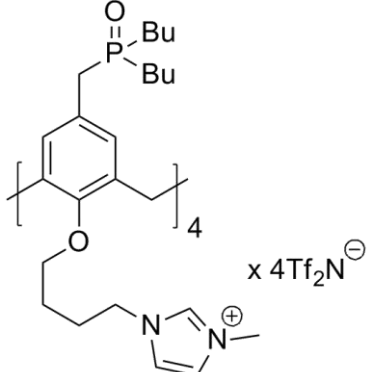
The aim of the extraction experiments is to gather extraction data as a function of several chemical parameters ($[H^+]$ value, ligand concentration, addition of salt etc.) to get some insights into the extraction mechanism. In this work the FILs with phosphine oxide, carbamoyl phosphine oxide and the one on the calixarene basis were investigated (see Table 1). More specifically, first the aim was to qualify whether the FILs are capable of the radionuclides extraction, and then to compare the extraction ability for the series of TSILs having the phosphine oxide group on either cation or anion and more generally to compare with the phosphine oxide neutral compound. Additionally we wanted to study the effect of calix[4]arene platform: whether it enhances the complexing properties of phosphine oxide groups grafted to the calix[4]arene-IL.

By doing so, it is expected to get at least indications to answer the following questions:

- Do FILs functionalized on the cation and the anion extract metallic entities?
- Do they extract according to the same mechanism?
- How do they compare to the neutral compound in terms of efficiency and mechanism?
- What is the influence of calix[4]arene platform

Table 1. List of compounds tested for the extraction

Chemical formula	Chemical name	Ordinal number	Abbreviated name
	Tributylphosphine oxide	commercial compound	TBPO
	1-Methyl-3-[4-(dibutylphosphinoyl)butyl]-3H-imidazol-1-ium bis-trifluoromethyl-sulphonylimidate	2.6 (Chapter II)	SM1006
	1-Decyl-3-methylimidazolium dibutylphosphinoylbutyl-1,2,3,4-tetrazolate	2.12e (Chapter II)	DM01
	1-Decyl-3-methylimidazolium 5-butyl-1H-tetrazolate	4.2 (Supplementary data)	Model compound

	1-Methyl-3-(octylphenylphosphinoylacetyl)propyl-3 <i>H</i> -imidazol-1-ium bis-trifluoromethanesulfonimide	2.15 (Chapter II)	CMPO-IL
	5,11,17,23-Tetrakis(dibutylphosphinoylmethyl)-25,26,27,28-tetra(4-(1-methylimidazolium)butoxy)calix[4]arene tetra-(bis(trifluoromethanesulfonyl)amide)	2.21 (Chapter II)	Calix-IL

III.2 Extraction experiments

Two different ILs have been used as diluents: C₁C₄imTf₂N and C₁C₁₀imTf₂N. This is because the compounds do not possess the same imidazolium cation, in the case of anionic FIL (DM01) C₁C₁₀im⁺ was used in order to increase its lipophilicity, while cationic FILs were based C₁C₄im⁺. Therefore it was decided to favor similarities in cationic part rather than keeping a similar solvent in all experiments although we are aware these two IL-diluents may present different physicochemical properties (in terms of IL solubility in water, for the main part).

First, U(VI) extraction in absence of ligand has been performed, in order to check a possible effect of the pure IL phase towards the metallic entity. Basic experiments aiming at determining the water and H⁺ solubilities in the IL phase have been also performed. Then, as a rule, a common set of extraction experiments have been conducted for all extraction systems studied. These are:

- Variation of D_M as a function of initial nitric acid concentration, $[\text{HNO}_3]_{\text{init, aq}}$. Reason : gives indication on extraction, allows adjustment of ligand concentration
- $[\text{H}^+]_{\text{eq, aq}}$ as a function of ligand concentration for a fixed initial nitric acid concentration. Reason: shows protonation of ligand
- Variation of D as a function of ligand concentration, for two different initial nitric acid concentrations (low and high acidity). Reason: determining of the ligand stoichiometry
- Variation of D as a function of added salts, either C₁C₄imCl or LiTf₂N, at a fixed low acidity: *ca.* $[\text{H}^+] = 0.3 \text{ M}$
- Variation of D as a function of added salts, either C₁C₄imCl or LiTf₂N, at a fixed high acidity: *ca.* $[\text{H}^+] = 2.3 \text{ M}$

Reasons for the two last is to determine the impact of Cat^+ and A^- for mechanism determination.

Experimental results are presented for each ligand in the order: TBPO, SM1006, DM01, and finally calixarene-IL **2.21**. Malonamide FIL-MA is not presented here.

Part of these experiments has been performed by Mrs. Valérie Mazan, as a permanent staff of the Strasbourg group, while others have been performed by me, during my stay in the

Strasbourg group. In order to make it clear, plots of experiments performed by Mrs. Mazan are surrounded by a light gray panel.

III.2.1 Experimental results for neutral compound - tributyl phosphine oxide (TBPO)

Trialkylphosphine oxides are organophosphorus compounds with a chemical formula $R_3P=O$ (where R = alkyl). The phosphine oxide group possessing high electron density on the oxygen atom, demonstrates high donor properties, thus can form stable complexes with different metal cations. Trioctylphosphine oxide was tested in the processes of liquid-liquid extraction since 1960s [111, 112, 113]. Its solutions in nonpolar organic solvents as kerosene and dodecane were used for the extraction of uranium and transuranium elements from weakly acidic solutions. The efficiency was 99.9% for U(VI), 99.1% for α -emitters, > 99% for Cm(III) [114].

In this work, tributylphosphine oxide (TBPO) has been chosen as a model compound for comparison purpose of the extraction abilities of the phosphine oxide compounds synthesized. TBPO is a commercially available reagent, was used as received. The biphasic systems, containing TBPO $U(VI) / HNO_3 // TBPO / C_1C_4imTf_2N$ were investigated.

As it has been already observed, uranyl is not extracted by the $C_1C_4imTf_2N$ phase in the absence of extractant, even at the highest HNO_3 concentrations [115, 116]. Therefore all following uranyl extractions should be regarded as due to the ligand.

Figure III-1 shows the distribution ratio of U(VI) as a function of nitric acid concentration, at a fixed ligand concentration equal to 0.04M.

The curve of extraction does not have significant extremes, as it just decreases when HNO_3 increases. The shape of the curve is normal for the extraction in ILs

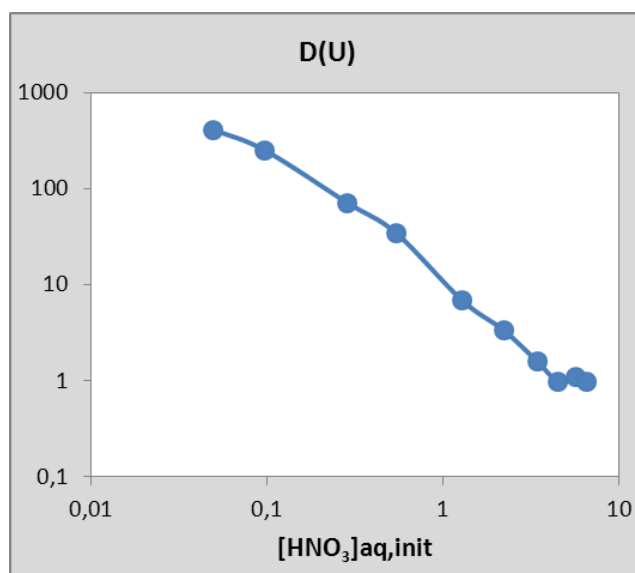


Figure III-1. $U(VI)/HNO_3//TBPO/C_1C_4imTf_2N$. D_U vs $[HNO_3]_{aq,init}$. $[U(VI)] = 4.96 \times 10^{-5}$ M; $[HNO_3] =$ variable; $[TBPO] = 0.04$ M

The equilibrium $[H^+]$ values have been measured for the system $0.3M HNO_3 // TBPO / C_1C_4imTf_2N$. Such results are displayed in Figure III-2 together with the expected equilibrium values $[H^+]_{aq,eq} = 0.94 \times [H^+]_{aq,init}$ as usually obtained in the absence of ligand [117].

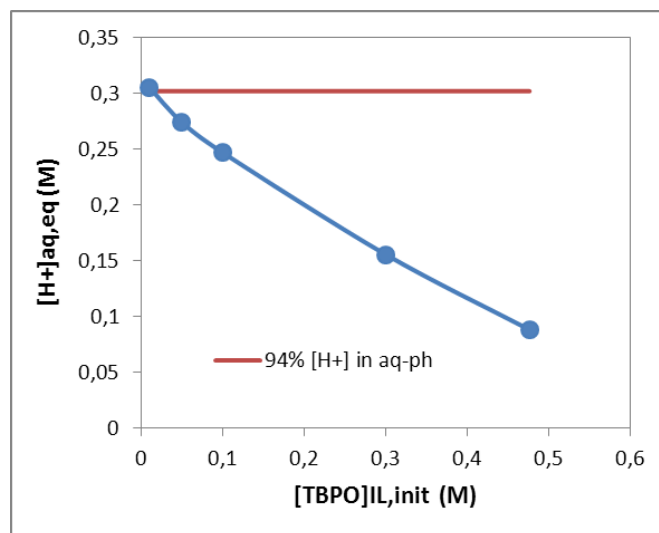


Figure III-2. $HNO_3/TBPO/C_1C_4imTf_2N$. $[H^+]_{aq,eq}$ vs $[TBPO]_{aq,init}$ $[U(VI)] = 0$ M; $[HNO_3] = 0.3$ M; $[TBPO] =$ variable. Horizontal line represents equilibrium $[H^+]$ without TBPO addition

A significant effect of TBPO on $[H^+]_{aq,eq}$ has been observed, what indicates a large protonation constant.

In order to investigate the mechanism of extraction experiments have been performed in 0.3M and 2.3M HNO_3 solutions, as a function of TBPO concentration. Figure III-3 presents the distribution ratios for these two ranges of acidities. The same data are given in Figure III-4 under $\log D_U$ vs $\log[TBPO]$ plot (slope analysis technique).

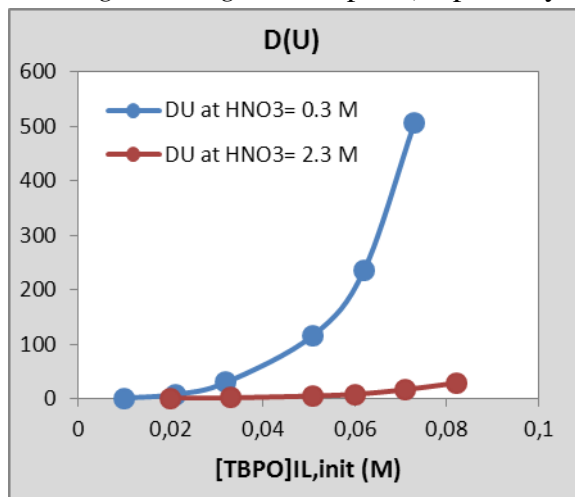


Figure III-3.

$U(VI)/HNO_3/TBPO/C_1C_4imTf_2N$. D_U vs $[TBPO]_{IL,init}$. : $[U(VI)] = 4.17 \times 10^{-5}$ M; $[HNO_3] = 0.3$ M (blue); $[HNO_3] = 2.26$ M (red); $[TBPO] =$ variable

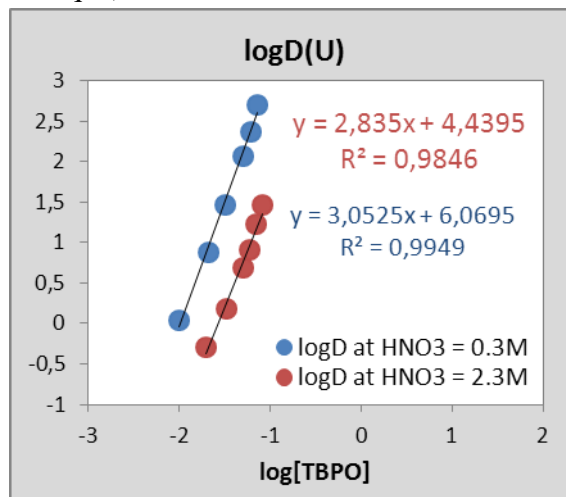


Figure III-4. log-log plot of data in Figure III-3

The log-log plots evidence very nice trends for both acidities: the slope is equal *ca.* 3 for $[H^+]_{aq,init} = 0.3$ M and 2.8 for $[H^+]_{aq,init} = 2.26$ M. This reflect a classical behaviour for IL and molecular solvents extracting systems.

To further study the extraction mechanism, the effects of the addition of the cation and the anion of IL were investigated at low acidity (Figure III-5 and III-6). $C_1C_4im^+$ was added in the form of C_1C_4imCl and Tf_2N^- in the form of $LiTf_2N$.

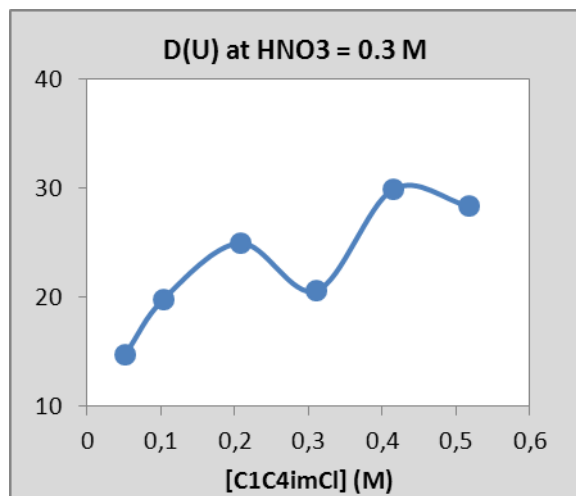


Figure III-5. $U(VI)/HNO_3//TBPO/C_1C_4imTf_2N$. D_U vs $[C_1C_4imCl]_{added}$. $[U(VI)] = 4.32 \times 10^{-5}$ M; $[HNO_3] = 0.293$ M; $[TBPO] = 20.5$ mM. $[C_1C_4imCl] = \text{variable}$

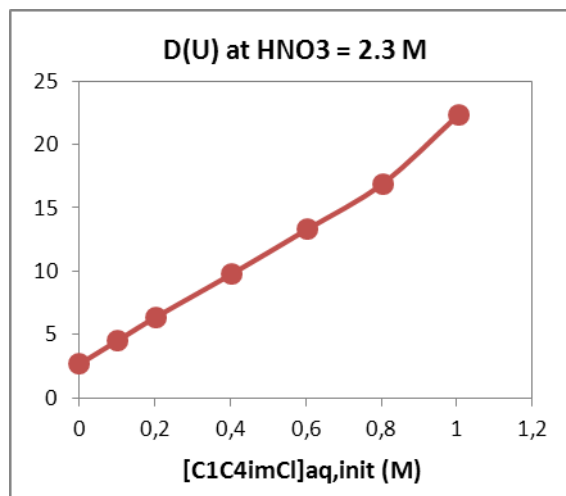


Figure III-6. $U(VI)/HNO_3//TBPO/C_1C_4imTf_2N$. D_U vs $[C_1C_4imCl]_{added}$. $[U(VI)] = 4.57 \times 10^{-5}$ M; $[HNO_3] = 2.245$ M; $[TBPO] = 40$ mM. $[C_1C_4imCl] = \text{variable}$

Similarly, the effects of the addition of the cation and the anion of IL were investigated at high acidity (Figure III-7 and III-8).

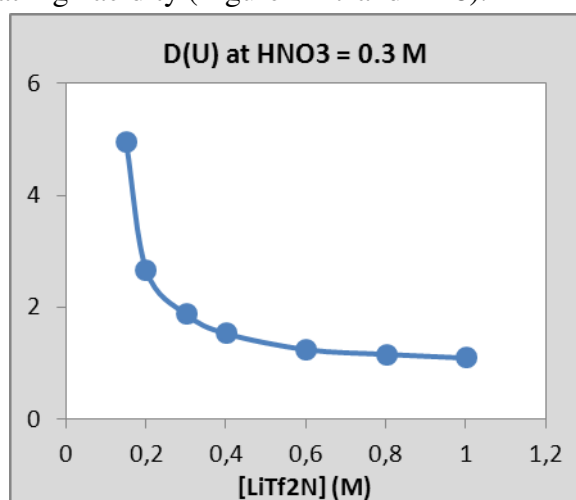


Figure III-7. $U(VI)/HNO_3//TBPO/C_1C_4imTf_2N$. D_U vs $[LiTf_2N]_{added}$. $[U(VI)] = 4.17 \times 10^{-5}$ M; $[HNO_3] = 0.289$ M; $[TBPO] = 21$ mM. $[LiTf_2N] = \text{variable}$

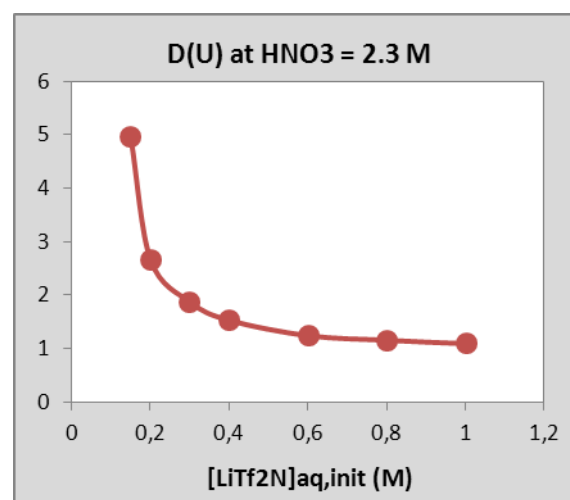


Figure III-8. $U(VI)/HNO_3//TBPO/C_1C_4imTf_2N$. D_U vs $[LiTf_2N]_{added}$. $[U(VI)] = 4.32 \times 10^{-5}$ M; $[HNO_3] = 2.27$ M; $[TBPO] = 60$ mM. $[LiTf_2N] = \text{variable}$

In Figure III-5 one data point is most probably outlier, thus the same trends are observed when $CatCl$ added: D variations are increasing at both acidic ranges, while right opposite effect is observed for $LiTf_2N$ added: D variations are decreasing. This is an indication of a similar mechanism of extraction by TBPO for all acidic range. Decrease of D as a function of LiA addition is explained in literature review (Chapter I) and corresponds to anionic exchange. Similarly, increase of D as a function of $CatCl$ added also corresponds to anionic exchange and related to the equilibria between $C_1C_nim^+$ and Tf_2N^- in aqueous phase. Thus, the experiments

with cation and anion additions give the same information causing opposite changes in D variations.

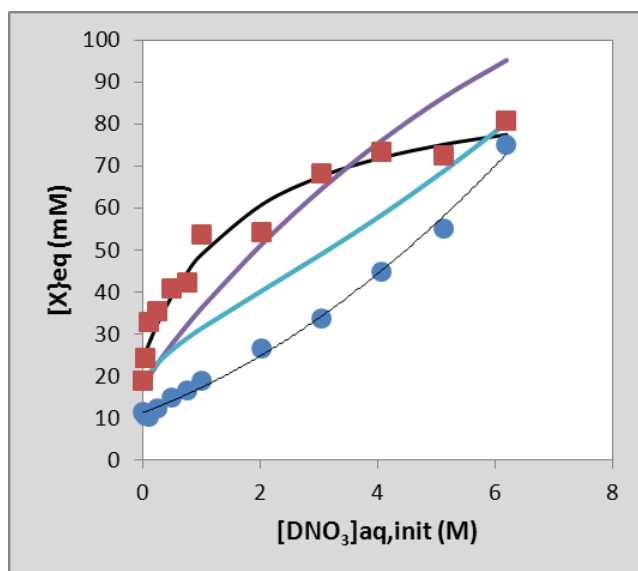


Figure III-9. $DNO_3//TBPO/C_1C_4imTf_2N$. $[C_1C_4im^+]_{aq,eq}$ or $[Tf_2N^-]_{aq,eq}$ vs $[DNO_3]_{aq,init}$. $[DNO_3]$ = variable; $[TBPO]=40$ mM, $[C_1C_4im^+]_{aq,eq}$ shown as red squares, $[Tf_2N^-]_{aq,eq}$ shown as blue circles; black lines are fit and polynomial trend line; violet line is variation of $[C_1C_4im^+]_{aq,eq}$ in the absence of ligand, blue line is variation of $[Tf_2N^-]_{aq,eq}$ in the absence of ligand

The addition of TBPO leads to changes in solubilities of Cat^+ and A^- in aqueous phases (Figure III-9), this is normal phenomenon for ILs [118].

III.2.2 Experimental results for cationic phosphine oxide FIL (SM1006)

The experimental data set is composed of several experiments performed for U(VI). Other extraction results obtained for Eu(III) and Am(III) were not conclusive, in the sense that a very low extraction was observed for Eu(III) and Am(III), whatever the nitric acid concentration (Figure IV-1 in Supplementary materials). As a consequence, no additional experiments were performed with these two elements and the distribution data are presented in the supplementary materials. All experiments presented here have been performed with the same stock of the ligand.

Figure III-10 displays the distribution ratio of U(VI) as a function of nitric acid concentration, at a fixed ligand concentration equal to 0.1 M.

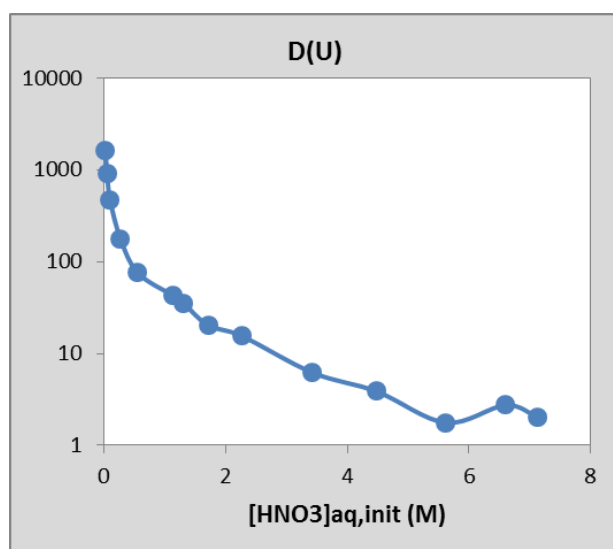


Figure III-10. $U(VI)/HNO_3//SM1006/C_1C_4imTf_2N$. D vs $[HNO_3]_{aq,init}$. $[U(VI)] = 4.71 \times 10^{-5}$ M; $[HNO_3]$ = variable; $[SM1006] = 0.1$ M

As in case of TBPO, the curve of extraction continuously decreases with increase of HNO_3 concentration. The shape of the curve is normal for the extraction in ILs.

The equilibrium $[H^+]$ value (i.e. once extraction has been performed) has been measured. Such results are displayed in Figures III-11 (a-c), together with the expected value $[H^+]_{eq} = 0.94 [H^+]_{init}$ as usually obtained in the absence of ligand in the IL phase.

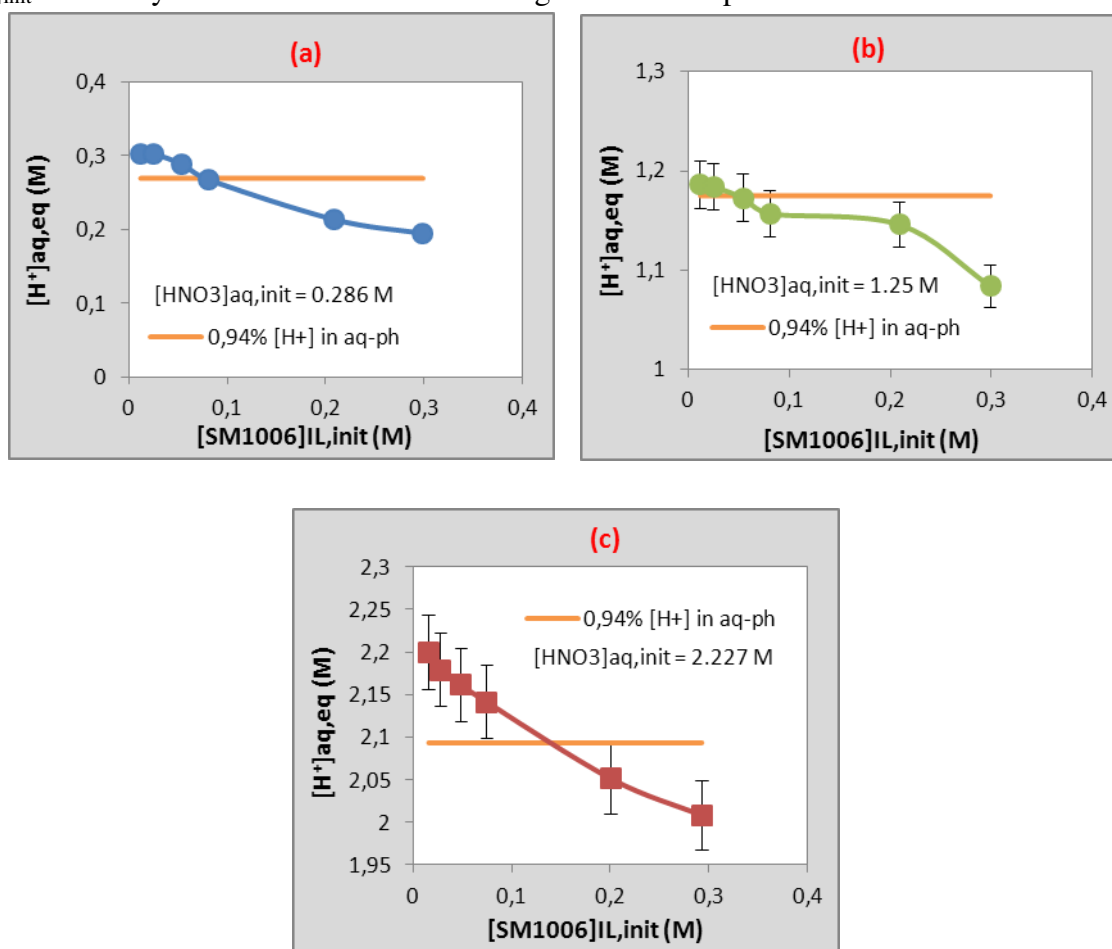


Figure III-11. $U(VI)/HNO_3//SM1006/C_1C_4imTf_2N$. $[H^+]_{aq,eq}$ vs $[SM1006]_{IL,init}$. $[U(VI)] = 4.71 \times 10^{-5}$ M; a) $[HNO_3] = 0.286$ M, b) $[HNO_3] = 1.25$ M, c) $[HNO_3] = 2.227$ M; $[SM1006]$ = variable. Horizontal line represents 94% of the initial $[H^+]$ value

The significant difference obtained at the highest ligand value, between the measured and the expected $[H^+]_{aq,eq}$ values is thus to be ascribed to the presence of the ligand.

Additional experiments have been performed at different acidity values. Figure III-12 gathers the distribution ratios obtained for three different fixed nitric acid concentrations ($[H^+] = 0.286$ M; 1.25 M and 2.227 M) and variable ligand concentration. The same data are displayed in Figure III-13 under a $\log D$ vs $\log[L]$ plot (slope analysis technique).

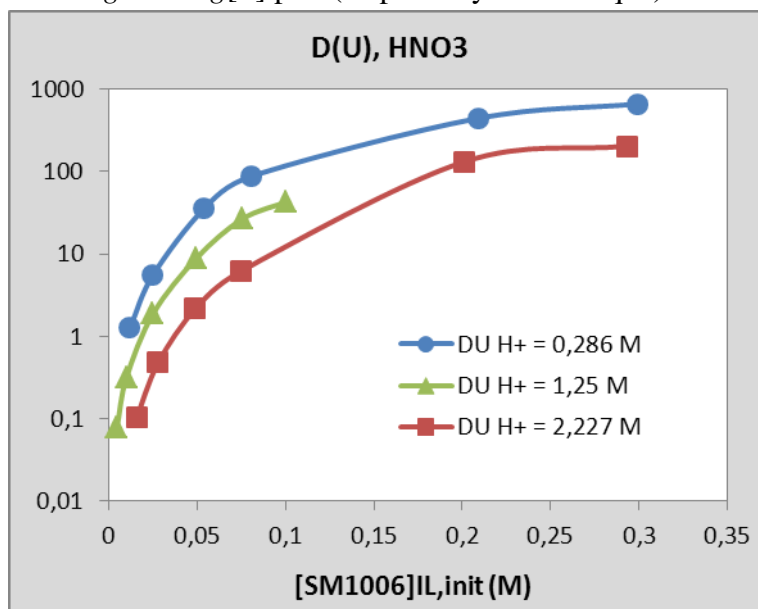


Figure III-12. $U(VI)/HNO_3/SM1006/C_1C_4imTf_2N$. D vs $[SM1006]_{IL,init}$. $[U(VI)] = 4.97 \times 10^{-5}$ M; $[HNO_3] = 0.286$ M (blue); $[HNO_3] = 1.25$ M (green); $[HNO_3] = 2.227$ M (red); $[SM1006] =$ variable

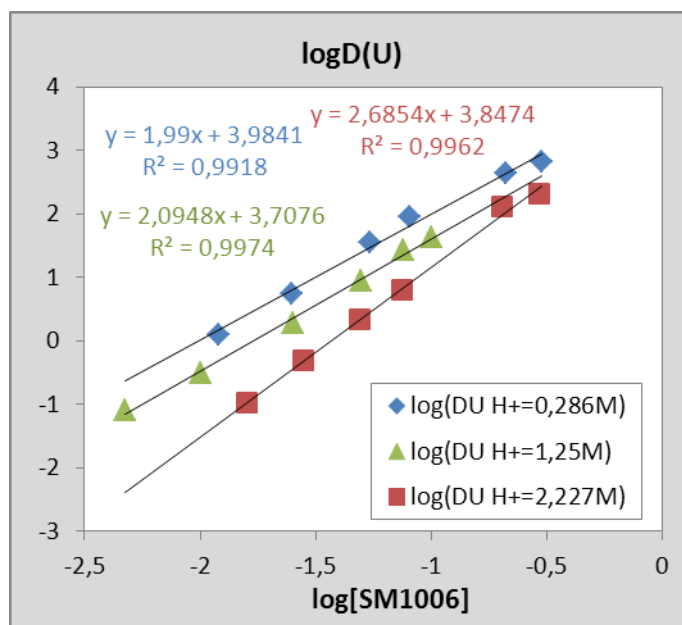


Figure III-13. $U(VI)/HNO_3/SM1006/C_1C_4imTf_2N$. $\log D_U$ vs $\log[SM1006]_{IL,init}$. $[U(VI)] = 4.97 \times 10^{-5}$ M; $[HNO_3] = 0.286$ M (blue); $[HNO_3] = 1.25$ M (green); $[HNO_3] = 2.227$ M (red); $[SM1006] =$ variable. Solid lines are linear fits of the data

For all three experimental sets, $D(U)$ is increasing as a function of L , which confirms the role of the ligand in the extraction process. The log-log plots evidence a very nice linear trend for any of the $[H^+]$ values and the slope is equal to *ca.* 2 for $[H^+] = 0.286$ M and 1.25 M, while it rises to 2.6 for $[H^+] = 2.227$ M.

In order to get some insights into the extraction mechanism, both salts were added at a fixed acidity value of $[H^+] = 0.29$ M as illustrated in Figure III-14 and III-15.

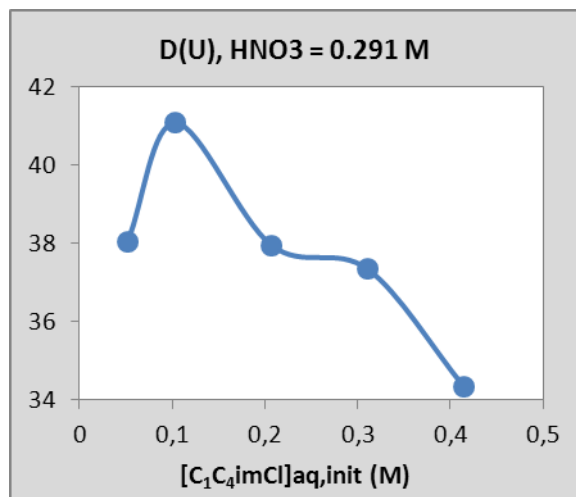


Figure III-14

$U(VI)/HNO_3/SM1006/C_1C_4imTf_2N$. D_U vs $[C_1C_4imCl]_{added}$. $[U(VI)] = 4.97 \times 10^{-5}$ M; $[HNO_3] = 0.291$ M; $[SM1006] = 40$ mM. $[C_1C_4imCl] =$ variable

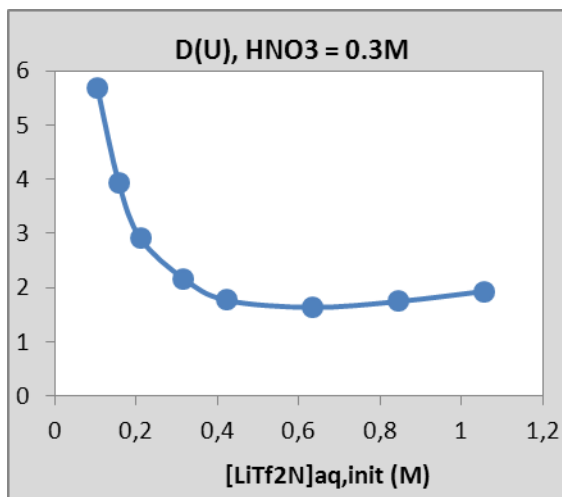


Figure III-15.

$U(VI)/HNO_3/SM1006/C_1C_4imTf_2N$. D_U vs $[LiTf_2N]_{added}$. $[U(VI)] = 4.32 \times 10^{-5}$ M; $[HNO_3] = 0.289$ M; $[SM1006] = 40$ mM. $[LiTf_2N] =$ variable

The effect of $LiTf_2N$ in high acidic range is displayed in Figure III-16.

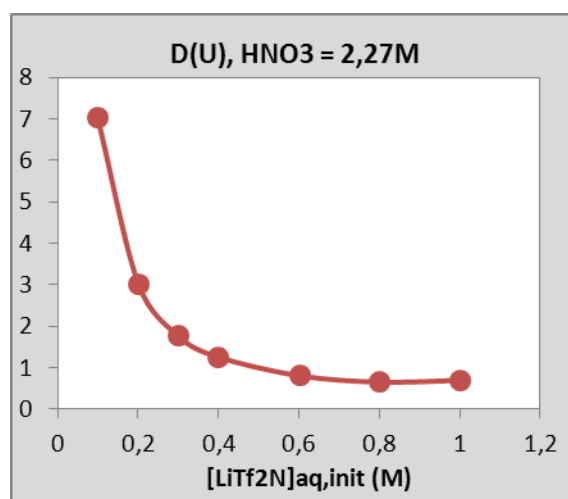


Figure III-16 $U(VI)/HNO_3/SM1006/C_1C_4imTf_2N$. D_U vs $[LiTf_2N]_{added}$. $[U(VI)] = 4.97 \times 10^{-5}$ M; $[HNO_3] = 2.27$ M; $[SM1006] = 0.1$ M. $[LiTf_2N] =$ variable

In the two data sets, $D(U)$ is decreasing as the concentration of the lithium salt is increased. Even though, the effect of C_1C_4imCl in high acidic range was not investigated, it should be similar to that in low acidic range, assuming the similarities for $LiTf_2N$ in both acidities.

Finally, Figure III-17 presents the impact of the acid nature onto the distribution ratio at a fixed ligand concentration equal to 0.1 M.

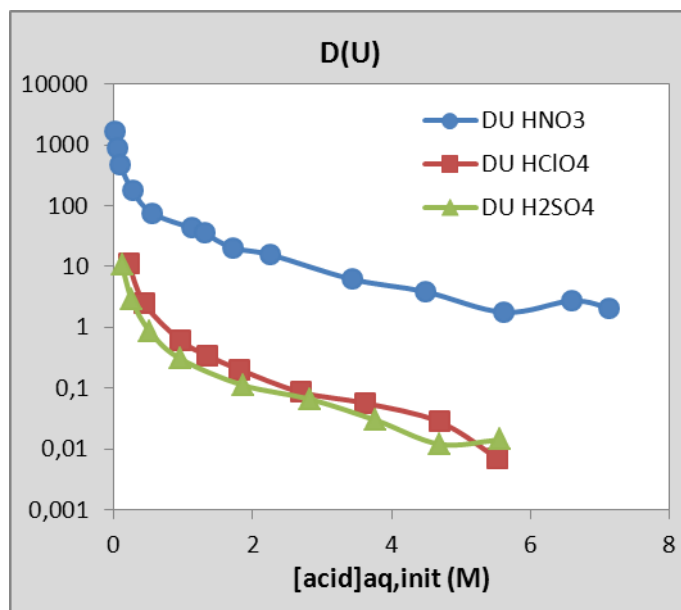


Figure III-17. $U(VI)/HNO_3//SM1006/C_1C_4imTf_2N$. D_U vs $[acid]_{aq,init}$. $[U(VI)]$ ca. 10^{-5} M; $[HNO_3]$ = variable (blue); $[HClO_4]$ = variable (red); $[H_2SO_4]$ = variable (green); $[SM1006] = 0.1$ M

Although the trend is that of a continuous decrease for all three acids, HNO_3 appears to enhance tremendously extraction as compared to the other two acids, while H_2SO_4 and $HClO_4$ lead to very similar low distribution values.

The last experiment concerns addition of $NaNO_3$ at fixed acid and ligand values ($[HNO_3] = 0.291$ M and $[SM1006] = 0.04$ M), see Figure III-18. An increase in $D(U)$ as a function of $[NaNO_3]_{added}$ is observed.

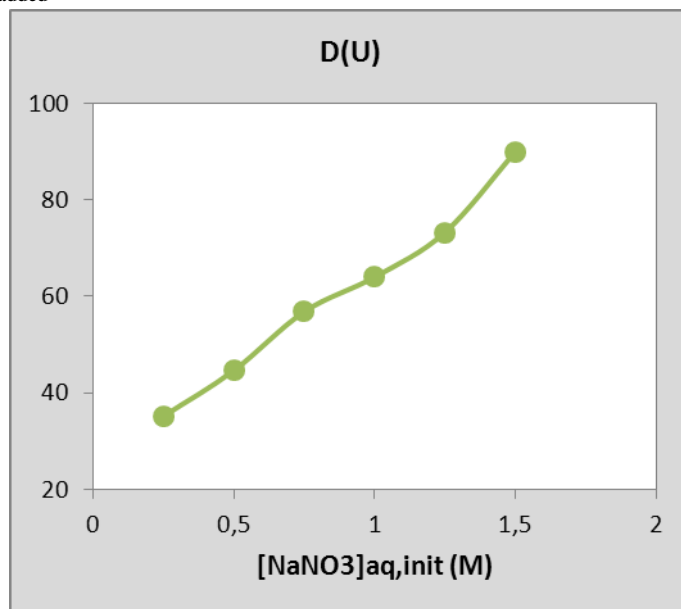


Figure III-18. $U(VI)/HNO_3//SM1006/C_1C_4imTf_2N$. D_U vs $[NaNO_3]_{added}$. $[U(VI)]$ 4.97×10^{-5} M; $[HNO_3] = 0.29$ M; $[SM1006] = 40$ mM

Apart from these extraction experiments, some data have been collected in order to quantify the behavior of the IL's cation and anion in the extraction system, that is in the presence of ligand. This refers to IL's cation and anion solubilities in the aqueous phase, that are of importance in case of cationic and anionic exchange, respectively (see Chapter I). The results

are displayed in Figure III-19, together with the corresponding data obtained in the absence of ligand for comparison purposes.

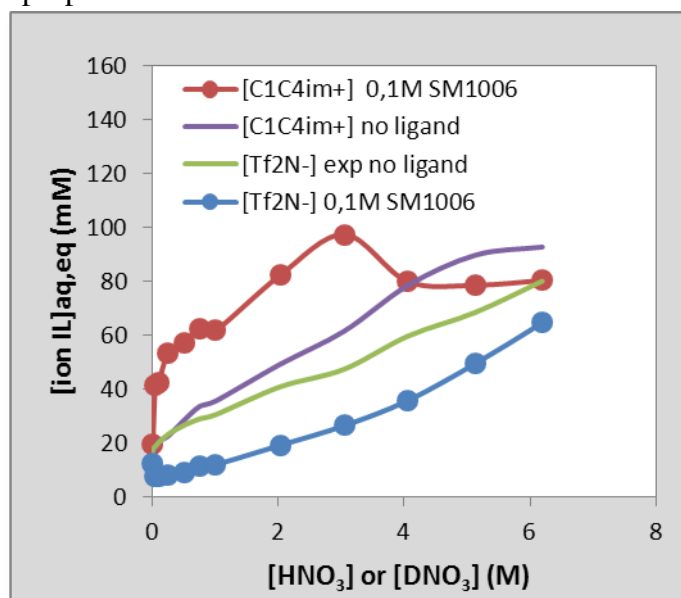


Figure III-19. $DNO_3(HNO_3)//SM1006/C_1C_4imTf_2N$. $[Cat^+]_{aq,eq}$ or $[A^-]_{aq,eq}$ vs $[DNO_3]_{aq,init}$ ($[HNO_3]_{aq,init}$). $[HNO_3]([DNO_3]) = \text{variable}$; $[C_1C_4im^+]$ shown in red when SM1006 added, $[Tf_2N^-]$ shown in blue when SM1006 added; $[C_1C_4im^+]$ shown as violet solid line in absence of ligand, $[Tf_2N^-]$ shown green solid line in absence of ligand

A tremendous effect of the ligand can be observed in Figure III-19, both for the cation and anion variations. In the absence of ligand, the cation solubility in the aqueous phase continuously increases as a function of acid concentration while, in the presence of 0.1 M SM1006. In the case of Tf_2N^- solubility, the most important difference in behavior is observed at very low acidity, as Tf_2N^- solubility increases in the absence of ligand, while it displays a minimum in the presence of ligand. It is important to note that in presence of ligand, the anion solubility only reaches values equal to those without ligand and no acid added at *ca.* 2.5 M of acid. This effect is thus non negligible in a wide range of acidities and should have a strong impact onto the extraction efficiency. Finally, as already described above (see Chapter I), the IL's cation and anion solubilities are very different from one another. This is only possible with a charge balance obtained through the other ions mutual solubilities (H^+ , NO_3^- , accordingly). These results confirm the huge complexity of such systems and the need for a complete analytical analysis of all the systems, which was not possible owing to the limited time allocated to this work.

III.2.3 Experimental results for anionic phosphine oxide FIL (DM01)

Similarly to $C_1C_4imTf_2N$, $C_1C_{10}imTf_2N$ has been checked for the extraction of uranyl under the conditions used in this work (temperature, shaking time). It was found that values of distribution ratio are very low (Figure III-20, see also comparison with extraction in presence of ligand, Figure III-24), and slightly increase with increase of nitric acid concentration, which can be explained by ion exchange, described forward.

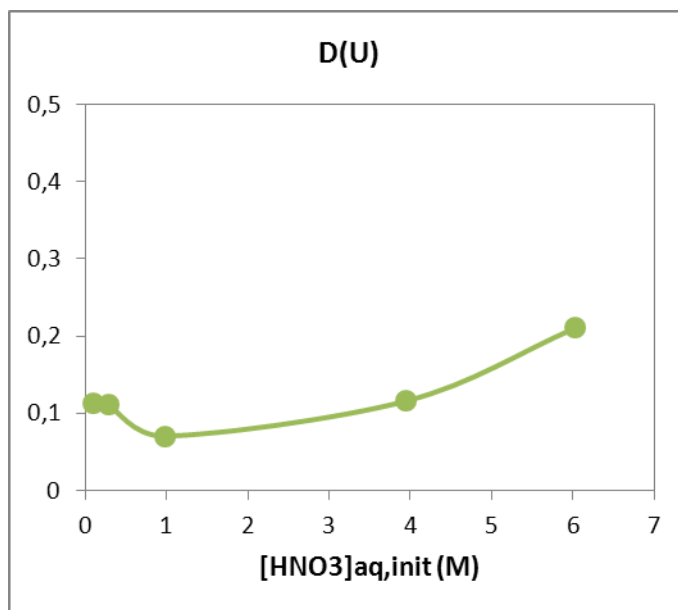


Figure III-20. $U(VI)/HNO_3/C_1C_{10}imTf_2N$. D_U vs $[HNO_3]_{aq,init}$. $[U(VI)] = 4.2 \times 10^{-5}$ M; $[HNO_3] =$ variable

Figure III-20 presents the D_2O amounts (red squares) in the IL-phases after pre-equilibration with aqueous phases, containing different DNO_3 concentrations, and the amounts of water in the IL-phases after U(VI) extraction experiments (blue diamonds).

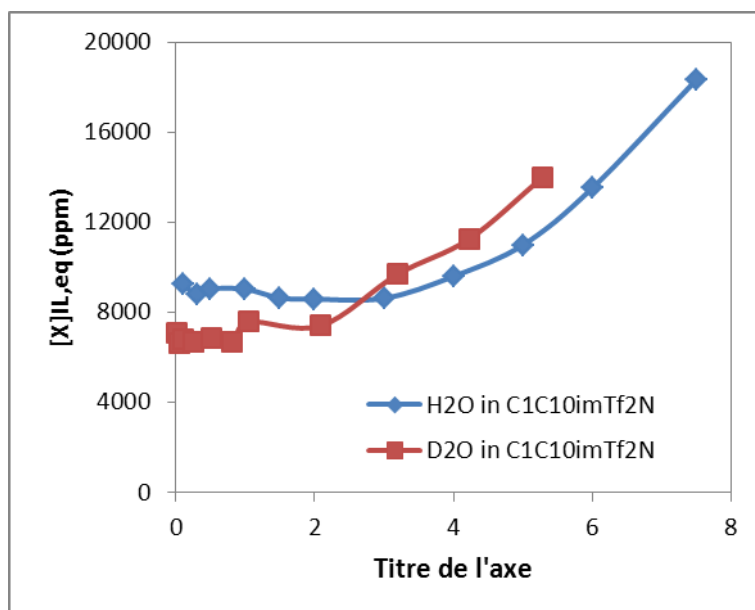


Figure III-21. $DNO_3(HNO_3)/C_1C_{10}imTf_2N$. Variations of H_2O or D_2O amounts in the IL phases as a function of nitric acid added

Figure III-22 presents the kinetic data for DM01 at two fixed acid concentration. This has been done because dry $C_1C_{10}imTf_2N$ is significantly more viscous than dry $C_1C_4imTf_2N$ so it was necessary to check that the usual equilibration time defined in the Strasbourg group for the latter IL was still relevant for the former IL.

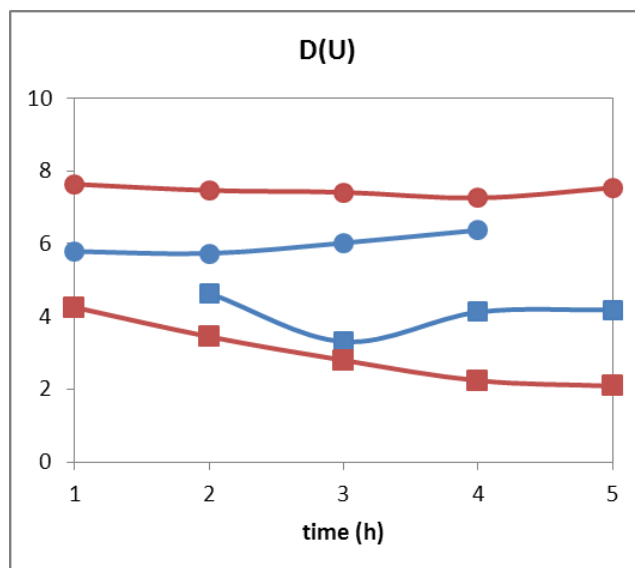


Figure III-22. $U(VI)/HNO_3//DM01/C_1C_{10}imTf_2N$. D_U vs time of equilibration. $[U(VI)] = 4.3 \times 10^{-3}$ M; ● circles $[HNO_3]_{aq,init} = 0.3$ M, ■ squares $[HNO_3]_{aq,init} = 2.3$ M; $[DM01] = 50$ mM

From the results obtained, we assumed that 3h is a sufficient time for U extraction by DM01 in $C_1C_{10}imTf_2N$, therefore, the equilibration time was fixed at 3 h in all other experiments.

Figure III-23 displays the variation of D as a function of initial nitric acid concentration for DM01. The extraction has been performed following the protocol described above. At very low concentrations, 3rd phase formation has been observed, therefore these data have been excluded (Figure III-24). In this case the D variations display so-called bell-shape, with a steep increase observed as $[HNO_3]_{aq,init}$ increases from 0.05 M to *ca.* 0.5 M and then a smooth decrease above $[HNO_3]_{aq,init} = 1$ M.

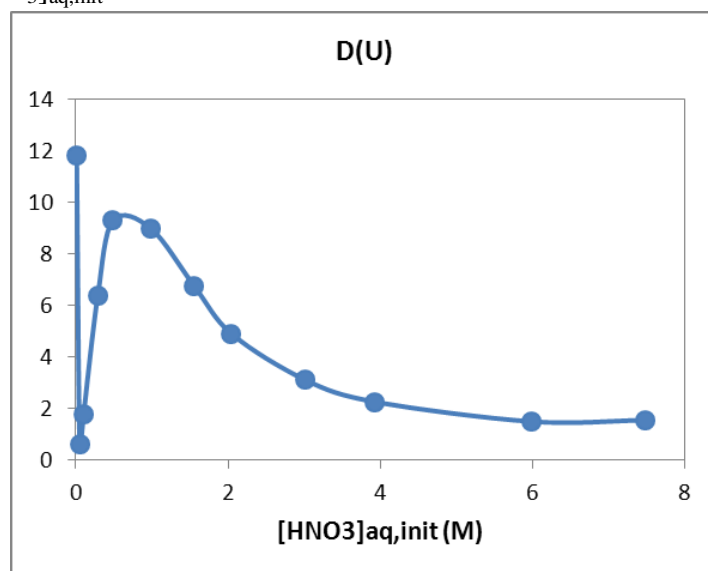


Figure III-23. $U(VI)/HNO_3//DM01/C_1C_{10}imTf_2N$. D_U vs $[HNO_3]_{aq,init}$. $[U(VI)] = 4.2 \times 10^{-5}$ M; $[HNO_3] =$ variable; $[DM01] = 50$ mM

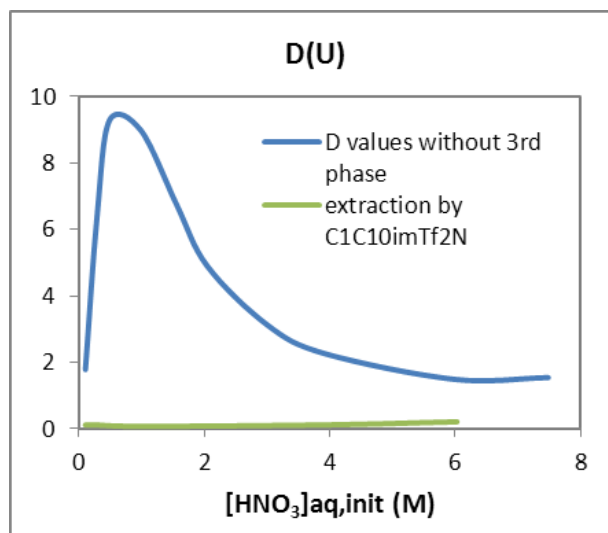


Figure III-24. $U(VI)/HNO_3//DM01/C_1C_{10}imTf_2N$. D_U vs $[HNO_3]_{aq,init}$. $[U(VI)] = 4.2 \times 10^{-5}$ M; $[HNO_3] =$ variable; $[DM01] = 50$ mM (blue); $[DM01] = 0$ M (green)

In Chapter II it was mentioned that tetrazoles may complex metal cations, in order to confirm or refute this fact the extraction experiment with a model tetrazolate FIL⁵ without phosphine oxide group has been performed. As it can be seen from Figure III-25, the tetrazolate pattern does not extract U, but responsible for the 3rd phase formation as discovered during the experiment.

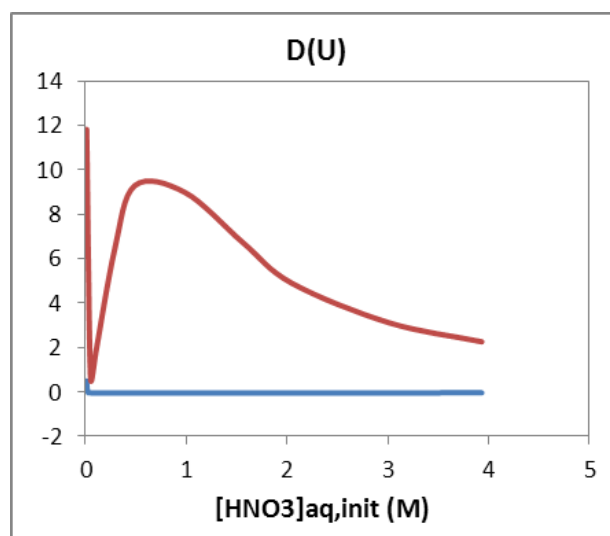


Figure III-25. $U(VI)/HNO_3//DM01/C_1C_{10}imTf_2N$. D_U vs $[HNO_3]_{aq,init}$. $[U(VI)]$ ca. 4×10^{-5} M; $[HNO_3] =$ variable; $[DM01] = 50$ mM (red); [model compound] = 50 mM (blue)

From these data, the first region was defined as the low acidic concentrations, $[HNO_3]_{aq,init} < 0.5$ M, and the second region - as the high acidic concentration, i.e. $[HNO_3]_{aq,init} > 0.5$ M. In order to study the mechanism of extraction, intermediate values of nitric acid concentration for each region have been chosen: $[HNO_3]_{aq,init} = 0.3$ M for low acidic region and $[HNO_3]_{aq,init} = 2.3$ M for high acidic region. Consequently, extraction has been performed for different ligand concentrations, as a function of initial nitric acidity (Figure III-24). The bell shape is evidenced in all three experiments.

⁵ The synthesis of the model compound is presented in Supplementary data

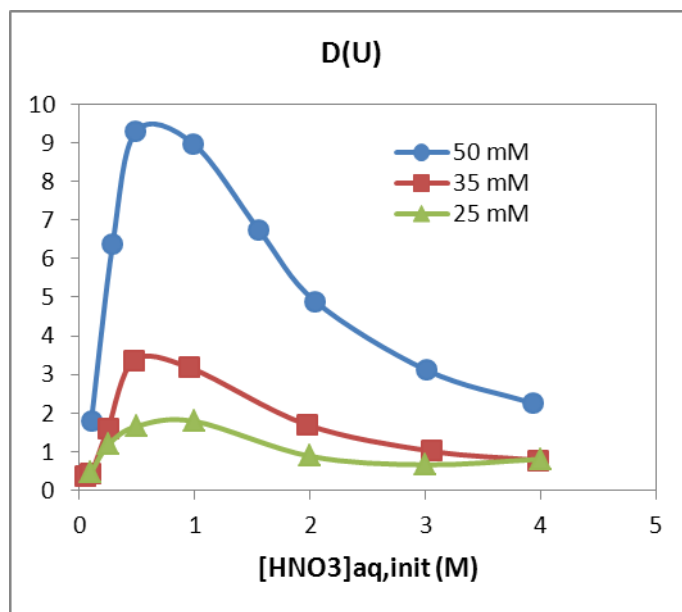


Figure III-26. $U(VI)/HNO_3//DM01/C_1C_{10}imTf_2N$. D_U vs $[HNO_3]_{aq,init}$. $[U(VI)] \approx 4 \times 10^{-5}$ M; $[HNO_3]$ = variable; $[DM01] = 50$ mM (blue); $[DM01] = 35$ mM (red); $[DM01] = 25$ mM (green)

Figures III-27 and III-28 illustrate the D increase as a function of DM01 concentration in region I and region II, ($[HNO_3]_{aq,init} = 0.3$ M, $[HNO_3]_{aq,init} = 2.3$ M).

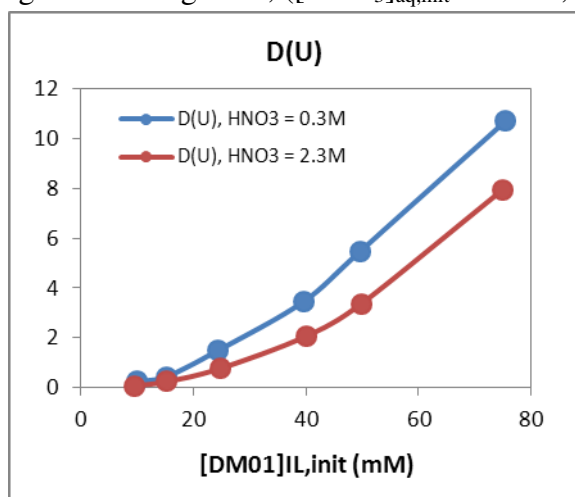


Figure III-27.
 $U(VI)/HNO_3//DM01/C_1C_{10}imTf_2N$. D_U vs $[DM01]_{IL,init}$. $[U(VI)] = 3.84 \times 10^{-5}$ M; $[HNO_3] = 0.3$ M (blue); $[HNO_3] = 2.3$ M (red)
 $[DM01]$ = variable

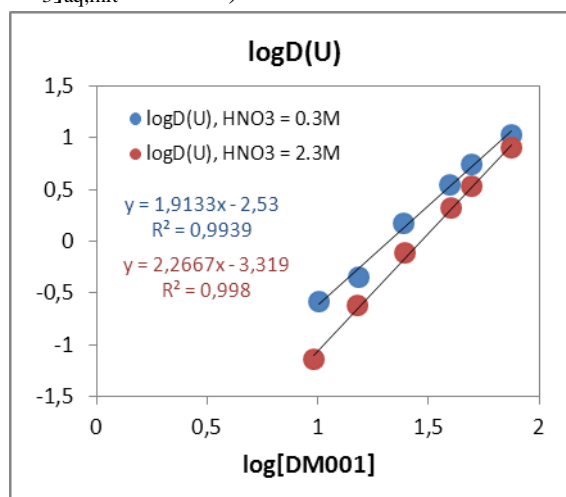


Figure III-28. Logarithmic representation of D_U vs $[DM01]_{IL,init}$; $[U(VI)] = 3.84 \times 10^{-5}$ M; $[HNO_3] = 0.3$ M (blue); $[HNO_3] = 2.3$ M (red)
 $[DM01]$ = variable

Then, Figures III-29 – III-32 present the D variation in both regions as a function of increasing amounts of a salt added to the aqueous phase. In Figure III-29 D coefficients (blue curve) were obtained from measurements of metal concentrations in aqueous phase (calculated from initial and equilibrium concentrations of metal), and D coefficients (green curve) were calculated from the data of both phases at equilibrium.

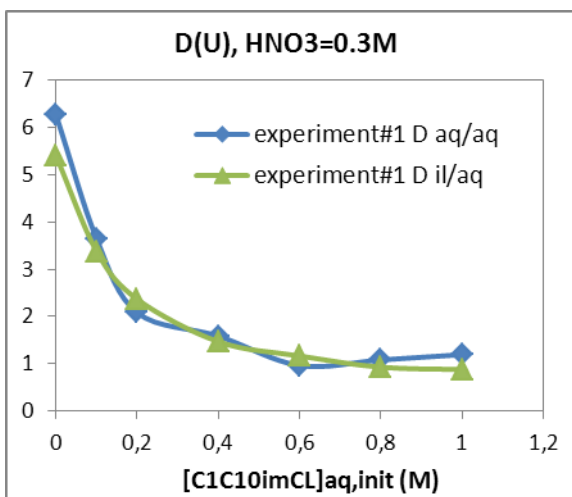


Figure III-29.

$U(VI)/HNO_3//DMO1/C_1C_{10}imTf_2N$. D_U vs $[C_1C_{10}imCl]_{added}$. $[U(VI)] = 3.84 \times 10^{-5} M$; $[HNO_3] = 0.3 M$; $[DMO1] = 50 mM$; $[C_1C_{10}imCl] = \text{variable}$

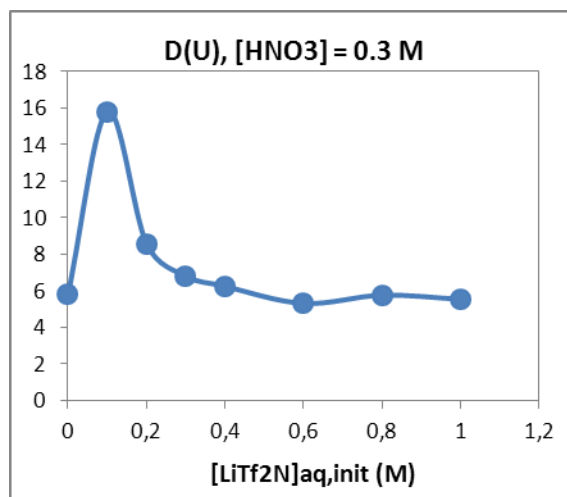


Figure III-30.

$U(VI)/HNO_3//DMO1/C_1C_{10}imTf_2N$. D_U vs $[LiTf_2N]_{added}$. $[U(VI)] = 4.37 \times 10^{-5} M$; $[HNO_3] = 0.3 M$; $[DMO1] = 50 mM$; $[LiTf_2N] = \text{variable}$

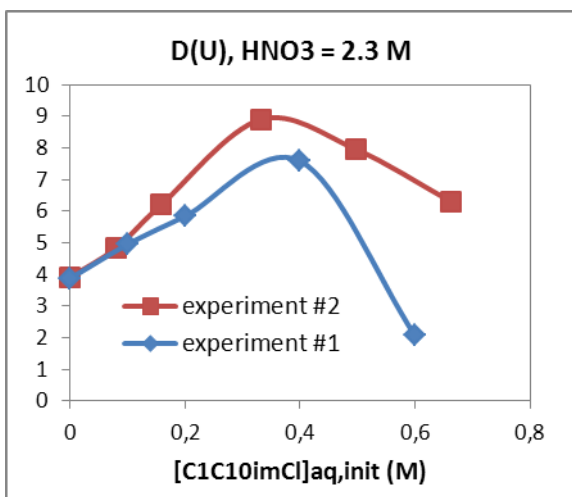


Figure III-31.

$U(VI)/HNO_3//DMO1/C_1C_{10}imTf_2N$. D_U vs $[C_1C_{10}imCl]_{added}$. $[U(VI)] = 3.84 \times 10^{-5} M$; $[HNO_3] = 2.3 M$; $[DMO1] = 50 mM$; $[C_1C_{10}imCl] = \text{variable}$

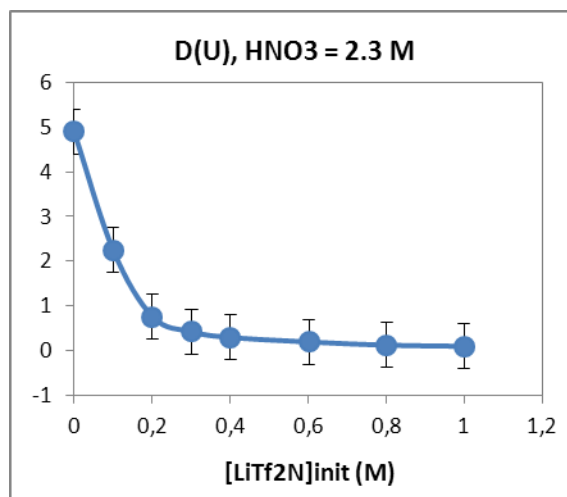


Figure III-32.

$U(VI)/HNO_3//DMO1/C_1C_{10}imTf_2N$. D_U vs $[LiTf_2N]_{added}$. $[U(VI)] = 4.27 \times 10^{-5} M$; $[HNO_3] = 2.3 M$; $[DMO1] = 0.05 M$; $[LiTf_2N] = \text{variable}$

Figure III-33 presents the D variations in region II, ($[HNO_3]_{aq,init} = 2.3 M$ and $[DMO1] = 50 mM$) as a function of $1/[Tf_2N^-]_{added}$. D is decreasing as $[Tf_2N^-]_{aq,eq}$ is increasing and the D vs $1/[Tf_2N^-]_{added}$ variation is linear (Figure III-33). As a complement, the possible transfer of the Tf_2N^- anion from the aqueous phase to the IL phase has been measured (Figure III-34).

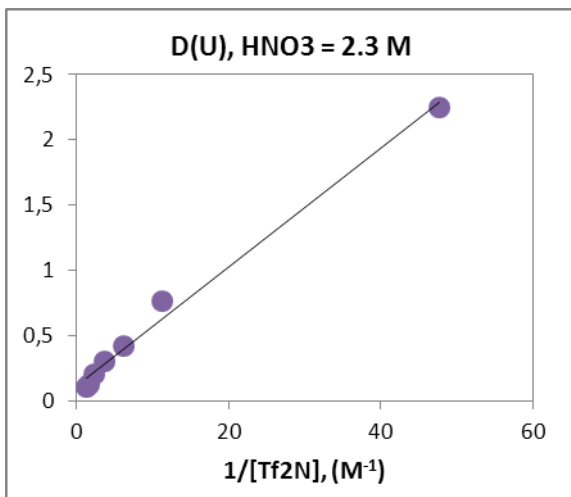


Figure III-33.

$U(VI)/HNO_3//DMO1/C_1C_{10}imTf_2N$. D_U vs $1/[LiTf_2N]_{added}$. $[U(VI)] = 4.27 \times 10^{-5}$ M; $[HNO_3] = 2.3$ M; $[DMO1] = 50$ mM; $[LiTf_2N] =$ variable. Solid linear line is a trend line for the data

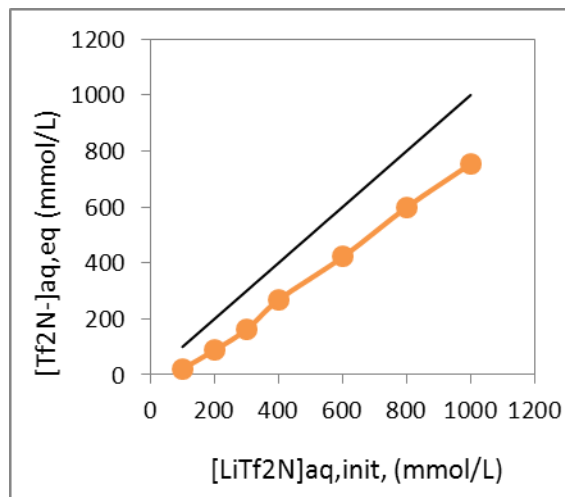


Figure III-34. $HNO_3//DMO1/C_1C_{10}imTf_2N$.

$[Tf_2N^-]_{aq,eq}$ vs $[LiTf_2N]_{added}$. $[U(VI)] = 4.27 \times 10^{-5}$ M; $[HNO_3] = 2.3$ M; $[DMO1] = 50$ mM; $[LiTf_2N] =$ variable. Solid black line corresponds to $y = x$

The addition of $LiTf_2N$ to the aqueous phase acidified with $[HNO_3]_{aq,init} = 2.3$ M leads to a non negligible transfer of Tf_2N^- ions to the IL phase, as shown in Figure III-34 with a transfer to the IL phase up to 80% of the initial added value. This anion transfer occurs in parallel with a very large increase of the water concentration in the IL phase (depending on the chemical conditions, up to 18 000 ppm), which adds to the *ca.* 8 600 ppm obtained at $[HNO_3]_{aq,init} = 2.3$ M (see Figure III-35).

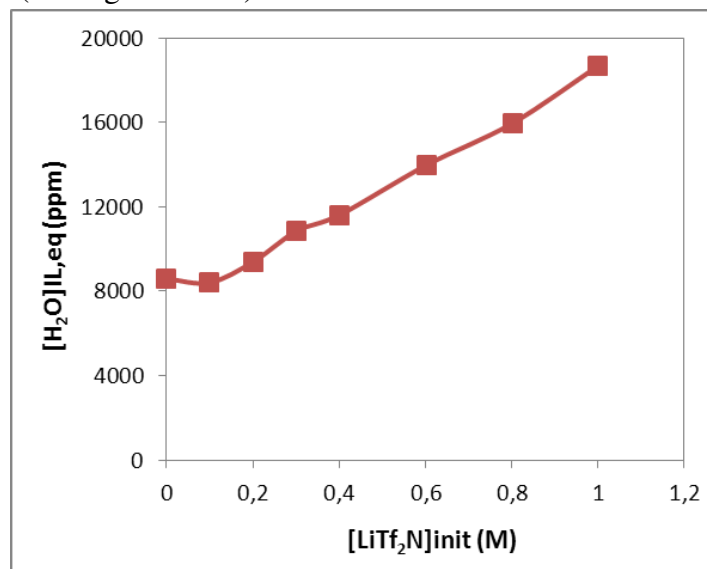


Figure III-35. $HNO_3//DMO1/C_1C_{10}imTf_2N$. $[H_2O]_{IL,eq}$ vs $[LiTf_2N]_{added}$. $[U(VI)] = 4.27 \times 10^{-5}$ M; $[HNO_3] = 2.3$ M; $[DMO1] = 50$ mM; $[LiTf_2N] =$ variable

III.2.4 Experimental results for cationic carbamoyl phosphine oxide FIL (CMPO-IL)

Figure III-36 displays the distribution ratio of U(VI) as a function of nitric acid concentration at fixed ligand concentration equal to 13 mM.

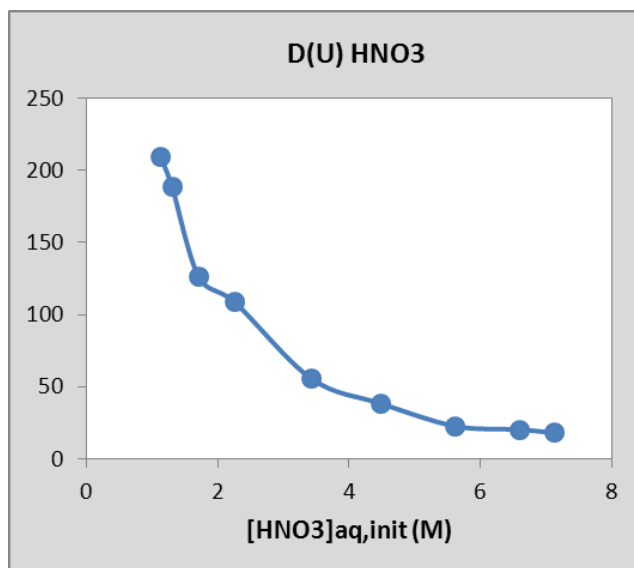


Figure III-36. $U(VI)/HNO_3//CMPO-IL/C_1C_4imTf_2N$. D_U vs $[HNO_3]_{aq,init}$. $[U(VI)] = 1.2 \times 10^{-5} M$; $[HNO_3] = \text{variable}$; $[CMPO-IL] = 13 \text{ mM}$

Similarly to the previous results, the curve of extraction shows continuous decrease, while nitric acid concentration is increasing.

The possible protonation of the ligand has been checked by increase of its concentration in the IL phase, at a constant acidity value, and measuring the equilibrium acidity in the aqueous phase (Figure III-37).

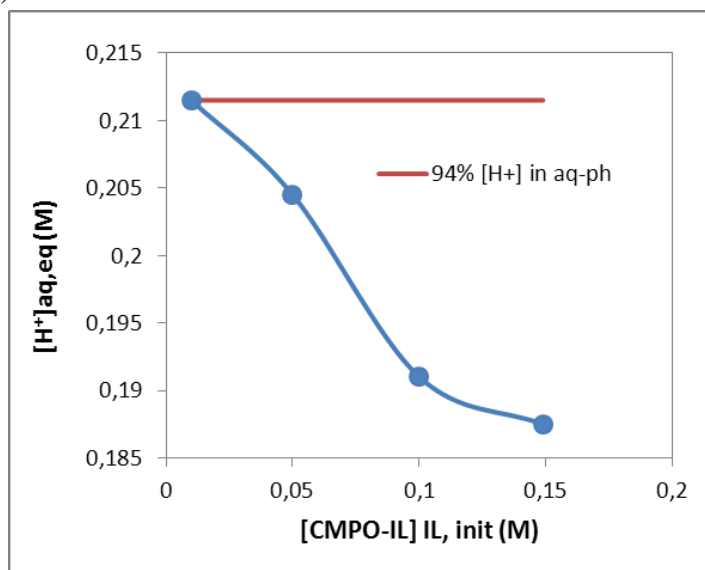


Figure III-37. $HNO_3//CMPO-IL/C_1C_4imTf_2N$. $[H^+]_{aq,eq}$ vs $[CMPO-IL]$. $[HNO_3] = 0.211 M$; $[CMPO-IL] = \text{variable}$

On the assumption of the graphic results, CMPO-IL undergoes protonation.

Prior to the extraction experiments with Am and Eu, the extractability of pure IL-phase toward them was checked in the presence of perchloric acid. These results consistent with those of our group, showing that Am is not extracted towards $C_1C_4imTf_2N$ from highly acidic $HClO_4$ aqueous solutions [119]. The identical behavior on that point was assumed for Eu and Am and therefore, the extraction data presented hereafter to be solely due to the presence of the OctPh-CMPO-IL moiety.

The extraction experiments with CMPO-IL have been performed for several metal cations, using either nitric or perchloric acid for aqueous phase (Figure III-38).

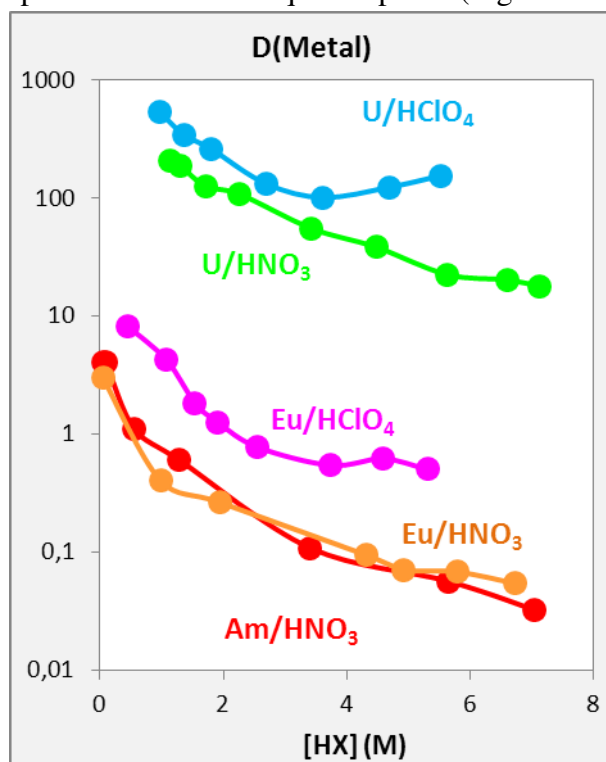


Figure III-38. $M/HX//CMPO-IL/C_1C_4imTf_2N$. $[U(VI)] = 1.2 \times 10^{-5}$ M (HNO_3); $[U(VI)] = 1.9 \times 10^{-5}$ M ($HClO_4$); $[Eu(III)] = 5.4 \times 10^{-5}$ M ($HClO_4$); Am=traces; $[CMPO-IL] = 13$ mM

From the Figure III-38 it can be seen that CMPO-IL is more efficient for the extraction of uranyl, especially in $HClO_4$.

Further experiments have been performed for the system $U(VI) / HNO_3 // CMPO-IL / C_1C_4imTf_2N$, involving salts addition.

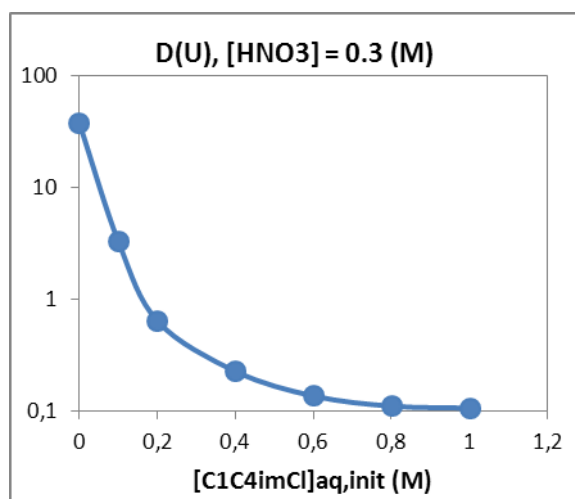


Figure III-39.

$U(VI)/HNO_3//CMPO-IL/C_1C_4imTf_2N$. D_U vs $[C_1C_4imCl]_{added}$. $[U(VI)] = 5.9 \times 10^{-5}$ M; $[HNO_3] = 0.3$ M; $[CMPO-IL] = 6.14$ mM

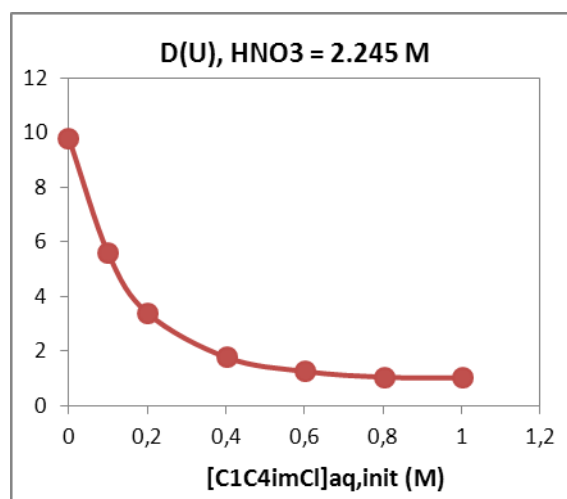


Figure III-40.

$U(VI)/HNO_3//CMPO-IL/C_1C_4imTf_2N$. D_U vs $[C_1C_4imCl]_{added}$. $[U(VI)] = 4.567 \times 10^{-5}$ M; $[HNO_3] = 2.245$ M; $[CMPO-IL] = 6.14$ mM

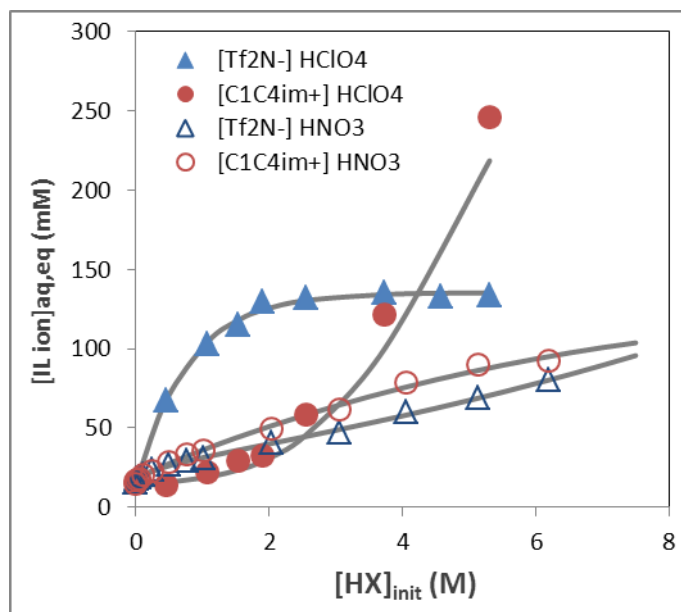


Figure III-41. Variations of the solubility of Tf_2N^- and $\text{C}_1\text{C}_4\text{im}^+$ in the aqueous phase as a function of acid initial concentration. Triangles: $[\text{Tf}_2\text{N}^-]$ variations; Circles: $[\text{C}_1\text{C}_4\text{im}^+]$ variations; Open symbols: HNO_3 data, Closed symbols: HClO_4 data. Solid lines: empirical fits (see text)

III.2.5 Experimental results for cationic calixarene-based phosphine oxide FIL (calix-IL)

The experiment has been performed by Dr. Ali Ouadi.

Figure III-42 displays the variation of D as a function of initial nitric acid concentration for Calix-IL. The extraction has been performed following the protocol described in paper [120]. The coefficients of extraction are rather low, and decreasing while the concentration of nitric acid increases.

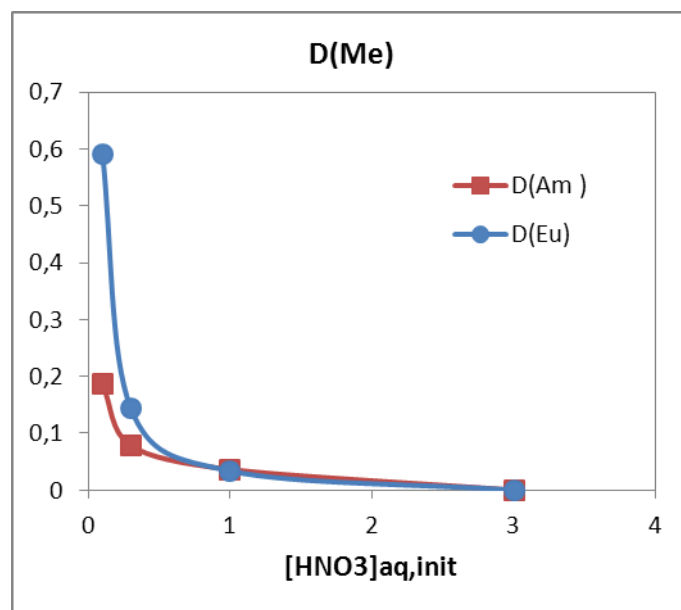


Figure III-42. $M/\text{HNO}_3//\text{Calix-IL}/\text{C}_1\text{C}_4\text{imTf}_2\text{N}$. D_{Me} vs $[\text{HNO}_3]_{\text{aq,init}}$. $[\text{Am}]$, $[\text{Eu}]$ = traces; $[\text{HNO}_3]$ = variable; $[\text{Calix-IL}] = 13.3 \text{ mM}$

III.3 Discussions

Prior to the discussion it should be mentioned that in this work the extraction results for malonamide FIL are not discussed, however they can be found in the paper⁶. As well as the additional extraction experiments with Calix-IL have not been performed due to the lack of the product, therefore any analysis of its extraction mechanism could not be performed.

At the beginning all U(VI) extraction results for the compounds TBPO, SM1006, DM01 and CMPO-IL have been gathered and displayed in a synthetic way (Figure III-X for D vs $[\text{HNO}_3]_{\text{aq,init}}$ and D vs addition of salts). This allows an overview of the results. From Figure III-X, it is obvious that DM01 behaves rather differently from the other compounds, as D vs $[\text{HNO}_3]_{\text{aq,init}}$ displays a maximum at low acidity, while all other compounds correspond to a continuous decrease of D as acidity is increased. This is ascribed to the appearance of a third phase at low acidity, together with the increased solubility of the compound in the aqueous phase as observed by ^1H NMR. It is therefore very difficult to precisely control the amount of ligand present in the IL phase so no further analysis of these results will be presented in this work.

Then, the remaining three compounds (TBPO, SM1006 and CMPO-IL) can be separated in two categories: the first TBPO and SM1006 behave similarly for addition of any of the salts, and at both low and high acidities. By contrast, CMPO-IL displays a decreasing trend at low and high acidities as a function of IL cation addition, which is opposite to the trend observed for TBPO and SM1006. Therefore the extraction results for TBPO and SM1006 will be discussed and analysed separately from those of CMPO-IL.

6 M. Bonnaffé-Moity, A. Ouadi, V. Mazan, S. Miroshnichenko, D. Ternova, S. Georg, M. Sypula, C. Gaillard, I. Billard, *Dalton Trans.* **2012**, 41, 7526-7536

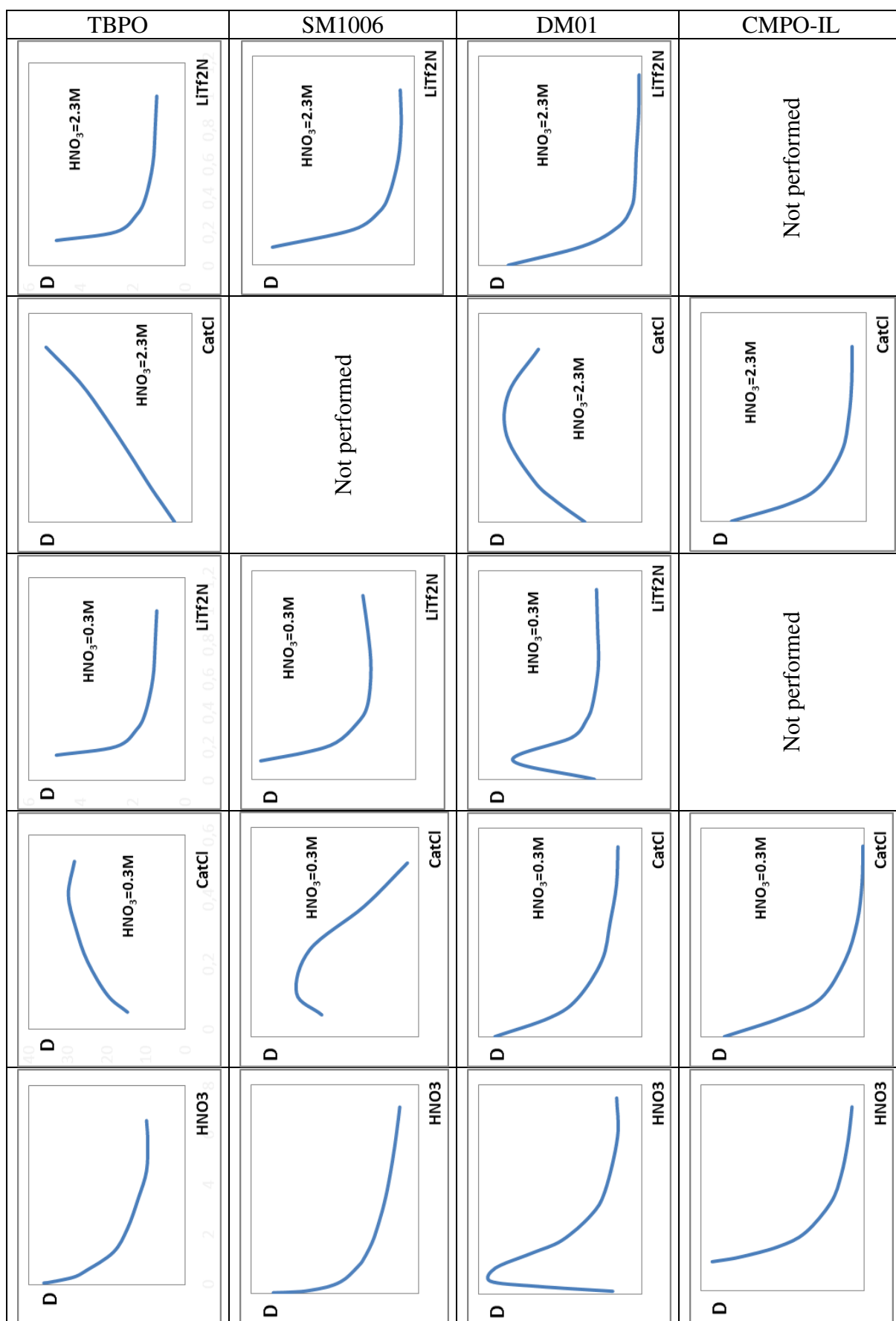


Figure III-X : Synthetic display of experimental results for TBPO, SM1006, DM01 and CMPO-IL: D vs $[HNO_3]_{aq,init}$ and D vs addition of salts

Prior to the quantitative discussions, the brief logic of the extraction experiments performed is to be provided. The first step in the extraction experiments is verification of complexing properties of the FILs synthesized in $M^{m+} / HNO_3 // FIL / C_7C_nimTf_2N$ extracting systems. On the basis of the results obtained we can conclude whether the FIL extracts or not, if yes the shape of D variations vs. $[HNO_3]$ is a first message about probable mechanism of extraction. The next step is quantitative determination of ligand stoichiometry by slope-slope analysis of D values as function of ligand concentrations in logarithmic form. The experiments with salts addition ($CatCl$ and/or LiA) are done to decipher the extraction mechanism (qualitative analysis). For the ligands possessing P=O group a protonation experiment is of high importance, and these data are required for the further quantitative analysis. In order to study the influence of ligand on the ionic liquid solubility in aqueous phase the NMR measurements of $[Cat^+]_{aq,eq}$ and $[A^-]_{aq,eq}$ are performed.

III.3.1 Qualitative analysis for TBPO and SM1006

Owing to the great similarities between the TBPO and SM1006 results, a unique explanation can account for all the data, with the restriction of the discrepancies observed in Figures III-5, III-14, that require some adjustments of the model from TBPO to SM1006.

First of all, it should be mentioned that the FIL, bearing the functional group on its cation, (SM1006) is even more capable of metal cation extraction than neutral TBPO, what at first sight contradicts the explanation given in the paper by Luo et al, which says that cationic TSIL is less efficient than neutral compound due to the coulomb repulsion between covalently attached imidazolium cation and metal cation [121]. In our case SM1006 undergoes protonation, which has a significant impact in decrease of extraction efficiency, thus in case of protonable ligands the coulomb repulsion may have a positive influence on the extraction, hindering protonation.

Both TBPO and SM1006 have phosphine oxide group, and as it was discussed in Section II.2.2, phosphine oxide group shows high donor properties in complexation of metal cations, however at the same time it possesses basic properties, which makes it protonable. It was assumed that protonation of TBPO would occur more readily due to the highest partial negative charge on the oxygen atom of the P=O group: in the case of TBPO P=O group has only butyl substituents, while SM1006 FIL also possesses covalently tethered imidazolium pattern, which due to the intra- and intermolecular interactions may shift the electron density, decreasing the basicity of phosphine oxide group.

Actually for TBPO a significant decrease in the $[H^+]_{aq,eq}$ values was observed from 0.3M to 0.1M as the ligand concentration was increased in the IL phase from 0.01M to 0.5M (Figures III-3, III-4). As well as for SM1006 smaller decrease in the $[H^+]_{aq,eq}$ values was observed: 1.186M to 1.084M at increasing ligand concentration from 0.012M to 0.3M. However, we assume an identical protonation process for both ligands, described through:



$$K_p = \frac{(\overline{LH^+})}{(\overline{L})(\overline{H^+})} \quad (III-2)$$

As it is already known, in the $C_1C_4imTf_2N$ biphasic systems H^+ distributes between the aqueous and IL phases such that 94% of initial H^+ concentration remain in the aqueous phase, therefore an equilibrium is established:



It was also observed that basic nature of the ligands affects solubility of IL in the aqueous phase, namely the distribution of ions $C_1C_4im^+$ and Tf_2N^- (Figures III-9, III-19). In Section I.3.2 it was discussed that ions of ILs dissolve not equally in acidified aqueous phases. At the presence of basic ligand this difference in the solubilities becomes even higher. It can be explained by its protonation, which causes the transfer of $C_1C_4im^+$ to the aqueous phase in order to compensate “extra” amount of H^+ used for the protonation. $C_1C_4im^+_{aq}$ in its turn induces re-equilibration of anions present in the aqueous phase: since $C_1C_4imNO_3$ is more soluble in aqueous phase than $C_1C_4imTf_2N$, the back transfer of NO_3^- from IL phase accompanied by exchange with Tf_2N^- appears to be very favorable, which is why we observe a decrease in the $[Tf_2N^-]_{aq}$ values as compared to the system without any ligand.

From Figure III-X (Synthetic display) it can be seen that TBPO and SM1006 display similar character of D variations as the salts (*CatCl* and/or *LiA*). The increase in D as $[C_1C_4imCl]_{aq}$ increased along with the decrease in D when $[LiTf_2N]_{aq}$ decreases is the signature of an anionic exchange. This is what is observed for TBPO (at low and high acidity) and for SM1006. Therefore the dominating extraction equilibrium applicable for the whole acidity range based on anionic exchange.

III.3.2 Quantitative discussion for TBPO and SM1006: Mathematical treatment, basic chemical considerations and fitting procedure

Due to the data obtained, the adequate mathematical modeling can be performed for three cases: $D=f(HNO_3)$, $D=f(L)$ at $[HNO_3] = 0.3$ M, $D=f(L)$ at $[HNO_3] = 2.3$ M. In the case of salt addition, there are unknowns, which cannot be taken in some approximation: The Tf_2N^- transfer may be accompanied by H^+ or Li^+ transfer or both, or by some back transfer of NO_3^- from the IL phase. $[Li^+]_{aq,eq}$ could not be measured, and considering the uncertainties for the nitrate determination by the colorimetric method used, which is quite sensitive to matrix effects, it was not possible to obtain a complete chemical description of the aqueous phases at equilibrium for the samples in which the $LiTf_2N$ salt was added. Similarly, when C_1C_4imCl is added, the equilibrium of the system is replenished by chloride anion, which was not measured. Respectively it is difficult to judge about NO_3^- distribution.

When a protonable ligand is added, it binds free H^+ of IL-phase (Equation III-1), causing re-equilibration of the system according to Equation III-2.

Thus the total concentration of ligand, which is assumed to be insoluble in aqueous phase:

$$L_0 = (\overline{L}) + (\overline{LH^+}) \quad (III-4)$$

The balance of total H^+ :

$$H_0 = H_{init}^+ = H_{eq}^+ + \overline{H_{eq}^+} + \overline{LH^+} \quad (III-5)$$

After mathematical transformations the equation:

$$K_p(1+K)(H_{eq}^+)^2 + H_{eq}^+(K_pL_0 - K_pH_0 + 1 + K) - H_0 = 0$$

There is only one solution of chemical meaning, expressing concentration of H^+ in aqueous phase at equilibrium:

$$H_{eq}^+ = \frac{-(K_pL_0 - K_pH_0 + 1 + K) + \sqrt{(K_pL_0 - K_pH_0 + 1 + K)^2 + 4H_0K_p(1+K)}}{2K_p(1+K)} \quad (\text{III-6(5)})$$

Thus H_{eq}^+ is a function of L_0 , H_0 , K_p and K .

Experimental data have been fitted to the equation, with one free parameter K_p . Results of fits are displayed in Figures III-43, III-44 and K_p values are gathered in Table 2. K is fixed according to 94% of remaining H^+ (in the absence of ligand).

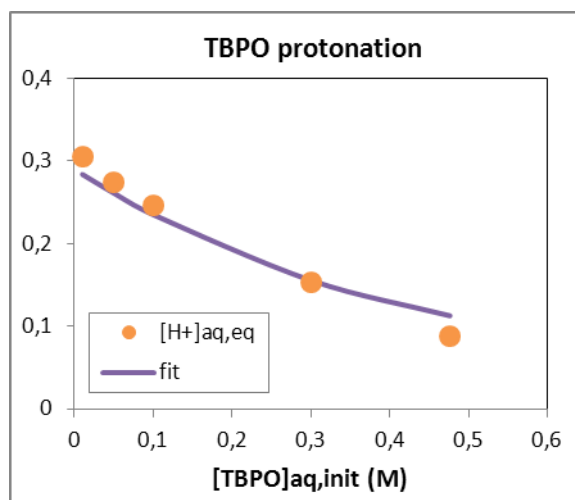


Figure III-43. Fit of TBPO protonation.
[HNO₃] = 0.3 M

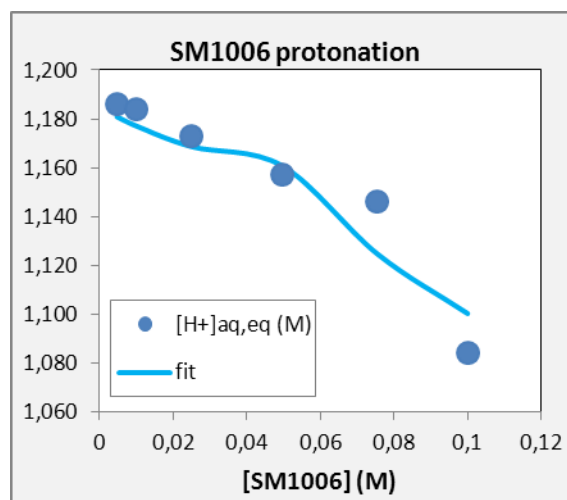


Figure III-44. Fit of SM1006 protonation.
[HNO₃] = 1.25 M

Table 2

Ligand	K_p
TBPO	97
SM1006	6.9
CMPO-IL	no significant protonation

Apart of ligand protonation, there are several other factors of negative or positive effect on the extraction efficiency. In order to evaluate impact of these effects and compare their orders of magnitude, the *sensitivity* study has been performed.

The two systems: $HNO_3 // C_1C_4imTf_2N / TBPO$ and $HNO_3 // C_1C_4imTf_2N / SM1006$ shown in Figures III-1 and III-10 were considered. In both cases the continuous descent in D values is observed while nitric acid concentration is increasing.

For TBPO the descent can be expressed by the ratio of D values at lowest and highest

$$[HNO_3]_{aq,init}: \frac{D_{low}}{D_{high}} = \frac{410.2}{0.97} = 425$$

For SM1006 even larger decrease in D values is observed:

$$\frac{D_{low}}{D_{high}} = \frac{1641.5}{2.0} = 820$$

Thus, the factors influencing the extraction are listed:

Protonation (negative effect):

On the basis of the table values, protonation of TBPO amounts to 97% at $\text{HNO}_3 = 6.6 \text{ M}$ this explains the significant decrease in D values. Similarly, the descent of the SM1006 curve is also attributed to the protonation: 72% of SM1006 is protonated at $\text{HNO}_3 = 7.1 \text{ M}$. In order to evaluate the effect of ligand protonation on D values, the simple model calculations (without taking into account complexation with nitrates, ions exchange, etc.) were performed. As it shown in Equations I-13, I-17: $D \sim (L)^p$, where p is a stoichiometry of a ligand. For the system $\text{HNO}_3 // \text{C}_1\text{C}_4\text{imTf}_2\text{N} / \text{TBPO}$ described in the Figure III-1 the concentration of non-protonated TBPO at the lowest acidity is 80.4%, while at the highest - 2.55%. Assuming TBPO stoichiometry $p = 3$ (Figure III-4), the ration of the $D(U)$:

$$\frac{D_{low}}{D_{high}} = \left(\frac{80.4}{2.55} \right)^3 = 3.1 \times 10^4$$

Similarly for $\text{HNO}_3 // \text{C}_1\text{C}_4\text{imTf}_2\text{N} / \text{SM1006}$ (Figure III-9) the calculated concentration of the ligand at the lowest acid concentration is 71.4%, at the highest is 28%. Taking into account the ligand stoichiometry $p = 2$ (Figure III-12), we obtain the ration of $D(U)$ coefficients for SM1006:

$$\frac{D_{low}}{D_{high}} = \left(\frac{71.4}{28.0} \right)^2 = 6.5$$

As it can be concluded from the calculations, the protonation has an enormous impact on the extraction efficiency in the case of TBPO, while for SM1006 it appeared to be less significant, however, its effect is still not negligible.

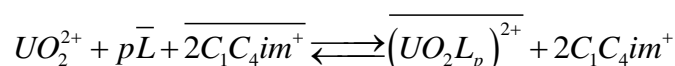
These calculated data are different from the real ratio for TBPO and SM1006, it means that other factors take part as well. And in case of TBPO another effect of positive impact affects the extraction, compensating the negative impact of the protonation. In contrast, for SM1006 another negative effect influences extraction, which leads to even larger decrease in D values as compared to just “pure” protonation effect.

Effect of cations (negative effect)

For IL extracting systems the extraction is implemented most probably by the ion exchange mechanisms. As it was already discussed, acid along with ligand change the equilibrium of both Cat^+ and A^- in the aqueous phase.

For both systems the concentrations of $\text{C}_1\text{C}_4\text{im}^+$ have been measured as shown in Figures III-9 and III-19.

Let us consider the cationic exchange with two imidazolium cations, neglecting all other possible factors:



$$D = K(\bar{L})^p \frac{1}{(\text{C}_1\text{C}_4\text{im}^+)^2}$$

If we assume the concentration of a ligand is constant, which means, no protonation occurs, then in rough approximation, impact on the extraction in term of cations concentration in aqueous phase is:

$$\text{For TBPO: } \frac{D_{low}}{D_{high}} = \left(\frac{Cat_{high}}{Cat_{low}} \right)^2 = \left(\frac{80.81}{18.74} \right)^2 = 18.6$$

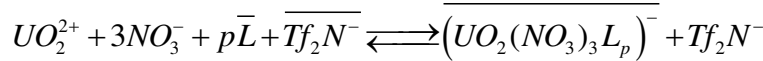
$$\text{For SM1006: } \frac{D_{low}}{D_{high}} = \left(\frac{Cat_{high}}{Cat_{low}} \right)^2 = \left(\frac{80.37}{19.7} \right)^2 = 16.6$$

As compared to protonation impact, the effect of ionic liquid cation as HNO_3 increases is negligible for TBPO and has similar value in case of SM1006.

Effect of anions (negative effect)

Similarly, for the anionic exchange the impact of Tf_2N^- anion has been calculated.

Again, assuming no protonation, and without taking into consideration nitrates concentration:



$$D = K(\bar{L})^p (\text{NO}_3^-)^3 \frac{1}{(\text{Tf}_2\text{N}^-)^2}$$

$$\text{For TBPO: } \frac{D_{low}}{D_{high}} = \left(\frac{A_{high}}{A_{low}} \right) = \left(\frac{74.94}{11.45} \right) = 6.5 \text{ (see Figure III-9)}$$

$$\text{For SM1006: } \frac{D_{low}}{D_{high}} = \left(\frac{A_{high}}{A_{low}} \right) = \left(\frac{64.69}{12.34} \right) = 5.2 \text{ (see Figure III-19)}$$

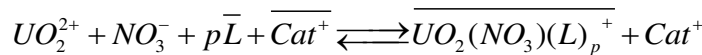
The order of the anion effect is similar with that of cation.

Effect of nitrates (positive effect)

The amount of nitrates participating in extraction equilibrium depends on the mechanism of extraction. Three mechanisms for each system have been considered:

For TBPO:

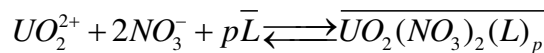
- 1) Cationic exchange



$$D = \frac{K(\bar{L})^p}{\text{Cat}} (\text{NO}_3^-)$$

$$\frac{D_{high}}{D_{low}} = \frac{(\text{NO}_3^-)_{high}}{(\text{NO}_3^-)_{low}} = \frac{6.58}{0.05} = 132$$

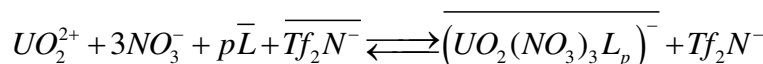
- 2) Ion pairing



$$D = \frac{K(\bar{L})^p}{\text{Cat}} (\text{NO}_3^-)^2$$

$$\frac{D_{high}}{D_{low}} = \frac{(\text{NO}_3^-)_{high}}{(\text{NO}_3^-)_{low}} = \left(\frac{6.58}{0.05} \right)^2 = 1.7 \times 10^4$$

- 3) Anion exchange

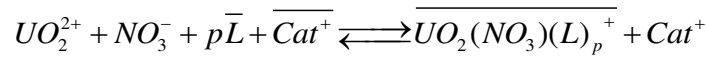


$$D = \frac{K(\bar{L})^p}{A^2} (NO_3^-)^3$$

$$\frac{D_{high}}{D_{low}} = \frac{(NO_3^-)_{high}}{(NO_3^-)_{low}} = \left(\frac{6.58}{0.05}\right)^3 = 2.2 \times 10^6$$

For SM1006:

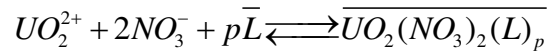
4) Cationic exchange



$$D = \frac{K(\bar{L})^p}{Cat} (NO_3^-)$$

$$\frac{D_{high}}{D_{low}} = \frac{(NO_3^-)_{high}}{(NO_3^-)_{low}} = \frac{7.13}{0.019} = 375.4$$

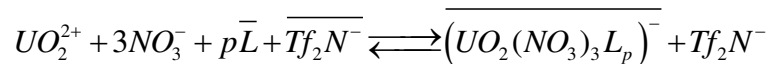
5) Ion pairing



$$D = \frac{K(\bar{L})^p}{Cat} (NO_3^-)^2$$

$$\frac{D_{high}}{D_{low}} = \frac{(NO_3^-)_{high}}{(NO_3^-)_{low}} = \left(\frac{7.13}{0.019}\right)^2 = 1.4 \times 10^5$$

6) Anion exchange



$$D = \frac{K(\bar{L})^p}{A^2} (NO_3^-)^3$$

$$\frac{D_{high}}{D_{low}} = \frac{(NO_3^-)_{high}}{(NO_3^-)_{low}} = \left(\frac{7.13}{0.019}\right)^3 = 5.2 \times 10^7$$

These rough calculations give the information on how much D is decreased at the highest H^+ value (as compared to the lowest H^+ value), however the curvature of the plot is also important. Furthermore, when complexation, protonation and extraction are considered together the relative matrix importance of the each effect has an impact on the final D values that cannot be handled by the raw estimates made above. Thus, calculations have been performed by use of the general program for the following mixed assumptions (association of HNO_3 is never considered). The following Figure III-45 vividly shows the results.

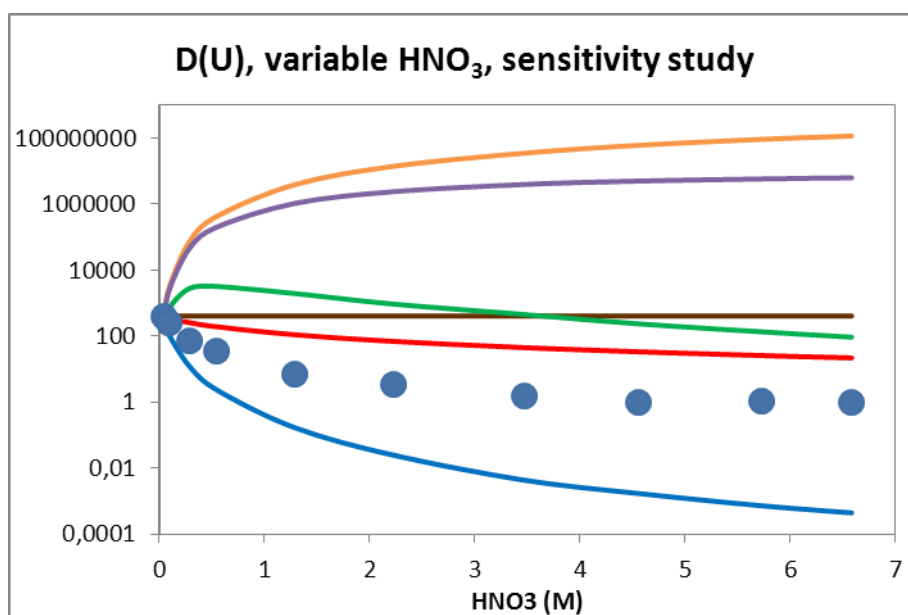


Figure III-45. Variations of D according to the influence of different factors (TBPO).

First of all, it should be defined that basic calculation means no complexation, no protonation and only one single extraction equilibrium. Further, a basic calculation can be modified by addition of different effects of negative or positive impact on extraction efficiency.

- 1) For the basic calculation#1 the cationic exchange with two H^+ was regarded, this is described in Figure III-45 by the brown curve.
- 2) Uranyl complexation with nitrates assumed for the basic calculation#1 is resulted in decrease, as displayed by the red curve.
- 3) Protonation of ligand in the basic calculation#1 gives the most significant decrease in D values, displayed by the blue curve.
- 4) Basic calculation#2 was performed assuming anion exchange with one Tf_2N^- as only extraction mechanism, and it results in a strong increase in D values, what is described by the orange curve.
- 5) Uranyl complexation compensates the positive effect of the basic calculation#2, what is displayed by the violet curve.
- 6) Protonation overbalances the basic calculation#2, leading to the decrease in D variations, this is described by the green curve.

The exact values are gathered in Table 3.

Table 3. Calculations for D values: TBPO extraction system

study	K_p	complexation	K_+	number of H^+ for cationic exchange	$K.$	ligand stoichiometry	comment
1)	0	no	1.57×10^9	2	-	3	basis#1 for comparison
2)	0	yes	1.57×10^9	2	-	3	basis#1 and 2 negative effects added successively
3)	97	yes	1.57×10^9	2	-	3	Basis#1 and protonation: D decrease is too strong as

							compared to the experimental data, but the curvature is correct
4)	0	no	-	-	6×10^8	3	basis for comparison
5)	0	yes	-	-	6×10^8	3	curvature at low acidity is not correct as compared to data
6)	97	yes	-	-	6×10^8	3	

Table 4. Fits for D values: TBPO extraction system

Fits	K_p	complexation	K_+	number of H^+ for cationic exchange	K	ligand stoichiometry	χ^2	comment
a)	97	yes	3.88×10^9	2	2.47×10^6	3.3	0.105	three fits are excellent, but very similar
b)	97	yes	6.49×10^6	1	2.5×10^6	3.3	0.108	
c)	97	yes	1.08×10^4	0	2.5×10^6	3.3	0.112	

As can be seen from Table 4 the best mathematical treatment for the data of $HNO_3 // C_1C_4imTf_2N / TBPO$ extraction system has been obtained on the assumption of anionic exchange along with cationic exchange. There are three possibilities for the cationic exchange with two cations, which can be H^+ and/or $C_1C_4im^+$. The three resulting fits interpret these data with high accuracy; however the fits are very similar, thus it is impossible to discriminate among them. The two extreme cases (exchange with two H^+ and with two $C_1C_4im^+$) are shown in Figure III-47.

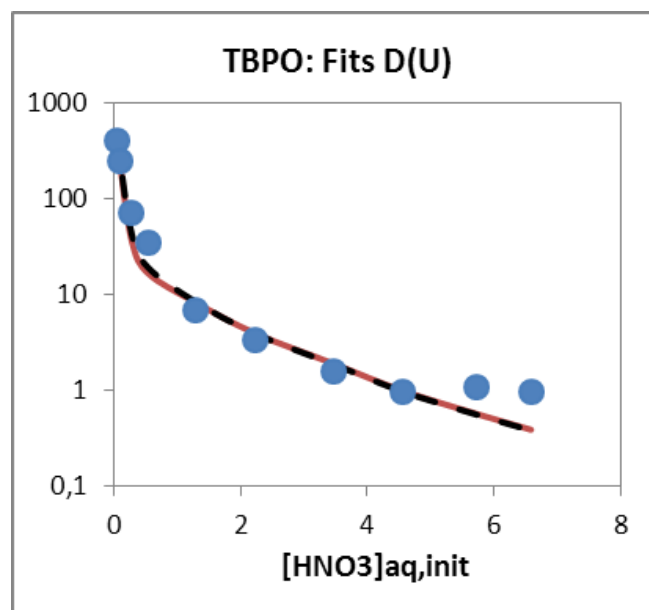


Figure III-46. Fits of D values for TBPO extracting system. A) Red curve; c) dashed curve

Similarly, for $HNO_3 // C_1C_4imTf_2N / SM1006$ extracting system the calculations and mathematical modelling have been performed. It was found that, the data could not be treated on the assumption of anionic exchange, while cationic exchange appeared to be sufficient (see Table 6).

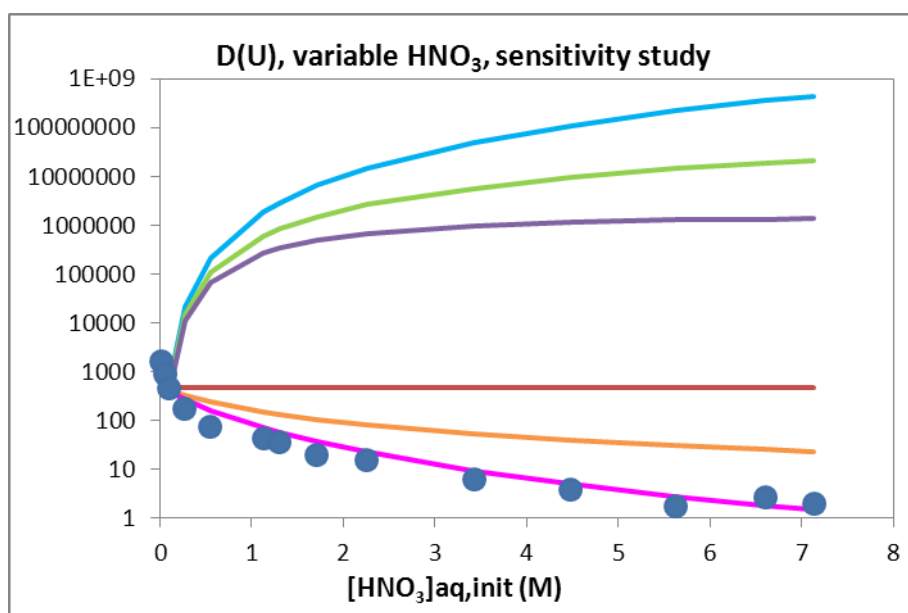


Figure III-47. Variations of D according to the influence of different factors (SM1006)

Table 5. Calculations for D values: SM1006 extracting system

study	K_p	complexation	K_+	number of H^+ for cationic exchange	K_-	ligand stoichiometry	comment
1)	0	no	1.16×10^7	2	-	2	cationic exchange basis#1 for comparison (red curve)
2)	0	yes	1.16×10^7	2	-	2	complexation with nitrates (orange curve)
3)	7	yes	1.16×10^7	2	-	2	cationic exchange along with protonation and complexation – almost perfect display (pink curve)
4)	0	no	-	-	1.3×10^7	2	anionic basis#2 for comparison (blue curve)
5)	0	yes	-	-	1.3×10^7	2	basis#2 along with nitrate complexation (green curve)
6)	7	yes	-	-	1.3×10^7	2	basis#2 along with complexation and protonation (purple curve)

Table 6. Fits for D values: SM1006 extracting system

Fits	K_p	complexation	K_+	number of H^+ for cationic exchange	K_-	ligand stoichiometry	χ^2	comment
a)	7	yes	8.08×10^6	2	none	2	0.105	three fits are excellent, but very similar
b)	7	yes	7.9×10^3	1	none	2	0.108	
c)	7	yes	6.08	0	none	2	0.112	

As it can be seen from Table 6, the contribution of anionic exchange does not help to fit the data in case of the SM1006 extracting system, and cationic exchange appears to be sufficient. Three fits have been performed on this basis, varying the number of H^+ exchanged. The fit, involving exchange with two H^+ is more acceptable in this case (see Figure III-48). The

data were fitted starting from 1 M HNO₃ concentration because some measurements were performed only after that acidic value.

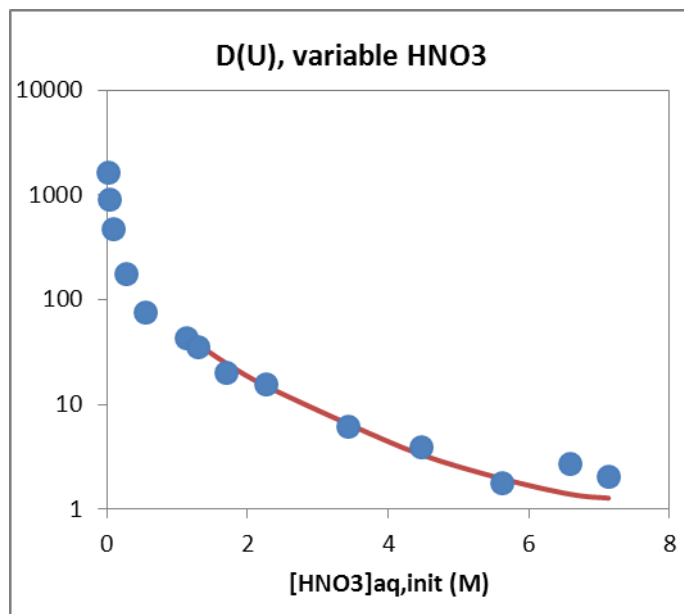


Figure III-48. Fits for D values for SM1006 extracting system. Red curve: fit a

The cationic exchange involved is in contradiction with the conclusion derived from salt addition experiments, which indicated anionic mechanism as dominating one. At the moment, no explanation can be provided for that, and some additional work should be performed before a complete understanding can be reached.

III.3.3 Qualitative analysis for CMPO-IL

As it is shown in the synthetic display (Figure III-X), in extraction of uranyl from nitric acid solutions CMPO-IL behaves rather differently from TBPO and SM1006 ligands, therefore it is discussed separately. The strategy for the investigation of the extracting properties of this ligand was different from that for TBPO and SM1006. The reasons for that are detailed below.

In aqueous radioactive wastes uranium exists in its stable hexavalent form UO_2^{2+} , this peculiar structure makes its extraction different from other elements. However extraction of other fission products is the one of the most challenging problems of radiochemistry, especially the extraction of hazardous long-lived radionuclides. In this respect, a traditional carbamoyl phosphine oxide is known to extract other actinides and lanthanides in the TRUEX process. Therefore, in this work apart of the set of uranyl extraction studies, the synthesized CMPO-IL was also tested for the extraction of Am and Eu (Figure III-36). Am and Eu are studied together because of the similar chemical behaviour, which make their separation difficult.

For the reason of relevance with real nuclear wastes, nitric acid is usually chosen as aqueous phase in the most of extraction experiment with radionuclides. In this case apart of acid strength, another very important factor is the role of the anion in complexation of metal cation. Thus, poly-atomic nitrate anion can have several modes of coordination to a metal cation, which can result in the formation of various complexes of different stoichiometry. In order to obtain a general model, which can characterize the extraction of metallic ions (by CMPO-IL) toward IL phases under various conditions, the comparison of the extracting properties toward U(VI), Am(III) and Eu(III) in different acids (HNO_3 and $HClO_4$) has been performed.

For the two previous ligands protonation has a strong influence on the extraction efficiency. In fact, the advantage of carbamoyl phosphine oxide group over phosphine oxide group lies in the presence of the carbamoyl fragment, which is important not so much for coordination to the metal, but for the ability to buffer the extractant against the effects of an acid [122]. It makes CMPO-containing ligands more resistant to protonation as compared to the phosphine oxide analogues. As listed in Table 2 CMPO-IL is not liable to significant protonation at the metal complexation site in the nitric acid range investigated. Similarly to the HNO_3 data, the $HClO_4$ uptake by the IL phase is increasing along with the increase of acid concentration. The $HClO_4$ remaining in the aqueous phase is equal 93% of its initial concentration, so the same behaviour of CMPO-IL toward protonation can be assumed for the perchloric acid solutions.

The previous section (TBPO and SM1006) has shown that despite a large corpus of experimental data (ligand concentration variations, additions of salts), there remains uncertainties regarding the exact mechanism of extraction. This could be due, in part, to the strong protonation of the investigated ligands: whatever the extraction mechanism, it cannot be deciphered because protonation hampers any extraction. In this section, we investigate other means of mechanism study (change in acid and in metallic element), while keeping the ligand concentration constant and getting rid of protonation.

The systems studied are:

$U(VI) / HNO_3 // CMPO-IL / C_1C_4imTf_2N$
 $U(VI) / HClO_4 // CMPO-IL / C_1C_4imTf_2N$
 $Eu(III) / HNO_3 // CMPO-IL / C_1C_4imTf_2N$
 $Eu(III) / HClO_4 // CMPO-IL / C_1C_4imTf_2N$
 $Am(III) / HNO_3 // CMPO-IL / C_1C_4imTf_2N$

We now turn to the qualitative part of this study, focussing on similarities and differences from one system to the other.

In the absence of extractant, it has been already observed that uranium is not extracted in the $C_1C_4imTf_2N$ phase, even at the highest HNO_3 concentration. The same has been confirmed for Am and Eu. Similarly, for $HClO_4$ neither uranyl nor Am were extracted to the IL-phase. The identical behavior for Eu was also assumed. Thus we consider the extraction data presented in this work to be solely due to the presence of CMPO-IL.

First, the differences induced by the change from HNO_3 to $HClO_4$ were examined. Perchloric acid is one of the strongest acids, however considering dissociation at concentrations used in this work the difference from nitric acid is very limited.

From Figure III-40 it can be seen that $HClO_4$ has different influence on the distribution of Cat^+ and A^- in aqueous phases. But, as it was found by the sensitivity study, the changes in Cat^+ and A^- distributions have less influence on the extraction equilibrium as compared to the effect of nitrates.

Another very important peculiarity of perchloric acid concerns complexation of metals. Perchlorate anion is known not to complex any of the metallic ions investigated [123, 124]. Therefore the idea of “locking the metal ion in a non-extractable form through complexation” is not possible in $HClO_4$ phases. Additionally, absence of complexation in a monophasic system does not imply impossibility of joint extraction metal cation along with anion in biphasic system. Considering HNO_3 media, the thermodynamic complexation constants for UO_2^{2+} with nitrates are 1.99 and 0.07, for Eu(III): 1.86 and 0.43, for Am only one complexation is known: 21.38 [35, 125, 126, 127]. Thus complexation with nitrates should be comparable for U and Eu and very limited for Am with HNO_3 .

As it was previously mentioned, the structure of uranyl cation UO_2^{2+} is different from metallic cations – Am^{3+} and Eu^{3+} , which is resulted in different coordination mode (6 for UO_2^{2+} , 8-9 for Am and Eu). It significantly influences extraction, and as it can be seen from Figure III-38, the extraction of uranyl from nitric acid solutions is superior to that of americium and europium.

With regard to the CMPO-functionalized ionic liquid, it should be mentioned that very often CMPO is called *bidentate ligand*, however many studies have reported that it can behave as monodentate as well. The binding mode depends on such conditions as acid nature, nature of the organic phase, nature of metal cation, ratio of $L:M$, etc. Thus, in order to get to know the binding mode of CMPO-IL in the system used, additional studies have to be performed. Furthermore, to our knowledge traditional CMPO ligand does not reveal high selectivity for Am vs Eu in biphasic ionic liquid systems.

On the basis of the discussion above, the differences and similarities in the extraction plots can be commented (Figure III-38).

The two systems $Eu(III) / HNO_3 // CMPO-IL / C_1C_4imTf_2N$ and $Am(III) / HNO_3 // CMPO-IL / C_1C_4imTf_2N$ do not display any significant differences in terms of D values in the whole acidic range. This should be expected on the basis of the well-known chemical similarities between Am and Eu but it also indicates that obvious differences in the nitrate complexing abilities for Am versus Eu have no significant impact on extraction. In conclusion, it would indicate that no nitrate is involved in the complexation, thus leading to extraction of the +3 species in both cases (cationic exchange). It also means the ligand by itself is not specifically conceived for being selective of Am vs Eu or vice versa.

By contrast, extraction with U is more efficient than Am/Eu extraction (HNO_3 medium).

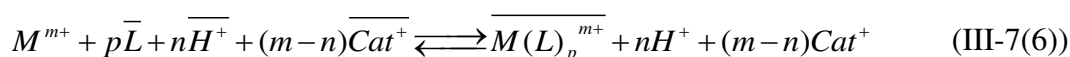
However, the most striking effect is seen in the change from HNO₃ to HClO₄: in nitric media, there is a continuous decrease for all three elements, as already observed for TBPO and SM1006 and U(VI), while HClO₄ medium induces the “usual” boomerang shape already observed in many cases. Thus, in HClO₄ medium, two distinct extraction mechanisms (at minimum) occur, while in nitric medium, there is no obvious argument against a single mechanism in the whole acidic range. This last fact is supported by the results obtained for the addition of salts (U case, HNO₃) indicating a cationic exchange at low and high acidity.

In conclusion, we propose cationic exchange for all 5 systems at low acidity, involving only the naked ions and in addition, in HClO₄ medium, an additional mechanism at high acidity, implying at least one ClO₄⁻ moiety, that would not be possible in nitric medium.

III.3.4 Quantitative discussion for CMPO-IL

In order to go a step further in the description of the data sets, some constraints should have been fixed to the various parameters of the general model before attempting fits. Furthermore, the number of parameters should be limited to a minimum.

First, the extraction of “naked” metallic cation through cationic exchange was considered:



For one given naked metallic ion, the corresponding extraction equilibrium does not explicitly depend on the nature of the acid used because the acid anion is not involved in the extraction equilibrium. However, we know that acid nature affects the ratio between H⁺ in the aqueous and IL phases, which in case of HNO₃ and HClO₄ are very similar (94% and 93% of H⁺ respectively remain in the aqueous phase). Also it was shown acid influences the distribution of Cat⁺ and A⁻ between two phases (see Figure III-41). Both phenomena, as it was demonstrated by sensitivity study, have smaller effect of the extraction efficiency as compared to complexation, for example.

In this case the maximum total number of exchanging cations is $m = 2$ for uranyl and $m = 3$ for Am and Eu. This is reflected in the extraction constant, which in case of triply charged species is slightly more dependent on the concentration of cations involved, than that of 2+ charge:

$$K(M, HX) = \frac{(\overline{ML}_p^{m+})(H^+)^n (Cat^+)^{(m-n)}}{(M^{m+})(\bar{L})^p (H^+)^n} \quad (\text{III-8})$$

The next question is how much of H⁺ participates in chemical equilibrium? The answer can be based on the two phenomena:

- 1) Availability of a cation: the relative amount of Cat⁺ in the ionic liquid phase is dramatically higher than that of H⁺.
- 2) But H⁺ is much more soluble in aqueous phase, thus, its transfer is more favorable.

The experiments with salt addition have proved the effect of Cat⁺ onto extraction of uranyl, it means that Cat⁺ participates in the extraction equilibrium.

The nature of element certainly does not affect the number of H⁺ (n), although charge from +2 (uranyl) to +3 (Am, Eu) means more exchanges to occur.

Extraction of naked ion occurs mainly at low H^+ , because when concentration of HNO_3 increases, the complexation becomes increasingly probable.

It was found (Figure III-41) that in the low region the solubility for HNO_3 is close to that of $HClO_4$. Therefore we can make an assumption about the number of H^+ :

$$n(U, ClO_4) = n(U, NO_3)$$

$$n(Eu, ClO_4) = n(Eu, NO_3) = n(Am, NO_3)$$

From Equation III-8 and above remarks it can be accepted that the constants of extraction $K(U, HNO_3) \approx (U, HClO_4)$. Also considering the chemical similarities between Eu and Am and their similar complexation with CMPO-IL: $K(Eu, HNO_3) \approx (Am, HNO_3)$.

The data for the 5 extraction systems have been fitted all together. The obtained results are shown in Figure III-49. As it can be seen, all the fits are in excellent agreement with the extraction data.

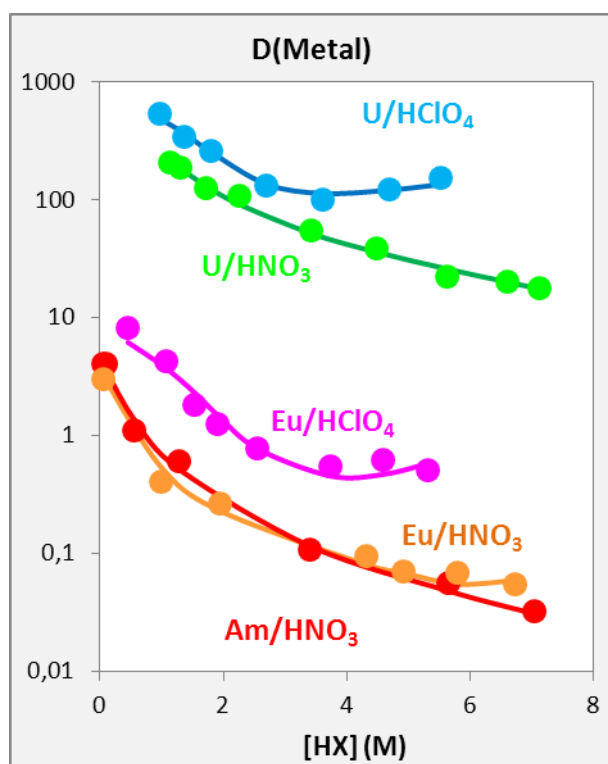


Figure III-49. CMPO-IL extracting systems. Circles: extraction data, solid lines: fits

Table 7. Parameter values corresponding to the best calculation, as depicted in Figure 2 (see text)

Extraction mechanism		Cationic exchange				Anionic exchange		Ion pair	χ^2		
metal	acid	extracted species	K_+	n	extracted species	K_+	n	$K.$			
U	HNO ₃	[UO ₂ L _p] ²⁺	0.18 ± 0.02	0	[UO ₂ (NO ₃)L _p] ⁺	0.47 ± 0.11	0	[UO ₂ (NO ₃) ₃ L _p] ⁻	stz	0.0474	
	HClO ₄				[UO ₂ (ClO ₄)L _p] ⁺	4.8 ± 10	1	[UO ₂ (ClO ₄) ₃ L _p] ⁻	ni	5.6 ± 1.8	0.0348
Eu	HNO ₃	[EuL _p] ³⁺	2.2×10 ⁻⁵ ± 0.2×10 ⁻⁵	0	[Eu(NO ₃)L _p] ²⁺	1.7×10 ⁻² ± 1.0×10 ⁻²	1	[Eu(NO ₃) ₄ L _p] ⁻	ni	1.9×10 ⁻³ ± 8.0×10 ⁻³	
	HClO ₄				[Eu(ClO ₄)L _p] ²⁺	0.83 ± 0.60	2	[Eu(ClO ₄) ₄ L _p] ⁻	stz	3.0×10 ⁻³ ± 2.0×10 ⁻³	0.0612
Am	HNO ₃	[AmL _p] ³⁺	3.0×10 ⁻⁵ ± 0.3×10 ⁻⁵	0	[Am(NO ₃)L _p] ²⁺	5.2×10 ⁻⁴ ± 1.3×10 ⁻⁴	0	[Am(NO ₃) ₄ L _p] ⁻	ni	3.0×10 ⁻³ ± 6.0×10 ⁻³	0.0465

stz : set to zero by the minimization procedure.

ni : does not improve χ^2

From Table 7 it can be seen that for all extracting systems the cationic exchange is involved: in the case of naked ions the exchange with two cations of the IL occurs, while for the extracting species, containing acid anion, the cationic exchange can occur involving different combinations of H⁺ and Cat⁺ depending on the system. Anionic exchange does not help to fit the data.

III.4 Conclusions

In this chapter the extracting results for the task-specific ionic liquids synthesized have been presented. It was demonstrated that these TSILs are capable of uranyl extraction (and in case of CMPO-IL and Calix-IL – also of Am and Eu), regardless the charge of the functionalized ion. The extraction by the TSILs occurs due to the functional group, which was responsible for metal complexation, and not due to the simple exchange with cation of the IL. The experiments have been performed with the FILs, containing either phosphine oxide or carbamoyl phosphine oxide functional groups. The last one appeared to be more stable under acidic conditions used in this study, while phosphine oxide group suffers from protonation, which significantly decreases its complexing properties when the acid concentration increases. The FIL on the calixarene platform basis did not demonstrate high extracting properties, however this still requires some additional experiments.

In order to make a qualitative and quantitative comparison of cationic, anionic FILs and neutral compound the mathematical modeling have been performed. Several extraction equilibria have been considered as possible mechanisms for the extraction by those compounds. It was found that cationic exchange is usually dominating equilibrium for all extracting systems studied. However, the general picture of the extraction in each case is rather complicated, and requires several equilibria, thus dozens of matching fits can be found, which cannot be truth for one extracting system. In order to have real limitations, the composition of the extracting complex has to be determined. This can be implemented by means of such techniques as EXAFS [128].

-
- 111 V.N. Kosyakov, E.A. Yerin, V.M. Vitutnev, *Journal of Radioanalytical chemistry* **1980**, 56,83-92
- 112 Nakhutin, I. E. (1971). *Zhurnal Obshchei Khimii* **41**, 5, 940–943 (in Russian)
- 113 E. K. Watson, W. A. Rickelton, *Solvent Extraction and Ion Exchange* **1992**, 10, 879-889.
- 114 T. A. Mastryukova, O. I. Artyushin, I. L. Odinets, I. G. Tananaev, *Ross. Khimicheskii Zhurnal* **2005**, XLIX, 86–96 (in Russian)
- 115 M. Bonnaffé-Moity, A. Ouadi, V. Mazan, S. Miroshnichenko, D. Ternova, S. Georg, M. Sypula, C. Gaillard, I. Billard, *Dalton Trans.* **2012**, 41, 7526-7536;
- 116 P. Giridhar, K. Venkatesan, S. Subramaniam, T. G. Srinivasan, P. R. V. Rao, *J. Alloys. Compds.* **2008**, 448, 104-108
- 117 V. Mazan, I. Billard, N. Papaiconomou, *RSC Adv.* **2014**, 4, 13371-13383
- 118 P. G. Rickert, D. C. Stepinski, D. J. Rausch, R. M. Bergeron, S. Jakab, M. L. Dietz, *Talanta* **2007**, 72, 315–320
- 119 A. Ouadi, B. Gadenne, P. Hesemann, J. J. E. Moreau, I. Billard, C. Gaillard, S. Mekki, G. Moutiers, *Chem. Eur. J.* **2006**, 12, 3074- 3081
- 120 I. Billard, A. Ouadi, C. Gaillard, *Anal. Bioanal. Chem.* **2011**, 400, 1555–66
- 121 H. Luo, S. Dai, P. V. Bonnesen, A. C. Buchanan, *J. Alloys Compd.* **2006**, 418, 195–199
- 122 D. G. Kalina, E. P. Horwitz, L. Kaplan, a. C. Muscatello, *Sep. Sci. Technol.* **1981**, 16, 1127–1145
- 123 L. Sémon, C. Boehme, I. Billard, C. Hennig, K. Lützenkirchen, T. Reich, A. Roßberg, I. Rossini, G. Wipff, . *J. Chem. Phys. Chem.* **2001**, 2, 591–598
- 124 G. Montavon, S. Markai, I. Billard, A. Nehlig, B. Grambow., *Radiochimica Acta* **2002**, 91, 289–296
- 125 S. Andersson, K. Eberhardt, C. Ekberg, J. O. Lijenzin, M. Nilsson, G. Skarnemark, *Radiochim. Acta* **2006**, 94, 469-474
- 126 A. Nehlig, M. Elhabiri, I. Billard, A. M. Albrecht-Gary, K. Lützenkirchen, *Radiochim. Acta* **2003**, 91, 37-43
- 127 R. Guillaumont, T. Fanghanel, J. Fuger, I. Grenthe, V. Neck, D. A. Palmer, M. H. Rand, *Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium*, Elsevier, Amsterdam, **2003**
- 128 Boon K. Teo, *EXAFS: Basic Principles and Data Analysis*, Springer, Berlin **1986**

GENERAL CONCLUSIONS

Liquid-liquid extraction is a key technique in reprocessing of radioactive wastes. The traditional industrial technology uses tributyl phosphate and kerosene as extracting organic phase, and allows the recovery of U and Pu up to 99% from nitric acid solutions. Nowadays much research is deduced to development and modification of this extracting technology. Usually the efforts are directed to the ligand improvement, as it was shown in the literature review by the diversity of complexing patterns designed either to be more efficient or more selective than traditional ones. Fantastic results have been obtained at this point, however this was often resulted in high cost, complex synthesis, fragile nature of the ligand (hydrolysis, radiolysis), or its low solubility. Only quite recently another concept has been launched, considering also the molecular solvent as a target for modifications [129]. These extracting systems developed became very complicated, thus difficult to handle. Moreover, they require the use of toxic and explosive organic solvents. Aiming to ecological safety ionic liquids (ILs) appear to be a new focus of the research. ILs are green solvents, characterised by low vapour pressure, thus non-volatile, as well as in most cases non-flammable, non-explosive and non-toxic. Furthermore in terms of liquid-liquid extraction their unique ionic nature allows unusual chemistry to occur. I would like to put an emphasis on the fact that ionic liquids are not just a group of chemical compounds, it is a concept, which opens broad horizons for synthetic chemistry. Thus the concept of ILs has been extended by task-specific ionic liquids (TSILs) – the ionic liquids modified for a specific task.

The development and investigation of the new TSILs for the extraction of radionuclides was the main object of this work. First, the preparative methods for the synthesis of cationic and anionic functionalized ionic liquids (FILs) have been developed. The compounds were incorporated with phosphine oxide, carbamoyl phosphine oxide or malonamide functional groups, capable of radionuclides extraction. To our knowledge, the grafting of the extracting pattern to the anion of IL has been realized for the first time. This allowed us to obtain the series of the cationic and anionic ILs bearing the same extracting pattern (dibutylphosphine oxide), thus to compare the influence of the ion on the extracting ability of the pattern. Moreover, this series was supplemented by the cationic FIL on the calixarene basis, thus the effect of the calixarene platform could be studied.

The neutral compound – tributylphosphine oxide appeared to be the most efficient in the series: *neutral phosphine oxide compound* > *cationic phosphine oxide FIL* > *anionic phosphine oxide FIL*. It means the extraction well occurs due to the extracting pattern, however the charge of ion influences it. Thus, lower efficiency of the cationic FIL compared to tributylphosphine oxide can be explained by the mutual electrostatic repulsion between positively charged imidazolium ring of the FIL and metal cation. Expected electrostatic attraction for anionic phosphine oxide FIL was offset by other factors. The anionic FIL synthesized contains tetrazolate anion, which was suffering from protonation in acidic media. And despite on its incorporation with very hydrophobic $C_{10}m^+$ cation, the FIL remained slightly water-soluble, that a part of the FIL is not available for extraction.

These phenomena make tetrazolate anion not suitable for the extraction under acidic conditions, therefore future synthetic research should be focused on the hydrophobic anions resistant to protonation.

Concerning the effect of the calixarene platform, the extraction was not significantly enhanced in case of calixarene-FIL. The possible explanation might lay in opposite effects: mobility of ionic liquid and rigidity of calixarene platform. However this needs better understanding, which is why future studies should be performed, involving various extraction experiments with different calixarene-FILs. In this respect the calixarene synthons obtained can be used for the synthesis of new calixarene-based FILs.

Also it was confirmed that phosphine oxide group undergoes protonation in ionic liquid medium, and this phenomenon significantly diminish extraction when acidic concentration is increasing. Considering these phenomena, the general mathematical model, which can be used for various IL extracting systems (different metal cations, ligands protonable and non-protonable, acid, etc), has been developed. Nevertheless, the computer modelling may provide several suitable fits due to the complexity of IL extracting systems. In this case the composition of the extracting complex has to be determined. It can be implemented by means of the EXAFS experiments. Thus, the use of the mathematical modelling along with EXAFS studies will allow determining of extraction mechanisms with high precision.

¹²⁹ S. Bourg, *SACSESS, EURATOM Collaborative Project on the Safety of Actinide Separation Processes*, CEA Marcoule, **2012**

SUPPLEMENTARY DATA

Chemicals and solutions:

All aqueous solutions have been prepared with ultrapure water (18.2 M Ω ·cm). Other chemicals are provided by:

C₁C₄imTf₂N (Solvionic, France, 99.5%), C₁C₁₀imTf₂N (Solvionic, France, 99.5%), HNO₃ (Merck, 65%), TBPO (Aldrich, 95%), NaNO₃ (Prolabo, 99.5%), LiTf₂N (Solvionic, France, 99%), H₃PO₄ (used as a standard for ³¹P-NMR), C₁C₄imCl (Solvionic, France, 98%), C₁C₁₀imCl (Aldrich, >95.5%), CF₃COONa (Alfa Aesar, Germany, 98%).

All metallic salts were used in stock solutions:

²³⁸U was introduced as UO₂(NO₃)₂·6H₂O with concentration of [UO₂²⁺] = 1.7×10⁻³ at 1 M HNO₃.

Europium was introduced as its nitrate salt at an initial concentrations 5.4×10⁻⁵ M (HNO₃) or 3.5×10⁻⁵ M (HClO₄). ²⁴¹Am is from an acidic aqueous solution of [HNO₃] = 1 M.

All the ILs used were carefully dried in vacuum within 1h at 60° C and 2h at ambient temperature before an experiment. This lowers the water content, which is necessary for the reproducibility of H₂O measurements. ILs solutions were prepared by weight as for the IL amount.

Extraction protocols:

For a typical uranyl extraction experiments equal volumes (0.8 ml) of aqueous and IL-phases have been first pre-equilibrated by mechanical shaking during 3 hours. Then 20 μ l of the stock solution of uranyl nitrate (with concentration [UO₂²⁺] = 1.7 × 10⁻³ M) were added by injection to each sample. Therefore, uranyl concentration in the aqueous phase prior to extraction was equal to *ca.* 4×10⁻⁵ M, (and HNO₃ ranged from 0.01 M to 7 M). Mechanical shaking has been applied for 3 hours. Before phase separation mixture has been centrifuged (3 min, 4000 rpm).

All extraction experiments have been performed at $t = 22 \pm 2$ °C.

For the extraction of americium and europium, a glove box has been used in a dedicated building. Equal volumes (0.8 ml each) of IL phase and aqueous phase were shaken for 3h, then layers were centrifuged and separated.

Measurement of distribution ratio

Uranyl concentrations were determined by ICP-MS with Tl as a standard (Agilent 7500i, error: $\pm 2\%$, LD = 0.001 μ g/l, LQ = 2 μ g/l) and uranyl distribution ratio, $D(U)$, was calculated from the concentration values of uranyl in the aqueous phase before and after extraction, according to:

$$D_{UO_2^{2+}} = \frac{[UO_2^{2+}]_{aq,init} - [UO_2^{2+}]_{aq,eq}}{[UO_2^{2+}]_{aq,eq}}$$

Additionally in few cases the $D(U)$ values were checked for both phases after extraction:

$$D_{UO_2^{2+}} = \frac{[UO_2^{2+}]_{IL,eq}}{[UO_2^{2+}]_{aq,eq}} \text{ (shown in Figure III-29)}$$

For all extraction experiments the volumes of the aqueous and IL phases were assumed as equal, neglecting the volume changes caused by mutual solubilities.

Their radioactivities were assayed by counting 0.5 ml aliquots of both phases in a γ -scintillation counter with a well type NaI(Tl) crystal. The distribution ratio D was determined as the ratio of radioactivity of the IL phase to that of aqueous phase.

γ -counting was performed using an Eurysis high purity germanium detector equipped with the ITech Instruments InterWinner 6.0 software. The γ -line at 59.5 keV was examined for ^{241}Am . Both aqueous and IL phases were measured. The peak surface ratio gives readily the distribution ratio. Owing to auto-absorption of photons below 100 keV, especially in the IL phases, the uncertainty on $D(\text{Am})$ is equal to *ca.* 15 %.

$$D = \frac{A_{IL}}{A_{aq}}$$

Other measurements

The concentration of water in the IL-phase has been measured by the Karl-Fischer technique (coulometer by Metler-Toledo DL 32, 10% uncertainty).

Nitrate and acidic concentrations have been determined solely in the aqueous phases as direct titration of H^+ and NO_3^- in the IL phase is not possible, due to the lack of assessed methods in such media.

Acidity of the aqueous solutions has been measured by means of an automatic titrator (Schott, titroline, error: $\pm 2\%$).

Quantitative ^1H and ^{19}F NMR experiments

All spectra were recorded on a Bruker 300MHz located at the Institut de Chimie, Strasbourg University, France, with a probe 5 mm QNP $^1\text{H}/^{13}\text{C}/^{31}\text{P}/^{19}\text{F}$ Z-GRD.

^{19}F -NMR: each NMR-sample contained 100 μl of aqueous phase taken from extraction experiment and 100 μl of a standard ($[\text{CF}_3\text{COONa}] = 52.65 \text{ mM}$), diluted with 450 μl of D_2O .

The spectral window for ^{19}F it was centred at -80 ppm with a width of 80 ppm to limit background acquisition. The uncertainty is equal to 5%.

The concentration of $\text{C}_1\text{C}_n\text{im}^+$ in the aqueous phases was measured by ^1H NMR using the solutions of internal standarts.

FORTTRAN

The fits were performed by using a Fortran subroutine included in the CERN package "MINUIT", which uses simplex and migrad algorithms for convergence.

Extraction of Am(III), Eu(III) by SM1006

The biphasic systems, containing $M(\text{III}) / \text{HNO}_3 // \text{SM1006} / \text{C}_1\text{C}_4\text{imTf}_2\text{N}$ were investigated. The extraction coefficients were always lower than 0.1, what characterizes the Am(III), Eu(III) extraction process extraction as inefficient.

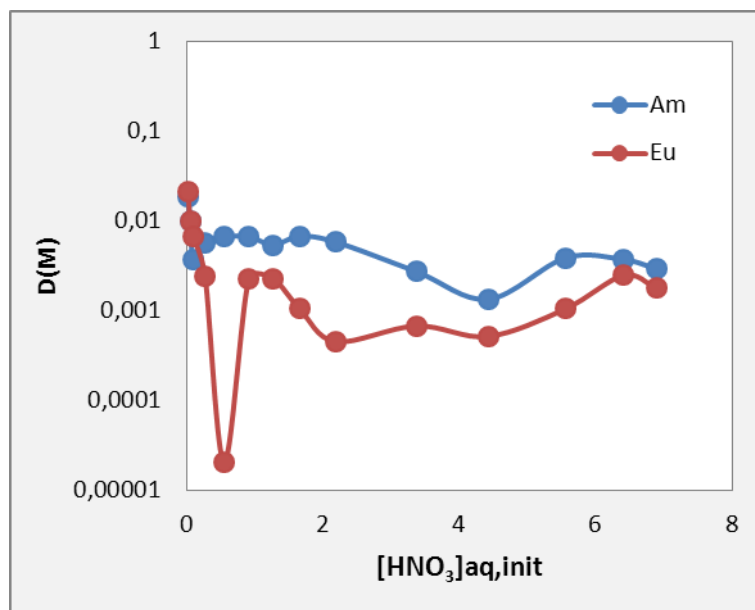


Figure IV-1. $M(III)/HNO_3/SM1006/C_1C_4imTf_2N$. D vs $[HNO_3]_{aq,init}$. $[M(III)] = \text{traces}$; $[SM1006] = 0.1 \text{ M}$

Synthesis of Model compound (Figures III-24, III-25)

For the investigation of complexing properties of tetrazolate ring the model ionic liquid on the basis of tetrazolate anion without phosphine oxide group has been synthesized.

Synthesis of 5-butyl-1H-tetrazole 4.1

The reaction mixture containing pentanenitrile (1.22 ml, 12 mmol), sodium azide (1.17 g, 18 mmol), and ammonium chloride (1.3 g, 24 mmol) in 15 ml of dry DMF was stirred for 24h at 120 °C. The solvent was removed in vacuum. To the residue 20 ml of H₂O were added. The product was isolated by extraction with chloroform. The combined organic layers were dried over Na₂SO₄, then filtered and dried in high vacuum (0.01 mm Hg). The viscous product was triturated in 20 ml of hexane, and then filtered. Colorless powder was obtained (Yield 1.21 g, 80.1%).

¹H NMR (299.943 MHz, CDCl₃): δ 0.93 (t, 3H, -CH₂-CH₃), 1.37-1.49 (m, 2H, -CH₂-CH₂-CH₃), 1.82-1.92 (m, 4H, -CH₂-CH₂-CH₃), 3.11 (t, 2H, -CH₂-CH₂-CH₂-CH₃), 13.64 (br s, CN₄H)

1-Decyl-3-methylimidazolium 5-butyl-1H-tetrazolate (model compound) 4.2

The compound was synthesized following the general procedure for the preparation of tetraazolates described in Chapter II, Section II.4.

Viscous transparent compound, (Yield 95 %)

¹H NMR (300.130 MHz, CDCl₃): δ 0.84-0.93 (m, 6H, -CH₂-CH₃ in Im, -CH₂-CH₃ in Tz), 1.16-1.32 (m, 14H, N-CH₂-CH₂-(CH₂)₇-CH₃), 1.32-1.44 (m, 2H, N-CH₂-CH₂-CH₂-CH₃), 1.72-1.89 (m, 4H, N-CH₂-CH₂- in Im, N-CH₂-CH₂- in Tz), 2.92 (t, 2H, N-CH₂-CH₂- in Tz), 4.01 (s, 3H, N-CH₃ in Im), 4.22 (t, 2H, N-CH₂-CH₂- in Im), 7.19 (s, 1H, C5H in Im), 7.26 (s, 1H, C4H in Im), 10.25 (s, 1H, N=CH-N).

ACKNOWLEDGMENTS

This research was performed within the framework of Cotutelle PhD program between Ukraine and France. The work was carried out in the Phosphoranes chemistry department of the Institute of organic chemistry in Kiev and Radiochimie group of the Institute Pluridisciplinaire Hubert Curien in Strasbourg.

First of all, I would like express my special appreciation and thanks to my both supervisors. Professor Vitaly Kalchenko for the encouragement to start my PhD and further guidance, expert advice, and valuable comments during the whole thesis. Doctor Isabelle Billard, who was taking care of me from my first days in Strasbourg, thank you for opening new horizons in chemistry and helping me to gain a lot of new skills. I have learnt so much from you!

For the financial support of my studies I would like to thank and acknowledge Ukrainian Academy of Science, University of Strasbourg along with the French Embassy in Ukraine.

I would also like to express my gratitude to the committee members for their willingness to participate in the examining of my PhD thesis: Professor Agilio Padua from the Clermont-Ferrand Chemistry Institute, Doctor Alexander Kostyuk from the Institute of organic chemistry in Kiev, Doctor Eric Chainet from Grenoble LEPMI in Grenoble, Doctor Véronique Hubscher from the University of Strasbourg and Doctor Clotilde Gaillard from the Lyon Institute of Nuclear Physics.

I am very grateful to all members of both research groups!

Especially I would like to thank Doctor Stanislav Miroshnychenko, my laboratory boss with golden hands and great heart. Thank you for teaching me applied organic chemistry, for your help and support. I also thank Doctor Atamas Lyudmila for providing several starting materials for my synthesis and valuable pieces of advice. Special thanks to Lidia Soloveivna, who was taking care of me during these years.

I would like to express my gratitude to Valérie Mazan from Radiochimie group for teaching me new skills in analytical chemistry and her great work. Special thanks to Ali Ouadi, who shared his unique experience concerning the synthesis of ionic liquids.

Also I would like to thank Sylvia Georg for ICP-MS analysis, expert advice, and really good time we spent together with her family in Strasbourg and Kiev. Indeed I was very lucky to have colleagues, who are also friends! My thanks to Doctor Michal Sypula from neighboring Poland, with whom we were sharing office, thus, were discussing many things from extraction to pierogi-vareniki. Doctor Maria Boltoeva from another neighboring country, Russia, thank you for the fruitful scientific (and non-scientific) discussions, your friendly support and care. Almost-Doctor Mauricio Torres from Colombia, thank you for sharing your life experience in many questions, and being a very good friend.

The years in Strasbourg were very special for me. And for this I am very grateful to my friends, who I met here: Georgios Voutsinas, without his encouragement this dissertation would not have been possible, Artem Osypenko, who was taking care of me like a brother, Nataliia Voievoda, who inspired me by her example, defending her PhD just two months before mine, Dmitry Komissarenko, who influenced my cultural level by attending together concerts of classic music and art galleries, Ievgen Shulov, who showed me Strasbourg and Kehl, when I just arrived, Oleksandr Koniev, who taught me lessons of nihilism, entertaining math and ice skating, also Sergii Kolodych, Marianna Sholokh, Iuliia Konko, Iuliia Karpenko, Viktoria

Postupalenko, Iryna Lysova, Marian Dryzhakov, Andrey Klymchenko, Katerina Trofimchuk, Lesia Kovalenko, Vasyl Kilin, Leonid Andronov. Dear friends, thank you for all those beautiful moments!

Finally, I would like to express my cordial gratitude to my family, especially my mother, and grandparents, for their love, care, and endless support throughout my life.

Dariia Ternova,
September, 2014
Strasbourg

Introduction

L'énergie nucléaire fournit environ 12 % de l'électricité consommée sur la planète. Dans le monde, il y a des promoteurs (World Nuclear Association, IAEA¹) et des opposants (Greenpeace International, NIRS²) à la production d'énergie par voie nucléaire mais, quoiqu'il en soit, à ce jour, 31 pays utilisent l'énergie nucléaire pour générer jusqu'à trois quarts de leur électricité ce qui conduit à 435 réacteurs nucléaires en fonctionnement tandis que 75 nouveaux réacteurs sont en construction [1, 2]. Les avantages de l'énergie nucléaire sont une absence quasi totale d'émission de gaz à effet de serre et une quantité somme toute faible de déchets radioactifs. De plus, c'est la seule industrie de production d'énergie à grande échelle qui prenne soin de toute la chaîne de ses déchets.

Parmi les déchets nucléaires, ceux dits de haute activité (HA en français, HLW, high-level waste en anglais) sont ceux qui méritent l'attention la plus soutenue. Les déchets de haute activité sont issus du combustible nucléaire utilisé et sont constitués principalement d'uranium (95%), de plutonium (1%), d'autres actinides (0.1%) et de produits de fission (3–4%). Deux stratégies de gestion sont employées pour le combustible nucléaire utilisé. Dans la première, le combustible est retraité pour en extraire les matériaux recyclables (uranium et plutonium) pour du combustible neuf. Dans l'autre, le combustible utilisé est simplement considéré comme un déchet et est entreposé en l'état en attendant un stockage définitif.

La première stratégie est appliquée en France, Russie, Chine, Inde et Japon, pays dans lesquels le combustible utilisé subit un retraitement avant son stockage. Le but premier du retraitement est la séparation de l'uranium et du plutonium pour un réemploi dans le cycle suivant du combustible. La séparation est mise en œuvre via le procédé PUREX (plutonium uranium extraction), qui est basé sur l'extraction liquide/liquide. Le procédé PUREX utilise du phosphate de tributyle dilué dans du kérosène et permet la récupération de 99% de U et Pu, mais les déchets contiennent encore d'autres éléments dangereux: Np, Am, Cm, I-129, Tc-99, Cs-135, Sr-90. Leur séparation et transmutation (Partitioning and transmutation, en anglais, P&T) est une étape importante dans la réduction de la toxicité des déchets. Selon des rapports de l'IAEA, séparation et transmutation peuvent aider à réduire le temps pendant lequel les déchets nucléaires doivent être isolés de la biosphère de 130 000 ans à environ 500 à 1500 ans [3].

Par conséquent, de nos jours, la recherche d'extractants sélectifs est d'une importance scientifique et industrielle capitale. **Cette thèse est donc une contribution au développement de nouveaux extractants, impliquant la synthèse de ligands originaux basés sur un canevas liquide ionique**, et ensuite dilués dans des liquides ioniques.

Le choix de ces deux composants des systèmes d'extraction (liquides ioniques en tant qu'extractants originaux et liquides ioniques en tant que nouveaux solvants) a été fait sur la base des arguments suivants:

- Les procédés modernes d'extraction liquide/liquide impliquent l'utilisation de solvants organiques qui sont explosifs ou inflammables, volatils et toxiques. Il y a une forte

¹ International Atomic Energy Agency; Agence Internationale pour l'Energie Atomique AIEA

² Nuclear Information and Resource Service

incitation pour des procédés industriels « verts » à travers la réglementation REACH³ (entrée en vigueur en 2007), qui, dans le futur, limitera l'utilisation des composés organiques volatils (COV) dans les procédés d'extraction liquide/liquide. Une alternative envisageable est l'emploi d'une nouvelle classe de solvants, appelés les liquides ioniques (LI). Ces solvants sont usuellement présentés comme étant non volatils et non inflammables. Certains les prétendent non toxiques, biodégradables, et même comestibles. De plus, du fait de leur structure chimique, les LI possèdent de fantastiques propriétés physico-chimiques autorisant des réactions chimiques inhabituelles. Par conséquent, les LI ont été choisis comme solvants pour les expériences d'extraction de ce travail.

- Un autre concept très prometteur est la création de liquides ioniques dits à tâches spécifiques (LIT ; task specific ionic liquids TSILs, en anglais). Les LIT sont des liquides ioniques qui, en plus de leurs propriétés ioniques et liquides sont conçus avec une certaine fonctionnalité. Dans le cas de l'extraction, ce sont des propriétés extractantes. La plupart du temps, les LIT sont synthétisés sur la base de liquides ioniques communs par fonctionnalisation de leur cation ou anion avec des motifs extractants. Ainsi, les LIT pour l'extraction sont-ils des extractants de nature ionique, qui peuvent être employés en phase pure ou dilués dans un LI similaire non fonctionnalisé. Avec les LI employés comme diluants, ce sont les analogues chimiques du couple extractant/solvant moléculaire.

³ Registration, Evaluation, Authorization and Restriction of Chemicals is a European Union Regulation

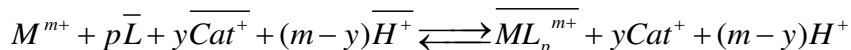
1 Revue de la littérature

L'extraction liquide/liquide (également appelée l'extraction par solvant) est un procédé de séparation qui est basé sur la distribution d'un soluté entre deux phases immiscibles, l'une d'entre elles étant usuellement une phase aqueuse et l'autre un solvant organique. Du fait de la différence de solubilités du soluté dans les phases aqueuse et organique, l'extraction par solvant peut être utilisée en vue de purification, enrichissement ou séparation.

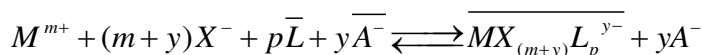
Dans cette étude, les LI ont été employés en tant que phase secondaire pour le procédé d'extraction liquide/liquide. Les LI sont des sels dont la température de fusion est inférieure à 100 °C. Du fait de leur nature ionique, ils possèdent une très faible pression de vapeur saturante, ce qui les rend non volatils, au contraire des solvants moléculaires, non inflammables et dans de nombreux cas, non toxiques. En dehors de leurs propriétés environnementales, les LI autorisent une chimie inhabituelle.

L'extraction liquide/liquide est caractérisée par un mécanisme d'extraction. L'extraction dans les solvants moléculaires a été étudiée depuis plusieurs décennies, ce qui fait que les mécanismes ayant lieu sont maintenant bien décrits et compris. Ils sont basés sur le simple fait que l'association ionique a lieu (formation de paires) ce qui implique que n'importe quelle entité transférant à travers l'interface en direction du solvant moléculaire est obligatoirement neutre (**mécanisme par extraction d'espèces neutres**) alors que la nature ionique des LI autorise des **mécanismes d'échanges ioniques**.

Echange cationique:



Echange anionique:



Il doit être signalé qu'un mécanisme par extraction d'espèces neutres est également possible dans les LI, quoique moins favorable en principe.

D'un point de vue quantitatif, pour caractériser l'extraction liquide/liquide d'un ion métallique, par exemple, on définit le coefficient de distribution, D, comme étant le rapport des nombre de moles de cet ion entre la phase organique et la phase aqueuse. Dans le cas de volumes identiques, ce rapport est identique au rapport des concentrations. Pour de nombreux ligands neutres dilués en solvants moléculaires, la compétition entre l'extraction de l'ion métallique et celle de l'acide conduit à des variations de D en fonction de l'acidité de la phase aqueuse ayant une forme de cloche caractéristique. Si le ligand n'extrait pas l'acide, l'extraction croît continûment.

La différence de mécanisme induite par les LI est très bien mise en évidence dans le travail de Shimojo et collaborateurs, dans lequel le comportement d'extraction de certains lanthanides III (Ln(III)) par l'extractant tétraoctyl-1,5-diglycolamide (par la suite dénommé TODGA) est à l'opposé de celui obtenu dans l'isooctane [4]. Dans l'isooctane, l'efficacité d'extraction pour Lu(III), Eu(III) et La(III) croît avec l'augmentation de l'acidité alors qu'au contraire, dans le LI C₁C₂imTf₂N, l'extraction est plus efficace à faible concentration en acide nitrique (Figure I-1).

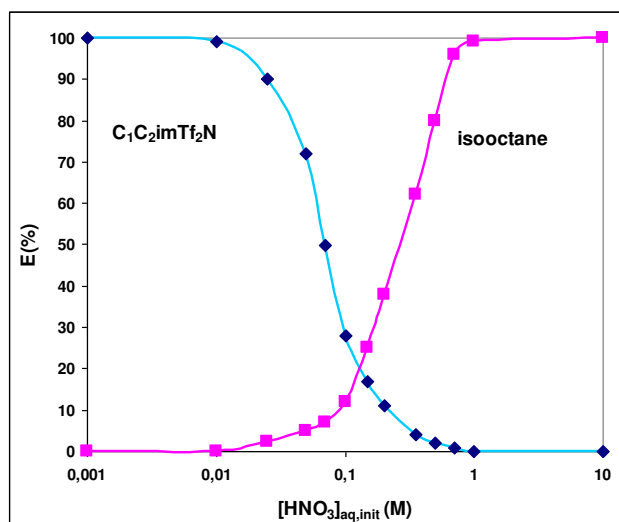


Figure 1-1. Variation schématique du pourcentage d'extraction E(%) d'un Ln(III) en fonction de $[HNO_3]_{aq,init}$ dans $C_1C_2imTf_2N$ et dans l'isooctane. D'après Shimojo et al. [4]

Un autre exemple caractéristique de l'influence particulière des LI sur le processus d'extraction liquide/liquide est la forme en boomerang de la variation de $D(M)$ en fonction de $[HX]_{aq,init}$. Ceci est assez fréquent dans la littérature. Une illustration de ceci peut être observée sur la figure I-2. Une telle forme est l'indication de deux mécanismes d'extraction différents dans les systèmes avec des LI.

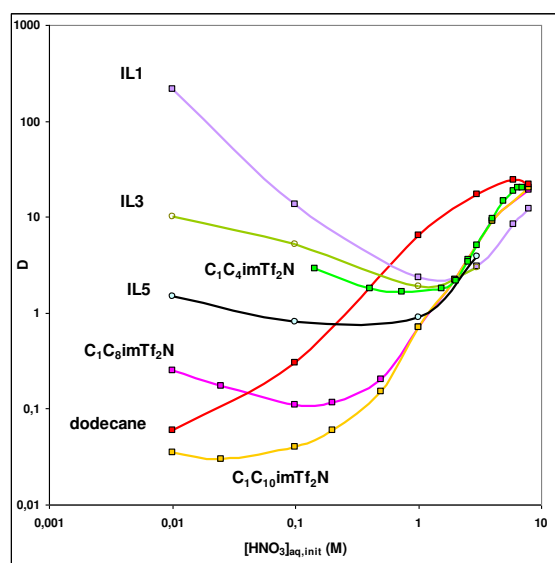


Figure 1-2. Comparaison du coefficient de distribution de UO_2^{2+} en fonction de $[HNO_3]_{aq,init}$ dans divers LI de la famille $C_1C_nimTf_2N$ et dans le dodécane, avec emploi de TBP. Les données pour LI1, LI3, LI5 et dodécane sont issues de [5], celles pour $C_1C_nimTf_2N$ ($n = 5, 8, 10$) sont tirées de [6] et celles pour $C_1C_4imTf_2N$ proviennent de [7]. IL1: $(CH_3)_3(CH_2CH_2OMe)NTf_2N$. IL3: $(CH_3)_3(CH_2CH_2Cl)NTf_2N$. IL5: $(CH_3)_3(CH_2C_6H_4NO_2)NTf_2N$

Un autre concept dans l'utilisation des LI en vue de l'extraction liquide/liquide est celui de LI à tâches spécifiques (LITS), encore appelés LI fonctionnalisés (LIF) et qui seront détaillés dans la suite de ce travail. L'extraction d'ions métalliques par des LITS a lieu selon des mécanismes d'échanges d'ions similaires à ceux observés dans les LI utilisés comme

diluants et contenant un extractant moléculaire [8]. Bien que peu de travaux se soient concentrés sur l'étude quantitative de cette question, des courbes d'extraction en forme de boomerang ont été observées dans les deux cas (ligand moléculaire ou LIF dilué dans un LI) [9].

La compréhension du mécanisme est un élément clef de la maîtrise fondamentale du procédé d'extraction.

Revue bibliographique sur les LIF

Il y a deux approches différentes pour la fonctionnalisation d'un LI. La première est celle d'une connexion covalente d'un motif extractant au cation ou l'anion du LI et la seconde est la formation d'un LIF par échange ionique avec un ion extractant. Si nous représentons un liquide ionique sous la forme $[Cat]^+[A]^-$, alors les liquides ioniques fonctionnalisés par connexion covalente sont du type $[Cat-E]^+[A]^-$ ou $[Cat]^+[A-E]^-$. Ce concept a été appliqué à la synthèse de mes LIF. La seconde approche est appliquée aux composés d'onium (cations ammonium ou phosphonium) et aux composés hétérocycliques portant des charges positives (pyridinium, pyrrolidinium). Ils sont combinés avec divers anions possédant des propriétés complexantes, conduisant à des LI fonctionnalisés. Ils peuvent être schématiquement représentés sous la forme $[Cat]^+[E]^-$.

- Exemples des LIF du type $[Cat]^+[E]^-$:

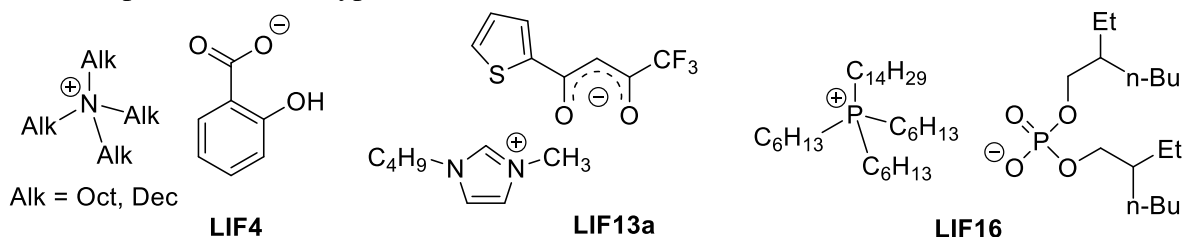


Schéma 1-1. LIF4 [10], LIF13a [11], LIF16[12, 13, 14]

- Exemples des LIF du type $[Cat-E]^+[A]^-$:

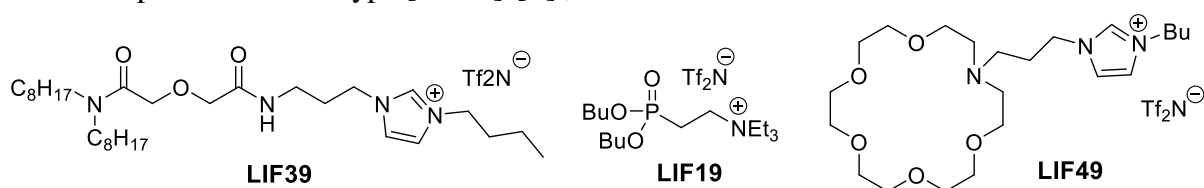
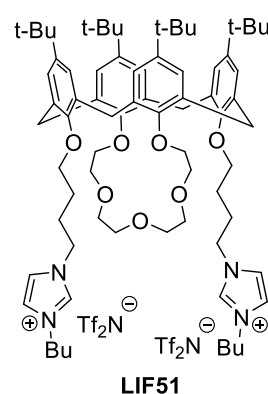


Schéma 1-2. LIF39 [15, 16], LIF19 [17], LIF49 [18]

Une autre idée très prometteuse est celle de la synthèse de LIT sur une base calixarénique.

Les calix[n]arènes sont une classe de composés macrocycliques obtenus par condensation cyclique de composés phénoliques *para* substitués par des formaldéhydes, où n est le nombre d'anneaux phénoliques [19]. Ils ont reçu une attention particulière, du fait de leur structure tridimensionnelle qui peut être modifiée avec différents groupes fonctionnels.

LIF sur une base calixarénique [20] :



2 Synthèses

Les LI $C_1C_4Tf_2N$, $C_1C_{10}Tf_2N$, qui ont été utilisés pour les expériences d'extraction en tant que milieu (seconde phase) ont été achetés chez Solvionic (France).

En revanche, les LIF de ce travail ont été synthétisés pour la première fois.

- Il doit être noté que ces LIF ont été synthétisés par connexion covalente d'un motif extractant (première approche de fonctionnalisation, comme décrit précédemment).

- Les LIF synthétisés sont de deux types: i) des LIF cationiques par fonctionnalisation du cation. En particulier, les cations imidazolium ont été modifiés par des groupements extractants variés ; et, ii) ce qui est important et très novateur, par fonctionnalisation de l'anion. Dans ce dernier cas, très peu de publications existent à ce jour.

Concernant l'extraction, dans tous les cas les anions ont été générés à partir d'extractants connus. C'est la seconde approche dans laquelle un anion, en dehors de porter une charge, possède des propriétés de complexation.

Liquides fonctionnalisés avec des malonamides⁴

Les malonamides sont des extractants donneurs oxygénés, qui sont utilisés pour l'extraction des An(III) et Ln(III) dans le procédé DIAMEX [21]. Ils appartiennent à la catégorie des extractants CHON, composés uniquement de carbone, hydrogène oxygène et azote, et qui peuvent être de ce fait totalement incinérés.

Considérant les propriétés extractantes et environnementalement bénignes des malonamides, elles apparaissent comme une base de développement de nouveaux LIT. Le composé *N,N'*-diméthyl-*N,N'*-dibutylmalonamide (DMDBMA) a été chimiquement modifié par les fragments imidazolium. La synthèse du composé résultant FIL-MA est décrite dans le Schéma 2-1.

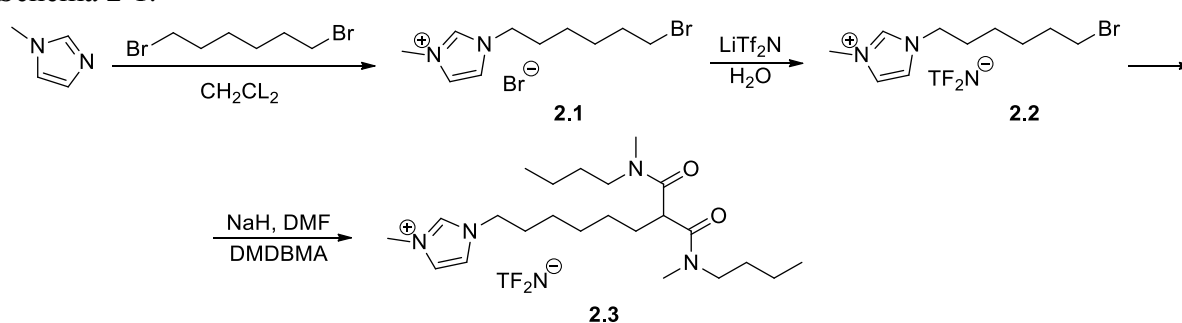


Schéma 2-1. Synthèse du malonamide FIL-MA

⁴ Ce paragraphe est basé sur l'article: M. Bonnaffé-Moity, A. Ouali, S. Miroshnichenko, V. Mazan, D. Ternova, M. Sypula, C. Gaillard, I. Billard, S. Georg, *Dalt. Trans.* **2012**, 41, 7526.

Liquides ioniques fonctionnalisés avec des groupements oxyde de phosphine

Les composés organophosphorés jouent un rôle clef dans le retraitement des déchets radioactifs. Depuis les années 1950, le phosphate de tributyl (TBP) est le principal composant pour la séparation de l'uranium et du plutonium des combustibles nucléaires usés. Cependant, le TBP a des capacités extractantes relativement faibles. Les extractants les plus efficaces parmi les composés organo-phosphorés monodentates sont les oxydes de trialkylphosphine (TAPO, en anglais).

LIF cationiques avec des groupements oxydes de phosphine

Au cours de la synthèse du LI cationique portant des groupements oxyde de phosphine, le composé oxyde de dibutyl-(4-chlorobutyl) phosphine **2.4** a été une substance clef (Schéma 2-2). La substance **2.4** a été synthétisée via la réaction d'Arbuzov du isopropyl-dibutylphosphinite avec un excès (rapport : 20) de 1,4-dichlorobutane à 100 °C durant 4h avec un rendement de 87 %.

Une méthode alternative pour obtenir le composé **2.4** est l'alkylation de l'oxyde de dibutylphosphine avec le 1,4-dichlorobutane dans un milieu DMSO / NaOH (50% de solution aqueuse), mais le rendement de la réaction est alors de moins de 30% [22]. Dans l'étape suivante, le 3-méthylimidazole a été alkylé avec l'oxyde de dibutyl-(4-chlorobutyl)phosphine (ratio des réactifs 1:1, 120 °C, 72 g, ampoule scellée sous vide), et le chlorure d'oxyde de dibutyl-4-(3-méthylimidazolium)butylphosphine **2.5** a été formé. La substance **2.5** a été utilisée pour la préparation du sel sans purification ultérieure: elle a été dissoute dans l'eau et un équivalent du bis(trifluorométhanesulfonyl)imide de lithium (LiTf_2N) a été ajouté à cette solution. Après la réaction, le plus lipophile bis-trifluorométhanesulfonimide **2.6** a été extrait avec du chloroforme et purifié sur charbon dans un mélange d'éthanol. Le composé **2.6** (rendement 72%) est un liquide fluide jaune bien soluble dans la plupart des solvants organiques.

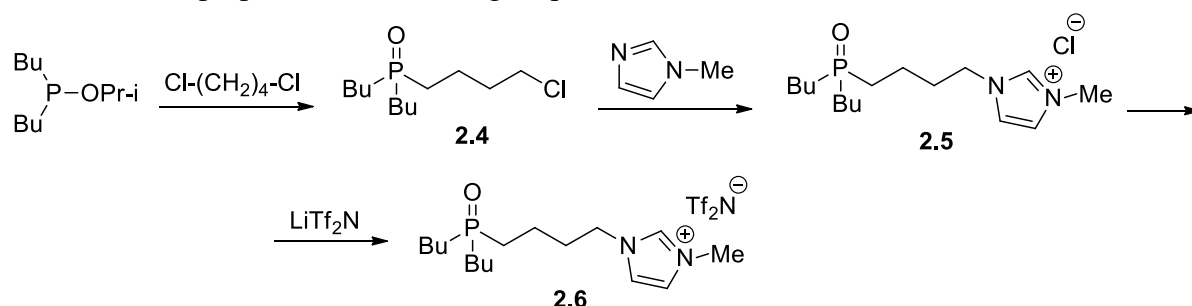


Schéma 2-2. Synthèse du LIF cationique avec du groupement oxyde de phosphine (SM1006)

LIF anioniques avec des groupements oxydes de phosphine

L'anion tétrazole a été choisi comme échafaudage pour les liquides ioniques oxydes de phosphine anioniques. Premièrement, le proton sur le groupement NH est relativement acide (pK_a égal à 5.63, 5.73 pour 5-méthyl- et 5-(*n*-octyl)tétrazoles respectivement; 4.90 pour tétrazole [23]) et se dissocie dans les solutions aqueuses neutres ou légèrement acides.

Deuxièmement, l'anion tétrazole peut être un ligand azoté multicentré et en y ajoutant l'atome d'oxygène du groupement P=O greffé, peut se lier aux cations actinides et lanthanides [24].

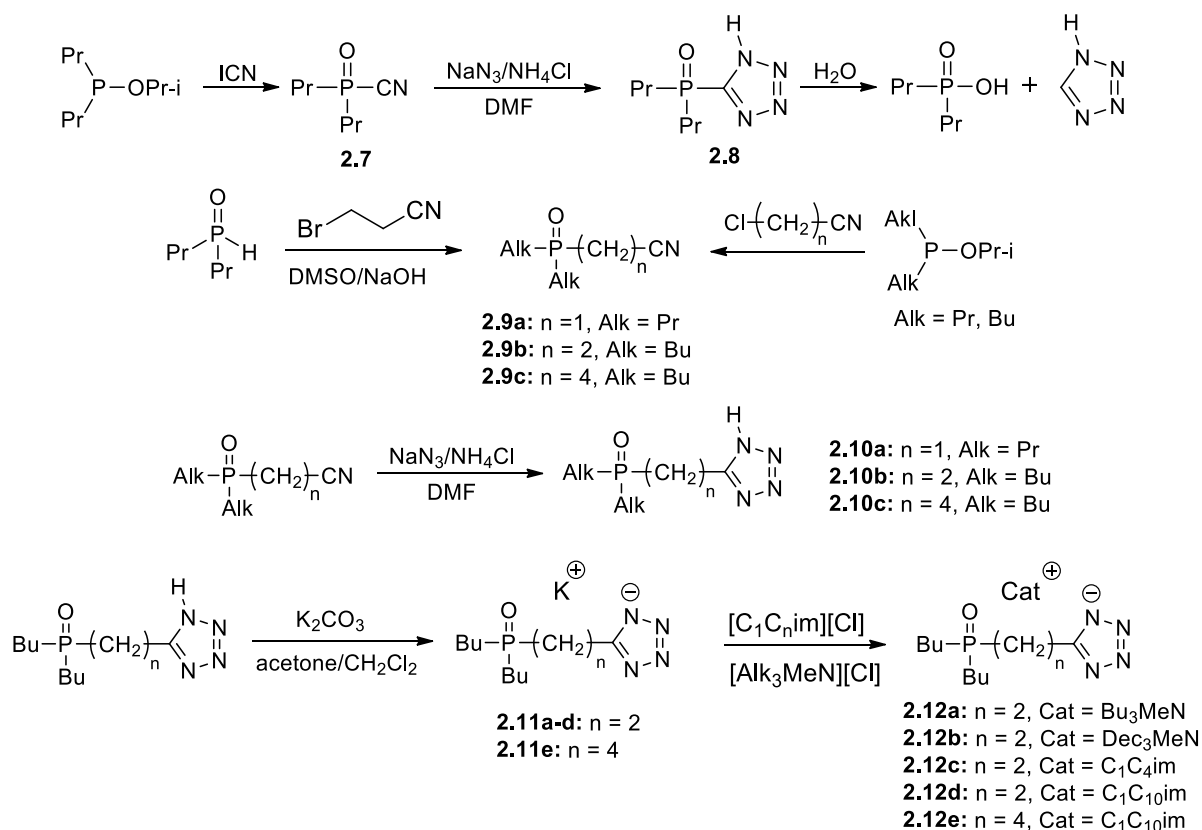


Schéma 2-3. Synthèse des LIF anioniques avec des groupements oxydes de phosphine

LIF avec un fragment CMPO

Le composé CMPO (oxyde de carbamoylphosphine, l'oxyde d'octyl(phényl)-*N,N*-diisobutylcarbamoylméthylphosphine) est un complexant bidentate, qui a été synthétisé en 1981 par deux groupes de recherche indépendants [25, 26]. Le composé CMPO trouve des applications dans le procédé TRUEX (transuranic extraction) en tant que second agent extractant en complément de TBP et permet d'extraire les éléments transuraniens (Np, Am, Pu, Cm, etc) [27].

De plus, dans les publications de Rout et Visser, il a été signalé que CMPO démontre de bien plus grandes valeurs de D pour les An dans les liquides ioniques C₁C₄imTf₂N et C₁C₄imPF₆ en comparaison des systèmes d'extraction avec du *n*-dodécane [28, 29].

La procédure pour la synthèse du liquide ionique CMPO (dénote par la suite CMPO-IL) ainsi que les structures des précurseurs sont résumées dans le schéma II-5. La substance clef CMPO-imidazole **2.13** a été obtenue par acylation du 3-aminopropylimidazole avec le méthyl (octylphénylphosphinyl)acétate (ratio des réactifs 1:2, 105 °C, 72 h, ampoule scellée). Ensuite, le CMPO-imidazole **2.13** a été alkylé avec de l'iodométhane (ratio des réactifs 1:1.5 en solution dans le dichlorométhane, température ambiante, 12h) pour donner l'iodure d'imidazolium iodide **2.14** en rendement quantitatif. Le CMPO-IL **2.15** a été obtenu par la réaction de métathèse de **2.14** avec une solution aqueuse de LiTf₂N (rendement 70%).

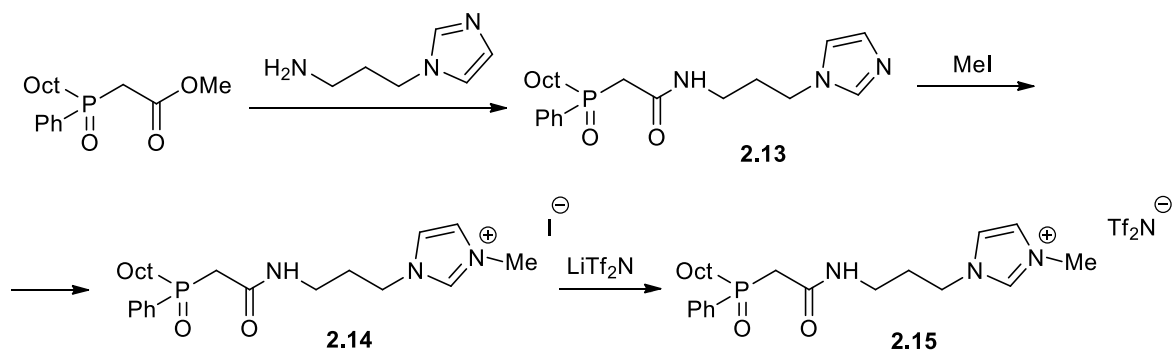


Schéma 2-4. Synthèse du LIF avec un fragment CMPO (CMPO-IL)

LIF avec des oxydes de phosphine calixaréniques

Le but suivant était de synthétiser des liquides ioniques à tâches spécifiques utilisant la plateforme calixarénique, qui permet d'augmenter les propriétés extractantes des groupes fonctionnels attachés, du fait d'effets coopératifs.

En vue d'obtenir de tels LIF, l'ahlogénure de calixarène a été modifié avec des groupements oxydes de phosphine sous les conditions de la réaction d'Arbuzov. La réaction se produit sélectivement quand 4 équivalents d'un phosphinite sont ajoutés graduellement (durant 10 – 15 minutes) à la solution refroidie (0-5 °C) du calix[4]arène **2.18** dans le chloroforme. Après 24 h d'agitation à température ambiante, le rendement de production était de 90-94%. L'introduction des fragments imidazolium sur la couronne inférieure de l'oxyde de phosphine calixarénique **2.19a** a été réalisée avec un excès de 1-méthylimidazole à 70 °C, conduisant à l'oxyde de phosphine calixarénique fonctionnalisé avec des imidazolium **2.20**. La substitution d'anions bromure dans **2.20** par les anions *bis*(trifluorométhylsulfonyle)imide dans la DMF conduit au calixarène **2.21** (Schéma 2-5). Malheureusement ce composé est un solide.

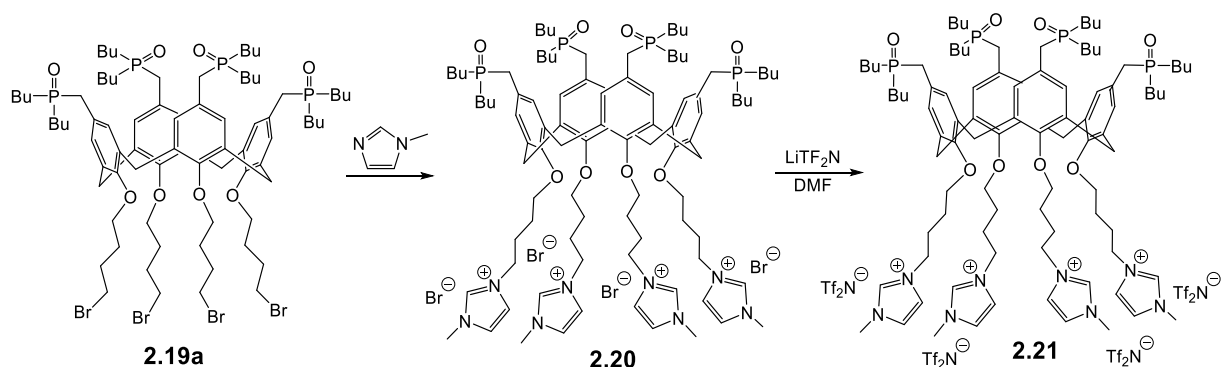


Schéma 2-5. Synthèse du LIF avec des oxydes de phosphine calixaréniques (calix-IL)

La synthèse de base a été également élargie par le nombre de synthons obtenus, qui peuvent être aisément transformés en les LIF correspondants en utilisant la seconde approche (lorsqu'une partie extractante porte une charge négative [Cat]⁺[E]⁻).

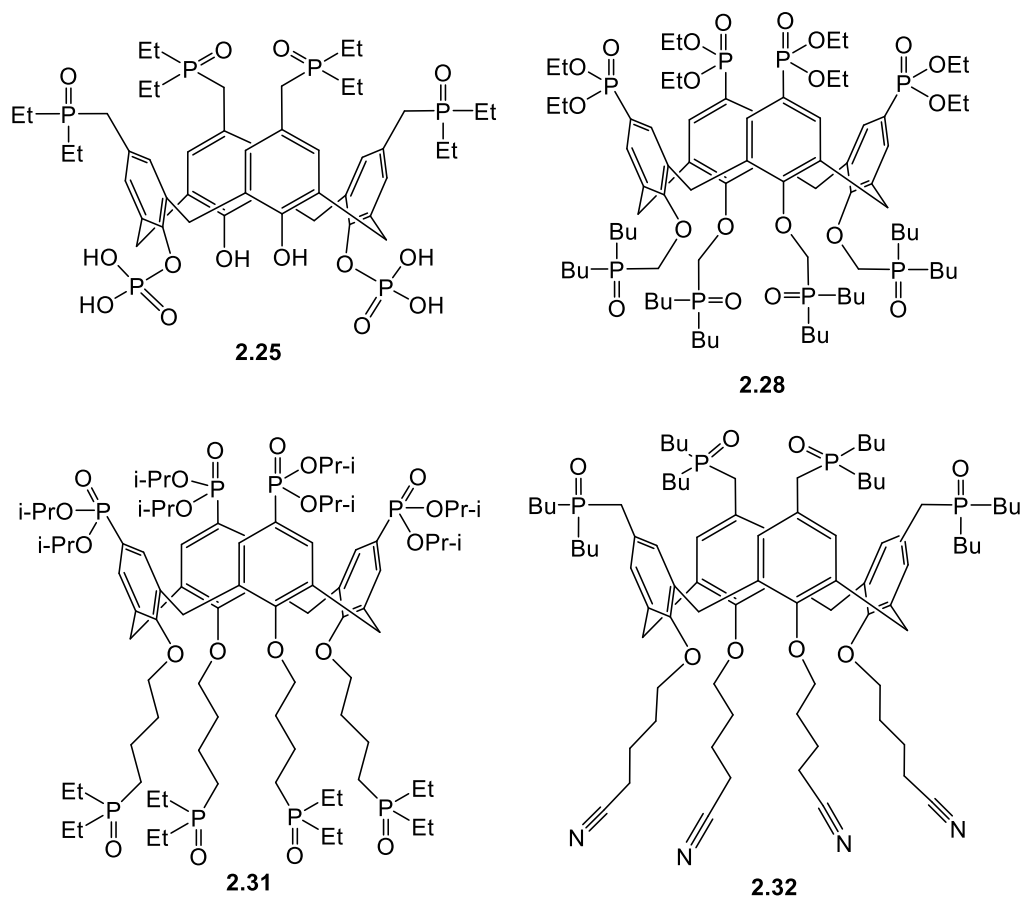


Schéma 2-6. Des synthons sur des bases calixaréniques

3 Extraction

Dans cette partie de l'étude, des expériences d'extraction liquide/liquide ont été réalisées.

Comme il a été mentionné précédemment, deux liquides ioniques ont été utilisés comme solvants : $C_1C_4imTf_2N$ and $C_1C_{10}imTf_2N$.

La phase aqueuse était toujours une solution acide de concentration connue. Le métal était ajouté à partir d'une solution mère.

Ainsi, le système d'extraction peut-il être noté : $M/HX//L$ (ou LIF)/IL.

M^{m+} – cation métallique

X^- – pour l'anion de l'acide minéral ($HX \rightleftharpoons H^+ + X^-$)

L – ligand (extractant synthétisé, complexant)

Expériences de déplacement d'équilibre d'extraction (ajout de $CatCl$ ou LiA)

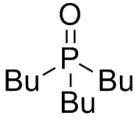
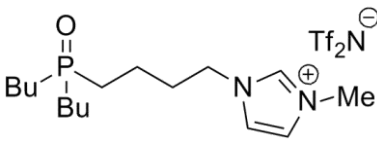
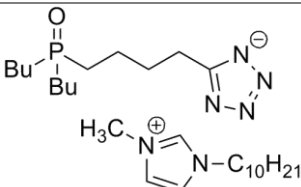
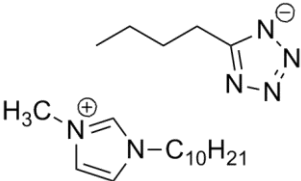
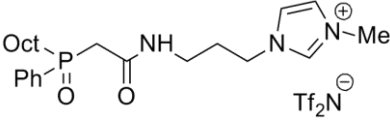
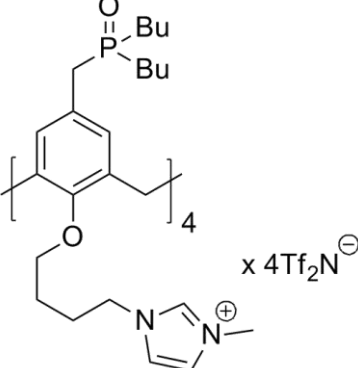
Cat^+ est le cation du LI,

A^- est l'anion du LI

Le but des expériences d'extraction est de rassembler des données en fonction de divers paramètres physico-chimiques (valeur de $[H^+]$, concentration en ligand, ajout de sel etc.) pour obtenir des informations quant au mécanisme d'extraction.

Dans ce travail, les LIF avec des oxydes de phosphine, des oxydes de phosphine avec le groupement carbamoyl et un calixarène ont été étudiés.

Tableau 1. List of compounds tested for the extraction

Formule chimique	Nom chimique	Nombre ordinal	Abréviation
	Tributylphosphine oxide	commercial compound	TBPO
	1-Methyl-3-[4-(dibutylphosphinoyl)butyl]-3H-imidazol-1-ium bis-trifluoromethyl-sulphonyl-imidate	2.6 (Chapter II)	SM1006
	1-Decyl-3-methylimidazolium dibutylphosphinoylbutyl-1,2,3,4-tetrazolate	2.12e (Chapter II)	DM01
	1-Decyl-3-methylimidazolium 5-butyl-1H-tetrazolate	4.2 (Supplementary data)	Model compound
	1-Methyl-3-(octylphenylphosphinoylacetyl-amino)propyl-3H-imidazol-1-ium bis-trifluoromethane-sulfonyl-imidate	2.15 (Chapter II)	CMPO-IL
	5,11,17,23-Tetrakis(dibutylphosphinoylmethyl)-25,26,27,28-tetra(4-(1-methylimidazolium)butoxy)calix[4]arene tetra-(bis(trifluoromethane-sulfonyl)amide)	2.21 (Chapter II)	Calix-IL

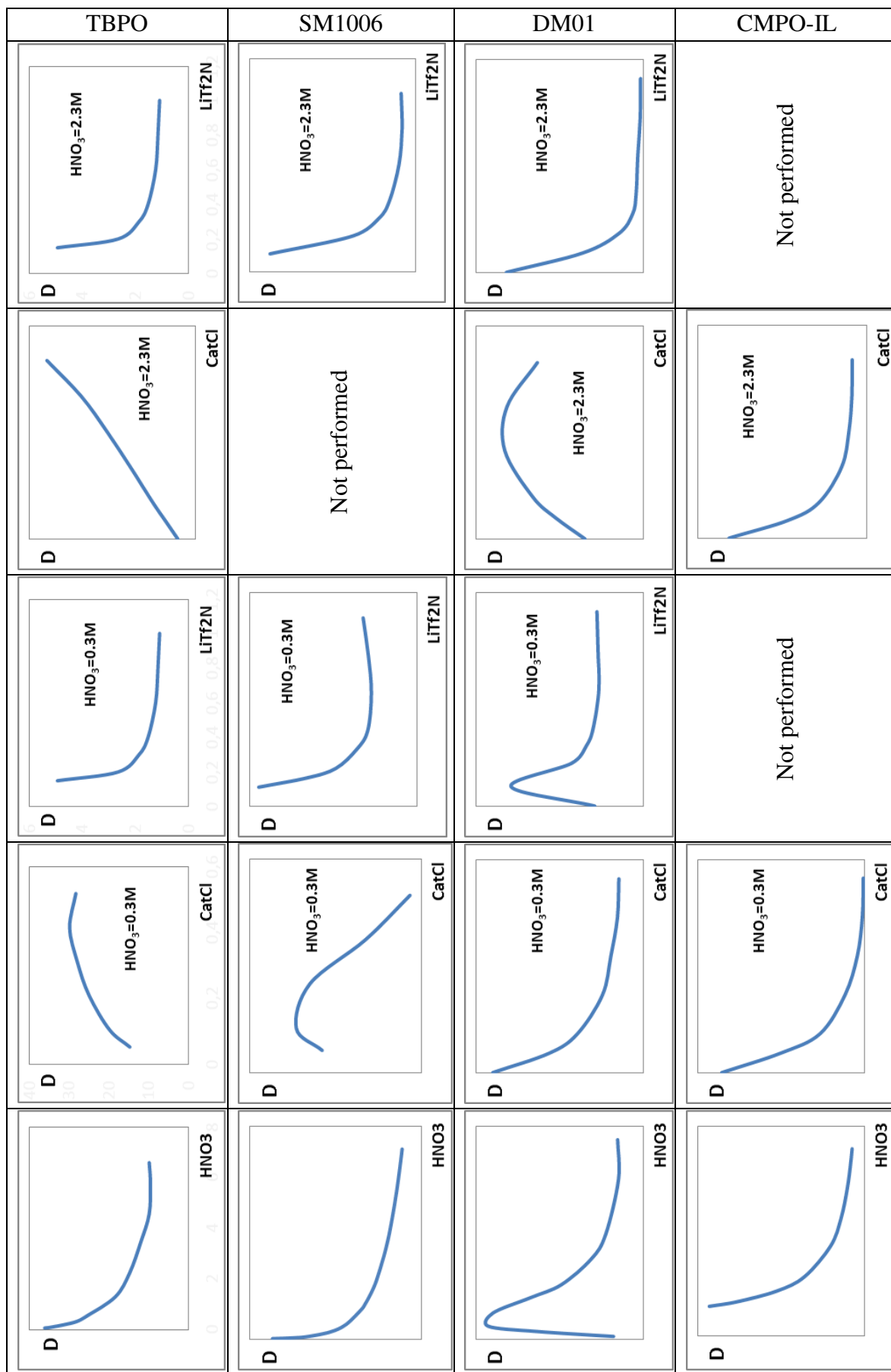


Figure 3-1 : Présentation synthétique des résultats expérimentaux pour TBPO, SM1006, DM01 et CMPO-IL: D vs $[HNO_3]_{aq,init}$ and D vs ajout de sels

La Figure 3-1, qui rassemble les données obtenues sous une forme synthétique, démontre que chaque système possède des capacités d'extraction spécifiques. Dans le but de progresser plus loin que la simple approche qualitative, des études quantitatives ont ensuite été menées :

- Facteurs influençant l'extraction : protonation, effets des cations et des anions du LI etc.
- Modélisation mathématique
- Etude de sensibilité (poids des différents sous mécanismes dans le résultat global)
- Ajustements mathématiques

Résultats

Dans l'optique d'effectuer une comparaison qualitative et quantitative des composés cationiques, anioniques et neutres, une modélisation mathématique, suivie d'un ajustement des données expérimentales ont été effectués. De nombreux équilibres ont été considérés en tant que mécanismes d'extraction possibles pour ces différents systèmes. Cette étude a montré que l'échange cationique domine les équilibres d'extraction de tous les systèmes étudiés. Cette modélisation a été effectuée sur la base des travaux antérieurs du groupe et en utilisant les programmes d'ajustement existants. Dans ce travail, il a été tenu compte de la dissociation de l'acide minéral, des complexations de l'ion métallique avec le contre-ion de cet acide, dans la phase aqueuse, de la protonation éventuelle du ligand, de l'équilibre, même en absence de métal, de l'ion H^+ entre les deux phases et enfin, de trois équilibres envisageables d'extraction : par échange de cation, d'anion ou par formation de paires. L'ajustement des données expérimentales à l'expression théorique de D en fonction de la concentration initiale en acide est effectué sur la base d'une méthode des moindres carrés. Des résultats typiques sont présentés dans le tableau suivant, où K_+ et K_- sont les constantes d'extraction cationique et anionique, respectivement.

Tableau 2. Ajustements des valeurs de D : système d'extraction avec SM1006.

Fits	K_p	complexation	K_+	Nombre de H^+ dans l'échange cationique	K_-	stoechiométrie du ligand	χ^2	commentaire
a)	7	oui	8.08×10^6	2	non	2	0.105	3 ajustements excellents et similaires
b)	7		7.9×10^3	1			0.108	
c)	7		6.08	0			0.112	

Comme on peut le voir d'après le tableau 2, l'hypothèse d'un échange anionique ne permet pas d'ajuster les données expérimentales dans le cas du système d'extraction avec SM1006, et l'échange cationique seul apparaît suffisant. Trois ajustements différents ont été effectués sur cette base, en variant le nombre de H^+ impliqués dans l'échange. L'ajustement pour lequel deux H^+ sont impliqués dans l'équilibre d'extraction est le meilleur dans ce cas (Figure 3-2). Les données ont été ajustées à partir de la valeur de 1M en HNO_3 parce que certaines des mesures additionnelles nécessaires à la modélisation n'ont pu être effectuées qu'à partir de cette valeur : typiquement, la concentration en H^+ transférée dans la phase LI à l'équilibre n'a pu être mesurée de façon fiable qu'au-delà de 1 M HNO_3 initial.

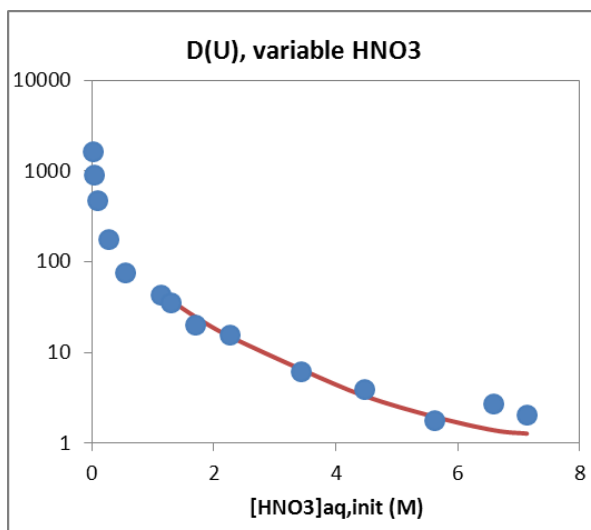


Figure 3-2. Ajustements des valeurs de D pour le système d'extraction avec SM1006. Courbe continue rouge: ajustement a) du tableau.

Il a été prouvé que tous les LIF étudiés au cours de ce travail sont capables d'extraire l'ion uranyle (et, dans le cas de CMPO-LI et du Calix-IL Am et Eu sont également extraits), quelle que soit la charge de l'ion fonctionnalisé. L'extraction via le LIF a lieu du fait du groupe fonctionnel, responsable de la complexation de l'ion métallique, et n'est pas due à un échange ionique entre le métal à extraire et la partie fonctionnalisée. En revanche, pour neutraliser la charge globale extraite et assurer l'électroneutralité de chaque phase, des ions du LI utilisé comme diluant sont quant à eux échangés, avec éventuellement des ions H^+ .

Conclusion

L'extraction liquide/liquide est une technique essentielle au retraitement des déchets radioactifs mais elle nécessite encore quelques modifications, afin de mieux répondre aux exigences environnementales de nos sociétés et pour être, si possible, encore plus efficace. Ceci justifie pleinement la recherche de nouveaux extractants et de milieu innovants. Une de ces alternatives est l'emploi de liquides ioniques en tant que milieu de réception des espèces à extraire, car ils sont plus efficaces et verts. Therefore the search of new extractants and media are of high scientific concern.

Au cours de ce travail nous avons tenté de fournir des systèmes répondant au mieux à ces différents besoins.

- Les LIF qui peuvent jouer le rôle d'extractant et de milieu de réception, ont été synthétisés par incorporation de divers groupes fonctionnels : malonamide, oxyde de phosphine et carbamoyl oxyde de phosphine.

- Selon les cas les cations et les anions ont été modifiés dans le but d'étudier l'influence de la charge sur le processus d'extraction.

- Les plateformes calixaréniques ont été introduites pour augmenter l'efficacité des groupements extractants.

- De nombreux synthons ont été obtenus, qui pourront être réutilisés à diverses fins de synthèses.

Les expériences d'extraction ont montré que tous les LIF étudiés étaient capables d'extraire des radionucléides.

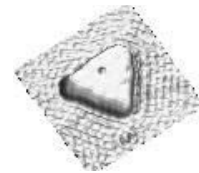
Cependant, le composé neutre tributyl phosphate, qui a été également employé en vue de comparaison est le plus efficace dans la série : *composé d'oxyde de phosphine neutre > oxyde de phosphine cationique > oxyde de phosphine anionique*. Ceci signifie que l'extraction a bien lieu du fait du groupement extractant mais que cependant la charge de l'entité qui le porte joue également un rôle non négligeable. Par conséquent, l'efficacité réduite de du LIF cationique comparée à celle de TBP peut être expliquée par des répulsions électrostatiques entre le cycle imidazolium chargé positivement du LIF et le cation métallique. Les attractions électrostatiques attendues entre le LIF anionique et ce même ion métallique sont anéanties par d'autres facteurs. En effet, le LIF anionique synthétisé contient l'anion tétrazolate qui subit une protonation en milieu acide et, en dépit de son incorporation avec un cation très hydrophobe $C_{10}H_{21}N^+$, reste malgré tout légèrement soluble dans l'eau. Si bien qu'une part non négligeable du LIF n'est plus disponible pour l'extraction.

Ces phénomènes rendent l'anion tétrazolate non indiqué pour une extraction en milieu acide si bien que la recherche future devrait se focaliser sur des anions hydrophobes résistants à la protonation.

Concernant les effets de la plateforme calixarénique, l'extraction n'a pas été significativement améliorée dans le cas du LIF-Calix. Une explication envisagée réside dans l'existence d'effets opposés : mobilité du liquide ionique et rigidité de la plateforme. Ceci nécessite cependant une étude plus approfondie, avec l'emploi de différents composés conçus à partir de ces plateformes. Dans cette optique, les nombreux synthons obtenus au cours de ce travail se révéleront très utiles.

Par ailleurs, il a été confirmé que le groupement oxyde de phosphine peut subir une protonation en milieu liquide ionique, et que ce phénomène diminue significativement l'extraction lorsque la concentration en acide initiale est augmentée. Les modèles mathématiques développés pour décrire l'extraction ont été écrits en tenant compte de ce phénomène. Malgré tout, il est possible d'obtenir plusieurs ajustements de bonne qualité du fait de la complexité inhérente aux systèmes étudiés. Dans certains cas, la nature du complexe extrait peut toutefois être déterminée grâce à des expériences d'EXAFS. La conjonction des informations obtenues par extraction, EXAFS et modélisation devrait permettre à l'avenir une détermination non ambiguë des mécanismes d'extraction.

-
- 1 <http://www.world-nuclear.org>
 - 2 <http://www.iaea.org/pris/>
 - 3 Technical report of IAEA series no.435 Implications of Partitioning and Transmutation in Radioactive Waste Management, 2004, INTERNATIONAL ATOMIC ENERGY AGENCY VIENNA, 2004
 - 4 K. Shimojo, K. Kurahashi, H. Naganawa, *Dalton Trans.* **2008**, *37*, 5083–5088
 - 5 T. J. Bel, Y. Ikeda, *Dalton Trans.* **2011**, *40*, 10125-10130
 - 6 M.L. Dietz, S. Jakab, K. Yamato, R.A. Bartsch, *Green Chem.* **2008**, *10*, 174-176
 - 7 I. Billard, A. Ouadi, E. Jobin, J. Champion, C. Gaillard, S. Georg, *Solv. Extr. Ion Exchange* **2011**, *29*, 577-601
 - 8 P. K. Mohapatra, P. Kandwal, M. Iqbal, J. Huskens, M. S. Murali, W. Verboom, *Dalton Trans.* **2013**, *42*, 4343–4347
 - 9 M. Bonnaffé-Moity, A. Ouadi, S. Miroshnichenko, V. Mazan, D. Ternova, M. Sypula, C. Gaillard, I. Billard, S. Georg, *Dalton Trans.* **2012**, *41*, 7526-7536
 - 10 V. M. Egorov, D. I. Djigailo, D. S. Momotenko, D. V Chernyshov, I. I. Torocheshnikova, S. V Smirnova, I. V. Pletnev, *Talanta* **2010**, *80*, 1177–1182
 - 11 A. Rout, K. a. Venkatesan, T. G. Srinivasan, P. R. Vasudeva Rao, *Solv. Extr. Ion Exch.* **2011**, *29*, 602-618
 - 12 X. Sun, Y. Ji, F. Hu, B. He, J. Chen, D. Li, *Talanta* **2010**, *81*, 1877–1883
 - 13 X. Sun, H. Luo, S. Dai, *Talanta* **2012**, *90*, 132–137
 - 14 X. Sun, H. Luo, S. Dai, *Dalton Trans.* **2013**, *42*, 8270–8275
 - 15 A. Sengupta, P. K. Mohapatra, M. Iqbal, J. Huskens, W. Verboom, *Sep. Purif. Technol.* **2013**, *118*, 264-270
 - 16 P. K. Mohapatra, A. Sengupta, M. Iqbal, J. Huskens, W. Verboom, *Chemistry* **2013**, *19*, 3230–3238
 - 17 A. Ouadi, O. Klimchuk, C. Gaillard, I. Billard, *Green Chem.* **2007**, *9*, 1160-1162
 - 18 H. Luo, S. Dai, P. V. Bonnesen, A. C. Buchanan, *J. Alloys Compd.* **2006**, *418*, 195–199
 - 19 C. D. Gutsche, *Calixarenes*, Cambridge: Royal Society of Chemistry, **1989**
 - 20 C. Jin, J. M. Shreeve, **2004**, *43*, 1215–1221
 - 21 C. Madic et al., Actinide partitioning from high level waste using the Diamex process, Nuclear Fuel Reprocessing and Waste Management, *Rep. CEA-CONF-12297*, **1994**, Marcoule
 - 22 E. N. Tsvetkov, N. A. Bondarenko, I. G. Malakhova, M. I. Kabachnick, *Synthesis* **1986**, *3*, 198-208
 - 23 a) G. I. Koldobskii, V. A. Ostrovskii, B. V. Gidasov, *Chem. Heterocycl. Compd.* **1980**, *16*, 665-674
b) L. D. Hansen, E. J. Baca, P. Scheiner, *J. Heterocycl. Chem.* **1970**, *7*, 991-996
 - 24 L. G. Lavrenova, S. V. Larionov, V. N. Ikorskii, Z. A. Grankina, *Zhurnal Neorganicheskoi Khimii* **1985**, *30*, 964 (in Russian)
 - 25 T. Ya. Medved, M. K. Chumatova, N. P. Nesterova, *Izvestia Akademii Nauk SSSR, Khimia*, 1981, *9*, 2121 (in Russian)
 - 26 D.G. Kalina, E.P. Horwitz, L. Kaplan, *Sep. Sci. Technol.* **1981**, *16*, 1127-1145
 - 27 G.F. Vandegrift, D. B. Chamberlain, C. Conner, J.M. Copple, J. A. Dow, L. Everson, J. C. Hutter, R. A. Leonard, L. Nufiez, M. C. Regalbuto, J. Sedlet, B. Srinivasan, S. Weber, D. G. Wygmans, Development and demonstration of the TRUEX solvent extraction process, Argonne, p.1045
 - 28 A. Rout, K. A. Venkatesan, T. G. Srinivasan, P. R. Vasudeva Rao, *Radiochim. Acta* **2009**, *97*, 719-725
 - 29 A. E. Visser, R. D. Rogers, *Solid State Chem.* **2003**, *171*, 109-113



Malonamide, phosphine oxide and calix[4]arene functionalized ionic liquids. Synthesis and extraction of actinides and lanthanides

Résumé

Le retraitement des déchets radioactifs est un problème crucial de nos jours. Ce travail est dédié au développement de nouveaux systèmes d'extraction des radionucléides sur la base de solvants 'verts', les liquides ioniques (LI).

Dans ce but, des LI ont été fonctionnalisés avec des motifs variés : oxyde de phosphine, carbamoyl oxyde de phosphine et fragments malonamides. De même, les plateformes calix[4]arènes ont été utilisées pour la synthèse de LI fonctionnalisés (LIF) et de leurs précurseurs. Des LIF de deux types (cationiques et anioniques) ont été obtenus.

Les LIF synthétisés ont été testés pour l'extraction liquide/liquide de radionucléides. Il a été montré que l'extraction est bien due aux motifs extractants. Toutefois, la charge de l'ion modifié influence l'extraction.

Différentes expériences d'extraction et une modélisation mathématique ont été effectuées pour déterminer les mécanismes d'extraction. Ces études ont montré que chacun des systèmes d'extraction est caractérisé par un ensemble d'équilibres d'extraction différent, basés essentiellement sur l'échange cationique.

Les mots-clés : extraction liquide-liquide, radionucléides, liquides ioniques, oxyde de phosphine, calix[4]arène

Résumé en anglais

Radioactive waste treatment is a crucial problem nowadays. This work was dedicated to the development of the new extracting systems for radionuclides on the basis of "green" solvents - Ionic Liquids (ILs).

For this purpose ILs were functionalized with various extracting patterns: phosphine oxide, carbamoyl phosphine oxide groups and malonamide fragment. Also the calix[4]arene platforms were used for the synthesis of functionalized ionic liquids (FILs) and their precursors. The FILs of both types - cationic and anionic have been obtained.

The synthesized FILs were tested for the liquid-liquid extraction of radionuclides. It was found that extraction well occurs due to the extracting patterns, however a charge of a modified ion influences extraction.

The various extracting experiments and mathematical modelling have been performed to determine the mechanisms of extraction. These studies showed that each extracting system is characterized by a different set of extracting equilibria, based mostly on cationic exchange.

Key words : liquid-liquid extraction, radionuclides, ionic liquids, phosphine oxide, calix[4]arene