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# Quaternary Ammonium and Phosphonium Ionic Liquids in Chemical and Environmental Engineering

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## 1. Introduction

Quaternary ammonium salts (quats) are an economically advantageous class of industrial compounds. They have surface-active properties, possess anti-microbial activity and are known to be bioactive (Boethling & Lynch, 1992; Juergensen et al., 2000). Contrary, reports regarding low melting tetraalkylphosphonium salts were relatively rare in the literature during the last decades (Bradaric et al., 2003).

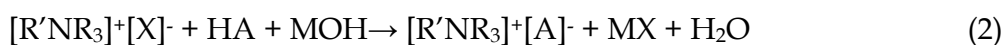
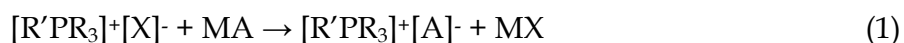
Although ILs based on quaternary ammonium cations have been known and produced for years, and also numerous phosphonium based ILs have been produced even in ton-scale, these groups of ionic liquids have been more or less “neglected” in the literature comparing to their imidazolium or pyridinium based counterparts. However, during the last decade significant work has been done, pointing out the advantages and broad application spectrum of these types of ionic liquids. Their improved thermal and chemical stability in comparison to e.g. pyridinium and imidazolium based ILs, their unique miscibility behaviour and solvating properties advances their use in specific applications (Rogers et al., 2002; Plechkova & Seddon, 2007; Chowdhury et al., 2007; Wasserscheid & Welton, 2008). Several ILs based on these classes of cations are already commercially available and have been successfully applied as phase-transfer catalysts, solvents, lubricants, gas capture agents, coating materials, or chemical sensors (Bradaric et al., 2003; Weng et al., 2006; Pernak et al., 2006; Yuan et al., 2007; Fraser & MacFarlane, 2009; Werner et al., 2010).

Tricaprylmethylammonium chloride (trade name Aliquat® 336), produced in ton-scale by Henkel, is nowadays widely used as metal extraction agent, phase transfer catalyst, surfactant, or antistatic agent. In contrast, trihexyl(tetradecyl)phosphonium chloride (trade name Cyphos® IL 101) was developed by Cytec Industries as a thermally stable phase transfer catalyst (Bradaric et al., 2003). Due to the relatively simple preparation route, Cyphos® IL 101 is produced in ton-scale and therefore represents a fairly cheap IL. Hence, due to their commercial availability and low prices, both Aliquat® 336 and Cyphos® IL 101 can be used themselves or represent favorable precursors for a series of ionic liquids. The goal of this chapter is to give some insight into the fascinating and fast-growing field of

these groups of ILs - especially based on cations of the cost-saving precursors Aliquat® 336 and Cyphos® IL 101 - concerning the field of chemical and environmental engineering.

## 2. Synthesis of ammonium- and phosphonium-based ionic liquids

Aliquat® 336 ([A336][Cl]) is prepared by methylation of a mixture of trioctyl/decyl amine (Alamine® 336, Cognis Corp.), whereas Cyphos® IL 101 ([P<sub>6,6,6,14</sub>][Cl]) is produced by Cytec Ind. in a quaternization reaction of trihexylphosphine with 1-chlorotetradecane (Robertson, 2001; Bradaric et al., 2003). A subsequent anion-exchange reaction between the quaternary ammonium/phosphonium halide and acid or salt (see Eqns. (1) and (2); R, R' = alkyl; X = halogen; M = alkali metal; A = desired anion) with corresponding anions leads to the desired ionic liquid (Bradaric et al., 2003; Mikkola et al., 2006a; Kogelnig et al., 2008; Fraser & MacFarlane, 2009).



However, the cation generation by alkylation reaction with halides and the following anion exchange often results in ILs comprising halide impurities, which results in alteration of their physico-chemical properties (Seddon et al., 2000). As chloride impurities are for example known to act as “catalytic poison”, ILs with halide contamination are unsuitable for catalytic reactions (Davies et al., 2004). To overcome the drawback of halide impurities, many literature protocols deal with synthetical approaches in which dialkylsulfates, carbonates, trialkylphosphates, alkyltosylates, methane sulfonates or fluorinated esters are used as alkylating reagents (Bradaric et al., 2003; Seddon et al., 2001; Kalb, 2005). However, since the main focus of this chapter lies on Aliquat® 336 and Cyphos® IL 101 based ionic liquids, different metathesis routes including these two commercially available ILs as precursors will be cited. Mikkola and co-workers (2006a) introduced the “new family” of ILs based on Aliquat® 336 as cation source by conducting a simple metathesis route utilizing appropriate sodium, potassium, or ammonium salts as anion source (see Eqn. 1). The authors obtained a series of hydrophobic ILs containing common anions like [PF<sub>6</sub>]<sup>-</sup>, [BF<sub>4</sub>]<sup>-</sup>, phosphate, nitrate or bis(trifluoromethylsulfonyl)imide ([Tf<sub>2</sub>N]<sup>-</sup>), but with a residual chloride content ranging between 0 and 6 wt%. On the other hand, the use of economically favorable Aliquat® 336 as a precursor may even justify the subsequent use of an anion exchanger in order to remove the residual chloride content, if necessary for specific applications. A well-established example of Eqn. (2) within the IL-community is the preparation of different phosphonium phosphinates (Robertson & Seddon, 2002). Trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (trade name Cyphos® IL 104) is commercially produced following this route (see Figure 1a, Bradaric et al., 2003). We also have shown recently (Kogelnig et al., 2008) that the simple deprotonation-metathesis route (Eqn. 1) under inert conditions leads to Aliquat-based ILs with sufficient purity (residual chloride contents between <0.1 and 0.8 wt%) for selected applications (see Figure 1b).

The slightly modified synthesis route (Stojanovic et al., 2010) could also be applied for the preparation of both ammonium- and phosphonium-based ILs containing functionalized anions like thiosalicylate, 2-(methylthio)benzoate, or phenyl(thio)acetate. All prepared ILs exhibited chloride contents below 0.9 wt%. However, due to the significantly high viscosities of the obtained ILs (up to 5242 mPas), the use of appropriate organic solvents was

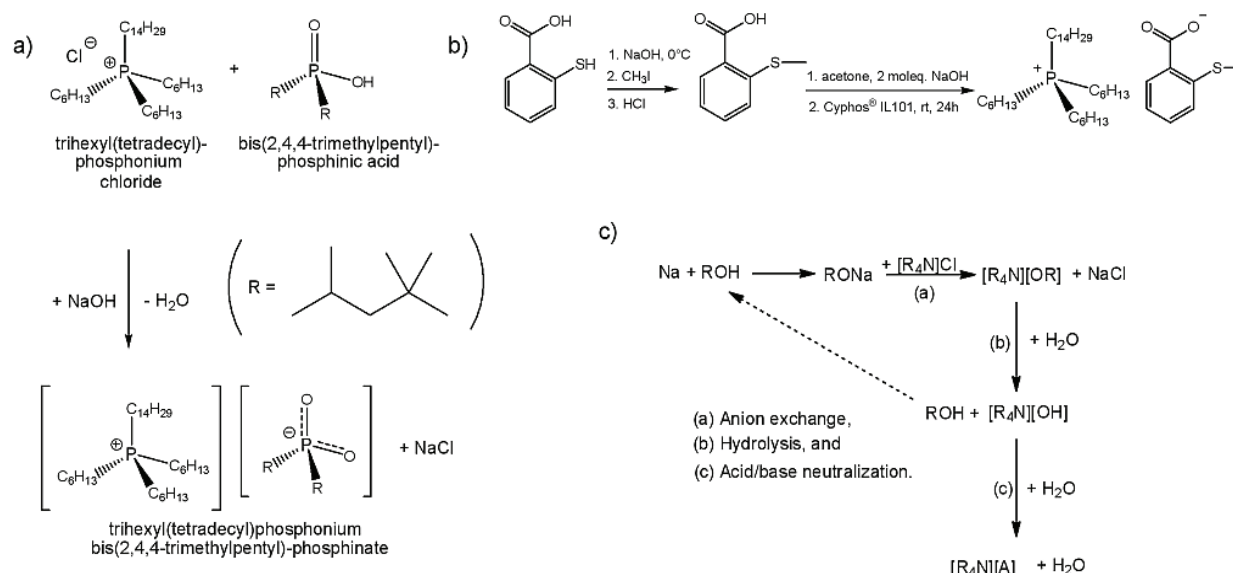


Fig. 1. a) Synthesis of Cyphos® IL 104 (redrawn from Bradaric et al., 2003) b) Synthesis of [P<sub>6,6,6,14</sub>] 2-methylthiobenzoate, [P<sub>6,6,6,14</sub>][MTBA] (redrawn from Stojanovic et al., 2010) c) Acid/base neutralization synthesis route (redrawn from Sun et al., 2010a)

inevitable to minimize loss of yield, which makes the preparation process in general more expensive and wasteful, limiting the industrial production of ILs. Sun et al. (2010a) recently presented a relatively simple preparation strategy which may alleviate industrial manufacturing of ammonium based ILs. Following the acid/base neutralization route shown in Figure 1c, the authors gained the IL tricaprylylmethylammonium nitrate, [A336][NO<sub>3</sub>], exhibiting a chloride content significantly lower than the same IL prepared via the conventional anion metathesis route. Although the obtained IL still contains a measurable amount of chloride, the described synthetic route may be attractive for large scale preparation since its reactants are cheap and easily available in contrast to halide-free intermediates.

### 3. Features of ammonium- and phosphonium-based ionic liquids

By now, numerous ILs based on both the Aliquat® 336 and the [P<sub>6,6,6,14</sub>] cation have been prepared using one of the synthesis routes described above. Several selected examples of common anions are presented in Figure 2.

The differences in physico-chemical properties of ammonium and phosphonium ILs begin with their stability towards degradation under various conditions, which differs clearly (Karodia et al., 1998; Wolff et al., 2000). Although both can decompose at elevated temperatures, phosphonium salts are generally more stable as their ammonium analogs (Wolff et al., 2000; Bradaric et al., 2003). Whereas ammonium salts undergo facile Hofmann- or β-eliminations in the presence of base (Hanhart & Ingold, 1927; Ingold & Vass, 1928), their phosphonium analogs decompose to tertiary phosphine oxide and alkane under alkaline conditions. Although the decomposition temperature of ILs depends strongly on the choice of anion, in most cases thermogravimetric analysis (TGA) of phosphonium ILs reveals a dynamic thermal stability even above 300°C (Bradaric et al., 2003; Fraser & MacFarlane, 2009). In contrast, corresponding ammonium-based ILs decompose at approximately 100°C lower temperatures. The enhanced thermal stability of phosphonium

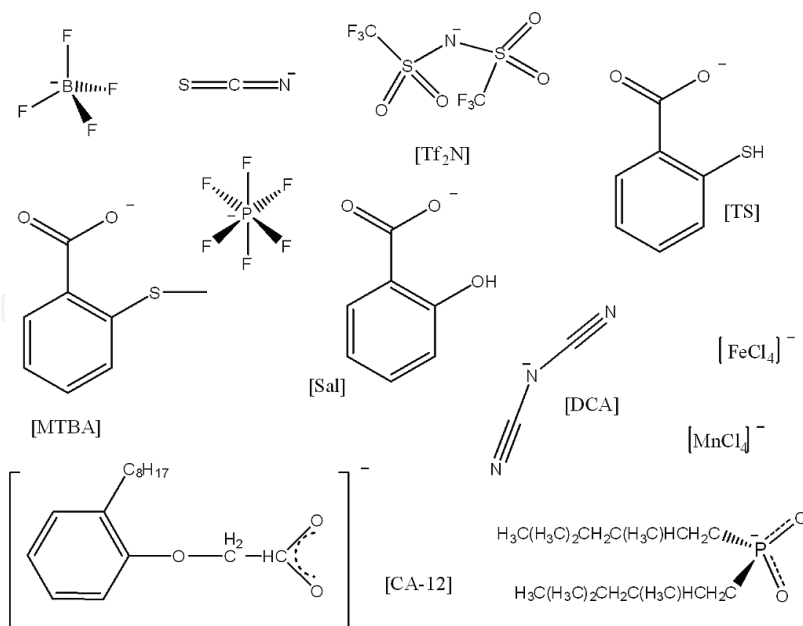


Fig. 2. Selected anions of phosphonium- and ammonium-based ILs

ILs play a crucial role when applied as solvents or catalysts for different reactions at high temperatures, or if the reaction products should be distilled from the ionic liquid at high temperatures. In general, the viscosity of Aliquat® 336-based ILs is significantly higher than that of  $[\text{P}_{6,6,6,14}]$  based ILs, but also strongly depends on the choice of anion. For example, the exchange of the chloride anion with thiosalicylate leads to an increase in viscosity, whereas the anion exchange with 2-(methylthio)benzoate leads to an increase in viscosity for the Aliquat® 336-based IL and to a decrease in viscosity for the corresponding phosphonium-based IL (Stojanovic et al., 2010). However, due to the strong temperature dependence, viscosities diminish extremely at temperatures typical for industrial applications (e.g. 70-100°C) (Bradaric et al., 2003; Kulkarni et al., 2007a; Stojanovic et al., 2010). Furthermore, phosphonium ILs generally depict higher electronic polarizabilities than their ammonium counterparts, indicating a difference in their solvation behaviour (Tariq et al., 2009; Stojanovic et al., 2010), whereas similarities can be found concerning the density. Both IL families exhibit densities ranging from 0.7 to 1.2 g cm<sup>-3</sup> with common values < 1 g cm<sup>-3</sup>. However, it is important to note that a reliable set of data regarding physico-chemical parameters of ammonium and phosphonium ILs is still missing, which limits their potential widespread industrial application (Atkins et al., 2004). On the other hand, even the available data sets should be considered carefully, since the properties of ILs strongly depend on their purity.

Besides an efficient and commercially favorable synthetic route, the determination of the purity level of obtained ILs accompanied with their purification plays a crucial role for their widespread use. Although the high-purity of ILs needs not to be achieved in every case, several authors observed negative effects of halide and water impurities on the rate and/or selectivity of reactions carried out in ionic liquids, on their catalytic performance as well as on their properties (Carmichael et al., 1999; Seddon et al., 2000; Gallo et al., 2002; Davies et al., 2004; Stark et al., 2006). From the engineering point of view, the presence of halide impurities in ILs can influence the choice of constitutional materials due to the corrosiveness of these anions. On the other hand, the presence of residual acid in ILs may have an impact on their performance in catalytic and separation processes (Werner et al., 2010). It also has been shown recently that the presence of impurities in ILs unambiguously narrows their apparent



electrochemical window, making the use of ultra high-purity ILs in electrochemical applications necessary (Buzzeo et al., 2004). Besides conventional methods like NMR, IR, ESI-MS, UV- spectroscopy, Karl-Fischer titration for the determination of water content, or elemental analysis, only a few analytical methods are dealing with the characterization of ammonium and phosphonium ILs. The absence of chromophoric UV-active groups in the Aliquat® 336 and Cyphos® IL 101 cations makes the conventional RP-HPLC with UV-detection unsuitable for these compounds, requesting more sophisticated coupling methods. Moreover, several difficulties arise in the course of the analysis of Aliquat® 336-based ILs as the cation depicts a mixture of quaternary ammonium cations with different alkyl chain lengths rather than a well-defined pure compound. This property makes the quantification of the Aliquat® 336 mix and hence all of its products more complicated. Lee et al. (1981) identified Aliquat® 336 as a mixture of quaternary ammonium cations with C<sub>6</sub>, C<sub>8</sub> and C<sub>10</sub> alkyl chain lengths applying gas chromatography. The distinct composition of the Aliquat® 336 mix was confirmed and quantitatively determined via Electro Spray Mass Spectrometry (ESMS), and revealed following mass percentages of different chloride components in Aliquat® 336:  $3.7 \pm 0.7$  % of methyl(n-hexyl)di(n-octyl)ammonium (A336<sup>+</sup><sub>C23</sub>),  $21.7 \pm 1.5$  % of methyltri(n-octyl)ammonium (A336<sup>+</sup><sub>C25</sub>),  $32.8 \pm 2.3$  % of methyl-di(n-octyl)(n-decyl)ammonium (A336<sup>+</sup><sub>C27</sub>),  $18.4 \pm 1.3$  % of methyl(n-octyl)di(n-decyl)ammonium (A336<sup>+</sup><sub>C29</sub>), and  $3.5 \pm 0.2$  % of methyltri(n-decyl)ammonium (A336<sup>+</sup><sub>C31</sub>) (Argiropoulos et al., 1998b). Recently, we developed an adequate, cost-saving and fast method for the purity determination of ammonium- and phosphonium-based ILs (Stojanovic et al., 2008), applying Reversed Phase High Performance Liquid Chromatography (RP-HPLC) with a serially coupled UV detector and a mass sensitive charged aerosol detector (CAD). This combination allows a simultaneous quantitative determination of non-chromophoric aliphatic cationic species and their aromatic, UV-active anionic counterparts. Further, a unified calibration can be applied with a single standard. Most notably, the resulting calibration function can be used for all other compounds or impurities for which no standards are available – which is particularly suitable for mixtures like Aliquat® 336. As it can be seen in Figure 3, all five components of the Aliquat® 336 cation could be efficiently separated and accurately quantified using an optimized step-gradient method, confirming the results obtained by ESI-MS measurements. The developed method was validated according to the ICH-guidelines ([www.ich.org](http://www.ich.org)) and successfully applied for the determination of molar ratios of ionic components of a series of Aliquat® 336- and Cyphos® IL 101-based ILs containing different aromatic anions.

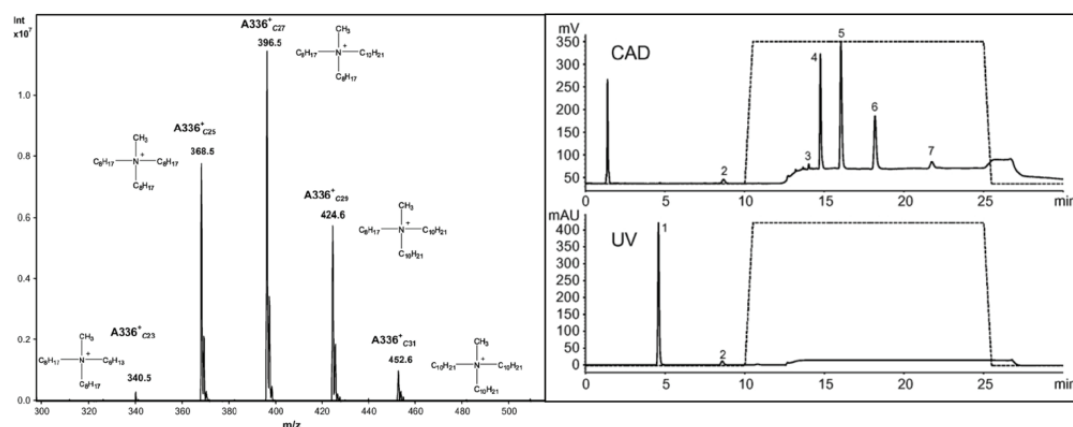


Fig. 3. ESI-MS spectrum of Aliquat® 336 (left) and chromatogram of IL [A336][TS] (taken from Stojanovic et al., 2008, Copyright © 2008 Elsevier B. V.)

#### 4. Ammonium- and phosphonium-based ionic liquids in extraction processes

Due to the hydrophobicity of Aliquat® 336- and [P<sub>6,6,6,14</sub>]-based ILs the formation of liquid-liquid biphasic systems with aqueous phases can be realized, making them suitable for such extraction processes. On the other hand, due to their polar nature many ILs show a pronounced miscibility gap with common apolar organic solvents. From the engineering point of view a severe drawback of ILs compared to conventional solvents is based on their high viscosity, requesting changes in the hydrodynamic design of extraction columns (Meindersma et al, 2007). However, very little is known about the behaviour of ammonium and phosphonium ILs in biphasic systems, e.g. about coalescence phenomena or micelle formation etc. (Werner et al., 2010).

##### 4.1 ILs as extracting agents for heavy metals

Already in the 1960's Seeley & Crouse highlighted the enhanced performance of Aliquat® 336 as liquid ion-exchanger for the removal of different metal species from hydrochloric acid solutions compared to conventionally used amine extractants like Alamine® 336 or Amberlite LA-1 (Seeley & Crouse, 1966). Since then Aliquat® 336 has been evaluated as extracting agent (in most cases dissolved in an appropriate organic solvent) for different metals from acidic aqueous solutions (e.g. Cd(II), Fe(III), Pt(II) and Hg(II) from hydrochloric acid solutions; El-Wakil et al., 1982; Hoh et al., 1985; de Mendonça Fábrega & Borges Mansur, 2007). Nayl (2010) presented a successful separation of Co(II) and Ni(II) from acidic sulfate solutions using Aliquat® 336 dissolved in kerosene. Further, Aliquat® 336 could be efficiently applied for the recovery of Co and Ni from spent Ni-MH batteries (Nayl, 2010). Aliquat® 336 dissolved in kerosene was also applied for the effective separation of Pt(IV) from Rh(III) from acidic chloride solutions (Lee et al., 2009). As Aliquat® 336 was first applied as extractant in the mining industry, it is not surprising that numerous studies are dealing with the evaluation of its extraction ability towards uranium, thorium and several lanthanides (e.g. Atanassova & Dukov, 2004; El-Nadi et al., 2005; Ali et al., 2007). In general, the extraction mechanism with Aliquat® 336 is based on the anion exchange/ion association of metal chloride/sulfate species; it therefore strongly depends on the composition of the aqueous phase (formation of different metal species) and pH (see Eqns. 4 and 5). Hence, effective metal stripping is mostly easily achieved by variation of pH, or via an efficient complexing agent like thiourea. In contrast, Cyphos® IL 101 has only recently been investigated as potential new IL extracting agent dissolved in toluene for the elimination of zinc and palladium from aqueous phases (Regel-Rosocka, 2009; Cieszyńska et al., 2007). Alguacil and co-workers (2010) investigated the transport of Cr (VI) through a pseudo-emulsion membrane from a feeding to an appropriate stripping phase using Cyphos® IL 101 as metal carrier. Additionally, we have investigated the separation of iron(III) and nickel(II) from hydrochloric acid solution (6 M HCl) with Cyphos® IL 101 dissolved in chloroform (Kogelnig et al., 2010a). The efficient back extraction was achieved with 0.5 M HCl solution. The conducted bulk liquid membrane (BLM) experiments as well as kinetic model data elucidated the transport mechanism as a combination of anion exchange and ion association (see Eqns. 4 and 5).



However, the application of Aliquat® 336 and Cyphos® IL 101 in liquid/liquid extraction processes has several disadvantages. Firstly, due to the high viscosity of ILs the use of organic solvents is inevitable, influencing both price and “greenness” of the process. Secondly, the extraction mechanism is based on anion exchange and hence strongly dependent on the composition of the aqueous phase. Further, the potential leachability of both IL and organic solvent in the aqueous phase may pose an additional environmental risk. Therefore, in order to overcome these drawbacks, two different approaches have been developed during the last years: 1) Avoiding of liquid/liquid extraction and hence increasing of the stability of the extracting agent may be achieved by immobilization of ILs onto different solid materials or via embedment of ILs into different matrices. However, the main challenge regarding these approaches is to attain the favorable performance of “liquid” ionic liquids. 2) In order to avoid anion exchange and to enhance the extracting ability, it is possible to combine favorable properties of quaternary ammonium and phosphonium cations like hydrophobicity and thermal stability with different functionalized anions containing functional moieties known for their affinity towards selected metals, and forming task specific ionic liquids (TSILs) as metal scavengers.

Generally, problems connected with solvent extraction, like inhibition of phase separation and product recovery by formation of difficult-to-separate emulsions, high consumption of organic reagents, solvent loss or shortcomings due to the flooding and loading in conventional column reactors may be overcome by so-called non dispersive solvent extraction (Gabelman & Hwang, 1999). Thereby hollow fiber membranes or so-called “supported liquid membranes” (SLMs), which consist of a porous polymeric (organic or inorganic) material whose pores are impregnated or in contact with an extractant or carrier, are used. Hollow fiber membranes impregnated with Aliquat® 336 as efficient ionic carrier were evaluated for removal of different metal species, e.g. cobalt(III), rhodium(III), or chromium(VI), from an aqueous feeding phase to an adequate stripping phase (Fontàs et al., 2000; Kao & Juang, 2005; Güell et al., 2008). The hollow fiber liquid membrane using Aliquat® 336 (35% v/v) as extractant and 0.5 M NaOH as stripping solution was successfully applied for the removal of arsenic ions in waste water from a gas separation plant. The extraction efficiency of Aliquat® 336 was thereby remarkably higher compared with other evaluated extractants (Cyanex® 923, tri-n-butylphosphate (TBP), bis(2, 4, 4-trimethylpentyl) dithiophosphinic acid (Cyanex® 301), tri-n-octylamine (TOA); Pancharoen et al., 2009). Myasoedova et al. (2008) evaluated different solid supports (polyacetonitrile, Amberlite XAD-7, hyper cross linked polystyrene or multi walled carbon nanotubes) with  $[P_{6,6,6,14}][Cl]$ ,  $[P_{6,6,6,14}][PF_6]$ , and  $[P_{6,6,6,14}][BF_4]$  as solid-phase extractants for Pt(IV), U(VI) and Pu(IV) from acid solutions, achieving the best performance with polyacrylonitrile impregnated with Cyphos® IL 101. Next to SLMs, polymer inclusion membranes (PIMs) were evaluated as solid supports for ILs. In contrast to SLMs, PIMs consist of a high molecular weight polymer to provide mechanical strength, a plasticizer to provide elasticity and a carrier molecule for facilitating the selective transport of the analytes (Nghiem et al., 2006). Polyvinyl chloride (PVC) and cellulose triacetate (CTA) are the most commonly used polymers for the preparation of PIMs, since they are able to embed carrier molecules and inhibit their leaching. It is also noteworthy that the mechanical properties of PIMs are quite similar to those of filtration membranes (Nghiem et al., 2006). Rahman and co-workers (2005) have shown that ionic liquids could be used both as a carrier as well as a stable plasticizer for PIMs. Until now, predominantly Aliquat® 336 has been evaluated as carrier for the extraction of different metal species (e.g. Au(III) (Argiropoulos et al., 1998a), Cd(II), Cu(II)



(Wang et al., 2000), Co(II) (Blitz-Raith et al., 2007), Pd(II) (Kolev et al., 2000), and Zn(II) (Juang et al., 2004)). Another interesting approach for the immobilization of ILs is the encapsulation of liquid extractants in polystyrene microcapsules. Yang et al. (2005) investigated the uptake of Cd(II), Cr(III), and Zn(II) from hydrochloric acid solutions by Aliquat® 336 encapsulated in polystyrene particles. The encapsulated extractant displayed high stability over a wide pH-range and the microcapsules could be successfully regenerated and reused several times, hence justifying their relatively extensive preparation. Furthermore, Guibal et al. (2009) selected another approach by choosing different biological materials such as alginate as “green” materials for encapsulation or immobilization of extractants. The prepared alginate particles were evaluated as efficient metal sorbents for Au(II), Hg(II), Pd(II), Pt(VI), or Bi(III) from hydrochloric acid solutions. The disadvantages of the method, however, still originate from the competition of metal ions capable of forming chloride complexes and the limitations associated with slow mass transfer when using dried resins.

A further approach regarding the advancement of metal uptake ability of ILs is the use of task specific ionic liquids as extracting agents. By anchoring different functional groups onto the anion, it is possible to combine the hydrophobicity of ammonium and phosphonium cations with the affinity of the functional group towards selected metal species, and hence enhancing both efficiency and selectivity of the extracting agent. For example, an ionic liquid based on the trioctylmethylammonium cation with thiosalicylate as anion, prepared via a halide free synthesis route, is commercially available and has been evaluated as extracting agent for heavy metals (e.g. Hg(II), Cu(II), or Pb(II)) from aqueous solutions with high distribution coefficients (Kalb, 2005; Kalb et al., 2006).

By a simple anion exchange of the chloride anion of Aliquat® 336 with a salicylate anion, Egorov et al. (2008, 2010) prepared a TSIL suitable for the extraction of Cu(II) and Fe(III) from aqueous solutions. During the last years we have prepared a series of hydrophobic ionic liquids based on Aliquat® 336- and  $[P_{6,6,6,14}]$  cations with functionalized aromatic anions (see Figure 2, Kogelnig et al., 2008; Stojanovic et al., 2010). The newly prepared IL tricaprylmethylammonium thiosalicylate,  $[A336][TS]$ , could be evaluated as highly effective extracting agent for Cd(II) from a natural river water matrix with a distribution coefficient  $>10^4$  (Kogelnig et al., 2008). The investigated IL exhibited high selectivity towards cadmium in the presence of naturally occurring alkali and earth alkali metals ( $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$ ). The same IL was efficiently applied for the removal of uranium traces from natural mineral water (Srncik et al., 2009). The selectivity of  $[A336][TS]$  towards alkali and earth alkali metals and a subsequent successful stripping of uranium with 2 M  $HNO_3$  makes this IL suitable as possible preconcentration agent for uranium for its subsequent analytical determination in natural waters. Further, thiol- and thioether functionalized ILs ( $[A336][TS]$ ,  $[P_{6,6,6,14}][TS]$ ,  $[A336][MTBA]$ , and  $[P_{6,6,6,14}][MTBA]$ ) seem to be suitable for the extraction of Pt(II) from aqueous solutions (see Figure 4, Stojanovic et al., 2010). The incorporation of aromatic anions significantly increased the stability of the investigated ILs in the aqueous phase, whereby ILs containing  $[MTBA]$  exhibited an extremely high stability with a leaching of the anion in the aqueous phase of max. 0.2 wt.%. Interestingly, the change from ammonium to phosphonium cations for methylthiobenzoate and thiosalicylate functionalized ILs resulted in different platinum uptake (see Figure 4). Whereas the highest uptake of Pt(II) was achieved with  $[P_{6,6,6,14}][MTBA]$ , only 40% of Pt(II) could be extracted with the ammonium analog. Therefore, also the physico-chemical properties of TSILs have to be considered in order to determine distinct reaction mechanisms, as the presence of a functional group is obviously not the sole factor influencing the extracting ability of TSILs.

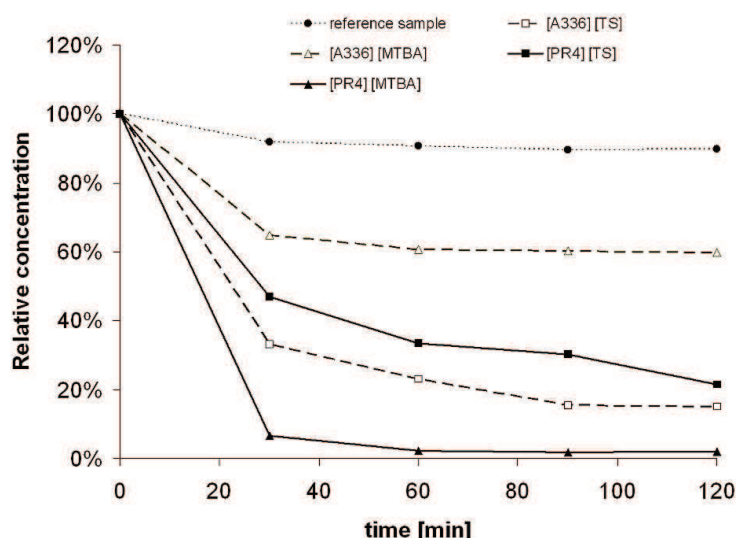


Fig. 4. Extraction efficiency of [A336][TS], [A336][MTBA], [PR<sub>4</sub>][TS], and [PR<sub>4</sub>][MTBA] for platinum(II) (Stojanovic et al., 2010, Copyright © CSIRO 2010)

A different concept of enhancing the extraction efficiency focuses on so-called bifunctional ionic liquids (bif-ILs). The idea behind this concept is the synergetic effect on the solvent extraction by combination of two extractants. An excellent example is given by the IL [P<sub>6,6,6,14</sub>][bis(2,4,4-trimethylpentyl)phosphinate] (trade name Cyphos® IL 104), as displayed in Figure 1a. In this case the synergetic effect on the solvent extraction is achieved by combination of Cyphos® IL 101 and bis(2,4,4-trimethylpentyl)phosphonic acid, which is known as excellent solvent for the extraction of cobalt and nickel from both hydrochloride and sulfate acidic solutions (Rickelton et al., 1984; Danesi et al., 1985), and is currently used to produce more than a half of the western world's cobalt (Rickelton & Robertson, 1982; Robertson, 1983; Rickelton et al., 1984). Sun et al. (2010b) investigated the separation of cobalt and nickel by synergetic extraction with the Aliquat® 336-based bifunctional IL [A336][CA-12] (see Figure 5). Their results indicated that the extraction abilities of the tricaprylmethylammonium cation ([A336]<sup>+</sup>) and the sec-octylphenoxy acetic acid group ([CA-12]<sup>-</sup>) can be remarkably enhanced by combining them in a corresponding IL. The same authors also investigated the synergetic effect of different bifunctional ILs (see Figure 2) for the extraction of europium and other rare earth elements from hydrochloric and nitric acid media (Sun et al., 2010a). On the other hand, Liu et al. (2010) evaluated the bif-IL

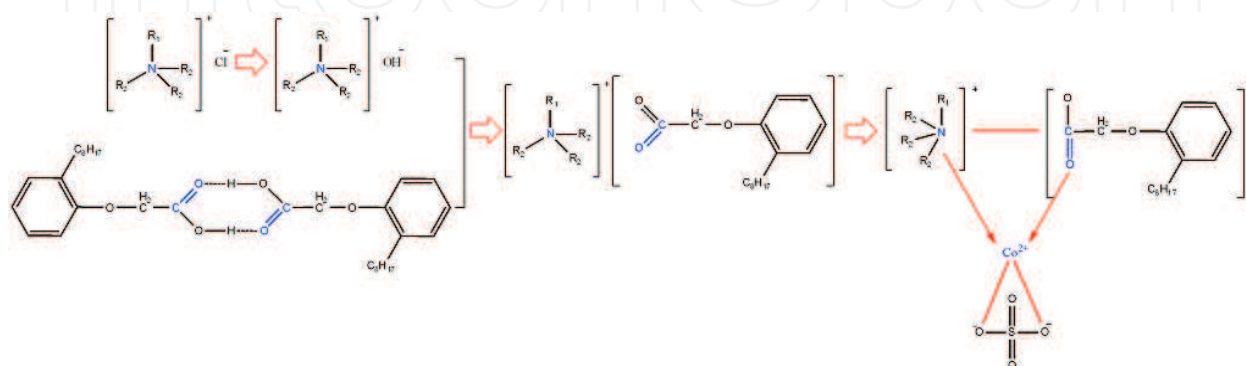


Fig. 5. Extraction of cobalt with the ionic liquid [A336][CA-12] (redrawn from Sun et al., 2010b)

Cyphos® IL 104, together with soybean oil methyl ester (SBME, biodiesel) as delutant, as extractant for rare earth elements from aqueous solutions. They achieved both enhanced extracting efficiency due to the presence of the bif-ILE and a diminished loss of IL due to the use of biodiesel as solvent.

In summary, the removal of heavy metals from aqueous solutions using phosphonium- and ammonium-based ILs both as anion exchanger and as functionalized TSILs depicts a field of extensive research and promising results. However, from the engineering and economic point of view, extensive research is needed regarding a complete recovery of the ionic liquid and the full isolation of the extracted metal from the loaded ionic liquid. Furthermore, the question of ILs' stability in aqueous phases and subsequently their possible toxicity towards the aquatic environment still needs more attention.

#### 4.2 Other separation processes with ammonium- and phosphonium-based ILs

Kulkarni et al. (2007b) investigated the absorption capacity of a series of Aliquat® 336-based ILs (see Figure 2) towards organic vapors (1,4-benzodioxane, biphenyl, xylene, and methanol) and received promising results with the ILs [A336][Tf<sub>2</sub>N] and [A336][DCA]. However, although both ILs showed remarkable absorption capacity, none of the tested ILs was able to provide sufficient selectivity regarding different organic solutes (see Figure 6). A possible solution may be a combination of different ILs in order to achieve the desired selectivity. The absorbed organic solutes were recovered by desorption under vacuum and preconcentrated by steam condensation. Compared to the relatively slow absorption process, the organic vapors could be desorbed very fast (<12h). The recycled ILs were also successfully reused. The same research group investigated the IL [A336][DCA] as capturing agent for dioxins from the vapor phase (Kulkarni et al., 2008), whereby the investigated IL absorbed 15.6 % by weight of dibenzo-p-dioxin in equilibrium. Due to the high thermal stability of ammonium ILs, dioxin was easily desorbed by vacuum distillation at 100°C, and the IL could be further reused.

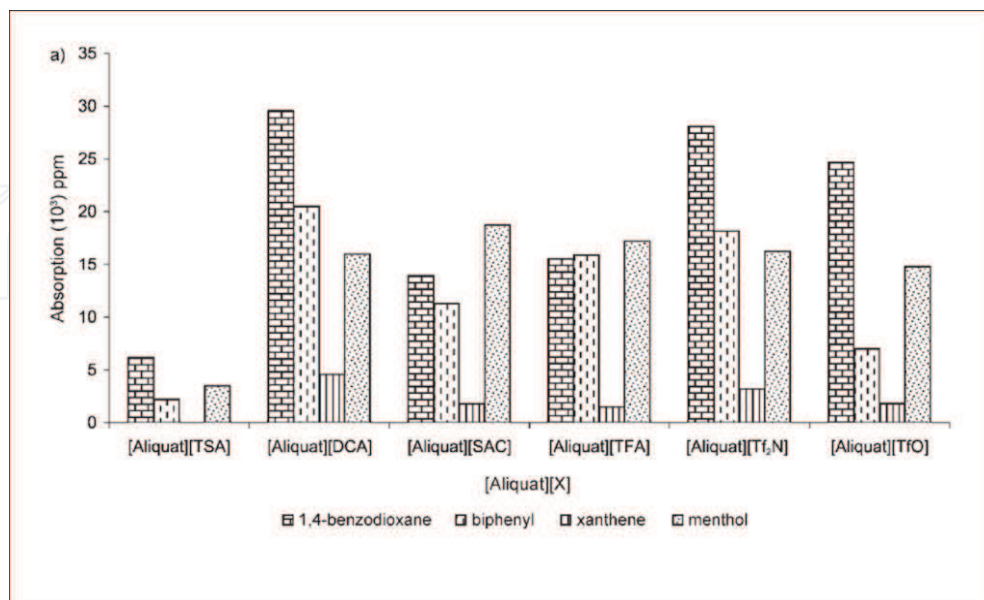


Fig. 6. Extraction efficiency of Aliquat® 336-based ILs for organic vapors (taken from Kulkarni et al., 2007b, Copyright© Wiley-VCH Verlag GmbH&Co. KGaA)

Furthermore, Egorov et al. (2008) investigated the extraction of eleven aromatic compounds (phenols and aromatic amines) from aqueous phases with the Aliquat® 336-based IL tricaprylmethylammonium salicylate, [A336][Sal] (see Figure 2). The best results were achieved for nitrophenols and naphthols, showing even better absorption capacities as common imidazolium-based ILs over the investigated pH-range. Recently, Aliquat® 336 and Cyphos® IL 101 were also evaluated as solvents for carboxylates and their extraction from aqueous phase (Rosatella et al., 2009). Whereas a large quantity of disaccharide mixtures was extracted, no satisfying extraction of monosaccharide mixtures was obtained. Further, the highly hydrophobic IL trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate, [PH<sub>3</sub>T][FAP], was evaluated as extraction agent for polycyclic aromatic hydrocarbons from the aqueous phase via single drop microextraction. Extremely high enrichment factors (680-2145) were achieved for compounds with high molecular weights and fused rings (Yao et al., 2009). On the other hand, Cyphos® IL 104 could be efficiently embedded in polysulfone resins and evaluated for the extraction of phenol from aqueous solutions. Prepared polysulfone resins exhibit remarkable mechanical stability and possess extremely high extractant loading capacity (0.83-0.88 cm<sup>3</sup>g<sup>-1</sup>) (Van den Berg et al., 2009). Due to the favorable features of polysulfone encapsulated ILs, this could be an interesting approach regarding the application of ILs in separation processes.

Another interesting application field is the removal of carboxylic acids from aqueous solutions. Both Aliquat® 336 and Cyphos® IL 101 have been investigated concerning their extracting ability for several acids, e.g. lactic, levulinic, glutaric, or amino acids (e.g. Uddin et al., 1990; Bora & Dutta, 1998; Kyuchoukov et al., 2005; Harington & Hossain, 2008; Hossain & Maisuria, 2008; Uslu & Kırbaslar, 2009; Pehlivanoglu et al., 2010). As an outstanding example the extraction of lactic acid with the bifunctionalized IL Cyphos® IL 104, should be mentioned. In contrast to distribution factors of about 1, which could be reached with trialkylamines (e.g. trioctylamine) as classical lactic acid solvents, distribution factors above 40 could be reached with Cyphos® IL 104. The assumed extraction mechanism suggests the coordination of lactic acid (LA) to the IL under formation of complexes (LAH)<sub>p</sub>(IL)(H<sub>2</sub>O)<sub>2</sub> (with p ranging from 1-3). The uptake of LA by Cyphos® IL 104 is directly connected with the water uptake of the IL, including the formation of reverse micelles in the IL and inclusion of water into hydrated complexes of lactic acid (Marták & Schlosser, 2007).

## 5. Applications as catalysts and solvents in organic synthesis

Since the pioneering work of Małosza, Brändström, and Starks (Małosza & Serafinowa, 1965; Brändström & Gustavilii, 1969; Starks, 1971), quaternary ammonium and phosphonium salts have been used as phase transfer catalysts in liquid/liquid biphasic systems. Bender et al. (2010) evaluated a series of ILs including Aliquat® 336 as phase transfer catalysts for the etherification reaction of 1-octanol with 1-chlorobutane. The conversions ranged from 87-96% with Aliquat® 336 catalysts. Whereas the use of Aliquat 336 as a phase transfer catalyst is widespread and extensively investigated (e.g. Baidossi et al., 1997; Villa et al., 2003; Rup et al., 2009), phosphonium ILs have only recently been investigated for this application. Yadav & Tekale (2010) evaluated the ILs [P<sub>6,6,6,14</sub>][Cl], [P<sub>6,6,6,14</sub>][Br], [P<sub>6,6,6,14</sub>][decanoate], and [P<sub>6,6,6,14</sub>][PF<sub>6</sub>] as phase transfer catalysts for selective O-alkylation of 2-naphthol. Thereby, the reactivity of ILs was strongly dependent on the anion attached to the phosphonium cation following the order Br<sup>-</sup> > Cl<sup>-</sup> > hexafluorophosphate >



decanoate, corresponding to the order of nucleophilicity for the anions. Hence,  $[P_{6,6,6,14}][Br]$  was chosen as most reactive catalyst. It depicted a good catalytic performance in the solid-liquid phase transfer catalyzed synthesis of p-nitrodiphenyl ether, leading to 100% selectivity towards the desired product (Yadav & Motirale, 2008).

Though Aliquat® 336 represents a widely used, economically favorable phase transfer catalyst with remarkable performance, the main drawback is its chemical and thermal stability. This could be overcome by the use of more stable phosphonium ILs, hence more fundamental research should be done in this direction.

Regarding the environmental pressure to reduce waste and to reuse material in terms of "green chemistry", one of the most problematic areas to create environmentally friendly solutions is the field of solution phase chemistry (Rogers et al., 2002; Fraser & MacFarlane, 2009). Phosphonium- and ammonium-based ILs may play a role in these efforts, as described in following selected examples (Fraser & MacFarlane, 2009).

The Heck cross-coupling reaction is a common reaction for the formation of carbon-carbon bonds between alkenes and organic halides (Heck & Nolley, 1972). Kaufmann et al. (1996) applied a phosphonium-based IL, trihexyl(tetradecylphosphonium) bromide ( $[P_{6,6,6,14}][Br]$ , trade name Cyphos® IL 162) as recyclable medium for the palladium-mediated Heck coupling of aryl halides with acrylate esters (see Figure 7) for the first time. Although relatively high yields were obtained, the reaction temperature was rather high (100°C) and more activated aryl halides were strongly favored. In contrast, the use of Cyphos® IL 101 seems more applicable for Heck coupling reactions of deactivated and sterically demanding aryl halides (see Figure 7). The reaction was conducted under moderate conditions (at 50°C within 2h), resulting in sufficiently high yields (Gerritsma et al., 2004). Further evaluation of different  $[P_{6,6,6,14}]$ -based ILs revealed the dominant role of the chosen anion on the yield of the reaction. Whereas ILs with chloride and decanoate anions seem to be suitable for high yield Heck reactions,  $[PF_6]^-$  and  $[BF_4]^-$  containing ILs resulted in significantly lower yields (Gerritsma et al., 2004). On the other hand, Aliquat® 336 was successfully applied as reaction media for the palladium-catalyzed hydroxycarbonylation of aryl halides and benzyl chloride derivatives (Mizushima et al., 2004), as its presence significantly enhanced the hydroxycarbonylation reaction. Furthermore, the catalyst in the IL phase could be easily recycled after extraction of the products with water.

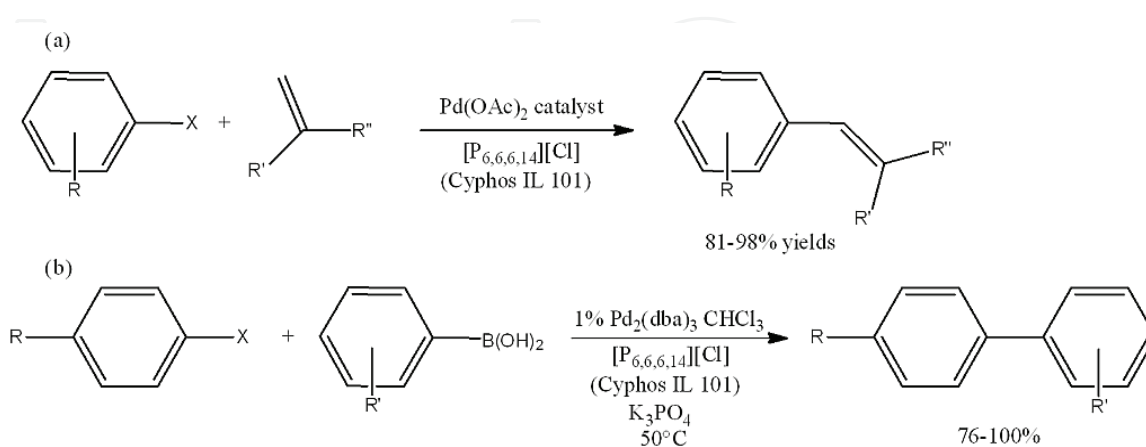


Fig. 7. (a)  $[P_{6,6,6,14}][Cl]$  ionic liquids reported as solvents in the Heck coupling reaction (redrawn from Fraser & MacFarlane, 2009). (b) Suzuki coupling carried out in a phosphonium ionic liquid (redrawn from Fraser & MacFarlane, 2009).



Several research groups investigated multiphase systems made by hydrogen, an aqueous phase, isooctane, Aliquat® 336 as phase transfer agent and a heterogeneous catalyst (e.g. Pd/C, Pt/C, Raney-Ni). These systems allow a variety of reduction reactions to be conducted under mild conditions ( $T = 50^{\circ}\text{C}$ ,  $p(\text{H}_2) = 1 \text{ atm}$ ), ranging from hydrodehalogenation of aryl halides (Tundo et al., 2001; Marques et al., 1994, 1995), hydrogenolysis of hydroxyls (Marques et al., 1995) up to aromatic hydrogenation (Marques et al., 1995; Selva et al., 1998). Perosa et al. (2002) for example studied the multiphase hydrogenolysis of benzyl methyl ether with different catalytic systems. It is noteworthy to mention that the relatively inexpensive Raney-Ni system is effective for debenzilation under such conditions while simpler systems require Pd/C as catalyst. This methodology enables difficult transformations to be carried out under mild conditions, using a less expensive catalytic system and allowing easy catalyst recovery and reuse. The same working group observed a tenfold acceleration of a Heck coupling of aryl iodides with electron poor olefins using a triphasic system containing Aliquat® 336 and Pd/C as catalyst (Perosa et al., 2004).

Another interesting example is the use of ILs in Suzuki cross-coupling reactions (carbon-carbon bond formation between an  $\text{sp}^3$  carbon or non- $\beta$ -hydride containing electrophile and a boronic acid derivative; Miyaura & Suzuki, 1995). Cyphos® IL 101 has been recently reported as an extremely successful medium for such types of reaction (see Figure 7, McNulty et al., 2002). The palladium catalyst ( $\text{Pd}_2(\text{dba})_3\text{CHCl}_3$ ) was dissolved in the IL, forming a stable solution in absence of oxygen, and hence could also be effectively recycled after solvent extraction of reaction products. The Suzuki reactions in Cyphos® IL 101 were efficient even under moderate conditions ( $50\text{--}70^{\circ}\text{C}$ ), whereas the use of imidazolium-based ILs in contrast requires elevated temperatures (up to  $110^{\circ}\text{C}$ ) (Mathews et al., 2000).

In general, ILs are also regarded as favorable solvents for Diels-Alder reactions, producing good to high yields (Welton, 1999). Janus & Stefaniak (2008) reported that Diels-Alder reactions carried out in the phosphonium IL  $[\text{P}_{6,6,6,14}][\text{Tf}_2\text{N}]$  under presence of catalysts occurs smoothly, in short time and with high yield and high stereoselectivity. Further advantages of the reaction originate from the good solubility of catalysts belonging to the group of metal chlorides, triflates, and bis-triflimides in  $[\text{P}_{6,6,6,14}][\text{Tf}_2\text{N}]$  and - due to the high thermal stability of the IL - from the easy separation of the product via distillation. Several authors have been investigating the use of phosphonium-based ILs as media for strong base mediated reactions such as Grignard reactions (Ramnial et al., 2005; Law et al., 2006; Fraser & MacFarlane, 2009). Ramnial et al. (2008) investigated the ILs Cyphos® IL 101 and trihexyl(tetradecyl)phosphonium decanoate,  $[\text{P}_{6,6,6,14}][\text{C}_9\text{H}_{19}\text{COO}]$ , as solvents for bases such as Grignard reagents, isocyanides, Wittig reagents (phosphoranes), and N-heterocyclic carbenes. The authors illustrated that ILs can be used for generating N-heterocyclic carbenes and their metal complexes and as solvent medium for the generation of Wittig reagents. The reactivity of Cyphos® IL 101 in Grignard reagent solutions with tetrahydrofuran-to-IL ratio of 1:3 was tested by the addition of anhydrous bromine resulting in the exclusive formation of bromobenzene. Furthermore, Cyphos® IL 101 seems to be stable in basic Grignard reagents solutions, since even after one month no deprotonation was observed (Ramnial et al., 2008). It should also be noted that the use of phosphonium-based ILs facilitates the separation of the product due to the formation of three-phasic systems of some IL/water/hexane combinations. This may reduce the use of ethereal solvents in this class of reactions and hence lead to a general “greening” of Grignard chemistry (Ramnial et al., 2005; Fraser & MacFarlane, 2009). However, phosphonium-based ILs may also undergo

deprotonation in the presence of strong base, similarly to the C-H activation of imidazolium based ILs (Fraser & MacFarlane, 2009). Tseng et al. (2007) clearly indicated that the  $\alpha$ -protons of  $[P_{6,6,6,14}]$  ions, although shielded, are still accessible to small bases such as  $OH^-$ . However, this exchange does not seem to produce a significant impact on the acidity of the cation.

Another promising field of phosphonium and ammonium ILs comprises the metal based ionic liquids. Following the idea of Hayashi and co-workers (Hayashi & Hamaguchi, 2004; Hayashi et al., 2006; Okuno & Hamaguchi, 2006). Del Sesto et al. (2008) prepared a set of transition metal based  $[P_{6,6,6,14}]$ -ILs. The simple reaction of Cyphos® IL 101 with  $FeCl_3$ ,  $CoCl_3$ ,  $MnCl_2$  or  $GdCl_3$  yields the corresponding ILs. All prepared ILs exhibited paramagnetic behavior as a sole property of ILs, and hence a series of hydrophobic, magnetic ILs was prepared. We have recently shown that the reaction of Aliquat® 336 with  $FeCl_3$  leads to the corresponding paramagnetic IL tricaprylmethylammonium tetrachloroferrate,  $[A336][FeCl_4]$  (Kogelnig et al., 2010b). The development of magnetic ILs opens a new field of possible applications (e.g. as catalysts, Bica and Gaertner, 2006; Nguyen et al., 2008).

One more aspect is worth mentioning regarding possible applications of ammonium and phosphonium ILs in environmental and chemical engineering: the environmental impact. Although ILs were often described as new „environmental benign“ and „green“ compounds due to their low (often immeasurable) vapor pressure and non-inflammability, many new ILs have shown to be toxic (e.g.) to aquatic organisms, or even explosive (Pham et al., 2010; Gao et al., 2009). In general, very little is known about the toxicity of ammonium and phosphonium ILs. Frade et al. (2009) investigated the toxicity of selected ILs in a human colon carcinoma cell line (CaCo-2). The evaluated Aliquat® 336-based ILs  $[A336][Cl]/[FeCl_4]/[TFA]/[TfO]$  are very toxic and can not be regarded as candidates for greener solvents. Interestingly, whereas  $[P_{6,6,6,14}][Cl]/[FeCl_4]$  were also very toxic, the dicyanamide ( $[DCA]$ ) anion led to a considerable decrease in toxicity. Kumar & Molhotra (2009) investigated the potential anti-cancer activity and cytotoxicity of selected ammonium- and phosphonium-based ILs. Cyphos® IL 101 may also be regarded as toxic in aquatic environment, exhibiting much higher ecotoxicity compared with common organic solvents (Wells & Coombe, 2006). The activity and cytotoxicity of investigated ILs were strongly influenced by alkyl chain length of and alkyl substitution on the cations. In general, phosphonium ILs were more active and less cytotoxic compared with ammonium ILs. Hence, ammonium and phosphonium ILs should not be a priori regarded as “green” solvents, and their behavior and environmental impact has to be extensively studied.

## 6. Conclusions

Ammonium and phosphonium ionic liquids undoubtedly represent a promising group of ILs. However, as it can be seen in examples presented in previous sections, many of the discussed applications and concepts are still in the early stage of development (with the exception of several widespread applications of Aliquat® 336, of course). This can be attributed mainly to the circumstance that ammonium- and phosphonium-based ILs have just recently gained attention both in the ionic liquid and engineering community. Hence most of the examples presented in the literature still deal with concept research. On the other hand the development of engineering applications of ILs generally requires a reliable and broad spectrum of knowledge concerning the nature of the IL itself and of relevant aspects regarding the attended application. At current stage of research much more information concerning fundamental IL properties and behavior is needed. In the further

stage of development aspects like efficiency of the recycling process, ionic liquid recovery and reusability, or the degree of ionic liquid degradation with time needs to be considered. Further, the toxicity and environmental impact of this group of ILs needs to be extensively studied as both Aliquat® 336 and Cyphos® IL 101 can not be regarded as “green” solvents.

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