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11

Ionic Liquids Recycling for Reuse

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1. Introduction

Ionic liquids (ILs) are unique new materials that offer novel solutions to the chemical industry as well as to its customers. They are organic salts composed entirely of ions, typically large organic cations and small inorganic anions. They have various striking features such as being liquid salts at ambient temperatures, thermally stable liquids over a range of 300 K, have very low vapor pressure at room temperature, and have the potential to replace many volatile organic solvents. They have judicious variation of the alkane chains on the organic cation, and may generate an infinite set of "designer solvents" because their physical properties can be modified according to the nature of the desired reactions by modification of their cations and anions [Candeias et al., 2009]. Since ILs have no detectable vapor pressure and do not emit volatile organic compounds (VOCs), they are expected to provide a basis for clean manufacturing "green chemistry." [Anonymous, 2004].

In addition, many ILs have unusual solubility and miscibility properties, attractive electric conductivity, quite interesting polarity nucleophilicity for catalysis, and remarkable tribologic properties [Werner et al., 2010]. The thermodynamics and reaction kinetics of processes carried out in ILs media are different from those carried out in conventional media. This creates new opportunities for catalytic reactions, separations, electrochemistry, and combined reaction/separation processes [Anonymous, 2004].

There has been an explosion of interest in ILs in the last decade that has resulted in the discovery of a vast number of new ILs with a wide range of applications. However, ILs may be sensitive to contaminants and may require frequent rejuvenation or replacement. The degree of sensitivity to impurities and the rate of degradation may have a large impact on IL functionality in industrial processes. Process engineering studies are required to obtain sufficient data on ILs stability under long-term exposure to process conditions and exposure to air, moisture, heat, corrosion products, trace impurities (e.g., SO_x, NO_x, etc.) and other key industrial application components. The useful lifetime (life-cycle costs), impact of water content, sensitivity to contaminants, thermal stability, aging, IL losses, etc., over time, as well as recyclability data, are crucial in evaluating ILs viability in commercial applications [Anonymous, 2004].

Rakita (2003) raised similar issues that need to be addressed to achieve efficient commercial synthesis of ILs and make them available on industrial scale. For example, what will the ILs look like after they have been used in a synthetic procedure? Are there contaminants left behind in the IL solvents? What are they? Do they matter, and if so, how can they be

removed? These questions need to be answered in the context of specific applications, not abstractly or in an absolute sense.

Despite the excitement of ILs, chemists are much too cautious about the propaganda of ILs' greenness. In the first major US meeting on ionic liquids, held in 2001 at the American Chemical Society meeting in San Diego, Robin Rogers (the Director of Center for Green Manufacturing at the University of Alabama in Tuscaloosa) said: "Before we can say that ionic liquids are green, we have to look at their entire life cycle. People are calling ionic liquids green because they are not volatile, but we have to look at how they are made all the way through to recycling and disposal" [Sen, 2006]. Rogers added: "Researchers also need to find better ways to recycle ionic liquids." Many processes for cleaning up ionic liquids involve washing with water or VOCs. "This needs more work. We don't want to create a secondary waste."

Although ILs are invariably described as highly stable green solvents, thorough investigations to quantify their environmental impact have lagged behind the pace of other research in the area [Scammells et al., 2005]. These issues are extremely important as well as the approaches for the recovery of the ILs (after their use) for further reuse (i.e., recycling). A very important challenge is to use the unique solvent properties of the ILs to develop efficient method for product separation and IL recycling [Galán Sánchez, 2008; Marsh et al., 2004; Gordon, 2001; Welton, 2004; Meindersma et al., 2005; Heintz, 2005; Olivier-Bourbigou & Magna, 2002; Wasserscheid & Keim, 2000; Wasserscheid & Welton, 2003; Wishart & Castner, 2007; Seddon et al., 2002; Holbrey & Seddon, 1999; Holbrey, 2004; Olivier, 1999].

Despite their extremely low vapor pressure that prevents IL emission to the atmosphere, they are, at least, partially miscible with water and will inevitably end up in the aqueous environment (as what happens in the application of ILs for the electro-deposition of metals). During industrial application, ILs will get mixed with other products that necessitate efficient separation and recycling of ILs for economical and ecological needs [Haerens et al., 2010].

Many researchers have pointed out the major concern in the use of ILs is their relative high cost, which makes their recycling an important issue for further study [Laali & Gettwert, 2001; Gonzalez et al., 2006; Verma et al., 2008]. Currently, ionic liquids are quite expensive in comparison with conventional molecular solvents, and large amounts of ILs are needed in the various applications, thus efficient recycling of ILs is important for their economic use, especially in large-scale applications [Wagner & Hilgers, 2008]. However, the cost of ILs is expected to decrease, due to their higher production levels, which is expected to render ILs economically competitive with organic solvents [Khodadoust et al., 2006].

To overcome the cost problem, some low cost and simple synthesis of the ILs are essential for their recycling and reuse. Attri et al. (2010), for example, recovered ILs from binary mixtures of ILs/N,N-dimethyl formamide (DMF) by the removal of the DMF component under vacuum. No appreciable change in the physical properties of the recovered ILs was observed and the recovered ILs were reused at least four times without loss of their purity.

Ionic liquids are now available from a number of commercial manufacturers and from many suppliers. However, IL preparation, work-up to separate/extract products and their recycling usually involve other solvents (e.g., VOCs) to extract unwanted residues, which are toxic persistent (to some extent). However, this diminishes the "green" aspect of their usage due to the cross-contamination arising from the use of organic solvents. Some ILs are certainly toxic and have been shown to have a detrimental effect on aquatic life that will tend to persist in local environment, on land/sea, etc. Thus there are worries about ILs end of life disposal, and materials incompatibility [Rayner, N.D.; Weatherley, N.D.]. One should

not forget that ionic liquids are quite different products compared to traditional organic solvents, simply because they cannot be easily purified by distillation, due to their very low volatility. This, combined with the fact that small amounts of impurities influence the IL properties significantly, makes the quality of ILs a quite important consideration for many applications [Seddon et al., 2000].
Also ionic liquids have to be much superior to conventional organic solvents where activity, selectivity and stability of the catalyst are concerned besides being environmentally benign [Song et al., 2001]. However, we have to keep in mind that organic solvents can be recycled and purified by distillation, while it is difficult to recycle ILs because immiscible organic solvents are required to separate the products [Fioroni et al., 2003; Hassan et al., 2006].
For academic researchers it is possible and desirable to obtain perfectly pure ILs with negligible amounts of impurities. However, such efforts are simply not necessary for most applications and would significantly add to the cost of ILs when produced on a commercial scale. Thus, once a customer has decided in which way to use a certain IL in a specific application, the set of specification parameters (purity, by-products, halide content, water content, color) have to be defined altogether [Wagner & Hilgers, 2008]. The recycling protocols usually make use of the low solubility of the ILs in organic solvents. This allows products and residual organics to be extracted using an organic solvent while the salt by-products present in the water-immiscible ILs can be washed out with water. On the other hand, water-miscible ILs are more difficult to recycle bacause inorganic by-products cannot be easily removed. Furthermore, if reaction products are sufficiently volatile they can be distilled directly from the IL, since ionic liquids are inherently non-volatile [Wagner & Hilgers, 2008].
Kanel (2003) mentioned some of the methods that have been developed to recover and reuse ILs like heating or evaporation of volatiles under vacuum, extractions with VOC solvents (obviate some of the advantages of using ILs), supercritical CO_2 ($scCO_2$) extraction, and distillation/stripping of the solute from the ILs (for thermally stable ILs).
In their Minireview, Wu et al. (2009) raised the question: do we understand the recyclability of ILs in a real sense? They have discussed various methodologies for the effective recycling of ILs and focused on the methods needed for the ILs separation from their "working" environment. They proposed that the appropriate separation method should be selected according to the different systems. To better understand the separation of ILs, fundamental research on the existence forms (ions, ion pairs or supermolecule) of ILs in solvents is vitally important.

2. Separation of solutes from ionic liquids by distillation/stripping

Distillation can be used to recover ILs from compounds with low boiling points, because of the ILs negligible vapor pressure. However, direct vacuum distillation protocol is energy-consuming, particularly for non-volatile compound/IL systems. Moreover, if the IL has a tendency to undergo hydrolytic decomposition, such as those that contain $[PF_6]^-$ ions, direct heating should be avoided or at least minimized [Wu et al., 2009]. Distillation can also be used to recover thermo-stable compounds with low boiling points from ILs [Han & Armstrong, 2007; Kanel, 2003]. The recycling of organic solvents requires that they can be purified by distillation, while the recycling of ILs is difficult because immiscible organic solvents are required to separate the products [Fioroni et al., 2003;. Hassan et al., 2006]. Kralisch et al. (2007) carried out the work-up by distillation, as well as the recycling of IL

solvents, using a rotary evaporator fitted with a water-bath. The pressure decay was adjusted to the boiling point of the solvent.
BASF (2011) pointed out that the recycling of ILs is easy if protonated cations (HY or RY) are used. In this case the ILs can be switched off by deprotonation (See Fig. 1). Imidazolium cations can be deprotonated by bases to form neutral carbene molecules. The resulting carbenes (amine or imidazole) are found surprisingly stable and can be distilled for recycling or purification purposes.

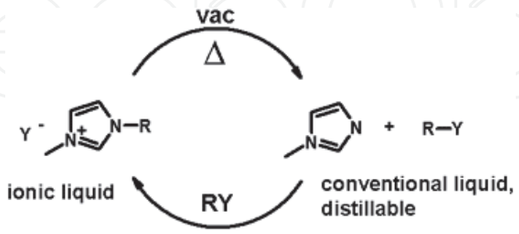


Fig. 1. ILs switching off by deprotonation

It is more difficult with alkylated cations. Apart from purification or recycling by liquid-liquid extraction, two principal "distillation" methods have been reported. The first is the formation of distillable carbenes [WO 01/77081; WO 05/019183] and the second is the back-alkylation of the anion (See Fig. 2) [WO 01/15175].

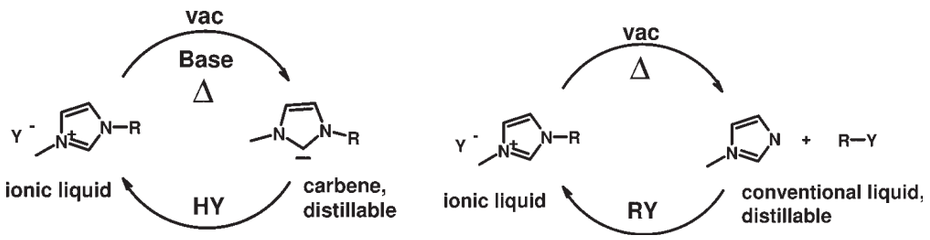


Fig. 2. Formation of distillable carbenes and back-alkylation of the anion

The IL can be recycled by further reaction of the carbene with an acid. The controlled decomposition reaction allows for a recycling or purification process of the IL [WO 01/15175]. In this case the IL is thermally cleaved. The neutral imidazole and alkylating agent are distilled, collected and re-reacted. However, in some cases it is even possible to distill the entire IL without decomposition. For example, the ionic liquid 1-Hexyl-3-methyl-imidazolium-chloride, [Hmim]Cl, can be distilled at 150 ^{o}C at 0.5 mbar [WO 2005/068404]. This has recently been demonstrated to be true also for fully alkylated cations [Earle et al., 2006]. These materials require higher temperatures of about 300 ^{o}C and 6 mbar vacuums.
Early before ionic liquids are adopted as solvents for the production of nitro-aromatics, Dal & Lancaster (2005) studied the nitration of aromatics using acetyl nitrate (HNO_3-Ac_2O) in two different ionic liquids, [bmpy][OTf] and [bmpy][$N(Tf)_2$], and developed a regime by which the solvent may be recovered and reused. The recycling of the IL was achieved by dissolving the post-reaction mixture into dichloromethane and adding water. It was then possible to extract any unreacted nitric acid, plus the acetic acid (HOAc) generated by the reaction with water. After removing the dichloromethane, the organics were removed from the IL by steam distillation, extracted from the water with dichloromethane and rotary evaporated to remove the solvent and substrate. The IL was recovered by extracting with

dichloromethane and then heating *in vacuo*. This process is illustrated in Fig. 3. The samples of the IL withdrawn after each run, and analyzed before being reused revealed that there was no difference between the recovered and the original IL [Dal & Lancaster, 2005].
The yield of chlorobenzene and the amount of IL [bmpy][$N(Tf)_2$] recovered after each reaction (after removal of the sample for NMR analysis) are shown in Table 1, which shows a steady loss of IL after each run. No degradation of the IL was observed during the reaction (as evidenced by the NMR spectra of the IL after each run and the fact that there was no discolouration). Therefore, Dal & Lancaster (2005) proposed that these losses are purely mechanical, arising from the washing procedure employed.

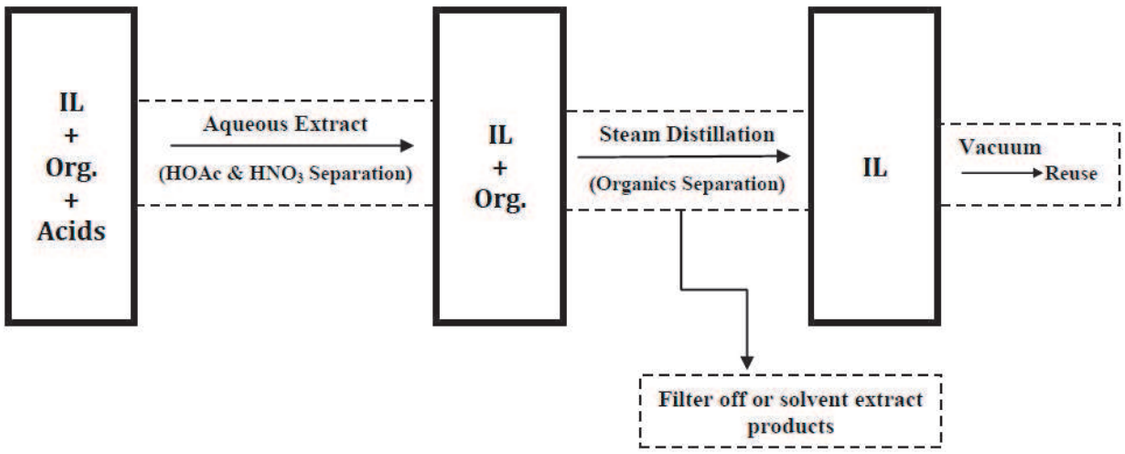


Fig. 3. Procedure for IL recycling from IL/Organic/Acid mixture [Reproduced from Dal & Lancaster, 2005].

Recycle #	Yield [%]	Mass loss of [bmpy][$N(Tf)_2$] recovered [g]
1	76	0.22
2	70	0.30
3	71	0.38
4	76	0.62
5	74	0.88

Table 1. Yield of chlorobenzene and recyclability of IL [bmpy][$N(Tf)_2$]

Dal & Lancaster (2005) admit that there is one major problem with the recycling of the IL as described above; the reliance on dichloromethane does not make this process appear green at first glance. Dal & Lancaster (2005) added that the role of dichloromethane in their work was to enable the determination of both product and recovery of the IL. In an industrial setting, it would be quite possible to perform a steam distillation of the entire reaction mixture. The organics will form a separate phase from the aqueous acids distilled and could probably be removed by simple decantation. And because this ([bmpy][$N(Tf)_2$]) IL is immiscible in water, it should be possible to decant any water from the IL and reuse it immediately. Thus recycling the IL does not require the use of dichloromethane [Dal & Lancaster, 2005].

3. Extraction with supercritical CO_2

Extraction of solutes from ILs with VOC solvents obviate some of the advantages of using ILs, but supercritical CO_2 ($scCO_2$) extraction may offer a promise. The "green" solvent $scCO_2$ may be a good choice for the recovery of solutes and the regeneration of ILs. Blanchard et al. [1999] demonstrated that $scCO_2$ exhibits high solubility in ILs whereas ILs show generally no detectable solubility in CO_2: The solubility of $scCO_2$ in ILs was determined to be less than 5×10^{-7} mole fraction [Blanchard & Brennecke, 2001]. This unique property of $scCO_2$ means that solutes can be isolated from ILs without cross-contamination of the gas phase with IL and also provides a means for recycling the ILs [Blanchard et al., 1999]. Recovery of the organic solute from ILs was near quantitative and achieved by simple expansion of the gas phase downstream. This efficient exchange between the two phases, coupled with the lack of mutual solubility seems to be ideally suitable for product separation and recycling of ILs [Gordon & Muldoon, 2008].

Blanchard et al. (1999) and Blanchard & Brennecke (2001) extracted aromatic and aliphatic compounds into a CO_2 phase from IL [bmim][PF_6]. Examples include separation of naphthalene from the [bmim][PF_6] [Blanchard & Brennecke, 2001] and methanol [bmim][PF_6] using pressurized CO_2 [Scurto et al., 2002]. A two-step extraction system (water/RTIL/CO_2) for trivalent lanthanum and europium was reported by Mekki et al. (2006) where the metal ions were extracted from the aqueous phase into $scCO_2$ via a RTIL/fluorinated β-diketonate mixture with high extraction efficiencies.

Taking into account the specific properties of carbohydrates, only hydrophilic ILs can be used [Murugesan and Linhardt, 2005]. This means that only apolar solvents or $scCO_2$ may be used to extract reaction products. Unfortunately, 5-hydroxy methyl furfural (HMF) was found to have a larger affinity for the IL 1-H-3-methyl imidazolium chloride than for the organic solvent (such as diethyl ether) or $scCO_2$. For the dehydration of fructose, Moreau et al. (2006) showed that HMF could be completely extracted with diethyl ether in a continuous or stepwise manner. But, their preliminary results using $scCO_2$ as extraction solvent do not seem to have better expected extraction properties.

Scurto et al. (2003) studied CO_2 induced separation of IL and water. If a pressure of CO_2 is placed upon a mixture of the IL and water, a second liquid phase can appear. In Fig. 4, the densest liquid is rich in IL (L_1), the next phase is rich in water (L_2) and the third phase is vapor (V), which is mostly CO_2 with a small amount of dissolved water. Scurto et al.(2003) demonstrated that water/[C_4mim]BF_4 solutions can be induced to form three phases in the presence of $scCO_2$.

Although the original solution of [C_4mim]BF_4 was quite dilute, the application of $scCO_2$ induced the formation of an additional liquid phase rich in [C_4mim]BF_4, indicating that the separation of [C_4mim]BF_4 from aqueous solutions by the application of $scCO_2$ is possible. In Fig. 4, the applied CO_2 pressure at which the second liquid phase appears (at a given temperature and initial concentration of IL in water) is called the *Lower Critical End Point* (LCEP). However, Wu et al. (2009) considered this effect as a pressure phenomenon, as well as due to a slight decrease in the dielectric constant upon addition of CO_2. In the opinion of Wu et al. (2009), a salting-out effect due to the formation of carbonate in the solution may also played a key role, since CO_2 reacts with water to form carbonic acid and its dissociation products.

Recycling of ILs with high efficiency is of key importance on going from the laboratory-scale to large-scale industrial application of these solvents [Wu et al., 2009]. It is noteworthy that

the efficiency of the recycling process for various ILs varies from quite poor [Seddon et al., 1999] to very good [Welton, et al., 2000; Handy & Zhang, 2001; Fukuyama et al., 2002]. The quality of the recovered IL should be assessed by some suitable technique [see for example, Wagner & Hilgers, 2008]. Even though ILs in some systems could be recovered efficiently, the yield of the product might decrease gradually with time (upon multiple usages) due to some impurities in the recovered ILs.

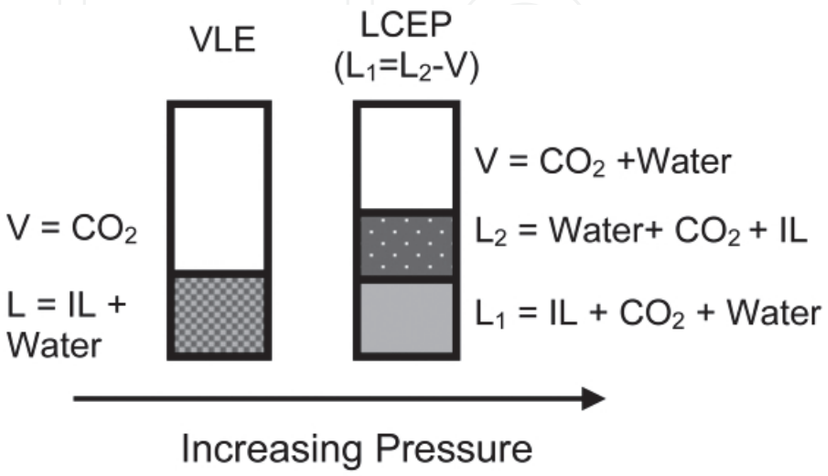


Fig. 4. Phase behaviour of IL/water/CO_2 mixture at increasing pressure at near-ambient temperatures (Adapted from Scurto et al., 2003)

Several procedures for the recycling of ILs have been reported in the literature. Depending on the IL used and the application where it is used, a variety of methods for recycling are possible. By picking the right purification steps, an individually optimized work-up procedure can be obtained [Wasserscheid & Welton, 2008]. However, if the customer does not feel comfortable with the task of recycling the IL there is a further option at hand: why not rent or lease the IL rather than buy it? The customers would in this case perform their application with the IL and send, the probably impure, IL back to the supplier, who has the expertise to recycle and clean it up [Wasserscheid & Welton, 2008]. This scenario could be interesting from an economic point of view for truly commercial applications on a large scale. *But will this be a practical solution?*

4. Ionic liquids as reaction media

Because of their negligible vapor pressure, thermal stability and easy recyclability, neutral ILs have been referred to as environmentally benign solvents. These ILs have been employed as excellent and recyclable medium for a wide array of reactions; e.g., Heck reaction [Park & Alper, 2003], Bischler–Napierlaski cyclisation [Judeh et al., 2002], Beckmann rearrangement [Ren et al., 2001], addition of thiols to unsaturated ketones [Yadav et al., 2003], l-proline catalysed aldol reaction [Loh et al., 2002], and Pechmann condensation of phenols and ethyl acetoacetate (EAA) catalyzed by $POCl_3$ in [bmim]PF_6 and [bmim]BF_4 ILs [Potdar et al., 2005]. Other examples where ILs have been used as a reaction media include, but not limited to, Diels-Alder reactions [Reinhardt, 2009; Doherty, 2004; Song, 2001], Friedel-Crafts alkylation and acylation reactions [Xiao, 2006; Xiao & Malhotra, 2005;

Ross & Xiao, 2002; Itoh, 2001; Stark et al., 1999], hydroformylation reactions [Magna et al., 2007; Sharma, 2009], Pd-mediated C-C bond formation [Park & Alper, 2003], alkene polymerisation [Hardacre et al., 2002], and biotransformations [Bornscheuer & Kazlauskas, 2006].

Bortolini et al. (2002) accomplished the recycling of [bmim][PF_6] by washing with an aqueous solution of $NaHSO_3$ and then with water. The uncoloured recovered IL was dried, analyzed by NMR and reused. Recycling of trihalide-based ILs was performed, after removal of the solvent used for product extraction, by addition of the consumed halogen, evaluated on the basis of the product yields.

The inability to successfully recycle morpholinium-based IL was reported by Kim & Shreeve (2004). Similar results were reported by Murray et al. (2003) after the fluorination of benzyl bromide using cesium fluoride (CsF) in [bmim][PF_6]. This suggests that recycling of ILs is limited for nucleophilic fluorination reactions using alkali metal fluorides. Although this system was not investigated in detail but it indicates that ILs cannot be recycled effectively when reaction is carried out under highly-basic conditions and higher temperatures.

Chrobok (2010) reported a new and efficient method for the synthesis of lactones involving the application of an oxygen/benzaldehyde system as the oxidant and ILs as solvents with the possibility of effective ILs recycling. After the Baeyere-Villiger (B-V) reaction, the recycling of the highly hydrophobic IL [bmim]NTf_2 was purified first with a saturated aqueous $NaHCO_3$ solution, and then with diethyl ether. The [bmim]NTf_2 was then concentrated and dried (60 ^oC, 8 h) under vacuum.

On the other hand, when hydrophilic ILs were used as reaction solvents, the product was first extracted with diethyl ether. Next, the organic extract was washed with a saturated aqueous solution $NaHCO_3$, dried and concentrated. Table 2 shows the results of reactions using three recycles of [bmim]NTf_2 in the oxidation of cyclohexanone. Alternatively, it is possible to distil the product from the crude reaction mixture [Chrobok, 2010**]**.

Recycle #	Yield of ε-caprolactone [%], as determined by GC	IL [bmim]NTf_2 recovery [%]
0	90	91
1	88	92
2	88	90
3	87	89

Table 2. Recyclability of IL [bmim]NTf_2 in the oxidation of cyclohexanone in the presence of benzaldehyde with oxygen and ACHN additive at 90 ^oC over 2.5 h reaction

The possibility of recycling the highly hydrophobic ILs [bmim]BF_4 and [Hmim]OAc used in the Baeyere-Villiger (B-V) oxidation of ketones with Oxone was also checked [Chrobok, 2010**]**. After the filtration of the post reaction mixture and the extraction of the product with ethyl acetate (for [bmim]BF_4) or dibutyl ether (for [Hmim]OAc), the ILs were concentrated, dried under vacuum (60 ^oC, 5 h) and reused. Table 3 shows four cycles of the oxidation of 2-adamantanone in ILs that are recovered and reused for further B-V reactions. No significant loss of activity of these solvents was observed. Additionally, ILs were recycled three times in a model reaction without significant loss of activity [Chrobok, 2010].

Recycle #	Yield [%] for 3 h reaction time using [bmim]BF_4	IL Recovery [%]	Yield [%] for 5.5 h reaction time using [Hmim]OAc	IL Recovery [%]
0	95	92	97	91
1	94	90	97	91
2	93	91	97	90
3	93	89	97	89

Table 3. Recyclability of ILs in the oxidation of adamantanone in the presence of Oxone at 40^{o}C

Gordon & McCluskey (1999) carried out the recycling of the IL used in the allylation reaction of benzaldehyde in the presence of tetraallylstannane catalyst following an extremely straight-forward protocol: The procedure employed was to dissolve the IL in ethyl acetate (10 ml), and wash with water (2x5 ml) and brine (5 ml). Addition of diethyl ether (20 ml) caused two layers to form, the lower being essentially pure IL. No decrease in the yield was observed in the runs carried out using the 'old' IL (see Table 4). Furthermore the products obtained were of the same purity as in the first run. In the case of the recycled [bmim][PF_6] salt, the purification removed all of the cloudy residue, while some cloudiness was observed in the recycled [bmim][BF_4] salt, but this did not seem to impair the performance of the IL [Gordon & McCluskey, 1999].

Recycle #	Isolated Yield [%] using [bmim][BF_4]	Isolated Yield [%] using [bmim][PF_6]
1	79	82
2	82	81
3	78	83

Table 4. Isolated yield using recycled ILs in the allylation reaction of benzaldehyde in the presence of tetraallylstannane catalyst

Potdar et al. (2005) employed *neutral* ILs such as [bmim]PF_6 or [bmim]BF_4 with catalytic amount of acid for synthesis of coumarin via Pechmann condensation of phenols and ethyl acetoacetate (EAA) under ambient conditions. They also carried out the reaction at high temperature in IL [bmim]PF_6, without the use of any acid catalyst and investigated the recycling of the ILs for reuse.

Potdar et al. (2005) also presented a general work up procedure for recycling of ILs: The reaction mixture was quenched with 10% aqueous NaOH solution and settled. The settled down IL was extracted with dichloromethane. Further, the dichloromethane layer was stirred vigorously with 10% aqueous NaOH in order to remove coumarin and acid traces. Further, dichloromethane layer was washed with water. The solvent was then evaporated and the resultant IL was subjected to consecutive extractions with diethyl ether to remove any organic impurities present. The resultant IL was then dried under vacuum at 60 ^{o}C and reused for subsequent reactions. When the IL [bmim]BF_4 was used, the reaction mixture was quenched by addition of water. The coumarin derivative separated as a solid was isolated by filtration. The IL was recovered by evaporation of water in a rotary evaporator. The above ILs have been reused for consecutive four cycles without loss in their efficiency [Potdar et al., 2005].

Potdar et al. (2005) found the yields of the above reactions obtained by employing chloroaluminate ILs or neutral ILs with catalytic amount of acid at room temperature compare well to those obtained at high temperature. They also found that the IL [bmim]PF_6 can be recycled efficiently and used consecutively for three runs without any considerable loss in its activity (see Table 5).

Recycle #	Yield [%] using [bmim]PF_6
1	95
2	92
3	94

Table 5. Recyclability of [bmim]PF_6 IL in Pechmann condensation performed at 100 ^{o}C

Xie & Shao (2009) studied the phosphorylation of corn starch was by reaction with sodium dihydrogenphosphate or disodium hydrogenphosphate using IL 1-butyl-3-methyl-imidazolium chloride (bmimCl) as reaction medium. The bmimCl was recovered by separating the product, and distilling the bmimCl under reduced pressure to remove the volatile compounds before being recycled and reused in the next phosphorylation reaction. The recycling test result is illustrated in Fig. 5 where it can be seen that a lower degree of solution (DS) of the starch was observed when the recovered IL was used for the subsequent cycle. However, the decline in the DS value was small even after five cycles. Therefore, the IL could be recovered and recycled without problem.\

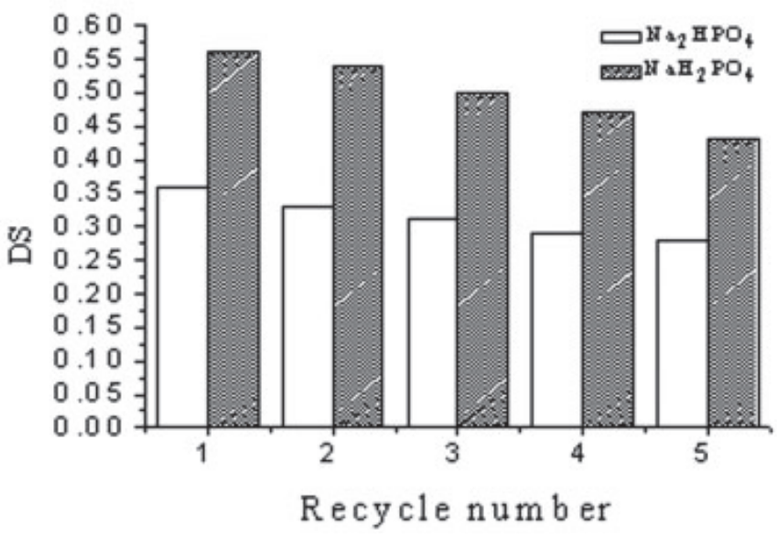


Fig. 5. Result of the ionic liquid recycle test. Reaction conditions: anhydride: urea: AGU molar ratio 3: 3: 1, reaction time 3 h, reaction temperature 1207C [From Xie & Shao, 2009]

The most studied examples are the 1,3-dialkylimidazolium-based ILs where the ionic solvent is usually recycled through several cycles of the reaction. Numerous examples describe the immobilization of a transition metal catalyst in the IL phase of a biphasic system [WO 01/77081, WO 05/019183, WO 01/15175, WO 2005/068404, Earle et al., 2006].

Faizee et al. (2007) presented the recovery of ILs used for the pretreatment of cellulose and lignocellulosic substrates using an ion exchange bed. This was carried out using Solid Phase Extraction (SPE) using Strong Cationic Exchange resins (SCX) or liquid-liquid extraction. As it is known, ionic liquids consist of an organic cation and an inorganic anion (chloride, in this case). The SCX is strongly acidic and exchanges the cation. The ion exchange bed then gets saturated with the cations and can be regenerated by passing hydrochloric acid-a process which allows for recovery of IL via the reverse ion exchange process.
Several groups have tested recycling of ILs as well as separation methods that would be suitable on an industrial scale, such as extraction with benign solvents like water, or $scCO_2$ or distillation [Itoh et al., 2003]. However the economics of commercially using ILs in industrial processes are still far behind and not clear. The currently published data on IL recovery do not allow for reliable extrapolation to industrial applications scale. However, it is clear that the ionic liquids which are proposed to be used as solvents need to be recycled and reused in order to have commercially attractive processes.
However, the scheme presented in Fig. 6 comprises a possible industrial application of the separation of ILs from other compounds. It can be used in breaking of azeotropes such as tetrahydrofuran (A) - water (B) mixture in the presence of an IL. Here the IL acts as an extractant (or entrainer) to wash down compound B and removed at the bottom of the column while compound A is released and distilled as a pure compound at the top of the column. In this case, the IL can be recycled into the process after removing residual B in a falling film evaporator [BASF, 2011; Maase, 2008].

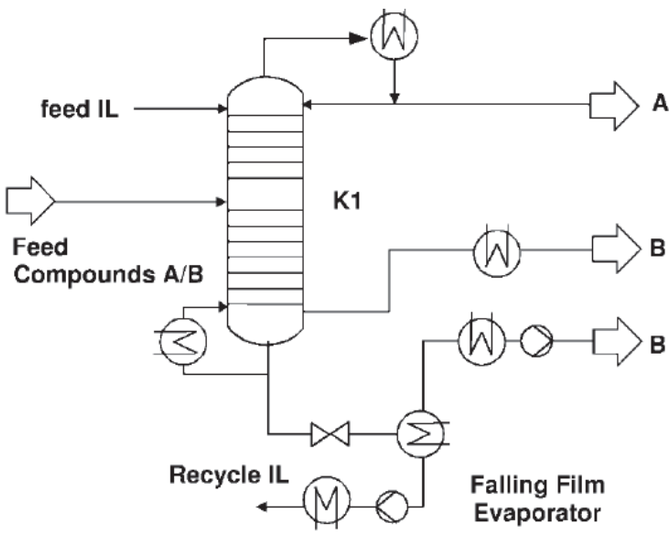


Fig. 6. Generic flow chart for the IL-based separation process [BASF, 2011; Maase, 2008]

Meindersma and Co-workers (2011) have their own experience with regenerating ILs, both on laboratory and pilot scales. They used a rotary evaporator (75°C, vacuum, 15 h) at the laboratory level and extraction column (6-m high, 0.06-m diameter, flux rate 8 $m^3/m^2.h$) in the pilot plant as a regeneration unit, which was, of course, not optimal. After the extraction experiments and after a phase separation between the IL and the organic extract phase, they bubbled hot nitrogen, 75°C, through the IL phase in the column. The complete regeneration of the IL was realized in (20-22) h. In a proper regeneration column, e.g. a falling film column, they expect that the process will be much shorter. They removed any remaining IL

from the raffinate phase by a one step washing with water. Both in the laboratory as in our pilot plant, they have used regenerated ILs, without loss of any activity. The colour of the IL changed, of course, from the original colour (e.g. yellow) to dark brown or black, probably due to some impurities. In one occasion, the fresh pyridinium-based IL smelled of pyridine. Table 6 compares several physical properties of the ILs before and after several regenerations [Meindersma & Co-workers, 2011].

Characteristic	New [3-mebupy]$N(CN)_2$	Regenerated [3-mebupy]$N(CN)_2$
Toluene distribution coefficient (10 wt%, kg/kg)	0.39	0.42
Viscosity (cP)	20	21
Density (kg/m^3)	1041	1040
Interfacial tension (mN)	13.3	13.4
Colour	Light red	Dark brown

Table 6. New IL vs. regenerated IL used for the extraction of toluene from alkanes at 313 K [Meindersma & Co-workers, 2011]

A review by Olivier-Bourbigou and Magna (2002) indicates that ILs have been successfully recycled in many reactions. Examples of reactions using recyclable IL included palladium-catalyzed Heck reactions (Ramnial, 2005; Carmichael, 1999] oxidations of benzaldehyde and alkylbenzene [Seddon & Stark, 2002], Friedel-Crafts reactions (Adams et al., 1998; Stark et al., 1999; Ross & Xiao, 2002], copolymerization of styrene and carbon monoxide [Hardacre et al., 2002], and dimerization of propene [Chauvin et al., 1990].

Recyclability requires rates and yields of reactions to be maintained at a reasonable level after repeated reactions. In particular, reactions containing a transition metal catalyst immobilized into the IL of a biphasic reaction system have proved to be recyclable. Generally, recycling is based on the non-volatile nature of ILs and the solubility differences between ILs, organic compounds and water. Products can be extracted from ILs with a non-polar solvent or they can be separated by distillation. A water-immiscible IL can be washed with water to get a water-soluble product or side products out of the reaction mixture [Kärkkäinen, 2007].

The major benefit of using ILs in the dimerization reaction is simplified separation of the products. ILs are polar, thus non-polar products are not miscible into them. The biphasic procedure enables separation of the products by decantation. The cationic nickel catalysts used showed good activity in ILs and they do not seem to leach from the IL phase to the product phase. This makes recycling of the IL and the catalyst possible. However, the sensitivity to air and water limits the use of $AlCl_3$-based ILs [Kärkkäinen, 2007].

Recycling studies indicated that the catalytic properties of an IL could be maintained for several hours. Kärkkäinen (2007) carried out the batch reaction in [C_4mim]Cl/$InCl_3$, with $InCl_3$ 0.58 mol%, at 120 ^oC for 1 hour. In these experiments the product layer was separated on the surface of the IL and decanted before a new batch of 2-methylpropene was fed in. The conversions of 2-methylpropene stayed at the same level in first three reactions, but the fourth one gave a 40% lower conversion.

Kärkkäinen (2007) carried out the dimerization reaction with a continuous feed of 2-methylpropene (1.5 mmol/min) in [C_6mim]Cl/$InCl_3$, x($InCl_3$) = 0.55 for 6 hours at 160 ^oC.

The amounts of the main dimers as a function of reaction time are shown in Table 7. The colour of the IL changed during the reaction; at the beginning the solution was clear, but after 6 hours it changed *from* yellow and orange to brown.

		Reaction time [h]					
Products	%	1	2	3	4	5	6
2,4,4-trimethyl-1-pentene	8	63	66	64	61	56	53
2,4,4-trimethyl-2-pentene	9	18	17	14	16	14	14
2,3,4-trimethyl-1-pentene	33	5	5	6	9	8	9
2,3,4-trimethyl-2-pentene	34	8	5	5	4	4	4

Table 7. Amount of main dimers formed as a function of reaction time in the continuous reaction of 2-methylpropene in $[C_6mim]Cl/InCl_3$, $x(InCl_3) = 0.55$, IL at 160 °C

The used catalytic IL was washed several times with hexane to purify it for the next reaction. After drying in a high vacuum it was analyzed with NMR. The 1H NMR spectrum indicated that the IL did not contain any products. In addition, indium content was analyzed from the hexane extract by elemental analysis and it showed the absence of $InCl_3$ indicating that it stayed in the IL and did not leach out from it. The IL was used again in a dimerization reaction and it catalyzed successfully the reaction. Excess $InCl_3$ did not leach out from the IL and recycling of the IL was possible. This method should be suitable for dimerizing other light olefins as well.

Xiao (2006) investigated the reusability and efficiency of ILs with and without catalysts. The recycling process involved washing the used ILs with diethyl ether. Any organic residue left in the IL layer could be separated by the ether wash. Two layers formed (IL and organics). The resulted IL layer was then separated and dried at 65 °C under reduced pressure (see Fig. 7).

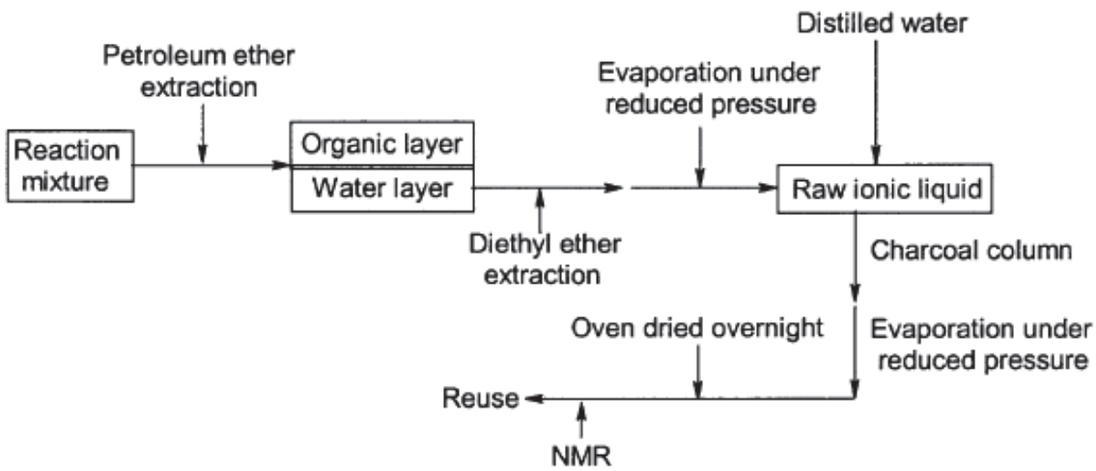


Fig. 7. Flow chart of recycling process of ILs [Xiao, 2006]

Successive runs were performed with the recovered IL, $[EtPy]^+[BF_4]^-$ or $[EtPy]^+[CF_3COO]^-$, for the Friedel-Crafts alkylation between benzene and 1-chlorobutane at 50 °C for four

hours. Table 8 shows that both ILs could be recovered quantitatively and almost without loss of activity and selectivity. This was evident from the fact that the conversion of the Friedel-Crafts alkylations was not affected even after the third run with the recovered IL.

Recycle #	Conversion [%] using $[EtPy]^+[BF_4]^-$	IL recovery [wt%]	Conversion [%] using $[EtPy]^+[CF_3COO]^-$	IL recovery [wt%]
0	45 (75)	-	55 (80)	-
1	43 (73)	94	53 (75)	93
2	44 (74)	92	51 (78)	92
3	41 (72)	93	50 (76)	93

Table 8. Recyclability of IL in the Alkylation of Benzene and 1-Chlorobutane. [Xiao, 2006]. Numbers in parenthesis isolated yields

However, yields of the IL recovery from the used $FeCl_3$ - IL system (Fig. 8) were relatively low. Table 9 shows that, although the ILs in $FeC1_3$-IL system can be recovered efficiently, the conversion dropped dramatically even with fresh $FeC1_3$. This was attributed to possible presence of some impurities in the recovered ILs. However, the product selectivity remained nearly the same [Xiao, 2006].

Recycle #	Conversion [wt%] using $FeC1_3$ - $[EtPy]^+[BF_4]^-$	IL recovery [wt%]	Conversion [wt%] using $FeC1_3$ - $[EtPy]^+[CF_3COO]^-$	IL recovery [wt%]
0	88 (87)	-	94 (94)	-
1	75 (84)	88	82 (92)	90
2	67 (83)	85	76 (90)	86
3	65 (81)	89	75 (91)	87

Table 9. Recyclability of $FeC1_3$-ILs in the Alkylation of Benzene and 1-Chlorobutane [Xiao, 2006]. Numbers in parenthesis isolated yields

[Xiao, 2006] also conducted successive runs for acylation between benzene and acetic anhydride at 50°C for four hours. Table 10 shows that both ILs could be recovered quantitatively with negligible loss of activity. Moreover, the acylation was not affected even after the third run with the recovered IL.

A similar study was also carried out with recovered $FeC1_3$-IL systems for the acylation of benzene with acetic anhydride [Xiao, 2006]. The IL recovery scheme is as presented in Fig. 8. The results of the acylation conversion using fresh IL and reused IL are shown in Table 11.

In this case, even though ILs in $FeC1_3$-IL system could be recovered efficiently, the yield of acylation product (Acetophenone) decreased gradually. This may be due to some impurities in recovered ILs.

Xiao (2006) also investigated the reusability of IL for the Friedel-Crafts reaction of N, N-dimethylaniline with ethyl glyoxylate catalyzed by the complex of (R)-BINOL-Br-Ti(O^iPr)$_4$. The recycling process involved washing the used ILs with diethyl ether. Any organic residue left in the IL layer could be separated by the ether wash. The IL layer was decanted and evaporated at 65°C under reduced pressure, then purified according to the schematic procedure shown in Fig. 9. Successive runs were performed with the recovered IL $[EtPy]^+[BF_4]^-$ or $[EtPy]^+[CF3COO]^-$ at room temperature for 24 hours.

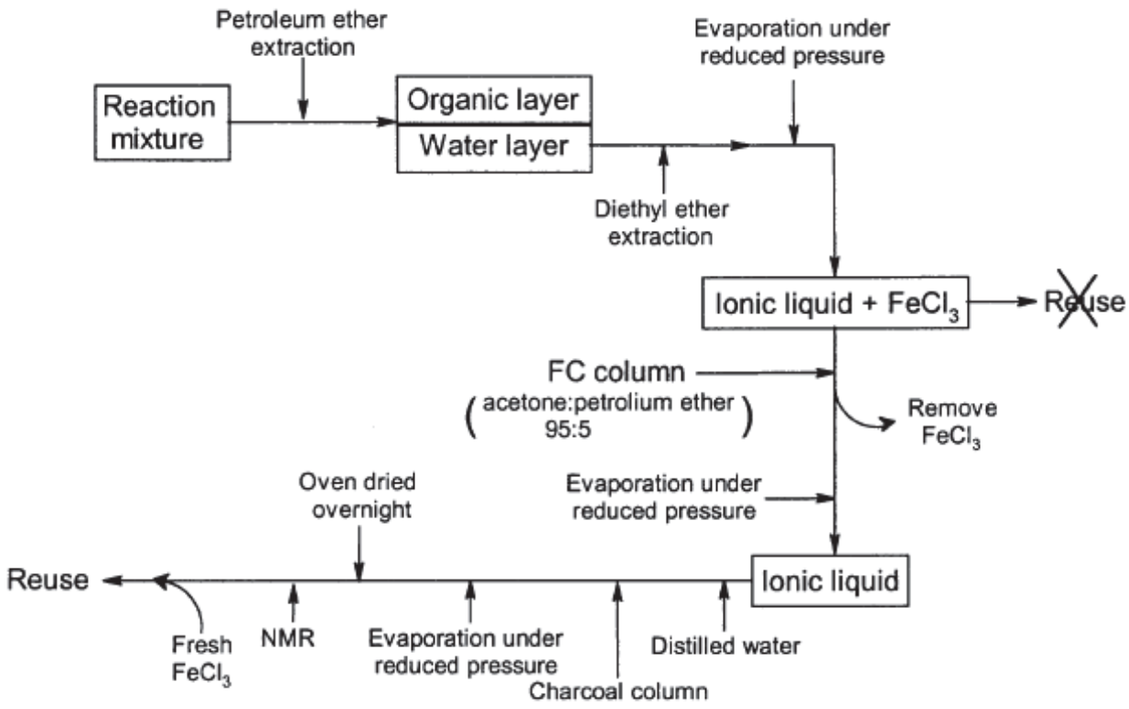


Fig. 8. Flow chart of recycling process of $FeC1_3$ - IL system [Xiao, 2006]

Recycle #	Conversion [wt%] using $[EtPy]^+[BF_4]^-$	IL recovery [wt%]	Conversion [wt%] using $[EtPy]^+[CF_3COO]^-$	IL recovery [wt%]
0	72 (97)	-	77 (99)	-
1	70 (97)	93	76 (98)	96
2	70 (95)	93	74 (97)	94
3	68 (96)	94	74 (98)	95

Table 10. Recyclability of Ionic Liquids in the Acylation of Benzene and Acetic anhydride [Xiao, 2006]. Numbers in parenthesis isolated yields

Recycle #	Conversion [wt%] using $FeC1_3$ - $[EtPy]^+[BF_4]^-$	IL recovery [wt%]	Conversion [wt%] using $FeC1_3$ - $[EtPy]^+[CF_3COO]^-$	IL recovery [wt%]
0	90 (94)	-	97 (97)	-
1	88 (91)	90	96 (94)	88
2	84 (89)	87	91 (91)	91
3	83 (88)	89	88 (92)	88

Table 11. Recyclability of $FeC1_3$-ILs in the Acylation of Benzene and Acetic Anhydride [Xiao, 2006]. Numbers in parenthesis isolated yields

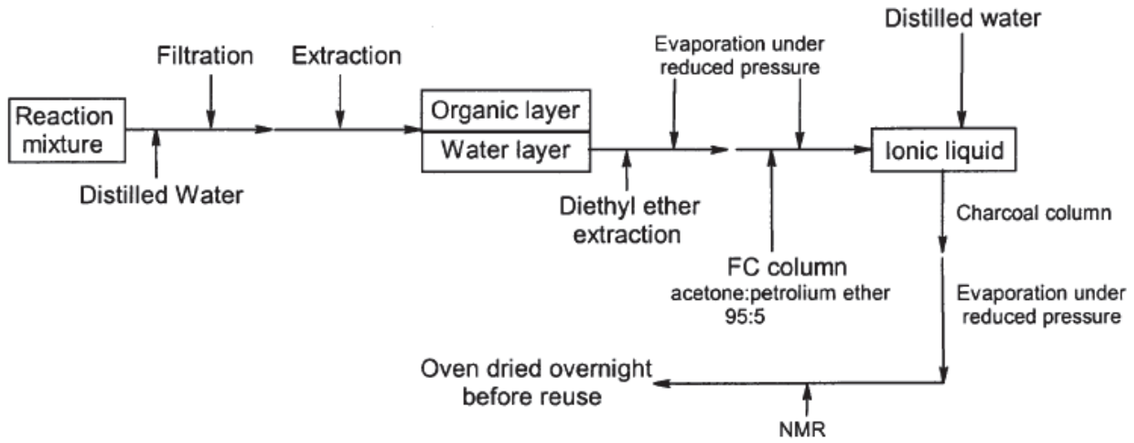


Fig. 9. Flow chart of recycling process of ILs used in the Friedel-Crafts reaction of N, N-dimethylaniline with ethyl glyoxylate catalyzed by the complex of (R)-BINOL-Br-Ti(O^iPr)$_4$ [Xiao, 2006]

Table 12 shows that both ILs could be recovered efficiently and utilized almost without loss of activity and selectivity. This is evident from the fact that the yield of the Friedel-Crafts acylations are not much affected even after the 5th run with the recovered IL.

Recycle #	Yield [wt%] using $[EtPy]^+[BF_4]^-$	IL recovery [wt%]	Yield [%] using $[EtPy]^+[CF_3COO]^-$	IL recovery [wt%]
0	74	-	86	-
1	72	92	84	93
2	73	94	83	93
3	72	91	82	92
4	71	93	83	94
5	69	92	82	92

Table 12. Recyclability and Reuse of Ils used in the Friedel-Crafts reaction of N, N-dimethylaniline with ethyl glyoxylate catalyzed by the complex of (R)-BINOL-Br-Ti(O^iPr)$_4$

Xiao (2006) also investigated the reusability of ILs for the asymmetric reduction of acetophenone catalyzed by the complex of (R)-BINOL-LAH. The recycling process involved washing the used ILs with diethyl ether. Any organic residue left in the IL layer could be removed by the ether wash. The IL layer was decanted and evaporated under reduced pressure at 65 °C, then purified according to the schematic procedure shown in Fig. 10. Successive runs were performed with the recovered IL $[EtPy]^+[BF_4]^-$ or $[EtPy]^+[CF_3COO]^-$ at room temperature for four hours.

The results show IL $[EtPy]^+[BF_4]^-$ could be recovered efficiently and almost without loss of activity and selectivity. This is evident from the fact that the yield was not affected much even after the 3rd run. In this reaction, however, $[EtPy]^+[CF_3COO]^-$ could not be recovered as efficiently as the previous cases. It may be because lithium aluminum hydride, as a powerful reductant, might react with carbonyl group of trifluoroacetate anion. The evidence is that a color change of $[EtPy]^+[CF_3COO]^-$ has been observed during experiments, which changed from colorless/light yellow to yellow, then to brown. See Table 13.

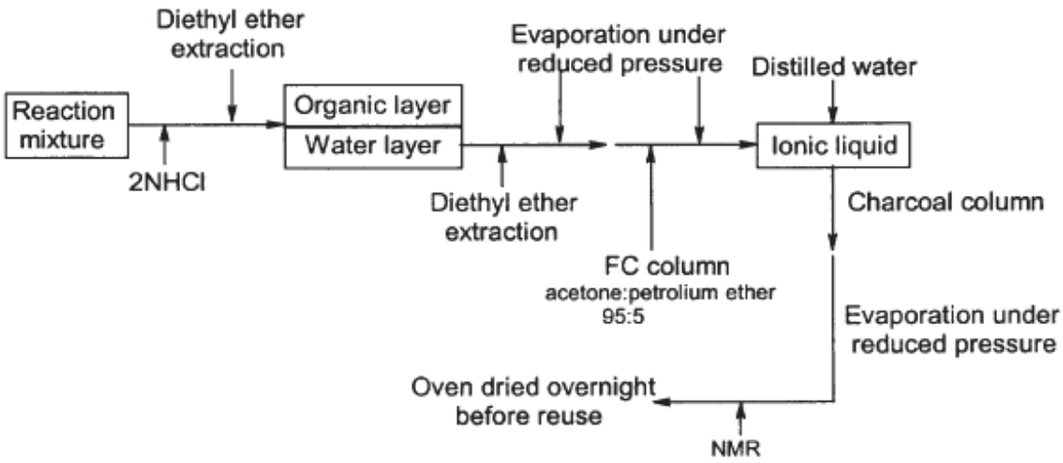


Fig. 10. Flow chart of recycling process of ILs used in the asymmetric reduction of acetophenone catalyzed by the complex of (R)-BINOL-LAH [Xiao, 2006]

Several aziridines in high yields with *cis* selectivity have been preparaed by using ILs [bmim][PF_6] and [bmim][BF_4] as reaction media. After each reaction the products were extracted with petroleum ether and ethyl acetate (5:1). It was found that the IL [bmim][PF_6] was easily recycled for five times with good conversions and high *cis* selectivities, although a gradual decrease in its activity was observed [Candeias et al. , 2009].

Recycle #	Yield [wt%] using IL $[EtPy]^+[BF_4]^-$	IL recovery [wt%]	Yield [wt%] using IL $[EtPy]^+[CF_3COO]^-$	IL recovery [wt%]
0	99	-	99	-
1	97	93	98	87
2	98	92	99	76
3	98	90	99	68

Table 13. Recyclability and Reuse of ILs used in the asymmetric reduction of acetophenone catalyzed by the complex of (R)-BINOL-LAH [Xiao, 2006]

In their reviw on the recovery of solutes extracted in ILs and regeneration of ILs, Han & Armstrong (2007) stated the following: Compounds with ionizable groups can be back-extracted into water at suitable pH values. Organic solvents that form two-phase systems with ILs can be used for the back extraction of neutral, thermally-unstable compounds [Blanchard et al., 1999; Blanchard & Brennecke, 2001]. Also the "green" solvent $scCO_2$ is a good choice for the recovery of solutes and the regeneration of ILs. $ScCO_2$ can dissolve in the ILs, while ILs cannot dissolve in $scCO_2$. This unique property means that solutes can be isolated from ILs without IL contamination. It also provides a means for recycling the ILs [Blanchard et al., 1999]. A methanol/[bmim][PF_6] mixture can be separated using pressurized CO_2 [Scurto et al., 2002]. Aromatic and aliphatic compounds were extracted into a CO_2 phase from [bmim][PF_6] [Blanchard et al., 1999; Blanchard & Brennecke, 2001].
Mekki et al. (2006) reported a two-step extraction system (water/RTIL/CO_2) for trivalent lanthanum and europium. The metal ions were extracted from the aqueous phase into $scCO_2$ via a RTIL/fluorinated β-diketonate mixture with high extraction efficiencies.

Docherty & Kulpa (2005) stated that the environmental benefits of ILs need to be carefully considered. Recent work demonstrated the toxicity of some ILs. More research is also needed on the long-term stability and recyclability of ILs. New ILs or novel applications of existing ILs can be developed that will further improve the capabilities of ILs for chemical separations. For example, the loss of ILs into aqueous media in metal ion extractions needs be suppressed.

New ILs and coating methods are being developed for high efficiency and high thermo-stability GC columns. Chiral GC stationary phases with high thermo-stability and broad enantiomeric selectivity are needed. One area that will continue to grow in importance is the use of ILs as absorbents in solid-phase extractions (SPE) and solid-phase micro-extractions (SPME). It is likely that ILs will fill the role of a polar absorbent for these techniques [Han & Armstrong, 2007].

Zhang et al. (2009) developed (3-aminopropyl) tributylphosphonium amino acid ILs for CO_2 capture, leading to 1 mol of CO_2 captured/1 mol of IL, and the ILs can be repeatedly recycled for CO_2 uptake. Nevertheless, the use of amine-functionalized ILs for CO_2 uptake shows several problems, with the main one being their high viscosities at ambient temperature, which are even larger upon complexation with CO_2 [Gutowski & Maginn, 2008]; this fact would hinder the CO_2 diffusion and uptake rate. Likewise, the synthesis of these ILs would require several synthetic steps [Bates et al., 2002], thus limiting their commercial viability [Karadas et al., 2010].

After the extraction of 5-hydroxy methyl furfural (HMF) with diethyl ether, the IL is recycled as such or after removal of the water formed during the course of the reaction (see Table 14). Such operation is rather important since three water molecules are produced during the course of the reaction. Under the operating conditions used, 5.55 mmol of fructose and 25.3 mmol of IL at 90 °C for 1 h, and although the amount of water formed after three cycles was twofold higher than that of the IL, the yield in HMF is not affected in a spectacular manner, but is more affected than after water removal where no significant loss in activity is observed within the experimental error [Moreau et al., 2006].

Recycle #	Yield of HMF [%] using as such IL	Yield of HMF [%] using after water removal IL
1	86	86
2	81	88
3	70	85
4	75	84
5	62	82

Table 14. Yield of 5-hydroxy methyl furfural (HMF) from fructose dehydration after recycling of IL 1-H-3-methyl imidazolium chloride

In order to have ILs that represent an ecological and further economic alternative to conventional solvent systems, their process advantages like solvent recovery are of particular importance. Ilgen (2009) investigated a particular process advantage of the IL $[C_6mim][BF_4]$ which was recycled and reused for 3 times. $[C_6mim][BF_4]$ was recycled via addition of cyclohexane or diethyl ether after reaction completion. The extract phase was afterwards separated. The extraction process was examined by gas chromatography, until no products or wastes were detected in the IL. Before each run, the IL was dried *in vacuo*. Mass losses and performance properties are listed in Table 15. After three recycling steps, a

mass loss of 5% was determined, while the solvent performance seems to remain unchanged [Ilgen, 2009]. Very similar results were reported for the use of the IL [C_6act like][BF_4] [Reinhardt, 2009]. See Table 16.

Recycle #	Mass loss [g]	Mass deviation [%]	Conversion of methyl acrylate [%] as determined by GC
1	-	-	92
2	0.52	3.1	96
3	0.72	4.3	97
4	0.84	5.0	97

Table 15. Mass loss and reaction conversion with recycled IL [C_6mim][BF_4] used in Diels-Alder reaction of methyl acrylate and cyclopentadiene [Ilgen, 2009]

Kralisch et al. (2007) carried out the work-up by distillation, as well as the recycling of solvents, using a rotary evaporator fitted with a water-bath, by placing 500 g of the respective solvent in a 1000 mL round bottom flask. For ethanol, n-heptane, xylene and cyclohexane, a temperature setting of T = 65 ^{o}C was chosen. Water and diethyl ether were distilled at T = 80 ^{o}C and T = 40 ^{o}C, respectively. The pressure decay was adjusted to the boiling point of the solvent.

Recycle #	Mass loss [g]	Mass Deviation [%]	Conversion methyl acrylate [%] as determined by GC
1	-	-	92.4
2	0.52	3	95.8
3	0.72	4	97.3
4	0.84	5	97.8

Table 16. Mass loss and conversion with recycled IL [C_6act like][BF_4] used in Diels-Alder reaction of methyl acrylate and cyclopentadiene [Reinhardt, 2009]

After the acetylation of cellulose, effective recycling of the solvent ILs is absolutely required. For example, at the end of the acetylation cornhusk cellulose in the presence of the IL AmimCl, the cornhusk cellulose acetates (CCA) product was precipitated with a large excess of water. The polymer was filtered off, and the residual IL in the filtrate was recovered by a simple evaporation, giving clean AmimCl. The purity of the recovered AmimCl was above 99%, confirmed by 1H NMR spectroscopy [Cao et al., 2007].
However, for the future industrial applications on a large scale, other methods suggested for removal of water may prove to be more practical [Wong et al., 2006; Swatloski et al., 2003]. These alternative methods include nanofiltration, reverse osmosis, pervaporation, and salting out of the IL. Apparently, the advantage of easy recycling of ILs will promote their industrial application in this field [Cao et al. (2007]. Based on the fact that the IL AmimCl can be effectively recycled after each acetylation, Swatloski et al. (2003) provides a technically feasible and environmentally acceptable method to prepare acetone-soluble cellulose diacetates in one step using relatively cheap cornhusk as cellulose resource.
The separation, post-reaction, of ILs and catalysts from reaction products is a challenge in the application of ILs to organometallic catalysis [Wong et al., 2006]. Suzuki reaction is a key step in the synthesis of active pharmaceutical ingredients. Separation of Suzuki reaction'

products from IL and homogeneous transition metal catalyst (TMC) via solvent extraction is the conventional choice [McNulty et al., 2002; Mathews et al., 2000; McLachlan et al., 2003] for obtaining IL (and catalyst in some cases) in a recyclable form (see Fig. 11.a). However, while solvent extraction is suitable for separation of apolar products, its use in separation of polar products is more problematic. For the latter case, a moderately polar extracting organic solvent is required, but since ILs tend to have significant partition coefficients into polar solvents, or are completely miscible with them, this can result in loss of IL to the product stream [Wong et al., 2006].

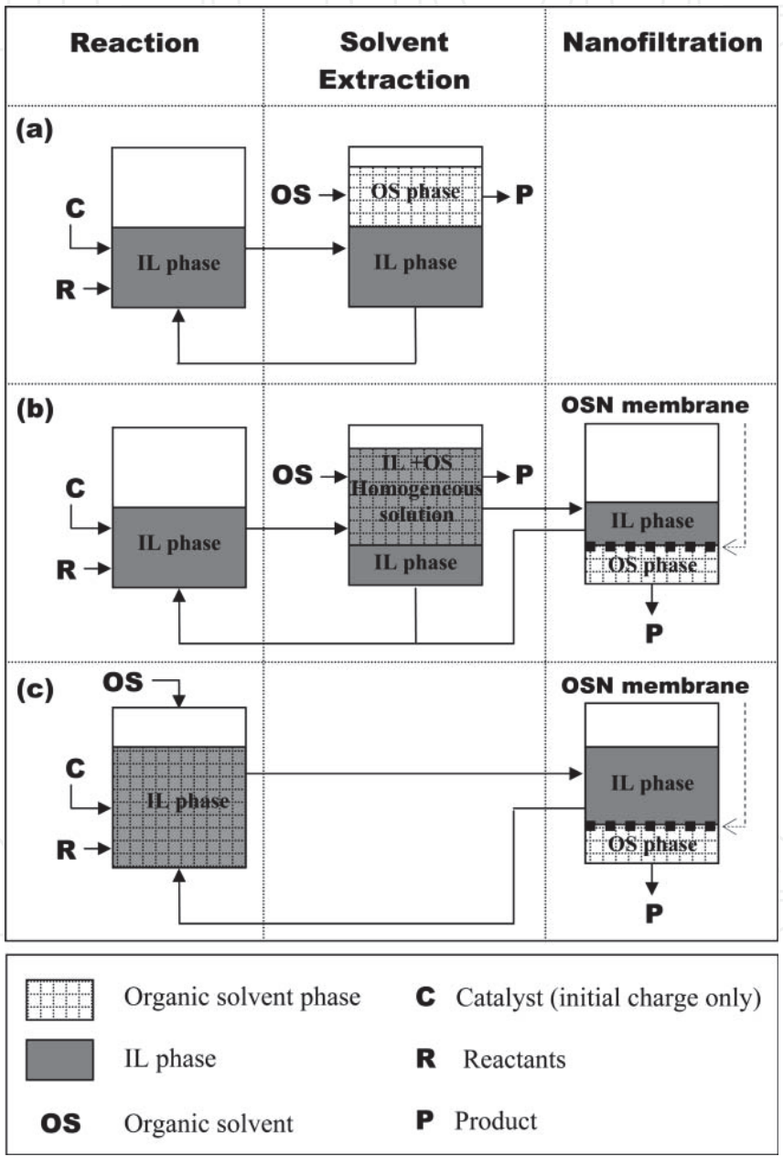


Fig. 11. Ionic liquid-transition metal catalyst recycle schemes for coupling reactions: (a) conventional product isolation via solvent extraction, (b) Organic Solvent Nanofiltration (OSN) used with a biphasic IL/organic system, and (c) Organic Solvent Nanofiltration (OSN) used with a single phase IL–organic solvent system [Wong et al., 2006].

Wong et al. (2006) stated that Organic Solvent Nanofiltration (OSN) can provide a separation solution which reduces these problematic losses. In this context, they envisaged two schemes for the use of OSN. In systems in which the IL and the moderately polar extracting solvent form a biphasic mixture, a significant amount of IL can partition into the organic solvent phase. The first scheme involves (see Fig. 11.b) separating the phases, and then applying OSN to the organic solvent phase to separate the product from the IL. The IL can be retained by the membrane, and then recycled to the reaction system. The second scheme (see Fig. 11.c) dispenses with the need for an intermediate solvent extraction. The reaction is carried out in a homogeneous solution of IL and organic solvent. The post reaction mixture is subjected to OSN, resulting in a permeate stream containing solvent and product, and a retentate stream containing solvent, TMC and IL.

Pure ILs can lower reaction rates due to unfavourable heat and mass transfer characteristics arising from their high viscosities. Using 50:50 wt% mixtures of organic solvent and miscible ILs avoided the problems associated with these high viscosities, while maintaining the beneficial effects of IL on the reaction [Wong et al., 2006]. Crucially, this means that IL can be recycled for use in subsequent reactions as a single phase mixture with organic solvent, as opposed to in the form of pure IL. In these cases, the scheme shown in Fig. 11.c is directly applicable.

Rasalkar et al. (2005) extracted the system of IL and l-proline with diethyl ether to remove all organic impurities and recharged it with a new batch of substrates. The IL acted as a reservoir for the catalyst. [MOEMIM]OMs containing l-proline was used for three runs consecutively. Though the yield of the product was comparable to that obtained in the first run, a decrease was observed in the *enantiomeric excess* of the *syn* isomer [%ee] in subsequent runs as shown in Table 17.

Recycle #	Isolated yield [%]	ee [%]
1	75	73
2	74	47
3	74	26

Table 17. Recyclability of IL and l-proline

In recent years, the use of ILs as a recyclable reaction medium, to replace volatile organic solvents has received considerable attention [Welton, 1999; Wasserscheid & Keim, 2000; Sheldon, 2001; Dupont et al., 2002]. Khan et al. (2003) recovered the ILs [bmim][PF_6] and [bmim][BF_4] used in chemoselective reduction of aromatic nitro and azo compounds using zinc and ammonium salts. After each cycle, the residue containing IL was dissolved in minimum amount of dichloromethane (CH_2Cl_2), or ethyl acetate (EtOAc), filtered through a filter paper, dried over Na_2SO_4 and the solvent was removed on a rotary evaporator. The IL was further dried at 70°C and 0.1 mmHg for 4 h. This reaction was repeated for 3 more cycles using the IL recovered from the previous run under identical conditions as for cycle 1. It was found that no decrease in yield or purity of the products when the ionic liquids were both reused. The results are listed in Table 18. The reduction of nitroarenes was performed with Zn (4 equiv.)/NH_4Cl (3 equiv.) under an inert atmosphere (in 10:1 [bmim][PF_6]/water for Method A) and (in 10:1 [bmim][BF_4]/water for Method B). The IL [bmim][BF_4] was also recycled effectively and reused for the reduction of azobenzene as shown in Table 19.

There are some disadvantages associated with the use of chloroaluminate ILs; they are moisture sensitive and cannot be recycled after the reaction. Potdar et al. (2005) adopted two

Recycle #	Yield [%], using [bmim][PF_6] (Method A)	Yield [%], using [bmim][BF_4] (Method B)
1	93	87
2	95	93
3	92	86
4	87	--

Table 18. Recyclability of ILs for the reduction of nitrobenzene to aniline

Recycle #	Yield [%] using [bmim][BF_4]
1	98
2	94
3	100
4	96

Table 19. Recyclability of the IL [bmim][BF_4] for the reduction of azobenzene

different approaches to the Pechmann condensation employing neutral ILs to establish cleaner synthetic methodologies. The IL [bmim]PF_6 that settled down, after quenching the reaction mixture with 10% aqueous NaOH solution, was extracted with dichloromethane. The dichloromethane layer was stirred vigorously with 10% aqueous NaOH in order to remove coumarin and acid traces. Further, dichloromethane layer was washed with water. The solvent was then evaporated and the resultant IL was subjected to consecutive extractions with diethyl ether to remove organic impurities present. The resultant IL was then dried under vacuum at 60 ^oC and reused for subsequent reactions. When [bmim]BF_4 IL was used for the reaction, the reactions were quenched by addition of water. The coumarin derivative separated as a solid was isolated by filtration. The IL was recovered by evaporation of water on a rotary evaporator. The IL was further purified *as per the procedure used* for the purification of IL [bmim]PF_6. Potdar et al. (2005) found that IL [bmim]PF_6 can be recycled efficiently and it was used consecutively for 3 runs without any considerable loss in its activity as shown in Table 20.

Recycle #	Yield [%] using [bmim]PF_6
1	95
2	92
3	94

Table 20. Recyclability of IL in Pechmann condensation performed at 100 ^oC

Because of their negligible vapour pressure, thermal stability and easy recyclability, neutral ILs have been referred to as environmentally benign solvents. These ILs have been employed as excellent and recyclable medium for a wide array of reactions; e.g., Heck reaction [Park & Alper, 2003], Bischler–Napierlaski cyclisation [Judeh et al., 2002], Beckmann rearrangement [Ren et al., 2001] addition of thiols to unsaturated ketones [Yadav et al., 2003] and l-proline catalysed aldol reaction [Loh et al., 2002].

5. Hydrophobic ionic liquid recycling

Among the published literature, it is generally recognized that ILs are easily recyclable. Undoubtedly, this is true for some specific biphasic systems that contain ILs, in particular for hydrophobic ILs, such as $[PF_6]^-$ and $[(CF_3SO_2)_2N]^-$ ILs [Wu et al. 2009]. In this case, liquid–liquid extraction is an efficient method for separation and has been used for recycling both the catalyst and the IL solvent in the course of palladium coupling reactions [Handy & Zhang, 2001; Mathews et al., 2000; Fukuyama et al., 2002]. The recyclability of these ILs is largely a result of their lack of solubility in some key organic solvents, such as diethyl ether. This lack of solubility allows products and residual organics to be extracted by using an organic solvent, while byproducts present in water-immiscible ILs can be washed out by using water with minimal loss of ILs [Wu et al. 2009].
In order to provide significant advantages over conventional technologies for extraction processes, Birdwell et al. (2006) developed a centrifugal solvent-extraction contactor recycle method successfully used for separation of dispersions containing immiscible organic IL/hydrocarbon/and aqueous systems. The systems tested are NaCl(aq)/$[C_4mim]NTf_2$, H_2O/$[C_4mim]$BETI and cyclohexane/$[C_4mim]$BETI (which was the most efficient, but still with slight loss of ILs).

6. Hydrophilic ionic-liquid recycling

Generally, *hydrophobic ILs* can be extracted with water to separate water-soluble solutes from the IL into the aqueous phase; however, this method is not suitable for *hydrophilic ILs*. Recovery of the hydrophilic ILs is more difficult in comparison to hydrophobic ILs, and the study in this field is in its infancy. To avoid cross-contamination of IL with water or vice versa, novel ways must be exploited. $ScCO_2$ was found to have the potential for the regeneration of hydrophilic ILs [Wu et al. 2009].

7. Membrane technology for ionic-liquid recovery

Membrane techniques have been applied to perform fine separation of undesirable constituents and these show promising results for the selective removal of volatile solutes from ILs [WO 2003/039719]. Haerens et al. (2010) investigated the use of pressure-driven membrane processes, nano-filtration, reverse osmosis and pervaporation, as a possibility to recycle ILs from water. They used Ethaline200 {a deep eutectic formed between choline chloride (a quaternary amine salt) and ethylene glycol} to perform these tests and compared their results with those found in the literature.
For concentrating ILs, the osmotic pressure was found to be the limiting factor when using nano-filtration or reverse osmosis. [Haerens et al., 2010] investigated pervaporation as an alternative and found it to have limited usability for this application as the water content was too high. For low water contents, pervaporation can be applied although the flux is very low due to the presence of the IL, which decreases the activity of the water and thus the flux through the membrane. The necessary membrane area would be very high and makes pervaporation rather impractical [Haerens et al., 2010].
The key among all performance advantages is that for the removal of salt and other materials that are in the ionic size range, only distillation processes can provide a similar level of fluid purity. Hence, this technology is vitally important in the case of recycling of ILs from nonvolatile compound/IL systems that are not suitable for distillation. Therefore, it

is necessary to explore novel membrane treatment process for IL recovery. As it is known, ILs exhibit distinctive fluid properties with high viscosity typically 2–3 orders of magnitude higher than water, rendering their separation, recovery and reuse from some reaction mixtures a difficulty [Wu et al. 2009].

ILs have been widely employed in extractions, as GC stationary phases, and as supported liquid membranes. In some cases, they can be considered "green" solvents, but they have many other benefits including unusual selectivities, high extraction efficiencies, dual-nature GC properties, durability, and resistance to thermal degradations [Han & Armstrong, 2007].

Since the phase behavior of ILs with gases will affect the attractiveness of using ILs in reactions and separations, understanding this phase behavior is of utmost importance. Anthony et al. (2002) presented the solubility of several permanent and reactive gases in various ILs and the separation of CO_2 from methane and nitrogen using ILs in a supported-liquid membrane system. They also showed that ILs can be recovered from organic or aqueous solutions using CO_2 as an anti-solvent. Solutions of ILs with organic and water can be induced to form three phases in the presence of CO_2, leading to the recovery of the ILs.

From their discussion, Wu et al. (2009) found that hydrophobic and hydrophilic ionic-liquid recycling techniques have their advantages and disadvantages. Their common drawback is that they are not amenable to industrial implementation. Membrane separation technology may be another alternative, since it is a mature technology and commercially available. Membrane separation has been widely applied in the field of water and wastewater treatment, food and beverage processing, and pharmaceutical and medical processes due to a number of performance and cost advantages over competitive technologies. Key among all performance advantages is that for the removal of salt and other materials that are in the ionic size range, only distillation processes can provide a similar level of fluid purity. Hence, this technology is vitally important in case of recycling ILs from non-volatile compound/IL systems that are not suitable for distillation. Therefore, it is necessary to explore novel membrane treatment process for IL recovery. As it is known, ILs exhibit distinctive fluid properties with high viscosity typically 2–3 orders of magnitude higher than water, rendering their separation, recovery and reuse from some reaction mixtures a difficulty [Wu et al. (2009)].

The dissolution of the hydrophilic ILs in the aqueous phase could represent a wastewater treatment challenge. Based on the inherent amphiphilic character of ILs, many measurements have been carried out to investigate the aggregation behaviour of ILs in water, which is very necessary for developing IL-regeneration methods, typically for membrane treatment technique [Wu et al. 2009].

Based on the different features of IL/H_2O mixtures with different concentrations, one can choose the most appropriate way for different IL recovery stages, leading to a combination of methods. For instance, in water- and ion-rich regions, in which the hydrated ions have a small radius but large ionization degree, the first choice may be electrodialysis technology, because this technology has been well developed, and it is energy-saving when the solution concentration is low. This also makes use of the property of ILs, that is, they composed entirely of ions. After the solution is concentrated in the salt-region, in which the target compound has a larger radius, then membrane separation can be employed; one can even use vacuum distillation at this stage. There are several different possible combinations and how to put every unit organically together to form a continuous process is open for debate. Certainly, the choice of any combination must be made on the basis of economical comparison and analysis [Wu et al. 2009] and more work is needed.

Gordon (2001) attempted to recycle the catalyst/IL system, but after the third cycle a decrease in yield and increase in reaction time was observed, suggesting that catalyst decomposition or leaching was occurring. Xiao & Malhotra (2005) recycled catalyst/IL systems to investigate the reusability and efficiency of ILs, with or without catalyst. Two ILs were examined, namely, $[EtPy]^+[BF_4]^-$ and $[EtPy]^+[CF_3COO]^-$. The recycling process involved washing the used ILs with diethyl ether to remove any leftover organic residues. Two layers formed (IL and organic). The resulted ILs were separated and the IL dried under reduced pressure at 65°C. Successive runs were used for acylation of benzene with acetic anhydride at 50 °C for 4 h. It is clear from the results are shown in Table 21 that both ILs could be recovered quantitatively with negligible loss of activity. Moreover, the acylation was not affected even after third run with the recovered IL.

Recycle #	Isolated yield of Acetophenone [%] using $[EtPy]^+[BF_4]^-$	IL Recovery [wt%]	Isolated yield of Acetophenone [%] using $[EtPy]^+[CF_3COO]^-$	IL Recovery [wt%]
0	70	–	76	–
1	68	93	75	96
2	67	93	72	94
3	65	94	73	95

Table 21. Recycling of ILs in the acylation of benzene with acetic anhydride [Xiao & Malhotra, 2005]

Xiao & Malhotra (2005) also carried out a similar study with the recovered $FeCl_3$-IL system, for the acylation of benzene with acetic anhydride. The results in Table 22 show that even though $FeCl_3$-IL system could be recovered efficiently, the conversion to acylation product dropped dramatically and the conversions obtained after the third trial were nearly the same as seen with pure IL alone (Table 21). This could be due to a loss in the catalytic activity of the $FeCl_3$-IL system [Xiao & Malhotra, 2005].

Recycle #	Isolated yield of Acetophenone [%] using $FeCl_3$ - $[EtPy]^+[BF_4]^-$	IL Recovery [wt%]	Isolated yield of Acetophenone [%] using $FeCl_3$ - $[EtPy]^+[CF_3COO]^-$	IL Recovery [wt%]
0	85	–	94	–
1	80	90	90	88
2	75	87	83	91
3	73	89	81	88

Table 22. Recycling of ILs-$FeCl_3$ in the acylation of benzene and acetic anhydride

Based on their good thermal stability, no vapor tension and no azeotrope formed, ILs may be separated from the products. Xie & Shi (2010) attributed the suitability of ILs for wood liquefaction to the functional groups of the ILs. After wood liquefaction in [BAIM][Cl/$AlCl_3$] or [BAIM][Cl] ILs, the product solution was extracted three times with ethyl ether at room temperature, and then dissolved in 1:1.6–1.8 volume ratio of acetonitrile: ethyl acetate and frozen at -20 °C for 24 h. Coarse ILs were dried at 90 °C under vacuum for 8 h. The results of reuse of the recycled ILs in wood liquefaction are shown in Table 23. It was found that both [BAIM][Cl] and [BAIM][Cl/$AlCl_3$] can be recycled (no less than five times) to maintain the original level of wood liquefaction rate with hardly any change in the activity of liquefaction [Xie & Shi, 2010].

Recycle #	Wood residue [%] using [BAIM][Cl] at 90 °C	Wood residue [%] using [BAIM][Cl/$AlCl_3$] at 70 °C
1	97.3	14.4
2	97.4	14.7
3	97.7	14.8
4	97.9	14.7
5	98.2	14.9

Table 23. Results of wood liquefaction using recycled ILs at a liquid/wood ratio = 6.5 and after 30 min

Li et al. (2010) reported on the dissolution of wood species in the ionic liquid [AMIM]Cl. The filtrate (after separating the regenerated wood) was condensed by rotary evaporation, dried under vacuum at 40 °C overnight to recycle the IL. It was found that as the reuse cycles of the IL increased, the wood regeneration yield increased, while certain wood components enriched within the recycled IL and the efficiency of cellulase enzymatic hydrolysis on the regenerated wood decreased.

8. Conclusions

Several procedures for the recycling of ILs have been reported in the literature. Depending on the IL used and the application performed on it, a variety of recycling methods were possible. By picking the right purification steps, an individually optimized work-up procedure can be obtained [Wasserscheid & Welton, 2008]. In this survey several procedures have been reported on how to recover ionic liquids from their solution. Among these methods are distillation/stripping at some suitable temperature (< 300 °C) and under vacuum, liquid-liquid extraction (using objectionable VOCs!), supercritical fluids (using CO_2 at room temperature and several MPa), and membrane separation (to separate nano size particles from ILs).

It was clear that ionic liquids will not provide advantages in all systems, but improvements in reactivity or selectivity are observed in many cases when the appropriate combination of cation and anion are selected [Gordon, 2001]. Despite this, the two factors that will ultimately decide whether reaction systems, when ILs are used, are viable on a larger scale are likely to be the ability to reuse the catalyst without a decrease in its activity, and whether the products can be separated efficiently without contamination from the ionic liquid or the catalyst. The combination of $scCO_2$ and ionic liquids seems to be a very promising approach to attain this goal. The simultaneous efficient nano-filtration recycling of ILs and homogeneous catalysts extends the possibilities of the practical application of these media in organic synthesis [Volkov et al. 2008]. Destruction of ILs and removal of extracted organic contaminants by photolytic degradation is possibly another method of recycling ILs [Yang & Dionysiou, 2004; Khodadoust et al., 2006].

Due to the current market size and the relatively high cost of ILs, the industrial production of ionic liquids is still small or limited to lab-scale (and sometimes pilot scale) applications and hence no industrial technology is yet available for ionic liquids recycling with the objective of reuse. Most of the published works on ionic liquids recycling are made at the bench scale where the investigators are trying to extract a solute from a mixture using some suitable ionic liquid then recover the ionic liquid for further reuse. The number of trial cycles in most cases was very few (3 to 5). Some other researchers were trying to recover a

catalyst from a reaction mixture where some ionic liquid was used. In this case, both the catalyst and the ionic liquid have to be recovered and recycled to the process for further cycles of the reaction. Again, the number of cycles was, in most cases, between 3 and 5.
Someone might say: If the customer does not feel comfortable with the task of recycling the IL, then why not rent or lease the IL rather than buy it? The customers, in this case, perform their application with the IL and send, the probably impure, IL back to the supplier, who has the expertise to recycle and clean it up [Wasserscheid & Welton, 2008]. This scenario could be interesting from an economic point of view for truly commercial applications on a large scale. But transferring of such possibly hazardous and contaminated materials from one place, or country, to another is not safe. Thus I think the recycling methods must be available and practicable for both parties; the customer and the supplier.
In summary, many authors and researchers agree that we are only at the very beginning of understanding the recyclability of ILs based on the available literature in the various application fields. Understanding of ILs volatility, purity, stability, biodegradability and toxicity is necessary for their recovery, since this determines whether an IL can be sustainably developed. In other words, there is a long way to go before large-scale implementation of ILs. Hopefully, this review could provide some clues to support a great deal of future research on ILs recycling and reuse.

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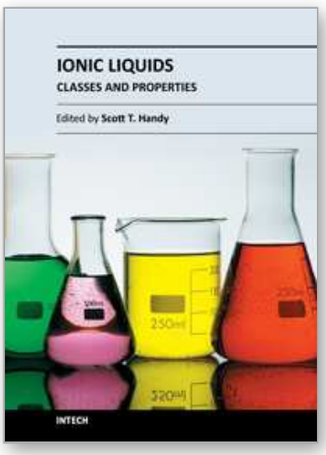
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Room temperature ionic liquids (RTILs) are an interesting and valuable family of compounds. Although they are all salts, their components can vary considerably, including imidazolium, pyridinium, ammonium, phosphonium, thiazolium, and triazolium cations. In general, these cations have been combined with weakly coordinating anions. Common examples include tetrafluoroborate, hexafluorophosphate, triflate, triflimide, and dicyanimide. The list of possible anionic components continues to grow at a rapid rate. Besides exploring new anionic and cation components, another active and important area of research is the determinination and prediction of their physical properties, particularly since their unusual and tunable properties are so often mentioned as being one of the key advantages of RTILs over conventional solvents. Despite impressive progress, much work remains before the true power of RTILs as designer solvents (i.e. predictable selection of a particular RTIL for any given application) can be effectively harnessed.

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