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Ionic Liquid-Mediated Liquid-Liquid Extraction

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1. Introduction

Liquid-liquid extraction is an important kind of separation method that is based on the distribution of chemicals between two different liquid phases. Compared to other separation methods, liquid-liquid extraction often has unique advantages for the separation of chemicals that have high or similar boiling points, with relatively large capacity and low consumption of material and energy (Treybal, 1951). However, the kinds of extractants that could be used for liquid-liquid extraction process are relatively small at present, so only limited separation efficiency could be achieved for the separation of many mixtures, especially those having similar structures. Besides, the volatility of existing extractants or extraction solvents not only can bring contamination to the environment, but also can lead to difficulty on the recovery of extractant and subsequent purification of products when the solutes are also volatile. These problems have limited the application of liquid-liquid extraction to more separation processes.

Using ionic liquids (ILs) as extractants may be a prospective solution to the above problems. The physicochemical properties of IL could be designed and adjusted task-specifically, so large separation selectivity may be achieved for various mixtures that need to be separated (Han & Armstrong, 2007). Moreover, the cohesive energy of ILs is always very large, so ILs are easy to form various immiscible liquid-liquid biphasic systems with other solvents (Marcus, 2010). Besides, the vapor pressures of ILs are extremely low, so ILs could be regarded as green extractants and the separation of ILs with volatile solutes could also be simplified (Welton, 1999). These characteristics have made ILs appropriate to be used as extractants in liquid-liquid extractions.

Liquid-liquid extraction using IL as extractant has been studied by many researchers in recent years since the partition of substituted-benzene derivatives between water and a hydrophobic IL 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim]PF_6$) was initially reported (Huddleston et al., 1998). These studies include the removal of sulfides and nitrides from diesel and gasoline (Holbrey et al., 2008; Xie et al., 2008), the separation of aromatics from aliphatics (Meindersma & de Haan, 2008), the removal of pollutants from water (Egorov et al., 2008; Vijayaraghavan et al., 2006), the isolation of biological substances from aqueous mixtures (Wang et al., 2007), the extraction of glycerol from biodiesel (Abbott et al., 2007), the extractive essential oil terpenless (Arce et al., 2006), and so on. From those works, ILs have been revealed to have the strong ability of interacting with organic

molecules through various mechanisms (e.g., π - π , dispersion, ionic exchange, hydrogen bonding). Moreover, these interactions can be finely adjusted by the change of IL's cation or anion task-specifically, thus often bringing on elevated separation efficiency compared with traditional solvents. IL-mediated liquid-liquid extraction has been studied not only at a lab scale but also a pilot scale, and has exhibited a great prospect for the industrial application. In this chapter, three subtopics will be introduced subsequently: liquid-liquid equilibrium of IL-molecular solvent mixtures; applications of IL-mediated liquid-liquid extraction; investigation of IL-solute interaction by quantum chemistry method. The extraction of metal ions, sulfides and nitrides using ILs as extractant are not included in this chapter because they are introduced in other chapters of this book.

2. Liquid-liquid equilibrium of ionic liquid-molecular solvent mixtures

Liquid-liquid extraction is a kind of separation technology based on immiscible liquid-liquid biphasic systems, so the liquid-liquid equilibrium of the mixtures consisted of IL with traditional molecular solvent has to be investigated. Currently, the liquid-liquid equilibrium of both binary and ternary IL-solvent mixtures has been reported.

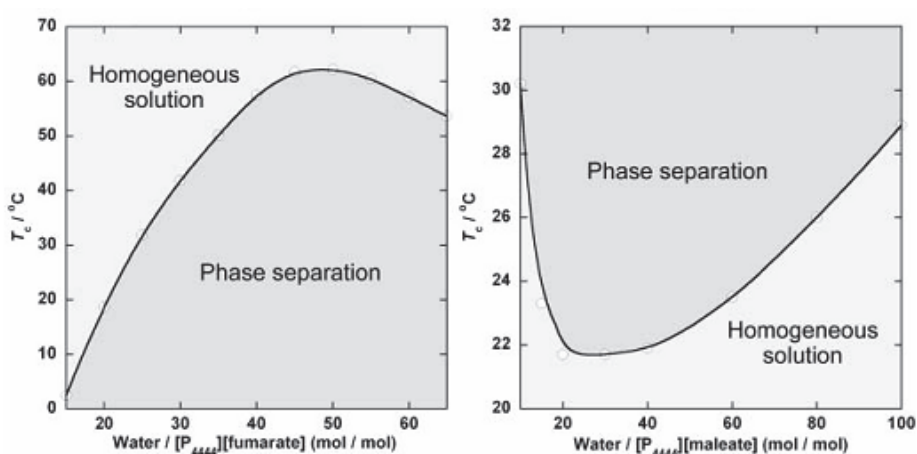


Fig. 1. Phase transition temperature T_c for ionic liquids/water mixtures at different water content. Left: tetra-*n*-butylphosphonium fumarate-water mixtures, UCST. Right: tetra-*n*-butylphosphonium maleate-water mixtures, LCST. Reprinted from reference which is downloaded from www.rsc.org (Fukaya et al., 2007).

As for the binary mixtures, liquid-liquid equilibrium has been reported for the mixtures of IL plus water, aliphatic alcohol, alkane, alkene, halogenated hydrocarbon, etc. (Crosthwaite et al., 2004; Domanska et al., 2006; Shiflett et al., 2009). Because ILs often have a relatively large polarity, the interaction between ILs and weak-polar solvents are often not strong and liquid-liquid biphasic systems with low immiscibility can be formed between ILs and those solvents. Different types of solubility curve have been found for IL-solvent binary mixtures. Most of the IL-solvent mixtures have a solubility curve with an ultimate critical solubility temperature (UCST). IL-aliphatic alcohol mixtures are typical examples that possess UCST-type solubility curves (Crosthwaite et al., 2004). In the immiscible region, the content of IL in the alcohol-rich phase is quite low. However, the content of alcohol in the IL-rich phase is much higher and could not be ignored. Due to different intermolecular interactions such as hydrogen-bonding, π - π and Van der Waals, the phase equilibrium can be effected by various

structural factors, including the alkyl side chain length of IL's cation, the kind of IL's anion, the length of alcohol, the branching of alcohol, and so on. Solubility curves with a lower critical solution temperature (LCST) were found for several IL-solvent mixtures. Ohno et al. found LCST in the mixtures of water plus amino acid-functionalized ILs those possess a carboxyl group in the anion (Fukumoto & Ohno, 2007), as well as the mixtures of water plus tetra-*n*-butylphosphonium maleate (Fukaya et al., 2007, Figure 1). The mixtures of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ($[C_n\text{mim}]\text{NTf}_2$) plus aromatics may have different phase diagrams depending on the length of alkyl chain in the cation (Lachwa et al., 2006), whose solubility curve could change from LCST type to UCST type with the increase of chain length.

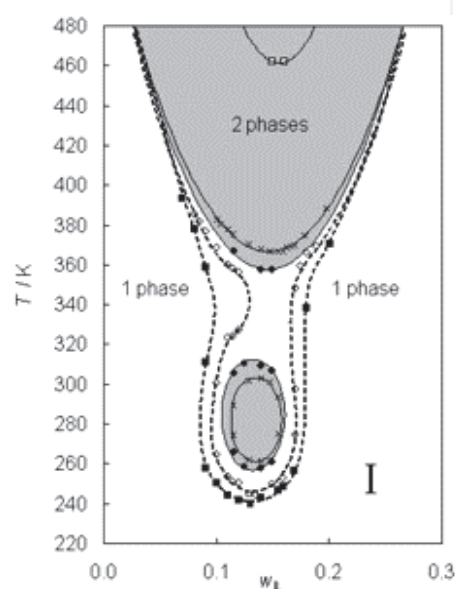


Fig. 2. Phase equilibria of $[C_n\text{mim}]\text{NTf}_2\text{-CHCl}_3$ mixtures; w_{IL} is weight fraction of IL. (\square) $n = 5.000$; (\times) $n = 4.337$; (\bullet) $n = 4.330$; (\circ) $n = 4.320$; (\blacksquare) $n = 4.300$. The shaded areas depict the demixing regions for $n = 4.330$. Reprinted from reference which is downloaded from pubs.acs.org (Lachwa et al., 2005).

Liquid-liquid equilibrium of IL-molecular solvent ternary mixtures has also been determined. Those mixtures are usually consisted of one IL and two molecular solvents, such as IL + aromatic + aliphatic, IL + ether + alcohol, IL + alkane + alkene, and so on (Arce et al., 2004; Letcher & Deenadayalu, 2003). In fact, most of those works are also complete liquid-liquid extraction studies themselves, where distribution coefficients and selectivity can be obtained directly from the triangle phase diagrams. Besides, Swatloski et al. studied the phase equilibrium of $[C_4\text{mim}]\text{PF}_6$ + ethanol + water ternary mixture (Swatloski et al., 2002). Although $[C_4\text{mim}]\text{PF}_6$ could not be fully miscible with either ethanol or water, it could be fully miscible with the mixture of ethanol + water when the composition of the ethanol-water mixture was within certain range. With the increase of water content in the $[C_4\text{mim}]\text{PF}_6$ + ethanol + water mixture, the UCST of mixture decreased first and then increased (Najdanovic-Visak et al., 2002). Therefore, through adjusting the content of water and ethanol in the $[C_4\text{mim}]\text{PF}_6$ + ethanol + water system, different kinds of liquid-liquid biphasic systems including fully miscible, partially miscible and fully immiscible systems could be obtained. Phase diagrams containing a closed loop at low temperature and a high-

temperature immiscible region were found in the ternary or so-called *quasi*-binary mixtures of $[C_n\text{mim}]\text{NTf}_2$ plus chloroform (Figure 2), where n was not a integer due to the mixing of two different ILs that had different n values (Lachwa et al., 2005). The closed loop was accounted the result of a delicate balance between enthalpic and entropic contributions to the Gibbs energy of a mixture.

3. Applications of ionic liquid-mediated liquid-liquid extraction

3.1 Extraction of organic compounds from aqueous phase

Extensive studies have been conducted for the extraction of organic compounds from aqueous phase with ILs, depending on the affinity between hydrophobic ILs and organic solutes. The extraction mechanism includes ion exchange, hydrogen bond, Van der Waals interaction, and so on.

Khachatrya et al. reported the extraction of phenolic compounds from aqueous solution into $[C_4\text{mim}]\text{PF}_6$, in which the solutes could be extracted nearly quantitatively at $\text{pH} < \text{pK}_a$ (Khachatryan et al., 2005). The relatively large distribution coefficient of phenolate anions indicated the ion exchange mechanism in the extraction that when phenolate anion entered into the IL phase, an equal amount of hexafluorophosphate anion was transferred to water.

The performance of a neutral IL *N*-butyl-*N*-methyl pyrrolidinium bis(trifluoromethanesulfonyl)amide as extractant was studied by Vijayaraghavan et al. for the removal of azo dyes from aqueous solutions (Vijayaraghavan et al., 2006). During the extraction, the azo dye went into the organic phase in its ionic form, and the distribution coefficient of the dye between IL and water was about 2.0. Repeated extractions (two to three times) with fresh IL proceeded to a removal fraction about 95% of the dyes from aqueous phase into the IL phase. The ion exchange mechanism was suggested again by Li et al. when investigating the extraction process of acid dyes from aqueous solution into $[C_4\text{mim}]\text{PF}_6$ (Li et al., 2007), in which the solvated part of IL played an important role as counter-ions for the anions of acidic dyes. Fan et al. investigated the suitability of imidazolium-based ILs, 1-methyl-3-alkylimidazolium hexafluorophosphate ($[C_n\text{mim}]\text{PF}_6$, $n = 4, 6, 8$) and 1-methyl-3-alkylimidazolium tetrafluoroborate ($[C_n\text{mim}]\text{BF}_4$, $n = 6, 8$), as a substitute for volatile organic solvents in the liquid-liquid extraction of selected phenols from aqueous solutions (Fan et al., 2006). The selected phenols included phenol, bisphenol A, pentachlorophenol, 4-octylphenol and 4-nonylphenol. A deep analysis of experimental results suggested the existence of strong hydrogen-bonding interaction between the anions of ILs and the phenols, which contributed to the high extraction efficiency of ILs for the phenols. As a result, the value of distribution ratio for phenol into $[C_n\text{mim}]\text{BF}_4$ was about 10 times as high as that into dichloromethane under the same conditions. The effect of aqueous phase pH on the partitioning of an indicator dye, thymol blue, was studied by Visser et al (Visser et al., 2000). A remarkable dependence of distribution ratio between $[C_n\text{mim}]\text{PF}_6$ and water on the pH value was revealed, suggesting a possible approach of separating ILs and extract after extraction (Figure 3).

Besides the extraction of organic pollutants from aqueous solutions, ILs can be also applied to the extraction of target products in biological conversion and separation process. For example, several ILs were reported as extractants to separate antibiotics and proteins from aqueous solutions (Cull et al., 2000; Tzeng et al., 2008).

Aqueous two-phase systems (ATPS) composed of salt solution and ILs can find its utilization in the extraction of certain organic compounds. For example, ATPS formed by

[C₄mim]BF₄ and KH₂PO₄ could be used to extract bovine serum albumin (Deng & Guo, 2006). High extraction efficiency could be achieved under the following conditions: the concentration of KH₂PO₄ was 80 g/L, the concentration of [C₄mim]BF₄ was in the range of 160-240 mL/L, the concentration of BSA was 30-50 mg/L, the acidity of the solution was pH = 4-8. Also, ATPS formed by [C₄mim]BF₄ and KH₂PO₄ exhibited high extraction efficiency of separation of penicillin G (Liu et al., 2005).

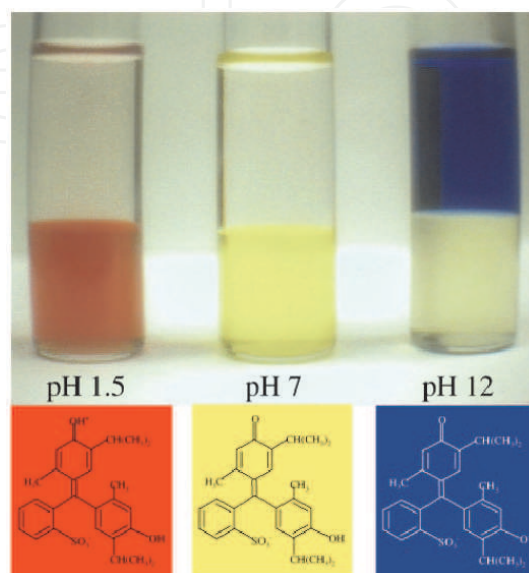


Fig. 3. Distribution of thymol blue in [C₄mim]PF₆-water biphasic system at different pH. Reprinted from reference which is downloaded from www.rsc.org (Visser et al., 2000).

3.2 Separation of mixtures with close boiling points and azeotropes

Extractive distillation serves as a useful solution for the separation of azeotropic mixtures and mixtures consisted of components which have small relative volatilities. The frequently-used extractants refer to solid salts and organic liquids. While the solid salts can corrode and block the distillation towers and the pipes, the volatility of organic liquids leads to larger solvent and energy consumption. ILs are liquid organic salts with negligible vapor pressure, so they can be used to overcome these shortages. Pereiro et al. studied the performance of 1-hexyl-3-methylimidazolium hexafluorophosphate ([C₆mim]PF₆) and 1-butyl-3-methylimidazolium methyl sulfate [C₄mim]CH₃SO₄ in the removal of heptane from its azeotropic mixture with ethanol (Pereiro et al., 2006; Pereiro & Rodriguez, 2008). Hu et al. studied ILs with tetrafluoroborate anion as solvent to separate ethyl acetate from its azeotropic mixture with ethanol (Hu et al., 2008), which included ILs 1-ethyl-3-methylimidazolium tetrafluoroborate ([C₂mim]BF₄), 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([C₂OHmim]BF₄), 1-ethyl-2,3-dimethylimidazolium tetrafluoroborate ([C₂dmim]BF₄) and 1-(2-hydroxyethyl)-2,3-dimethylimidazolium tetrafluoroborate ([C₂OHdmim]BF₄). It was found that the separation efficiency could be influenced by the hydrogen bond basicity of anions, the acidity of hydrogen at the C2 position of imidazolium ring, and the alkyl chain length of imidazolium cation (Figure 4). Seiler et al. showed the excellent performance of [C₂mim]BF₄ as entrainer for the separation of ethanol/water mixture. Compared to a conventional entrainer 1,2-ethanediol, [C₂mim]BF₄ could dramatically reduce the energy consumption of the separation process.

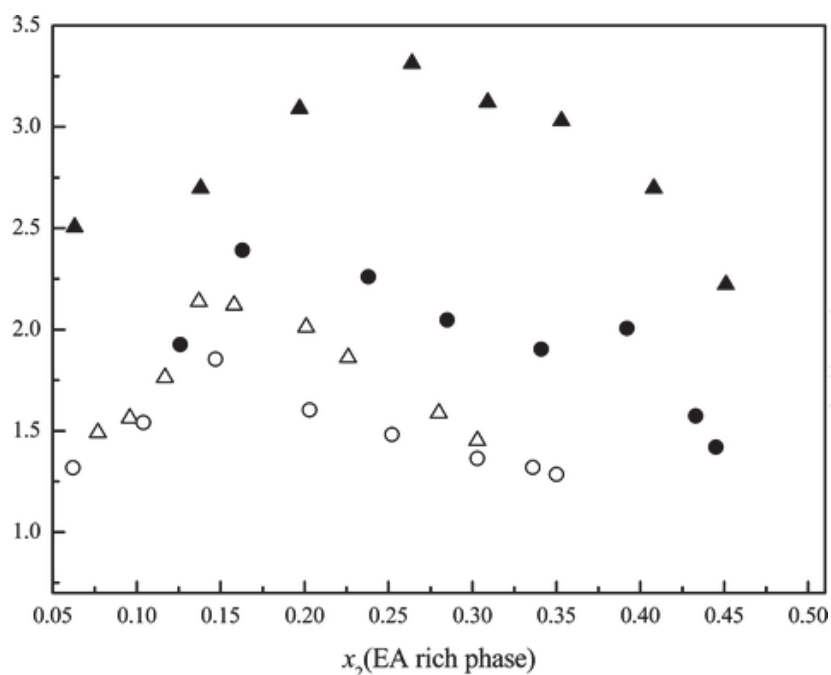


Fig. 4. Extraction selectivity of ethanol and ethyl acetate with different ILs. ▲, $[C_2OHmim]BF_4$; ●, $[C_2OHdmim]BF_4$; Δ, $[C_2mim]BF_4$; ○, $[C_2dmim]BF_4$. x_2 is the mole fraction of ethanol. Reprinted from reference which is downloaded from pubs.acs.org (Hu et al., 2008).

Since the boiling points of aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylene) and aliphatic hydrocarbons with four to ten carbons are really close (some even form azeotropic mixtures), it's of great difficulty to separate them from each other. For now, the common separation method in industry is liquid-liquid extraction with organic solvents such as *N*-methylpyrrolidone and sulfolane as extractant (Chen et al., 2000; Krishna et al., 1987), which often have low separation selectivity and high energy consumption. Nevertheless, the unique structure of ILs qualifies them as an alternative extractant for separation of aromatic and aliphatic hydrocarbons. On the one hand, one or more unsaturated functional groups in the structure of ILs entitle them to form π - π interaction with aromatic hydrocarbons, leading to a peculiar affinity of aromatic hydrocarbons for ILs. On the other hand, the relatively strong polarity of ILs induces a small solubility of alkanes. Meindersma et al. have given their efforts to the extraction of aromatics from aromatic/aliphatic mixtures in recent years (Meindersma et al., 2005; Meindersma et al., 2006; Meindersma et al., 2006; Meindersma & de Haan, 2008; Onink et al., 2010). They selected 4-methyl-*N*-butylpyridinium tetrafluoroborate ($[mebupy]BF_4$), 1-methyl-3-methylimidazolium methylsulfate ($[mmim]CH_3SO_4$) and several other ILs as novel extractants to separate toluene/heptane mixtures. The result showed that the separation selectivity when using IL as extractant could be 1.5 to 2.5 times higher than that when using sulfolane and the increase of polarity of ILs (i.e., the reduction of alkyl length on the cation, introduction of polar functional groups such as hydroxyl group) could improve the selectivity (Figure 5). What's more, since ILs are nearly non-volatile, the regeneration of ILs could be achieved by simple flash evaporation, which dramatically reduced the energy consumption compared to the distillation of sulfolane. Pilot research in a rotary disk column has been conducted and inspiring result was obtained.

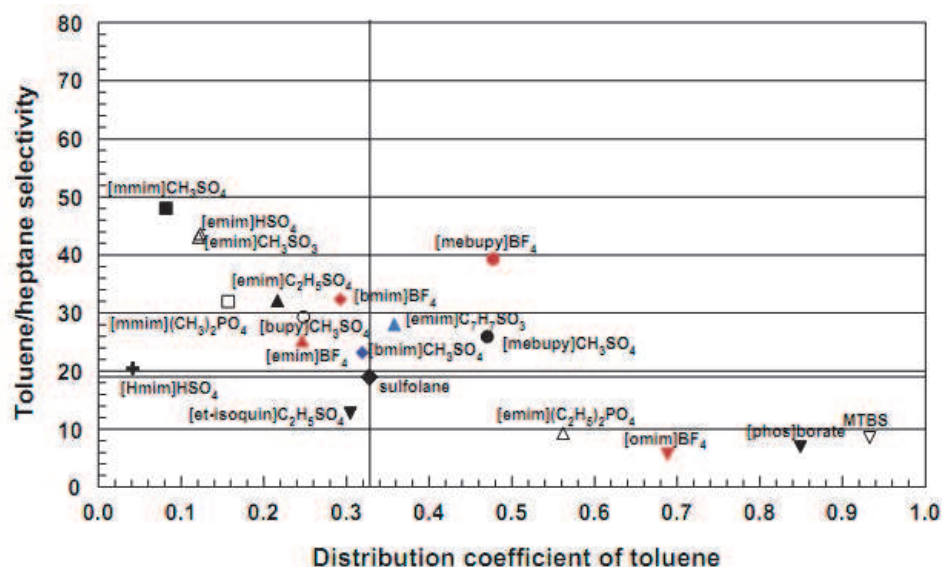


Fig. 5. Toluene/heptane separation with ionic liquids or sulfolane. Reprinted from reference which is downloaded from www.elsevier.com (Meindersma et al., 2005).

3.3 Separation of structurally related natural compounds

There is a growing interest in obtaining organic products from natural resources in recent years. Many of these natural products have certain physiological activities, which makes them as preferable components of medicine, health products and cosmetics. However, a common problem existing in obtaining chemicals from natural resources is that the product of interest often appears in a mixture with various structurally related compounds (Chen & Payne, 2001), so the effective separation of them is necessary and challenging (Sticher, 2008). For now, the widely-used methods for separating structurally related natural compounds are adsorption methods which base on the distribution equilibrium of chemicals between a solid adsorbent and a liquid solvent. Nevertheless, these methods have some shortages. First, since the active chemical structures are just located at the surface of solid adsorbent, their apparent density is very small, leading to a low throughput capacity and a large solvent consumption and energy consumption. Second, since the adsorbents always possess a lot of minute pores but the natural compounds often have a relatively large molecular size, the diffusion and transmission of compounds are difficult, which can improve the consumption of solvent and energy again. Although new approaches such as simulated moving bed chromatography and supercritical fluid chromatography could improve separation efficiency to some extent, they are not widely-used because of their requirement for special equipment (Rajendran et al., 2009; Taylor, 2009). So, novel separation methods besides adsorption are still desired.

Liquid-liquid extraction using ILs as extractant have been applied for the separation of structurally related natural compounds. Arce et al. studied the separation of limonene and linalool by extraction, using organic solvents or ILs as extractant (Arce et al., 2006). The separation of linalool from limonene is necessary for the production of citrus essential oil, and the common method is distillation. However, essential oils can be damaged by distillation, so liquid extraction may be a good alternative. Six types of organic solvents, and one type of IL were used as extractant in extraction, including 2-butene-1,4-diol, diethylene glycol, 1,2-propanediol, 1,3-propanediol, 2-aminoethanol, ethylene glycol, and 1-ethyl-3-methyl-

imidazolium methanesulfonate ($[\text{C}_2\text{mim}]\text{OMs}$). Based on the measured distribution ratio and selectivity (Figure 6), extraction process simulations were conducted for using these solvents. As shown by the results, although the IL did not get the highest linalool recovery, it provided the highest purity. Li et al. studied the extraction of α -tocopherol by IL-modified SBA-15 adsorbent (Li et al., 2008). Although the process seems not liquid-liquid extraction but solid-phase extraction from the macroscopic view, the mechanism is still based on the distribution of chemicals between IL and organic solvent. Very high adsorption selectivity for α -tocopherol was achieved by using 1-ethyl-3-methylimidazolium aminoacetate ($[\text{C}_2\text{mim}]\text{Gly}$)/SBA-15 as adsorbent, in which $[\text{C}_2\text{mim}]\text{Gly}$ was a kind of amino acid-functionalized IL possessing a glycine anion. The separation selectivity of α -tocopherol to the major interference component glyceryl triundecanoate was 10.5 and the concentration of α -tocopherol was elevated from 15.7% in the feedstock to 73.0% after stripping by diethyl ether in the first cycle.

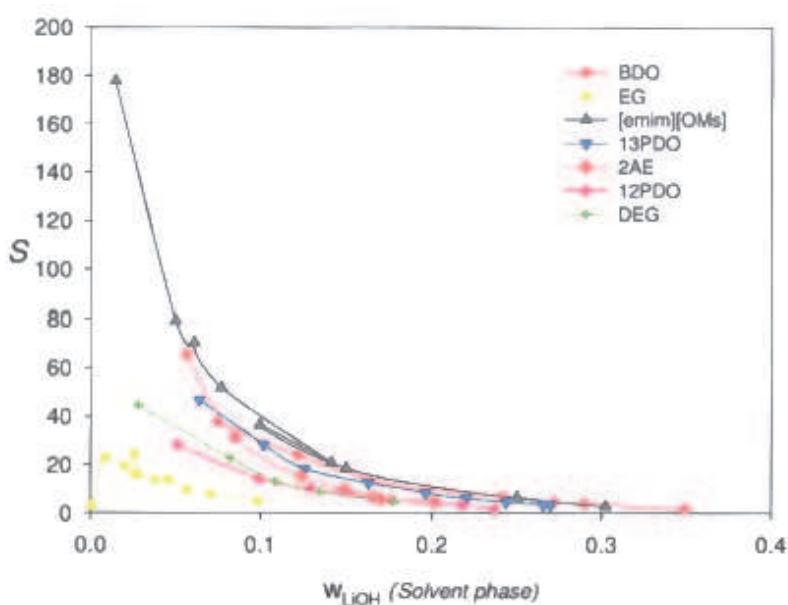
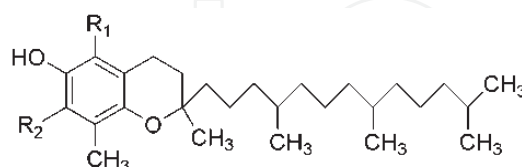


Fig. 6. Selectivity S for different solvents to extract linalool from its mixtures with limonene at 298.15 K. Reprinted from reference which is downloaded from onlinelibrary.wiley.com (Arce et al., 2006).

The separation of tocopherol homologues by IL-mediated liquid-liquid extraction have been investigated by Yang et al. in recent years and will be introduced in more detail hereinafter. Tocopherols are the main compositions of natural Vitamin E and play an important role in human health due to their antioxidative capacity and ability to act as free radical scavenger (Packer, 1984). Tocopherols are widely contained in many vegetables and fruits, and can be extracted as a mixture of four different homologues, viz. α -, β -, γ - and δ -tocopherol. These different tocopherols possess a same basic structure that consists of a chromanol head and an alkyl side chain, while differing in the number and position of methyl groups on the chromanol head (Figure 7). Since α -tocopherol has been reported to possess the highest biological activity, there is a strong need to separate it from the other forms of tocopherol (Hosomi et al., 1997). However, the separation of mixed tocopherol homologues has been very challenging because of their high structural similarity. The available methods for this problem mainly include various chromatographic technologies, such as high performance liquid chromatography (Ng et al., 2004; Pyka & Sliwoik, 2001), capillary electrochromatography

(Chaisuwan et al., 2008), microemulsion electrokinetic chromatography (Chang et al., 2006), nano-liquid chromatography (Fanali et al., 2002), supercritical fluid chromatography (Jiang et al., 2003) and low pressure column chromatography (Wan et al., 2008). Although these technologies could give effective separation for the tocopherol homologues, they are almost only applied at a laboratory scale on account of the low throughput capacity and large consumption of absorbents and solvents or the requirement for special equipment.



Compound	R ₁	R ₂
α -Tocopherol	—CH ₃	—CH ₃
β -Tocopherol	—CH ₃	—H
γ -Tocopherol	—H	—CH ₃
δ -Tocopherol	—H	—H

Fig. 7. The structures of tocopherols. Reprinted from reference which is downloaded from pubs.acs.org (Yang et al., 2009).

As an alternative to the chromatographic methods, Yang et al. carried out the liquid-liquid extraction of mixed tocopherol homologues with ILs (Yang et al., 2009). Since the four tocopherol homologues are likely to have different hydrogen bond acidities due to their structural difference in the number and position of methyl groups on the chromanol head, they may be effectively separated with each other by certain ILs via hydrogen bonding interaction. So, 1-butyl-3-methylimidazolium chloride ([C₄mim]Cl) was selected as a model extractant for the separation of tocopherol homologues, as it had a relatively strong ability of interacting with hydrogen bond donor molecules (Armstrong et al., 1999; Xie et al., 2008). (Armstrong et al., 1999; Xie et al., 2008) (Armstrong et al., 1999; Xie et al., 2008) (Armstrong et al., 1999; Xie et al., 2008) (Armstrong et al., 1999; Xie et al., 2008) [C₄mim]Cl was diluted with methanol before use as it was highly viscous or even solid near room temperature. Non polar solvent, hexane, was selected as the feedstock solvent for mixed tocopherols to form a biphasic system with IL-methanol solution. As the result presented in Table 1, significant difference among the distribution coefficients of each tocopherol homologue was found, which decreased as the order δ -tocopherol > β & γ -tocopherol > α -tocopherol (β and γ -tocopherols were considered as one combined component, because their structure and property were too similar to be distinguished in HPLC analysis). Especially, α -tocopherol exhibited a much lower value of distribution coefficient than the other forms of tocopherols. While most of α -tocopherol remained in the hexane phase, the other forms were much easier to distribute into the extract phase, resulting in large selectivities of α -tocopherol toward the other tocopherols. For example, while the mole ratio of [C₄mim]Cl to methanol was 1:1.3 and temperature was 303.15 K, the selectivity of δ -tocopherol to α -tocopherol was as large as 21.3 and the selectivity of β & γ -tocopherol to α -tocopherol was also higher than 8. Therefore, it is reasonable to consider that α -tocopherol could be selectively obtained from the mixture of various homologues in high purity by multi-stage extractions. And then, it was also showed in Table 1 that the selectivities of δ -tocopherol to α -tocopherol

and β & γ -tocopherol to α -tocopherol tended to increase along with the increase of IL's content in the IL-methanol solution, thus suggesting a key role of [C₄mim]Cl in the extractive separation. Since the differences among the tocopherol homologues just lie in the different structural environment around the hydroxyl group, it appears that the selective separation probably results from the hydrogen bonding interaction between the hydroxyl groups and the chloride anion as expected. The methyl group which exists around the hydroxyl group of tocopherol could reduce tocopherol's hydrogen bond acidity and weaken the affinity of tocopherol for [C₄mim]Cl, consequently resulting in a smaller distribution coefficient of α -tocopherol between IL phase and hexane phase.

Mole ratio of [C ₄ mim]Cl to methanol	Distribution coefficient			Selectivity		
	δ	β & γ	α	δ/α	β & γ/α	δ/β & γ
1:1.3	2.34	0.95	0.11	21.3	8.6	2.5
1:2.7	2.58	1.18	0.16	16.1	7.4	2.2
1:5.4	1.94	1.06	0.24	8.1	4.4	1.8
Pure methanol ^a	1.01	0.94	0.85	1.2	1.1	1.1
Pure [C ₄ mim]Cl ^b	0.23	0.09	0.01	18.8	7.7	2.4

Table 1. Extractive separation of mixed tocopherols using [C₄mim]Cl at 303.15 K. Initial concentration of tocopherol in hexane (mg/ml): δ 0.54, β & γ 0.53, α 0.11. Volume ratio of two phases: 1:1. a) methanol amount was adjusted to reach an equilibrium phase volume ratio about 1:1. b) carried out at 328.15 K, mixed for 18 h. Reprinted from reference which is downloaded from pubs.acs.org (Yang et al., 2009).

To clarify the hydrogen-bonding interaction mechanism proposed above, the authors investigated the extraction when the structures of IL and tocopherol were modified. First, to demonstrate the role of phenolic hydroxyl group in extraction, distributions of mixed tocopherol acetates in [C₄mim]Cl-methanol-hexane biphasic system were determined and the results were used for a comparison (Table 2). Since the hydroxyl groups on chromanol ring had been converted to ester groups, all of the tocopherol acetates were poor hydrogen bond donors and thus were expected to show weak affinity for [C₄mim]Cl. Well, the experimental results showed in Table 2 accord with this expectation. The distribution coefficients of tocopherol acetates are much smaller than those of tocopherols, as well as sharply decreased selectivities.

Then, to demonstrate the role of IL's anion in extraction, two other kinds of ILs with different anions were investigated for the extractive separation of tocopherol homologues. Consequently, the distribution coefficients of tocopherols in biphasic system varied with the order [C₄mim]BF₄ < [C₄mim]CF₃SO₃ < [C₄mim]Cl under the same conditions ([C₄mim]CF₃SO₃ refers to 1-butyl-3-methylimidazolium trifluoromethanesulfonate), and the selectivities of tocopherol homologues had the same order (Table 3). This order is consistent with the order of these ILs' hydrogen bond basicity strength (Anderson et al., 2002). Combined with the experimental results about tocopherol acetates, it was revealed that the hydrogen-bonding interaction between IL's anion and phenolic hydroxyl group played an important role on the separation selectivity.

Solutes	Distribution coefficient			Selectivity		
	δ	$\beta\&\gamma$	α	δ/α	$\beta\&\gamma/\alpha$	$\delta/\beta\&\gamma$
Tocopherols	2.10	0.89	0.11	19.1	8.1	2.4
Tocopherol acetates	0.002	0.002	0.002	1.0	1.0	1.0

Table 2. Extractive separation of mixed tocopherol acetates and mixed tocopherols using [C₄mim]Cl at 303.15 K. Initial concentration of tocopherol in hexane (mg/ml): δ 2.31, $\beta\&\gamma$ 2.27, α 0.46. Initial concentration of tocopherol acetates in hexane (mg/ml): δ 2.30, $\beta\&\gamma$ 2.25, α 0.46. Volume ratio of two phases: 1:1. Mole ratio of [C₄mim]Cl to methanol: 1:1.3. Reprinted from reference which is downloaded from pubs.acs.org (Yang et al., 2009).

IL	Distribution coefficient			Selectivity		
	δ	$\beta\&\gamma$	α	δ/α	$\beta\&\gamma/\alpha$	$\delta/\beta\&\gamma$
[C ₄ mim]BF ₄	0.02	0.01	0.003	6.7	3.3	2.0
[C ₄ mim]CF ₃ SO ₃	0.31	0.15	0.04	7.8	3.8	2.1
[C ₄ mim]Cl	2.34	0.95	0.11	21.3	8.6	2.5

Table 3. Extractive separation of mixed tocopherols using different ILs at 303.15 K. Initial concentration of tocopherol in hexane (mg/ml): δ 0.54, $\beta\&\gamma$ 0.53, α 0.11. Volume ratio of two phases: 1:1. Mole ratio of IL to methanol: 1:1.3. Reprinted from reference which is downloaded from pubs.acs.org (Yang et al., 2009).

The effect of temperature and concentration of tocopherols on extraction was investigated. As the temperature increased, both the distribution coefficients and selectivities tended to decrease. As the concentration of tocopherols increased, the distribution coefficients decreased slowly at the beginning but much more sharply after a certain concentration, where the equilibrium concentration of tocopherols in extract phase started to achieve saturation.

3.4 Regeneration of ionic liquids

The method of regenerating ILs varies according to diverse properties of different extracts. As for the solutes with low boiling points and good thermostability such as aromatics, short-chain aliphatic compounds and so on, distillation is suggested due to negligible vapor pressure of ILs. When it comes to the solutes which are less volatile or sensitive to heat, for example, aromatic sulfur compounds and natural bioactive products, ILs can be recovered by stripping with solvents. With respect to the solutes which can dissociate in water, such as phenolic compounds and organic acids, ILs can be regenerated by stripping with aqueous solution whose pH value is in a reasonable range. Moreover, supercritical CO₂, which is well-known as another variety of green solvent beside IL, can be used to separate the solutes from ILs (Blanchard & Brennecke, 2001).

4. Ionic liquid-solute interaction investigated by quantum chemistry method

Quantum chemistry based method have attracted more and more attention in separation science to get the understanding of underlying mechanism for experimental results and provide reasonable predictions before further experiments. The extractant-solute interaction is one of the most important factors that decide the distribution coefficient and separation

selectivity in liquid-liquid extraction, so the investigation of IL-solute interaction by quantum chemistry method is worth carrying out to improve the research and application on IL-based liquid-liquid extraction.

The interaction between thiophene and ILs $[\text{C}_4\text{mim}]\text{PF}_6$ and $[\text{C}_4\text{mim}]\text{BF}_4$ were investigated by *ab initio* calculations (Zhou et al., 2008), as a lot of attention has been paid to the extraction of sulfur-containing compound from fuel and $[\text{C}_4\text{mim}]\text{PF}_6$ showed a larger capacity of thiophene than $[\text{C}_4\text{mim}]\text{BF}_4$. The geometry optimization and electronic charge analysis were carried out at MP2/6-31G level, and energy calculation was finished at MP2/6-311G(d,p) level. Various interacting systems, including thiophene- PF_6^- , thiophene- BF_4^- , thiophene- $[\text{C}_4\text{mim}]^+$ and neat IL, were analyzed. Columbic attraction was found to dominate the interaction between thiophene and IL. Two factors mainly contributed to the larger capacity of thiophene in $[\text{C}_4\text{mim}]\text{PF}_6$ than $[\text{C}_4\text{mim}]\text{BF}_4$, of which one was the relatively stronger electron donation of phosphor atom to fluorine atoms in PF_6^- and the other was the lower compactness degree of $[\text{C}_4\text{mim}]\text{PF}_6$ compared to that of $[\text{C}_4\text{mim}]\text{BF}_4$.

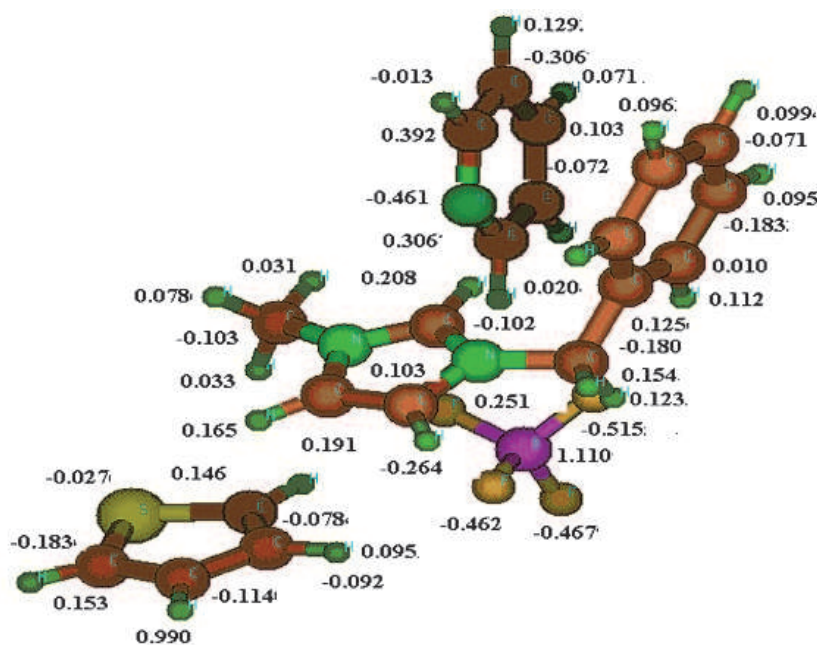


Fig. 8. Optimized geometries and partial charges for $[\text{Bemim}]\text{BF}_4$ -thiophene-pyridine. Reprinted from reference which is downloaded from www.elsevier.com (Anantharaj & Banerjee, 2010).

The simultaneous interaction of IL with thiophene and pyridine was studied by density functional theory (Figure 8), due to the requirement of simultaneous removal of aromatic sulfur-compounds and nitrogen-compounds from diesel oil (Anantharaj & Banerjee, 2010). Calculations were carried out to determine several global scalar properties such as HOMO/LUMO energies, HOMO-LUMO energy gap, chemical hardness, chemical potential, electronegativity, global hardness, global softness and electrophilicity index for clusters containing ILs with thiophene and pyridine, providing a prediction that the simultaneous removal followed an overall order 1-benzyl-3-Methylimidazolium tetrafluoroborate ($[\text{Bemim}]\text{BF}_4$) > 1-butyl-1-methylpyrrolidinium tetrafluoroborate ($[\text{C}_4\text{mpyr}]\text{BF}_4$) > 1-butyl-4-methylpyridinium hexafluorophosphate ($[\text{C}_4\text{mpy}]\text{PF}_6$) > 1-butyl-4-methylpyridinium tetrafluoroborate ($[\text{C}_4\text{mpy}]\text{BF}_4$) > 1-butyl-1-methylpyrrolidinium hexafluorophosphate

([C₄mpyr]PF₆) based on the combination of various scalar parameters. This trend was in accordance with that of infinite dilution activity coefficients of pyridine plus thiophene in ILs predicted by quantum chemical based conductor like screening model-real solvents (COSMO-RS) method. The CH- π interaction between the CH group in the imidazolium cation and the aromatic ring in the sulfur-compound was considered as the main interaction between imidazolium ILs and sulfur-compounds (Anantharaj & Banerjee, 2011).

Investigation was also conducted for the extraction of another common sulfur-compound, benzothiophene, from diesel oil (Varma et al., 2011). Both extraction experiments in IL-hexane biphasic systems and theoretical calculations with COSMO-RS method were performed. Based on the activity coefficients of component calculated by COSMO-RS method, the tie-lines for benzothiophene-IL-hexane ternary systems could be predicted with a good agreement with experimental results (Figure 9). The root mean square deviations were 4.36% and 7.87% for 1-ethyl-3-methylimidazolium ethylsulphate ([C₂mim]C₂H₅SO₄) and 1-ethyl-3-methylimidazolium acetate ([C₂mim]CH₃COO) based system, respectively. Besides, it was notable that the authors also utilized the COSMO-RS method for the prediction of quaternary liquid-liquid biphasic systems containing two ILs, benzothiophene and hexane.

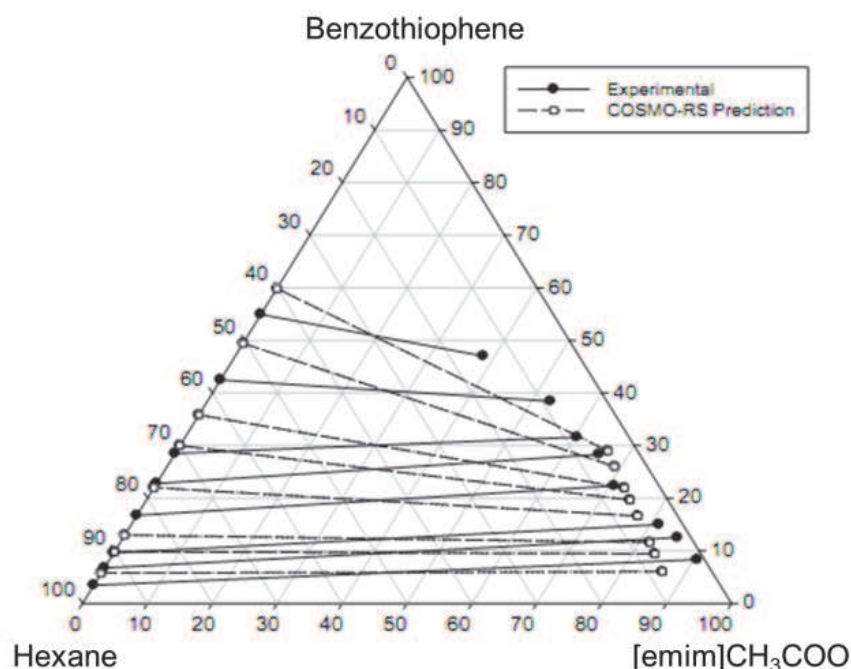


Fig. 9. Experimental vs. COSMO-RS predictions for the composition tie lines of the system [emim]CH₃COO-benzothiophene-*n*-hexane at 308.15K. Reprinted from reference which is downloaded from www.elsevier.com (Varma et al., 2011).

5. Conclusion

IL-mediated liquid-liquid extraction is receiving more and more attention now. In general, ILs can be regarded as “green” alternatives to common organic solvents, because their negligible volatility can reduce the air pollution and facilitate the regeneration from volatile components. Nevertheless, they can also be superior to common solvents in many cases not due to the nonvolatile features but to some other benefits such as the designable physicochemical properties against specific tasks and unusual liquid-liquid equilibrium

with common solvents. Overall, favorable distribution coefficient and separation selectivity, together with less energy consumption and less volatile pollution, may be achieved in liquid-liquid extraction using IL as extraction solvent.

It should be noted that the environmental impact of IL should be evaluated more carefully. Despite the non-volatility, some amount of ILs may move into water and soil inevitably during the extraction process, especially for a large-scale application in industry. More research is needed on the leach of IL to environment, enrichment of IL in environment, toxicity of IL and degradability or recovery of IL. Dynamics and transport properties in IL-based extraction require more attention, which is of special significance due to the large viscosity of ILs compared with common solvents. Recent work on the hydrodynamic behavior analysis of a rotating disc contactor for aromatics extraction with [mebupy]BF₄ by an experimental and numerical analysis has been reported (Onink et al., 2010). More research should be carried out on the diffusion of components, dispersion of biphasic systems, interfacial transport, process intensification, and so on. Moreover, quantum chemistry and molecular dynamic simulation methods are expected for a further development to improve the design of new ILs and novel applications of current ILs. As the variety of IL is considered a very huge number, it seems unreasonable to develop IL-mediated applications just by numerous experiments.

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Applications of Ionic Liquids in Science and Technology

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This volume, of a two volume set on ionic liquids, focuses on the applications of ionic liquids in a growing range of areas. Throughout the 1990s, it seemed that most of the attention in the area of ionic liquids applications was directed toward their use as solvents for organic and transition-metal-catalyzed reactions. Certainly, this interest continues on to the present date, but the most innovative uses of ionic liquids span a much more diverse field than just synthesis. Some of the main topics of coverage include the application of RTILs in various electronic applications (batteries, capacitors, and light-emitting materials), polymers (synthesis and functionalization), nanomaterials (synthesis and stabilization), and separations. More unusual applications can be noted in the fields of biomass utilization, spectroscopy, optics, lubricants, fuels, and refrigerants. It is hoped that the diversity of this volume will serve as an inspiration for even further advances in the use of RTILs.

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