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Do We Understand the Recyclability of Ionic Liquids?

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Abstract: Recyclability is one of the reasons why ionic liquids (ILs) are attracting the attention of a growing number of scientists and engineers, but do we understand the recyclability of ILs in a real sense? For this purpose, this review focuses on the methods need for their separation from their “working” environment. Here we proposed that the appropriate separation method should be selected according to 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.

Keywords: aggregation • ionic liquids • membranes • recyclability

Introduction

Ionic liquids (ILs) are attracting the attention of a growing number of scientists and engineers due to their unique characteristics as “green” solvents: recyclability, negligible vapour pressure, non-flammability and low melting point.[1] Although investigations on physicochemical properties of ILs, in particular their thermodynamic and thermophysical properties, are still unsystematically studied, remarkable progress has been made in recent years in the synthesis of ILs and the study of chemical reactions in ILs as well as electrochemistry. This is somewhat surprising, because their easy recyclability, a key property responsible for their increasing popularity, has not yet been extensively studied, besides their purity, stability, biodegradability and toxicity.

Owing to the lack of volatility, ILs do not contribute to the release of harmful vapour into the atmosphere, but their release to aquatic environments could cause severe water contamination, because of their potential toxicity and inaccessible biodegradability. Therefore, researchers need to find alternative ways to recycle ILs, as many processes for cleaning up ILs involve washing with water or volatile organic compounds (VOCs), which creates waste stream. Furthermore, ILs still remain very expensive in comparison to conventional alternatives. This is why although ILs have shown great potential on the laboratory scale, there has not yet been any known large-scale industrial application of these solvents. To offset their expense as well as to accentuate their green properties, many chemists have sought to recycle ionic liquids, and noted that cost will be less important if ionic liquids can be recycled. Clearly, recycling is an important issue not only from the point of view of the economics of IL usage, but also for concern about IL disposal, biodegradation and toxicity. To date, however, there has been no paper on special discussion of ILs recovery. To keep the length manageable, this review is highly selective, and for what it is worth, we try to give our opinion throughout the paper. We apologise if your results have been misunderstood, but we hope this will generate more stimulating discussion in the future.

Hydrophobic Ionic-Liquid Recycling

Among the published literature, it is generally recognised that ILs are easily recyclable. Undoubtedly, this is true for some specific biphasic systems that containing ILs, in particular for hydrophobic ILs, such as $[PF_6]$- and $[CF_3SO_2)_2N]$-ILs. In this case, liquid–liquid extraction (l/l extraction) is an efficient method for separation and has been used for recycling both the catalyst and IL solvent in the course of palladium coupling reactions.[2–4] The recycling ability of these ionic liquids 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.

To provide significant advantages over conventional technologies for extraction processes, Birdwell et al.[5] have developed a centrifugal solvent-extraction contactor recycle method successfully used for the following systems: NaCl(aq)/$[C_4mim]NTf_2$ and $H_2O/[C_4mim]BETI$ {$[C_4mim]NTf_2$ = 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide; $[C_4mim]BETI$ = 1-butyl-3-methylimidazolium bis(perfluoroethanesulfonyl)imide}. They found the last system (cyclohexane/$[C_4mim]BETI$) was the most efficient, but still with slight loss of ILs.

For l/l extraction, admittedly, ILs can be recovered by using conventional organic solvents. However, this diminishes the “green” aspect of their usage due to the cross-contamination arising from the use of organic solvents. Alternatively, distillation can be used to recover ILs from compounds with low boiling points, because of their negligible vapour 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 minimised. However, supercritical fluids (SCFs) may solve these problems. The advantages of using SCFs as extraction medium include low cost, nontoxic nature, recoverability and ease of separation from the products.

Supercritical CO_2 ($scCO_2$) is the most widely used SCF owing to its nontoxic and non-flammable characteristics. It

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is a good choice of "green" solvent for the regeneration of ILs,[6] since $scCO_2$ can dissolve in the ILs, while ILs cannot dissolve in $scCO_2$. This unique property implies that ILs can be isolated from ILs/solute systems without IL cross-contamination; that is, it provides a means for recycling ILs. Scurto et al.[7] have demonstrated that separation of hydrophobic imidazolium-based ILs from aqueous solutions by the application of $scCO_2$ was possible and $[C_4mim][PF_6]$ was separated from an IL-saturated aqueous solution at 293 K and at a CO_2 pressure of 4.9 MPa. Blanchard et al.[6] found did not detect any $[C_4mim][PF_6]$ in naphthalene after extraction with CO_2 at 13.8 MPa and 313 K. The experimental work of same research group[8] demonstrated that a wide variety of solutes can be removed from $[C_4mim][PF_6]$ with $scCO_2$, with recoveries greater than 95%. When the extraction experiments were conducted at 313 K and 13.8 MPa, recovery of some organic solutes was as high as 98%. The recovery rate was considered to be related to the dipole moments of solutes and the amount of CO_2 used for extraction.

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, novel ways must be exploited.

Supercritical-CO_2 ($scCO_2$) also has potential for the regeneration of hydrophilic ILs. Scurto et al.[7] have studied the use of $scCO_2$ as a separation switch for IL/H_2O mixture. They demonstrated that the solutions of water and $[C_4mim]BF_4$ can be induced to form three phases in the presence of $scCO_2$. Although the original solution of $[C_4mim]BF_4$ is quite dilute, application of $scCO_2$ induces the formation of an additional liquid phase that is rich in $[C_4mim]BF_4$ (Figure 1), indicating that separation of $[C_4mim]BF_4$ from aqueous solutions by the application of $scCO_2$ is possible. The author considered this effect as a pressure phenomenon, as well as due to a slight decrease in dielectric constant upon addition of CO_2. In our opinion, a salting-out effect due to the formation of carbonate in solution may also play a key role, since CO_2 reacts with water to form carbonic acid and its dissociation products.

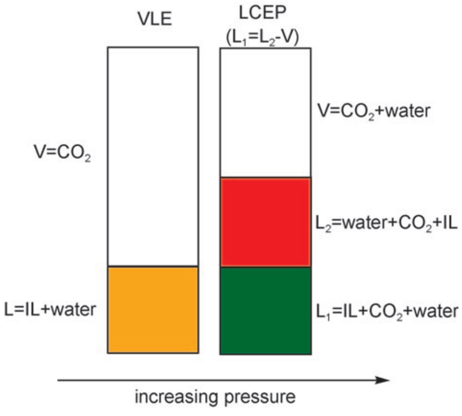

Figure 1. Phase behaviour of IL/water/CO_2 mixture at increasing pressure at near-ambient temperatures (adapted from reference [7]).

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Replacing water with methanol, the same research group have found the similar phenomenon during CO_2-induced separation.[9] They investigated the factors that control the liquid–liquid–vapour equilibrium in $[C_4mim]BF_4$/methanol/CO_2 ternary systems at 313 K.[10] The results showed that the lowest critical endpoint pressure (LCEP) was dependent on the choice of IL and the initial concentration of IL in methanol, while the *K* point pressure was independent of the type of IL.

Thereafter, Wu et al.[11] investigated the triphasic behaviour of $[C_4mim]BF_4$/water/CO_2 system in detail. They found that increase of pressure and decrease of temperature are favourable to the separation of the $[C_4mim]BF_4$ and water. However, CO_2 cannot induce complete separation of $[C_4mim]BF_4$ and water even when the pressure is as high as 20 MPa, at which the maximum concentration of $[C_4mim]BF_4$ in IL-rich phase is 75.63 wt %. The reason is that the intersolubility of CO_2 and water is very low even at high pressure. Up till now, therefore, there is no example of this method being used to recycle hydrophilic ILs, that is, it remains technically demanding.

Recently, Rogers and co-workers[12] demonstrated that the addition of the water-structuring salt, K_3PO_4, to an aqueous solution of $[C_4mim]Cl$, a hydrophilic ionic liquid, produced an aqueous biphasic system (ABS), forming an upper IL-rich phase and a lower K_3PO_4-rich phase (Figure 2, left). The authors suggested that the formation of the $[C_4mim]Cl$/salt ABS resulted from the increase of dielectric constant of the aqueous phase caused by addition of kosmotropic salts, forcing the low dielectric $[C_4mim]^+$ ions to the upper phase with concurrent transfer of chloride anions. This salting-out effect provides the potential for recycling hydrophilic ILs from aqueous solution. As far as we known, however, there is no report on the recycling of ILs with this system. The most important reason is that the introduction of inorganic ions (K^+ and PO_4^{3-}) complicates the recycling process, since hydrophilic ILs also dissociate into ions in aqueous solutions.

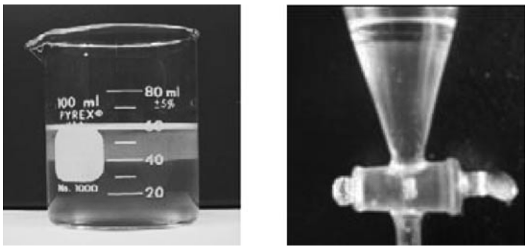

Figure 2. Phase behaviour induced by salting-out. Left: IL/salts. Right: IL/saccharides.[12]

Taking this into account, we replaced inorganic structuring salts with covalent compounds, that is, saccharides, which are also kosmotropic and can be removed more easily in comparison to inorganic ions.[13,14] Our group proposed a novel and environmentally benign ABS composed of hydrophilic ionic liquids {1-allyl-3-methylimidazolium chloride ([Amim]Cl), 1-allyl-3-methylimidazolium bromide ([Amim]Br), and $[C_4mim]BF_4$} and saccharides (sucrose, glucose, xylose, fructose), forming an upper IL-rich phase and a lower sucrose-rich phase (Figure 2, right). For the first time, we utilised this novel ABS for separating hydrophilic ILs from aqueous solutions. In a very recent study, we found lowering the temperature is favourable for the formation of ABS.[15] This indicates that recycling efficiency can be enhanced by decreasing temperature, whereby we deduced that this ABS is entropy-driven process. Although the recycling efficiency is not high, this novel ABS was used as an instructive example to separate and recycle hydrophilic ILs from aqueous solutions.

Membrane Technology for Inonic-Liquid Recovery

From the above discussion, it is found that each of these techniques has its 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 we 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. Gan et al.[16] investigated the potential application of microfiltration process in IL separation based on experimental studies of fluid properties and filtration characteristics of $[C_{10}mim]NTf_2$ and $[N_{8881}]NTf_2$ {$[C_{10}mim]NTf_2$ = 1-decyl-3-methylimidazolium trifluoromethanesulfonate and $[N_{8881}]NTf_2$ = methyltrioctylammonium bis(trifluoromethylsulfonyl)imide}. It was found that direct filtration of the pure ionic liquids through nuclepore microfiltration membranes yielded very low permeation rate. The viscosities of ILs can be drastically reduced by mixing with a small volumetric proportion of methanol and ethanol, and the mixed solution permeated through the microfiltration membranes with ease.

Based on this finding, a series of organic-solvent-stable nanofiltration membranes (STARME^{MTM}) were employed by Livingston et al.[17] to recycle ILs (CYPHOS IL 101 and ECOENG500) from Suzuki cross-coupling reaction mixtures. They found that STARME^{MTM} membranes showed good rejections for CYPHOS IL 101 and ECOENG 500 in methanol and ethyl acetate, and the performance of STARME^{MTM} 122 was best. After evaporation of methanol and ethyl acetate, a maximum recovery of 83 wt% CYPHOS IL 101 can be obtained. Evidently, this result is far from the requirement of industrial implementation.

Fernandez et al.[18] recently put forward recovery of the 3-octyl-1-methylimidazolium chloride ([C$_8$mim]Cl) from waste water through aggregation control by addition of FeCl$_3$. Their motivation is based on the fact that [C$_8$mim]$^+$ should show inherent amphiphilicity and exhibit aggregation behaviour analogous to the properties of surfactants.

These membrane processes are lacking in theoretical treatment, such as neglecting the importance of the charge and concentration polarisation effect on the IL filtration. In our latest unpublished work,[19] we use non-equilibrium thermodynamics to analyse the results of [C$_4$mim]BF$_4$ and [C$_4$mim]Br nanofiltration experiments. It was found that the values of reflection coefficient for both ILs are lower than those of the NaCl/water system, although the ion sizes of [C$_4$mim]$^+$ and Br$^-$ (or BF$_4^-$) are larger than that of Na$^+$ and Cl$^-$, respectively. We thought this behaviour was ascribed to the difference of the extent of hydration of the ions. A hydrated ion has a definite geometric structure. When the hydrated ion is pressured through the pore of the membrane, the hydrated ion's geometric structure is crushed out of shape, that is, the water molecules around the ion have been partially dehydrated. The stronger the hydrated structure, the more difficult it is to crush it out of shape under the same conditions. The hydration of NaCl is stronger than [C$_4$mim]BF$_4$ and [C$_4$mim]Br; the hydration numbers (hydration number = the number of molecules of water with which an ion can combine in an aqueous solution of given concentration) are 5.5, 2.9 and 2.7 for NaCl, [C$_4$mim]Br and [C$_4$mim]BF$_4$, respectively.[20] Thus, it is easier for ILs to go through a membrane, and thereby the values of reflection coefficient are smaller.

Apart from the nanofiltration, Afonso and co-workers[21] have demonstrated that pervaporation is capable of quantitatively removing water and organic solutes directly from [C$_4$mim]BF$_4$ (removal rate $>99.2\%$), more effectively and under milder operating conditions than distillation. Choosing the appropriate membrane for the individual separation problem, pervaporation proved more versatile than solvent extraction processes as well as more efficient and energetically more advantageous than evaporative techniques. This method was used successfully to enhance esterification conversion in ILs.[22]

From the above discussion, we find that the efficiencies of the different IL recycling processes vary. Therefore, it may be not suitable to repute IL easy recovery, particularly for hydrophilic ILs. In this respect, the combination of the aforementioned separation techniques is necessary and seems to be the most promising way to recycle ILs, since we are still far from a situation in which we can recycle ILs by only one method. To this end, it is necessary and important for us to put our emphasis on the solution properties. Taking hydrophilic IL recovery from aqueous solution as an example, we need to know more about the state of ILs in aqueous solution, including solution structure and aggregation behaviour. These properties can be obtained from the results of thermodynamic, spectroscopic, light scattering, and even computer simulation techniques. In the following section we interpret this topic clearly with our present research results, coupled with some excellent studies on aggregation behaviour from other research groups.

Fundamental Research for Ionic Liquid Recovery

As mentioned above, dissolution of the hydrophilic ILs in the aqueous phase could represent a waste-water treatment challenge. Hence we address the solution properties of aqueous hydrophilic ILs solution in this section. 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. For the sake of brevity, in this section we do not plan to review some excellent work in detail,[23–28] but mainly show fundamental research by our group in the field of IL recyclability.

It is known that [C$_4$mim]BF$_4$ is macroscopically 100% miscible with water in any molar ratio. However, Figure 3 clearly shows that the mixture of water and [C$_4$mim]BF$_4$ is not microscopically as homogeneous as we thought. Recently, Bowers et al. showed that the mixing of [C$_4$mim]BF$_4$ and water is incomplete at the microscopic level, on the basis on their small-angle neutron-scattering measurements.[28]

We also tried to study the mixture of [C$_4$mim]BF$_4$ and water by light-scattering characterisation. It is shown that only a single relaxation was observed when the concentration of [C$_4$mim]BF$_4$ is lower than 0.3749 g mL^{-1}, at which point the solution is full of dissociated ions, [C$_4$mim]$^+$ and BF$_4^-$ hydrated by water molecules, resulting in a narrow distribution of hydrodynamic radius (Figure 3, top).

As the concentration of [C$_4$mim]BF$_4$ increase to 0.3749 g mL^{-1}, another fast relaxation mode becomes evident in which the distribution of the unhydrated ions is much smaller. This can be explained as follows: as the concentration increases, the ionisation degree of [C$_4$mim]BF$_4$ decreases and formation of microstructure with smaller hydrodynamic radius is ascribed to the existence of unhydrated ions. That is, the appearance of a fast mode could be interpreted as the unhydrated ions.

As the concentration increases, in the case of 0.6495 g mL^{-1}, the slow mode becomes weaker, accompanied by the wide distribution of particles with much larger size, while the fast mode has the opposite trend. This is because [C$_4$mim]BF$_4$ acts as solvent in this case with water as the solute, and thus water molecules are solvated by [C$_4$mim]BF$_4$, causing the rest [C$_4$mim]BF$_4$ associated. Thus, the unionised part aggregates with hydrated ions to form clusters, leading to an increase of hydrated ionic volumes (Figure 3, bottom right). In other words, the slow mode

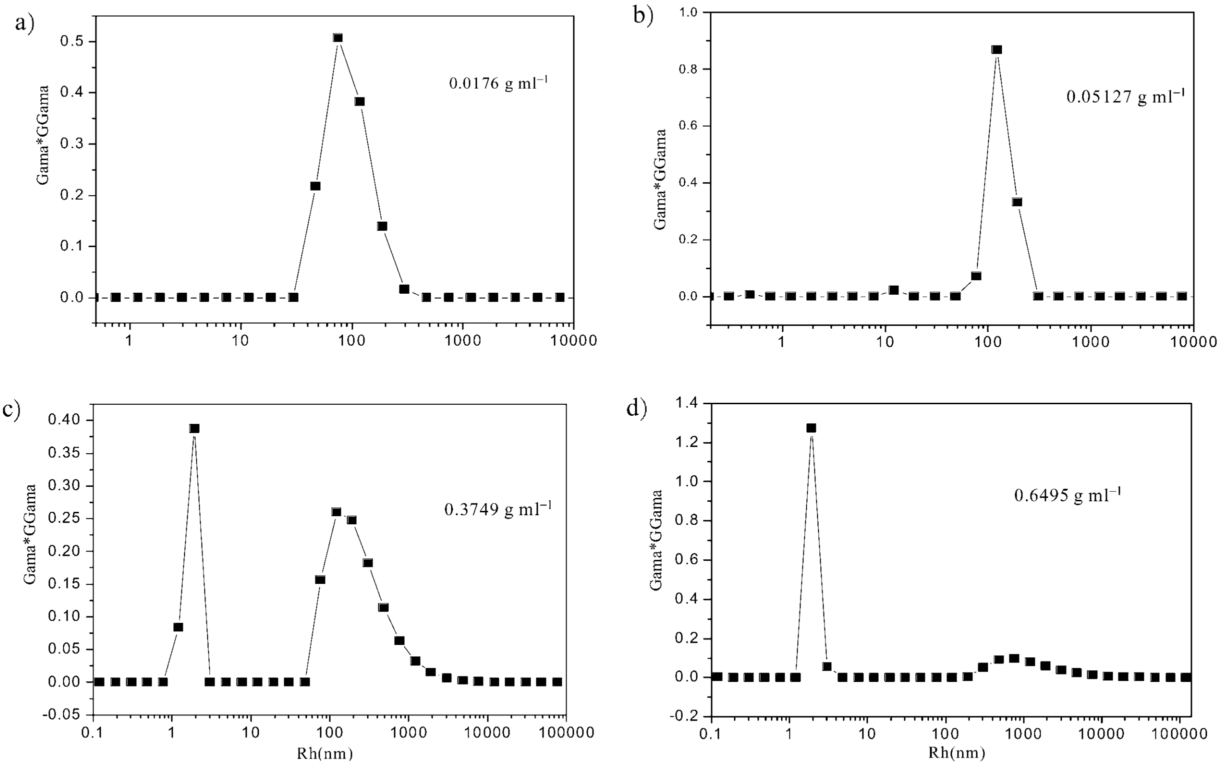

Figure 3. The hydrodynamic radius of the aqueous solution of [C_4mim]BF_4 and its distribution.

could be interpreted as the dynamics of large aggregates or clusters.

These findings can be demonstrated macroscopically in the variation of specific conductance with [C_4mim]BF_4 concentration (Figure 4).[29] It is observed that the conductivity increases sharply with [C_4mim]BF_4 concentration as expected, and followed by a maximum conductivity of 47.10 mS cm^{-1} at the mole fraction of [C_4mim]BF_4 of 9.7 %, after which conductivity decreases linearly. This can be ascribed to two effects: 1) increase of viscosity and therefore reduction of the mobility of the charge carriers and 2) reduction of the number of the charge carriers due to aggregate formation. The latter become dominant at higher concentration, thus leading to a strong decrease of conductivity.

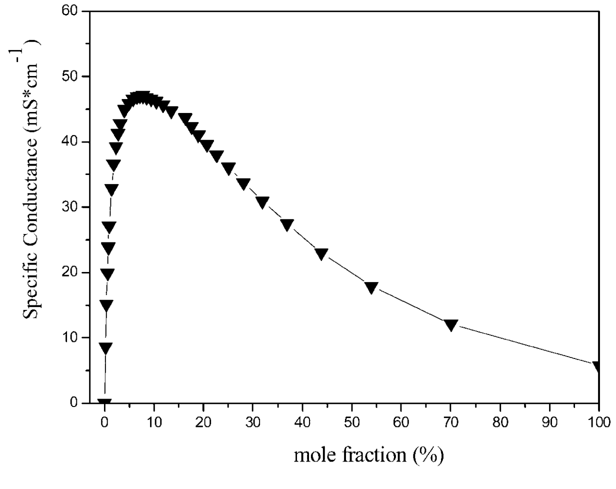

Figure 4. Concentration dependence of specific conductivity for aqueous [C_4mim]BF_4 solutions.[29]

By combining the light-scatting and conductance results, we propose a schematic model to explain the changes of the solution properties of aqueous [C_4mim]BF_4 over the whole concentration range, leading to a water-rich region (Figure 5, top left), an ion-rich region (Figure 5, top right) and a salt-rich region (Figure 5, bottom).

In the water-rich region, the aqueous solution of [C_4mim]BF_4 is dilute, [C_4mim]BF_4 dissociates into free anions and cations; the distribution of hydrodynamic radius is narrow and the specific conductance increases upon addition of [C_4mim]BF_4. In the ion-rich region, the association between the anions and cations leads to a reduction of the number of the charge carriers, accompanied by a decrease of the increase amplitude of conductance. In salt-rich region, the mole fraction of [C_4mim]BF_4 is much greater than that of water, thus the former acts as solvent and the latter is solvated. Accordingly, [C_4mim]$^+$ and BF_4^- are almost in the state of ion pairs. The associated part aggregating with hydrated ions forms a supermolecular structure that strongly resembles to the structure of pure [C_4mim]BF_4, which is the most important reason for sharp decrease in conductance.

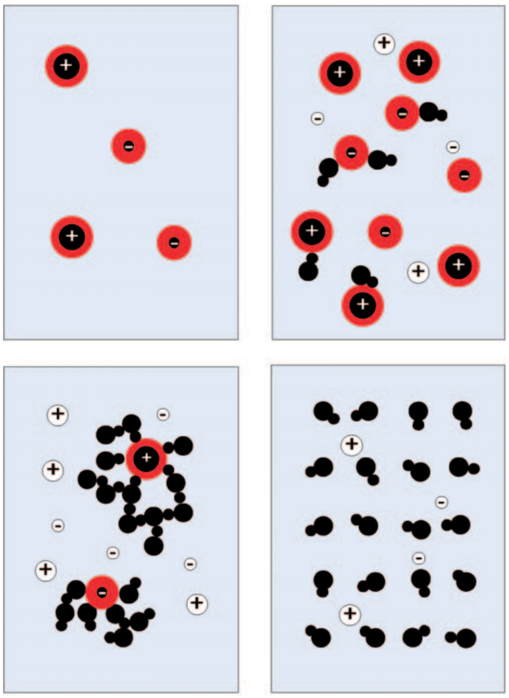

Figure 5. Aggregation model for aqueous solution of [C_4mim]BF_4: Top left: the water-rich region; top right: ion-rich region; bottom: the salt-rich region. ⊕: unhydrated cation; ⊖: unhydrated anion; black co-joined circles: associated ion pairs; ⊕ surrounded by red: hydrated cation; ⊖ surrounded by red: hydrated anion

Summary and Outlook

Based on the different features of IL/H_2O mixtures with different concentrations, we 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 ionisation 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; we 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 combination must be made on the basis of economical comparison and analysis, and more work is in progress.

In summary, we are only at the very beginning of understanding the recyclability of ILs based on the available literature in this field. We hope this review could provide some clues to support a great deal of further research. For IL recovery, understanding of volatility, purity, stability, biodegradability and toxicity of ILs is necessary, since this determines whether ILs can be sustainably developed. In a word, there is a long road ahead for large-scale application of ILs.

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