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**RECOVERY OF IONIC LIQUIDS FROM LIGNOCELLULOSIC
SAMPLES**

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ABSTRACT

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RECOVERY OF IONIC LIQUIDS FROM LIGNOCELLULOSIC SAMPLES		
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<p>Ionic liquid is a kind of liquid which is composed entirely of ions, such as KCl, KOH solids can change into liquid at a high temperature. Ionic liquids were formed by organic cation and inorganic anion (chloride, in this thesis). The recovery was significant because ionic liquids should be recycled in the process and they disturbed or hinder the chemical analysis.</p> <p>The aim of this thesis was to recover of ionic liquids [AMIM][Cl] and [BMIM][Cl] from the pretreatment of cellulose and lignocellulosic samples (substrates). In the experiment part, although the result was not so good, how to recover the ionic liquids was clearly showed in laboratory.</p> <p>Ionic liquid has already been applied in many chemical reactions, such as polymerization, acylation, esterification and electrochemical synthesis. And these reactions have showed fast rate of reaction, high conversion rate, exact reaction electivity, catalytic system can be recycled reused and other advantages.</p>		

Key words

Ionic liquids (IL), recovery, recycling.

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1 INTRODUCTION

An ionic liquid is a kind of liquid which is composed entirely of ions , such as KCl, KOH solids which can change into liquid state at a high temperature. At or near room temperature a substance consists of ions in liquid state, these liquids can be called room temperature ionic liquids, room temperature molten salts or organic ionic liquids. In ionic compounds, the force between the anion and the cation is Coulomb force. The size of Coulomb force is related to the charge number and radius of anion and cation. Ionic compounds have a larger ionic radius and smaller force between them, so that ionic compound has a lower melting point. (Audrieth 1936.)

Theoretically, there are one trillion kinds of ionic liquids. Chemists can choose the ionic liquids which are suited to the needs of their work. Ionic liquids are not the same as organic solvents. They cannot be evaporated into gases. Therefore, ionic liquids cannot create new air pollution or harmful gases in chemical experiments. Chemists are interested in the use of ionic liquids which can be recycled several times. (Seddon 1999.)

Ionic liquids are environmentally friendly solvents. They can replace volatile organic compounds because they have almost no vapor pressure. Ionic liquids have demonstrated their potential ability, and they are also a unique design of solvents. The properties of ionic liquids can be adjusted by the cation/anion structure to satisfy specific application requirements. (Qiao 2004.)

It has been found that ionic liquids have a good ability for dissolving cellulose. To improve the saccharification rate of ionic liquids which dissolve cellulose, the solution can be pretreated with acid hydrolysis or enzymatic hydrolysis cellulose.

However, it is necessary to recycle and reuse these ionic liquid solvents in order to make ionic liquids that have commercial values. (Qiao 2004.)

In the 19th century, scientists had begun studying ionic liquids. However, there was no cause for widespread interest in ionic liquids, Walden (1914, 1800) reported that he got $(\text{EtNH}_3)\text{NO}_3$ melting point 12°C . Concentrated nitric acid reacted with amine to produce $(\text{EtNH}_3)\text{NO}_3$. However, $(\text{EtNH}_3)\text{NO}_3$ was so unstable that it easily exploded. The discovery of this kind of ionic liquid was not attractive to chemists. This was the first ionic liquid. In general, ionic compounds melting into liquid require high temperatures in order to overcome the astrict of ionic bond. This state is called "flux". (Walden 1914.)

The force of the ionic bond will get weaker in ionic compounds when the cation radius increases and the melting point decreases. For most substances, the mixture melting point is lower than the pure material melting point. For example, the melting point of NaCl is 803°C , and the melting point of mixed system consisting of 50%LiCl-50%AlCl₃ (mole fraction) is only 144°C . If increase the volume of cations or anions and the structure of the asymmetry, and decrease the force between anions and cations, this salt will be a liquid at room temperature and that is an ionic liquid. According to this principle, Hurley and Wier (1951, 203) first synthesized an ionic liquid at liquid state. They chosen ethyl imidacloprid Sa ion to be the cation. Synthesized ionic liquid is a mixture which consists of ethyl bromide imidacloprid Sa and aluminum chloride at room temperature. However, this kind of ionic liquid has a relatively narrow liquid temperature range, and when aluminum chloride ionic liquids contact with water, they will emit hydrogen chloride so that HCl stimulates the skin of human beings. (Wier 1951.)

In the 20th century early 70s, Wilkes (1982, 1263–1264) began to research ionic liquids. He developed a better battery which was used for missiles and space probes. In his research, he found that an ionic liquid can be used as liquid for electrolyte batteries. He used 1-methyl-3-ethyl-imidazole as the cation. Chloride was synthesized by 1-methyl-3-ethyl-imidazole. In the mole fraction were 50% of the AlCl₃ presence and its

melting point reached 8°C. After that, the application of ionic liquids has really been widely carried out. Recent research studies of scientists also show that using ionic liquids can effectively extract the industrial emissions of carbon dioxide. (Wilkes 1982.)

The aim of this thesis is to recover ionic liquids [AMIM][Cl] and [BMIM][Cl] from the pretreatment of cellulose and lignocellulosic samples (substrates). Ionic liquids are formed by organic cation and inorganic anion (chloride which is used in this thesis). The recovery is significant because ionic liquids should be recycled in the process and they disturb or hinder the chemical analysis. The recovery could be carried out using strong cationic exchange resins (Strong Cation Exchanger, SCX e.g. Amberlite) or the liquid-liquid extraction. The SCX has a strong acidity and it is used to exchange the saturated cations. SCX can be regenerated by using the hydrochloric acid. This system is used for recovery ionic liquids by the reverse ion exchange process. The parameters affecting the regeneration process must be discussed and presented. What is the best way to recover the ionic liquids? How to recover ionic liquids? What is the recovery rate?

2 PROPERTIES OF IONIC LIQUIDS

Ionic liquids have many important properties in physics and chemistry such as the melting point, viscosity, density, hydrophilicity and thermal stability. Different cations and anions are selected to prepare different ionic liquids, and the compatibility of ionic liquids with water also can be changed. Ionic liquids as reaction a medium can separate the products. (Wang 2007.)

2.1 The melting point of ionic liquids

The melting point is one of the most important properties of ionic liquids. Ionic liquids require a low melting point, which means that they are in liquid state at room temperature. Different melting points of chlorides show that the structure characteristic of cations has a visible impact on the melting point of ionic liquids. The lower symmetry structure of the cation is the weaker interaction force between ions. If the cationic charges are uniformly distributed, the melting point will decrease. When the size of anions increases, the melting point of ionic liquids also reduces. Therefore, ionic liquids with low melting points are formed by cations which have the following characteristics: a low symmetry, weak intermolecular forces and unify distributed cation charge. (Wang 2007.)

2.2 The solubility of ionic liquids

Ionic liquids can dissolve organics, inorganic substances and polymers. Ionic liquids are good solvents in many chemical reactions. The successful to use of ionic liquids, their dissolution characteristics need to be studied. The solubility of ionic liquid is intimately bound up with the properties of cations and anions. The effect of cations on the solubility of ionic liquids can be seen from the solubility of quaternary ammonium. Ionic liquid

dissolve N-octyl-enein tosylate anions, which with the cationic side chains of the quaternary ammonium ionic liquid become larger, and the solubility of N-octyl-ene increases more quickly. Thus, the solubility of ionic liquids can be adjusted by changing the alkyl of cations. The anions affect the solubility of ionic liquids. Water is fully miscible with [BMIM][CF₃SO₃], [BMIM][CF₃CO₂] and [BMIM][C₃F₇CO₂], but [BMIM]PF₆, [BMIM][(CF₃SO₂)₂N] with water can form two-phase mixture. At 20°C, saturated water with [BMIM][(CF₃SO₂)₂N], the content of [BMIM][(CF₃SO₂)₂N] in water is only 1.4%. This kind of ionic liquid and water miscibility gap can be used for liquid - liquid extraction separation technology. The limits of the dielectric constant of ionic liquids have more than one characteristic. Ionic liquids are completely miscible with organic solvents. (Le 2007.)

2.3 The thermal stability of ionic liquids

The thermal stability of ionic liquids is limited by the interaction force between hetero atoms and carbon atoms, the interaction force between hetero atom and hydrogen bonds. The composition of cations and anions is also related to the structures and properties of ionic liquids, for example, by using aluminum oxide to determine a variety of imidazole ionic liquids, the initial thermal decomposition temperature of imidazole ionic liquid is about 400 °C. When the anion is the same, the second place of imidazole salt cation replaced by alkyl, the ionic liquids starting thermal decomposition temperature is markedly improved. When the substituent on the third place of nitrogen is a linear alkyl, it will make this ionic liquid more stable. The order of the stability for the corresponding anions is PF₆ > Beti > Im ≈ BF₄ > Me ≈ AsF₆ ≥ I, Br, Cl. As well as, the content of water has a slight effect for the thermal stability of ionic liquid. (Le 2007.)

2.4 The density of ionic liquids

The density of ionic liquids is related to the volumes of anions and cations. Comparison with the density of chlorine aluminate which included different substituent-imidazole cations, shows that the density of ionic liquids has a linear relationship with the length of the N-alkyl chain which is in the imidazole cations. The larger volumes of organic cations are, the smaller density of ionic liquids. The density of ionic liquids can be slightly adjusted by the structure of cations. Anions have more obvious effects on the density of the ionic liquids. When the volumes of anions become larger, the density of ionic liquids will be higher. Therefore, designing different density of ionic liquids can select different cations and anions. In fact, the pH of ionic liquids is determined by the anion which is in the ionic liquid. (Le 2007.)

2.5 The viscosity of ionic liquids

The viscosity of ionic liquids mainly depends on the capacity of hydrogen bonds formation in ionic liquids and the magnitude of van der Waals forces. The relationships between the van der Waals forces and the viscosity of ionic liquids can be found by changing the anions of 2,3-dibutyl-2-methyl-imidazolium ionic liquid. When the anion CF_3SO_3^- is changed into $\text{C}_4\text{F}_9\text{SO}_3^-$ and CF_3COO^- is also changed into the $\text{C}_3\text{F}_7\text{COO}^-$, it will significantly increase the viscosity of ionic liquids because $\text{C}_4\text{F}_9\text{SO}_3^-$ and $\text{C}_3\text{F}_7\text{COO}^-$ anions have stronger van der Waals forces. (Dymek & Stewart 1989.)

2.6 The vapor pressure of ionic liquids

Compared with other molecular solvents, the inside of ionic liquids has a large Coulomb force. The interaction energy between monovalent anion and cation is 100 kJ / mol, which is 10 times bigger than the water. They have a very low vapor pressure even at the higher

temperature in vacuum. Ionic liquids have a strong polarity and a unique solubility for a wide range of organics, inorganics and polymeric materials. The ionic liquid is the only solvent which can dissolve hydrides (such as NaH and CaH_2), carbide, nitride, various oxides and sulfide and other solvents. (Reichardt 1987.)

3 SYNTHESIS OF IONIC LIQUIDS

According to the different anions in ionic liquids, they can be divided into two categories: halide salt ionic liquids and new ionic liquids.

When the solid halide salts mix with the AlCl_3 aqueous solution, the preparation method can be obtained by using halide salt ionic liquids. This reaction is an exothermic reaction. Two kinds of solids will be added little by little into the halide salt ionic liquids so as to facilitate heat dissipation. These kinds of ionic liquids are researched early. Halide salt ionic liquids as solvents have been used in many research chemical reactions. Halide salt ionic liquids have many advantages over normal ionic liquids, but the disadvantage of these ionic liquids is that they are extremely sensitive to water. This kind of ionic liquids must be completely treated and applied in vacuum or inert atmosphere. Furthermore, when AlCl_3 ionic liquids are coming in contact with water, they can emit hydrogen chloride gases. (Wasserscheid & Welton 2002.)

Another type of ionic liquids are named new ionic liquids. They were developed after finding $[\text{EMIM}]\text{BF}_4$ ionic liquid which melting point is 12°C . New ionic liquids are different from the AlCl_3 ionic liquids. They have a fixed composition, and many of them are stable in water and air. In new ionic liquids, the cations are usually alkyl substituted imidazole ions $[\text{R}_1\text{R}_3\text{IM}]^+$, or $[\text{BMIM}]^+$, and the anions used are BF_4^- , PF_6^- , CF_3SO_3^- , $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, $\text{C}_3\text{F}_7\text{COO}^-$, CF_3COO^- , $(\text{CF}_3\text{SO}_2)_3\text{C}^-$, $(\text{C}_2\text{F}_5\text{SO}_2)_3\text{C}^-$, $(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}^-$, SbF_6^- . (Wasserscheid & Welton 2002.)

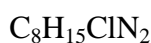
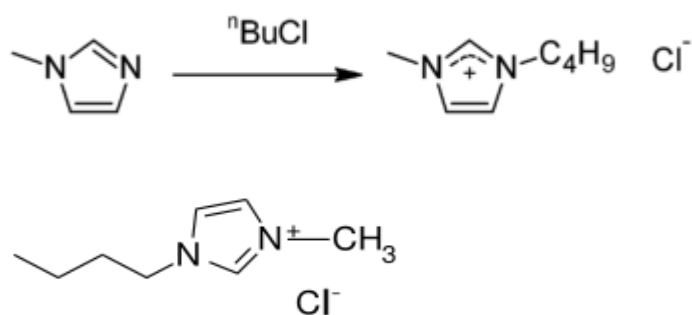
By changing the combinations of cations and anions different ionic liquids can be synthesized. In general, the cations of ionic liquids are organic ions. The common types of ionic liquid cations are alkyl ammonium cation, alkyl onium cation, N-alkyl-pyridine cation and N, N'-2-alkyl imidazole cation. The most common one is the N, N'-2-alkyl

imidazole cation. There are two kinds of methods to synthesize ionic liquid: direct synthesis and two-step synthesis ionic liquids. (Wasserscheid & Welton 2002.)

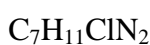
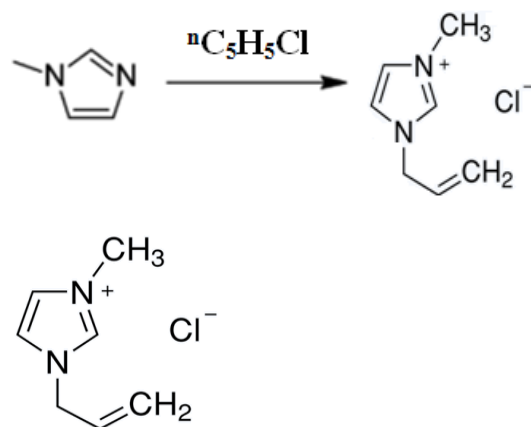
3.1 One step synthesis to make ionic liquids

Ionic liquids can be synthesized directly through the acid–base neutralization reaction or quaternary ammonium reaction. The operation method is easy and economical, and there are no by-products in the synthesis process. The products are easily purified. For example, nitro ethylamine ionic liquid can be synthesized by letting an ethylamine aqueous solution reacting with nitric acid in a neutralization reaction. After neutralization reaction, excess water can be removed from ionic liquids in vacuum, in order to keep them pure. In addition ionic liquids can be dissolved into organic solvents such as acetonitrile and tetrahydrofuran. Then ionic liquids are treated by activated carbon. Finally, organic solvents are removed in vacuum in order to synthesize new pure ionic liquids. In addition, the quaternary ammonium reaction can also synthesize a variety of ionic liquids in one step, such as 1-butyl-3-methyl-imidazoleonium salt [BMIM], $[\text{CF}_3\text{SO}_3]$, [BMIM]Cl. (Wang 2007.)

[BMIM] -Cl is synthesized by alkylating 1-methylimidazole with 1-chlorobutane.



[AMIM]-Cl is synthesized by alkylating 1-methylimidazole with 1-chloropropene.



3.2 Two-step synthesis to make ionic liquids

If the one step method cannot obtain the goal ionic liquids, two-step synthesis method must be used. Firstly, halogen salts which contain the target cation ([cation]X ionic liquids) should be synthesized in a quaternisation reaction. Secondly, the target Y^- anion will exchange the X^- anion or the goal ionic liquids are obtained by adding metal salts (MY) or strong protonic acids (HY). Metal salts (MY) are used with AgY or NH_4Y . The production precipitations (AgX) or gases (NH_3 and HX) can be easily removed during the reaction. When strong protonic acids (HY) are added into [cation]X ionic liquids, they must be mixed at low temperature. Then the ionic liquids should be washed many times by water until the ionic liquids are neutral. After that ionic liquids can be extracted by using organic solvents. Finally the organic solvents are removed in vacuum, so that pure ionic liquids can be received. It should be considered that the reaction is completed when the target Y^- anions replace the X^- anions of [cation]X ionic liquids, in order that there are no X^- anions remaining in the target ionic liquids. The purity of ionic liquids is very important for their applications and the characterization of their physical and chemical properties. (Wang 2007.)

4 ADVANTAGES OF IONIC LIQUIDS

Ionic liquids are odourless and non-flammable solvents. They have a very low vapour pressure, so they can be used in high vacuum systems, while reducing environmental problems from volatilization. Ionic liquids have a good solubility for organic and inorganic minerals. The reaction can be going on at homogeneous conditions, while reducing the volume of equipments. The range of the operational temperature of ionic liquids is -40 to 300 °C. They have a good thermal and chemical stability. Ionic liquids can be easily separated from other materials so that they will be recycable. (Le 2007.)

Ionic liquids as solvents have a successful performance in many organic reactions, such as polymerization, alkylation, and acylation reactions. An ionic liquid is not the same as a typical organic solvent, and there are no neutral molecules in ionic liquids, and all ions are cations and anions. Ionic liquids have a good thermal stability and conductivity, and they are excellent solvents for most inorganic, organic and polymer materials. In general, ionic liquids are not able to become steam, so they cannot produce harmful gases for atmospheric pollution in the chemical process. The prices of ionic liquids are relatively cheap. Because the majority of ionic liquids are stable to water, they are easily synthesized in the aqueous phase. Ionic liquids also have good designability. A special feature of the ionic liquid can be received through molecular design. In conclusion, ionic liquids are an ideal replacement of traditional volatile solvents. The use of ionic liquids effectively avoids environmental pollution, health, safety and equipment corrosion problems. Ionic liquids are truly environmentally friendly green solvents. They are suitable for the current advocate of clean technologies and sustainable development requirements. Ionic liquids have been already accepted and approved more and more widely for human beings. (Le 2007.)

5 APPLICATIONS OF IONIC LIQUIDS

Because ionic liquids have unique properties, so they are widely used in various fields of chemical research at present. Ionic liquids as reaction solvents have been applied in many types of reactions.

5.1 Ionic liquids are used in cellulose processing

Cellulose as a bio-renewable resource is the most widely distributed in the world. For the first time ionic liquids in cellulose processing was applied by Graenacher in 1934 when ionic liquids were made of 1-ethylpyridinium chloride and free nitrogen containing bases. Now Robin Rogers and co-workers have found that real solutions of cellulose can be produced at technically useful concentration by using ionic liquids. Although the technology that ionic liquids dissolve cellulose has been presented as a new idea, this technology opens up great potential for cellulose processing. (Swatloski, Spear, Holbrey & Rogers 2002.)

Cellulose processing is content dissolve of cellulose and the subsequent disposal. For the dissolving of cellulose, the great volumes of various chemical auxiliaries can be reduced to use by using the ionic liquids such as carbon disulfide (CS_2). For the subsequent disposal, the process can be greatly simplified by the use of ionic liquids. They as a solvent can be completely recycled. (Raoa, Venkatesana, Nagarajana, Srinivasan & Vasudeva Rao 2007.)

5.2 Ionic liquids are used in hydrogenation reaction

Many ionic liquids have already been used in hydrogenation reactions. The use of ionic liquids has two advantages in the hydrogenation reaction. The rate of reaction rate by using ionic liquids is several times faster than using conventional solvents. The mixture solution of ionic liquids and catalysts which have already been used can be recycled utilization. As research has shown, ionic liquids can play in two roles of solvents and catalysts in the hydrogenation reaction. (Qiao 2004.)

Ionic liquids can dissolve parts of the transition metals. Homogeneous reactions use ionic liquids which dissolve transition metals as a catalyst. In the hydrogenation reactions of ionic liquids fields, the homogeneous reaction has been mostly applied. In addition, the ionic liquids are easily separated and sublimated when they are used in diesel fuel which mainly contained aromatics of the hydrogenation reaction. At the same time, ionic liquids will not pollute the environment. (Qiao 2004.)

5.3 Ionic liquids are used for the separation and purification technology

Because ionic liquids have unique physical and chemical properties as solvents, they are very compatibly used for separation and purification technologies. Now there are a lot of reports about ionic liquids are used in separations and purifications. For instance, butanol can be extracted from the fermentation broth by using ionic liquids. In an ionic liquid, the non-volatile organic compounds can be extracted by using supercritical CO₂. Deng (2006, 232–235) reported that Chinese chemists have researched in the field, and they found that an ionic liquid can be applied in the solid–solid separation field. This method used [BMIM]PF₆ as leaching agent to separation taurine and sodium sulfate solids mixture. It has great applications, and the ionic liquid recovery rate is 97%.

6 RECOVERY AND RECYCLING OF THE IONIC LIQUIDS

Ionic liquids have a very good solubility with organic materials and inorganic salts. They can be miscible with a variety of compounds. Ionic liquids are usually recycled in two ways.

6.1 Liquid-liquid extraction

Firstly, if the mixture solution of ionic liquid only contains water, ethanol, acetone or other common solvents, by reducing pressure and distillation, they will be removed and ionic liquid will be pure and then reused. From the cellulose dissolved experiments, the mixture solution was mixed by ionic liquids and water, and then the ionic liquid could be purified and recycled by this method. (Turner , Spear , Huddleston , Hokbrey & Rogers 2003.)

It means: cellulose is dissolved in the ionic liquid and the solution was heated to 70~130 °C in an oil bath. Vacuum degassing of the warm cellulose ionic liquid solution is coated on a glass plate and use another piece of glass plate is used to cover on the top. Then the system is put into distilled water and soaked a period of time. After that the template was opened slowly and the ionic liquid is washed and the regenerated cellulose membrane is removed. The mixture of water and ionic liquid is decompressed and distilled, and then it is placed in a vacuum dryer for more than 24 h in order to remove water. The recovery rate of ionic liquids is 96.120%. The result of Swatloski's (2002) work shows that the recovery rate of ionic liquids is high. The recovered ionic liquids can be re-used.

Secondly, the mixture solution of the ionic liquid contains inorganic salts. Some K_3PO_4 solution can be added into the mixture solution. After that salting-out will happen. The upper layer is the ionic liquid and the lower-layer is K_3PO_4 solution with salt. Through the

liquid separation treatment, a pure ionic liquid is obtained by further purification steps. (Turner, Spear, Huddleston, Hobbrey and Rogers & Biomacromolecules 2004.)

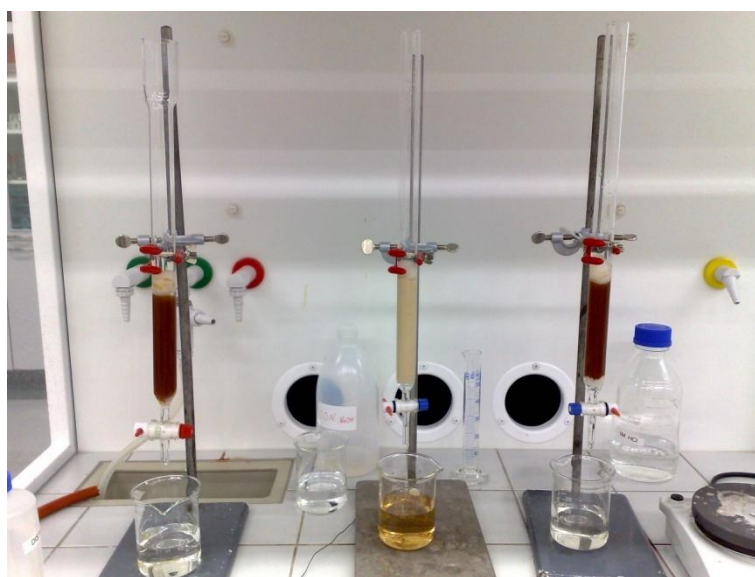
6.2 Solid-phase extraction

In solid phase extraction, the cations in the mixture solution of the ionic liquids are exchanged by ions in resin. Firstly, ionic liquids are diluted by distilled water, and then SCX cartridges are used to ion exchange. Secondly, after solid phase extraction pre-concentration, the samples are eluted by orthophosphoric acid. If there are some salts or organic solvents in the solution such as methanol or acetonitrile and acid solutions, they will be extracted by using phosphoric acid in the ionic liquid solution. Finally, the acidification of a saturated salt solution has a very effective elution system. This also shows that ionic liquid resins have certain hydrophobicity and it is used for solid-phase interactions. In solid-phase extraction, the breakthrough volume is very important, because it limits the attainable detection. (Stepnowski, Müller, Behrend, Ranke, Hoffmann & Jastorff 2003.)

7 THE EXPERIMENT OF RECOVERING IONIC LIQUIDS

Six samples containing ionic liquids were used in this experiment. Three of them contained [BMIM]Cl, and the others contained [AMIM]Cl. Each sample contained 5 g of the ionic liquid and 20 ml water. All of these ionic liquids were mixed with water.

At first ion exchange was used during the experiment. Three ion exchange systems were built. First one was filled with Amberlite IR-120 resin, second one was filled with Lewatit SP-112 resin, and the third one was filled with Dowex resin. There was 31 g dry ion exchange resin in each system. The exchange capacities of these resins are 4.3-4.5 mmol/g. So 31g ion exchange resin can exchange from 133.3 mmol to 139.5 mmol cations.



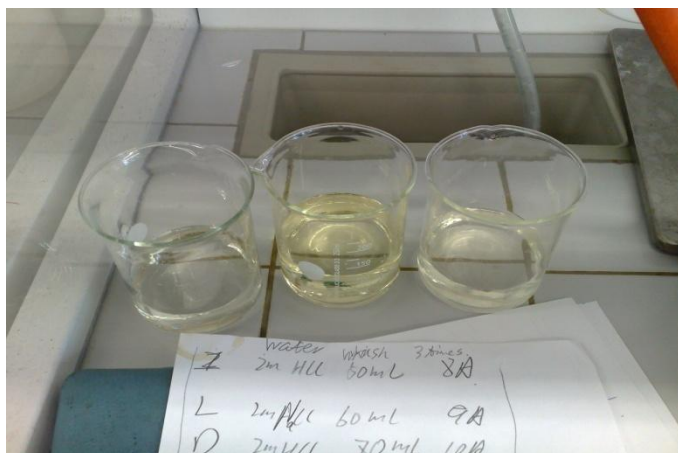
GRAPH 1. Three ion exchange systems (Photo: author)

Amberlite IR-120 resins and Dowex resins released H^+ and Lewatit SP-112 resins released Na^+ . Two solutions were prepared, namely a HCl solution and a NaCl solution. The concentrations of these two solutions were 2 M.

Distilled water was used for wetting the three ion exchange systems. 70 ml HCl solution was filled in both of the Amberlite IR-120 and the Dowex systems, and 70 ml NaCl solution was filled in the Lewatit SP-112 system. Afterwards the Cl^- of each ion exchange system was removed by using distilled water. The washed solution was tested by using AgNO_3 solution. Cl^- ions of tested samples could react with Ag^+ ions to form AgCl white precipitates after adding AgNO_3 solution. If there were some white precipitate in the tested sample, the system should be washed until there was no white precipitate in the tested sample.

One ionic liquid sample was added into the system. After that 70 ml HCl solution was added into the system again in order to exchange out the ionic liquid. The exchanged solution was kept. The system was washed until there were no white precipitates in the washed solution when one drop of AgNO_3 solution was added. 70 ml NaCl solution was added the Lewatit SP-112 system. Next the same procedures were repeated in Lewatit SP-112 system, only 70 ml HCl solution could be replaced by 70 ml NaCl solution.

Because HCl solution easily volatilized, the exchanged samples were heated, in order to remove HCl. NaCl was hardly removed, so the samples which contained NaCl could be washed by 30% K_3PO_4 solution. After 30% K_3PO_4 solution was added and then the mixture solution was shaken as well as possible. The solution was delaminating. In the upper solution was ionic liquid, and the lower was 30% K_3PO_4 solution with NaCl. Then the ionic liquid could be extracted. In theory 80% to 90% salts of ionic liquid could be removed. Thus the ionic liquid solution should be washed 2 to 3 times to ensure receiving a pure ionic liquid solution.



GRAPH 2. Three exchanged samples (Photo: author)

The same procedures should be repeated for the [AMIM]Cl samples. After that six exchanged solutions could be obtained. Heidolph Rotary Evaporator Laborota 4010 digital was used to remove the water. It could offer a low pressure system so that it could decrease the boiling point of water. The six samples were moved to six boiling flasks. Both one sample and the receiver flask were connected to the machine. The cooling system was opened. The pump was opened for pumping the air in order to offer a low pressure circumstance. Then the air valve was closed to make a closed system. The turning speed was chosen 100 rpm and the highest temperature was 40°C. After 40 minutes the water almost was removed, a very pure ionic liquid was gained. When the sample was changed, the rolling and heating was turned off. The air valve was slowly opened. When there was no sound of air flow, the pump could be closed. The sample was replaced by a new one. The other five samples were repeated with the same process.



GRAPH 3. Heidolph Rotary Evaporator Laborota 4010 digital (Photo: author)



GRAPH 4. The sample after drying (Photo: author)

After drying the ionic liquids, they were weight and the mass of them was in Table1.

TABLE 1. The mass of six recovered samples

	By Amberlite IR-120	By Lewatit SP-112	By Dowex
[BMIM]Cl	0.5 g	0.7 g	0.4 g
Recovery rate	—	—	—
[AMIM]Cl	1.6 g	2.3 g	1.5 g
Recovery rate	—	—	—

As it shows in Table 1, these three kinds of ion exchange resins are unsatisfactory. Lewatit SP-112 resin is better than the other two resins. The recovery rate still was too small. Ionic liquids are recovered by using ion exchanges. The result has shown that normal ion exchange resins are unsatisfactory. Other salts are added into ionic liquids by ion exchange resins. In Graph 2 the three samples have different colors. The mid one which is using Lewatit SP-112 resins for exchange have more yellow color, the other two are lighter than the mid one. The yellowiest contain more ionic liquid, which means that the Lewatit SP-112 resins are better than the other two.

If the ionic liquid is mixed only with water, then low pressure and distilled water can be used. After distillation, the samples are put in a vacuum dryer for drying 24 hours then a pure ionic liquid can be gained. If the ionic liquid solutions not only contain water but also other salts, they can be removed by using 30% K_3PO_4 solution. The ionic liquid should be washed several times so that the salts can be removed. If there are two kinds of ionic liquids or even more ionic liquids in the solution, the wanted cations can be exchanged by the strong cations exchanger. The extraction, distillation and drying were done again in order to get a pure ionic liquid.

8 DISCUSSION AND CONCLUSIONS

In this thesis, physical properties of ionic liquids, the manufacture method, advantage of ionic liquids and the application of ionic liquids were briefly introduced. This thesis experimental part shows how to recover the ionic liquids in the laboratory although the result was unsatisfactory.

The aim of this thesis is to recover [AMIM][Cl] and [BMIM][Cl] ionic liquids from the pretreatment of cellulose and lignocellulos. Ionic liquids are recovered by using ion exchange. But the result has shown that normal ion exchange resins are unsatisfactory. Other salts are added into ionic liquids by ion exchange resins. Ionic liquids are recycled in three ways.

If ionic liquid is only mixed with water, then low pressure can be used to take off the water. After distillation, the samples are put in a vacuum dryer for drying 24 hours then a pure ionic liquid can be gained.

If the ionic liquid solutions not only contain water but also other salts, the salts can be removed by 30% K_3PO_4 solution. The ionic liquid should be washed several times so that almost the salts can be removed. After distillation, the samples are put in a vacuum dryer for drying 24 hours then a pure ionic liquid can be gained.

If there are two kinds of ionic liquids or even more ionic liquids in the solution, the wanted cation can be exchanged by strong cations exchanger. The salts can be removed by 30% K_3PO_4 solution. The ionic liquids should be washed several times so that the salts can be removed. After distillation, the samples are put in a vacuum dryer for drying 24 hours then a pure ionic liquid can be gained.

By using these three methods ionic liquids can be recovered. But these three methods only

can be used in laboratory. An economical method and a clean technology for the recovery of ionic liquids in industry need further research.

Ionic liquids have their own properties, which makes them usable in clean technologies. Ionic liquid has already been applied in many chemical reactions, such as polymerization, acylation, esterification and electrochemical synthesis. In addition these reactions have shown a fast rate of reaction, high conversion rate, exact reaction electivity, catalytic system and the ionic liquids can be recycled, reused and other advantages. In addition, functional natural polymer materials are prepared by using ionic liquids. Ionic liquids as reaction media can synthesize different types of cellulose derivatives. These cellulose derivatives play a big role in forthcoming research.

Ionic liquids have many excellent properties. They are expected to replace the original organic solvents in many ways. Ionic liquids are considered the most promising green solvents in the twenty-first century. To become a green solvent, the problem of recycling and reuse of ionic liquids must be solved. Ionic liquids have very good solubility and can soluble with a variety of compounds, so that their recovery becomes more difficult in future.

The ionic liquids are recyclable and non-volatile. When the ionic liquid dissolves cellulose, its reaction conditions are moderate, and the equipment is easy to control. Regenerated cellulose by ionic liquid retains more natural characteristic of cellulose, and the product is superior to the traditional viscose process. Cellulose which is in the ionic liquid can make a homogeneous derivative reaction. An ionic liquid as a new cellulose solvent has fast dissolution velocity, large solubility, and small degree of degradation for cellulose, the solvent simply can recovery and have a high rate of recovery characteristics. Regenerated cellulose also has good mechanical properties. Therefore, the ionic liquid as a new cellulose solvent has great potential in the production of cellulose. There are not that many ionic liquids which can be used to dissolve cellulose, and many aspects need further research, as well as for a new regenerated cellulose.

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Calculations of the mass of 31g resins

Exchange capacity of these resins is 4.3–4.5 mmol/g. 31g ion exchange resins can exchange 133.3 mmol–139.5 mmol cations. The mole of ion exchange resins should be 3-5 times more than the mole of ions.

Prepared solutions:

Prepared 2 M HCl solution was and the volume was 1000 ml by using 7 M HCL solution.

Prepared the concentration of NaCl solution was 2 M and the volume was 500 ml

The mass of 1mol NaCl solid was calculated.

Prepared the volume of 30% K_3PO_4 solution was 500 ml.

$$\rho_{\text{water}} = 1 \text{ g/ml}, V_{\text{water}} = 500 \text{ ml}.$$

$$m_{\text{water}} = \rho_{\text{water}} * V_{\text{water}} = 1 \text{ g/ml} * 500 \text{ ml} = 500 \text{ g}$$
