

Full Research Paper

Hydrolysis and Partial Recycling of a Chloroaluminate Ionic Liquid

Ming-Hong Fang and Li-Sheng Wang*

School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing, China

* Author to whom correspondence should be addressed. E-mail: lishengwang@btamail.net.cn;
Fax: +86-10-68911040.

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Abstract: Hydrolysis of the ionic liquid $\text{Et}_3\text{NHCl}\cdot 2\text{AlCl}_3$ and a process for recycling the triethylamine were studied. When the hydrolysis was carried out at a relatively high temperature, the released HCl could be absorbed more easily. With addition of sodium hydroxide to the aqueous hydrolysis solution, a feasible process for recycling triethylamine was developed, involving first distillation of triethylamine, followed by filtration of the aluminium hydroxide. The yield of recovered triethylamine was about 95%. The triethylhydrogenammonium chloride prepared from the recycled triethylamine was of good purity and could be reused to synthesize new chloroaluminate ionic liquids.

Keywords: Ionic liquid, hydrolysis, triethylhydrogenammonium chloride, triethylamine recovery.

1. Introduction

Green Chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances [1]. With the rapid advancements in the field of synthetic organic chemistry, more and more environment friendly processes are being developed a rapid rate. Recently, there has been an upsurge in interest in ionic liquids (ILs). It is generally accepted that ILs have relatively low melting points and are less viscous than molten salts [2]. The acidity of a chloroaluminate ionic liquid can be modulated with changing the amount of AlCl_3 [3]. They have low vapor pressures, are considered by many authors to be environmentally friendly and can be applied in

many organic reactions [4-7]. Due to these excellent characteristics of ILs which makes them superior to other organic solvents, scientists have done much work on their applications in electrochemistry, liquid-liquid extraction and catalysis, including biocatalysis and polymerization [8-12]. Up to now, some important chemical reactions such as the Diels-Alder reaction [13], cracking and isomerization reactions [14], the Friedel-Crafts reaction [15,16], and hydrogenation reactions [17] have been successfully carried out in ILs. An important chloroaluminate ionic liquid, $\text{Et}_3\text{NHCl}\cdot 2\text{AlCl}_3$, is prepared by combination of Et_3NHCl with AlCl_3 in a 1:2 molar proportion. Due to its good performance as a Lewis acid catalyst and relatively low price, it is widely used in the Friedel-Crafts reactions [18-20], and shows good catalytic performance. However, in many instances, deactivation of the chloroaluminate ionic liquid after it had been recycled several times has been noted. A method must be found for recycling the ionic liquid and to the best of our knowledge such a method has not been reported in the literature.

In this article, the hydrolysis of a chloroaluminate ionic liquid and a process for recycling the triethylamine were studied. The recovered triethylamine was used to prepare triethylhydrogenammonium chloride with good purity. The obtained triethylhydrogenammonium chloride was used to synthesize a new chloroaluminate ionic liquid. Based on the results of this study, it is hoped that a similar process can be used for the recycling of other chloroaluminate ILs.

2. Experimental Section

2.1 Materials

Triethylhydrogenammonium chloride (AR 99+ %), aluminum trichloride (AR 98.5 %), ethanol (95 %), sodium chloride, potassium acid phthalate, nitric acid (65 %-68 %, m/m), mercuric nitrate, bromophenol blue, phenylazoformic acid 2-phenylhydrazide, hydrochloric acid (36 % - 38 %, m/m), sodium hydroxide, phenolphthalein, were all purchased from VAS Chemical Reagent Corporation Ltd., Beijing. An electronic balance with precision of 0.1 mg was used to determine the mass of the materials. Some solutions and indicators were prepared as follows:

(1) 1:1 Nitric acid was prepared with a 1:1 volume ratio of nitric acid (65 % - 68 %, m/m) to deionized water and 1 mol/l nitric acid was prepared with nitric acid (65 % - 68 %, m/m, 63 ml) diluted to 1l in a volumetric flask.

(2) Bromophenol blue indicator was prepared by dissolving bromophenol blue (0.1 g) in ethanol (20 %) to 100 ml in a volumetric flask.

(3) Phenylazoformic acid 2-phenylhydrazide indicator was prepared with phenylazoformic acid 2-phenylhydrazide (0.5 g) dissolved by ethanol (95 %) and made up to 100 ml in a volumetric flask.

(4) Phenolphthalein indicator was prepared with phenolphthalein (0.5 g) dissolved by ethanol (95 %) and made up to 100 ml in a volumetric flask.

2.2 Preparation of $\text{Et}_3\text{NHCl}\cdot 2\text{AlCl}_3$ ionic liquid

In a round-bottomed flask equipped with a magnetic stirrer and a gas inlet valve, under nitrogen, anhydrous AlCl_3 (266.7 g, 2 mol) was slowly added to triethylhydrogenammonium chloride (138 g, 1 mol). The mixture was stirred at 70 °C for 6 hours to ensure a complete reaction and then kept under reduced pressure (about 13.3 kPa) for 3 hours.

2.3 Hydrolysis of the ionic liquid

A beaker was used as reactor to ensure HCl free vaporization during the hydrolysis process. The hydrolysis is a strongly exothermic reaction, so for safety reasons, the appropriate temperature was carefully determined. The hydrolysis of an equal amount of ionic liquid in different amounts of water was also investigated.

2.3.1 Hydrolysis

Ionic liquid (100 g) was added dropwise to H₂O (25 °C, 200 g) in a beaker. The beaker was cooled with ice to absorb the heat released by the fiercely exothermic hydrolysis. This operation was carried out in ventilated cabinet. During the hydrolysis process HCl was released. The temperature of the solution was controlled at 45 °C. After it was cooled to room temperature, the concentration of chlorine ion was analyzed according to the method described in literature [21]. Hydrolysis at high temperature was carried out according to the same procedure, but the temperature was controlled between 80 -110 °C.

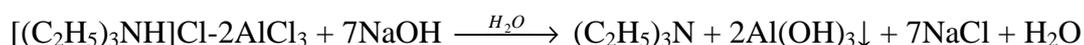
All of the measurements reported in this paper were repeated three times under parallel conditions, and the average value was taken. Concentrations of chlorine ion of different solutions are listed in Table 1. From this data it was found that after hydrolysis of equal amounts of ionic liquid in equal amounts of H₂O, the concentration of chlorine ion was higher when hydrolysis was carried out at a higher temperature, where molecules were much more active. When the ionic liquid was dropped into the solution, it was dispersed easily and the HCl released by the hydrolysis reaction was well absorbed. This lead to a high concentration of chlorine ion in the solution. On the contrary, in low temperature solutions, drops of ionic liquid were not easily dispersed and this lead to a very high concentration of HCl in a limited volume of the solution, so less HCl was absorbed by the solution and more HCl was easily released. This lead in turn to a low concentration of chlorine ion in the solution. The heat released by the exothermic hydrolysis reaction raised the temperature of solution, helping the solution absorb more HCl during the hydrolysis process, so for the measurement of the calibration curve of chlorine ion concentration given below, the hydrolysis was carried out at a relatively high temperature.

Table 1. Effect of hydrolysis temperature on chlorine ion concentration of aqueous IL solutions.

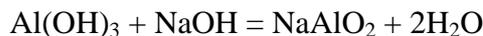
| | T/°C | Cl ⁻ /(mol/l) |
|------------------------------------|--------|--------------------------|
| Hydrolysis of | 25-45 | 6.225 |
| 100 g IL in 200 g H ₂ O | 80-110 | 6.618 |
| Hydrolysis of | 25-45 | 4.903 |
| 100 g IL in 300 g H ₂ O | 80-110 | 4.979 |

2.3.2 Calibration curve of chlorine ion concentration

The theory behind recycling of the triethylamine is based on the chemical reaction below:



The molar number of Cl⁻ ions is equal to the molar number of sodium hydroxides. When too much sodium hydroxide was added to the solution, the excess was wasted and would react with aluminium hydroxide.



On the contrary, when not enough sodium hydroxide was added, the rate of recycle of triethylamine would be affected. The exact amount of sodium hydroxide added can be specified, according to the chlorine ion concentration of the solution, so it is very important and meaningful to acquire a calibration curve of chlorine ion concentration vs. the amount of water for the hydrolysis. Measurements were carried out seven times with an equal amount of ionic liquid and different amounts of H₂O. The temperature of water at beginning was 25 °C and 110 °C when the hydrolysis was finished. After solutions were cooled to room temperature, the chlorine ion concentration was analyzed according to the method described in the literature [21]. The experimental results are listed in Table 2. The dependence of chlorine ion concentration of the water consumption was correlated to a second-order polynomial, and the result is shown in Figure 1.

Table 2. Dependence of chlorine ion concentration of aqueous solution on the water consumption.

| H ₂ O consumption of per gram IL/(g) | C(Cl ⁻)/(mol/L) |
|---|-----------------------------|
| 1.8600 | 6.7753 |
| 2.0000 | 6.6181 |
| 2.9571 | 4.9789 |
| 3.4078 | 3.8200 |
| 4.1210 | 3.1126 |
| 5.4322 | 2.4366 |
| 6.2673 | 2.2480 |

After the calibration curve was determined, hydrolysis of ionic liquid (90 g) in water (200 g) was carried out according to the same method described above. The concentration of chlorine ion determined by titration was 6.076 mol/l and the result calculated from the second-order polynomial was 6.088 mol/l. The relative deviation (RD %) of experimental data from the smoothed result was 0.2 %. The result based on the second-order polynomial thus predicted well the chlorine ion content of the aqueous solution. With the second-order polynomial, the chlorine ion concentration can be obtained without titration when the amount of water for per gram ionic liquid is specified in the hydrolysis.

2.4 Process for recycling triethylamine

Triethylhydrogenammonium chloride and aluminum trichloride are the raw materials for synthesizing chloroaluminate ionic liquid. The triethylhydrogenammonium chloride is synthesized from triethylamine and hydrochloric acid. A feasible method was suggested to recover the triethylamine from the aqueous solution after the hydrolysis, with aluminium hydroxide and sodium chloride being obtained as by-products.

After hydrolysis of 100 g of ionic liquid in 300 g H₂O, the volume of the aqueous solution was 369 mL. Then the solution was transferred into a 1000 ml round-bottomed three-necked flask equipped with a stirrer and a thermometer. The chlorine ion concentration was 4.6543 mol/l (calculated according to the second-polynomial with $x = 3$).

According to the chlorine ion concentration, the necessary amount of sodium hydroxide aqueous solution was added dropwise to the flask. The temperature was strictly controlled at 50 °C in order to prevent the vaporization of triethylamine. Without filtration of Al(OH)₃, the mixture in the flask was directly heated to distill off the triethylamine. When the mixture was heated from 80 °C to 105 °C the triethylamine and H₂O were collected and weighed. The aluminium hydroxide precipitate was filtrated and dried. Thus 0.237 mol triethylamine (yield: 95.87 %), 31.626 g Al(OH)₃ (yield: 82.0 %) and 72.2 g sodium chloride (yield: 71.34 %) were obtained. Figure 2 shows the flow chart and material balance of the above procedure.

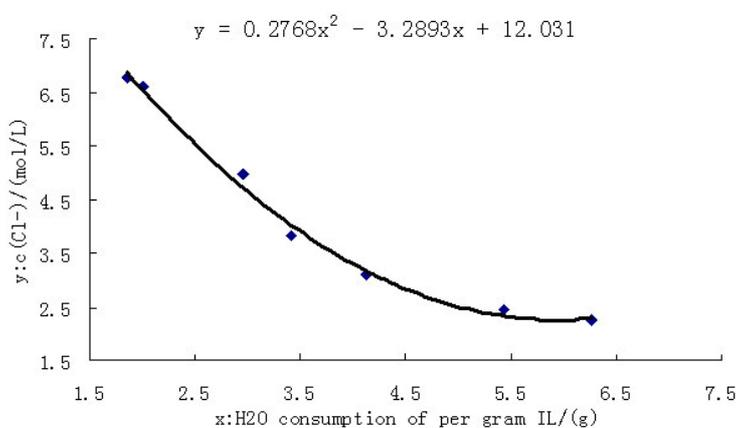


Figure 1. Chlorine ion concentration of aqueous solution vs. water consumption

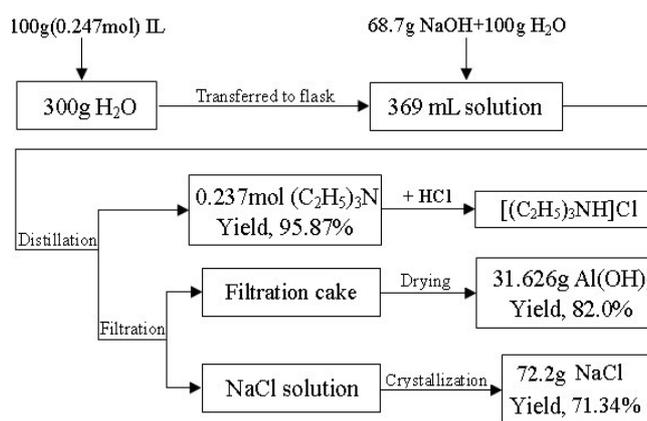


Figure 2. Process for recycling triethylamine.

2.5 Titration of the concentration of triethylamine solution

After distillation, triethylamine was collected in a flask. Enough deionized water was added to the flask until the biphasic disappeared. Acid-base titration based on the following chemical reaction was applied to determine the concentration of triethylamine solution:



The triethylamine solution was titrated with standard hydrochloric acid using bromophenol blue as indicator. The concentration of triethylamine solution was calculated according to following equation:

$$c_{(C_2H_5)_3N} = \frac{c_{HCl} V_{HCl}}{V_{(C_2H_5)_3N}}$$

2.6 Preparation of triethylhydrogenammonium chloride from the recovered triethylamine

After the triethylamine solution was collected, enough hydrochloric acid was added to react with it. The solution was concentrated and then triethylhydrogenammonium chloride (Et₃NHCl) was obtained upon cooling the solution. The purity of the obtained Et₃NHCl was investigated by ¹H-NMR (using D₂O as solvent) and elemental analysis. The ¹H-NMR spectra were at δ = 3.146, 3.153, 3.164, 3.200 ppm, the quadruplet peak corresponded to the CH₂ proton absorptions. The ratio of the number of hydrogens to carbons was 9:6, in agreement with the structure of Et₃NHCl. Elemental analysis: found %: N, 10.28; C, 51.86; H, 11.01 and calculated: N, 10.18; C, 52.35; H, 11.74. The elemental analysis results indicated that the recovered Et₃NHCl prepared from recycled triethylamine was of good purity, and it could be used for synthesizing new chloroaluminate ionic liquid. The obtained ionic liquid has been successful used as a catalyst to produce dichloride phenylphosphine in an industrialized scale [22].

3. Conclusions

(1) The influence of temperature of hydrolysis of the Et₃NHCl-2AlCl₃ chloroaluminate ionic liquid on the chlorine concentration of the obtained aqueous solution was studied. The concentration of chlorine ion was higher in the solutions where hydrolysis of the ionic liquid was carried out at a higher temperature. The aqueous solution with a higher temperature could absorb HCl released by the hydrolysis more easily and was beneficial to the safety of industrial processing.

(2) In the recovery of triethylamine, when the aluminum hydroxide precipitate was filtered before distillation, the yield of triethylamine was only 12 %-18 %, due to the fact that some of the triethylamine was volatilized and some of it remained in the filtration cake. The sharp smell of triethylamine emitted by the cake proved this point. When the mixture was directly heated to distill triethylamine before filtration, the yield was as high as 95.87 %. The sequence of distillation and filtration in the process was the key factor to achieve a high yield of triethylamine recovery.

(3) The aqueous NaCl solution obtained from the above the hydrolysis process could not be reused due to the crystallization of NaCl that would happen after a small amount of ionic liquid was added, so the NaCl solution was directly heated to recover the NaCl crystals. In all, triethylamine was recycled well; aluminium hydroxide and sodium chloride were obtained as by-products. This is in accord with the spirit of Green Chemistry.

References and Notes

1. Anastas, P.T.; Kirchhoff, M.M. Origins, Current Status, and Future Challenges of Green Chemistry. *Acc. Chem. Res.* **2002**, *35*, 686-694.
2. Seddon, K. R. Ionic Liquids for Clean Technology. *J. Chem. Tech. Biotech.* **1997**, *68*, 351-356.

3. Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH, Weinheim, **2003**.
4. Welton, T. Room-Temperature Ionic Liquids: Solvents for Synthesis and Catalysis. *Chem. Rev.* **1999**, *99*, 2071-2083.
5. Earle, M.J.; Seddon, K.R. Ionic liquids. Green Solvents for the Future. *Pure Appl. Chem.* **2000**, *72*, 1391-1398.
6. Seddon, K.R. Biocatalysis in Ionic Liquids. *Green Chem.* **2002**, *4*, 147-151.
7. Dupont, J.; Consorti, C.S.; Spencer, J. Room Temperature Molten Salts: Neoteric "Green" Solvents for Chemical Reactions and Processes. *J. Braz. Chem. Soc.* **2000**, *11*, 337-344.
8. Kazarian, S.G.; Briscoe, B.J.; Welton, T. Combining Ionic Liquids and Supercritical Fluids in situ ATR-IR Study of CO₂ Dissolved in Two Ionic Liquids at High Pressures. *Chem. Commun.* **2000**, *20*, 2047.
9. Blanchard, L.A.; Hancu, D.; Beckman, E.J.; Brennecke, J.F. Green Processing Using Ionic Liquids and CO₂. *Nature* **1999**, *399*, 28.
10. Nanjundiah, C.; McDevitt, S.F.; Koch, V.R. Differential Capacitance Measurements in Solvent-Free Ionic Liquids at Hg and C Interfaces. *J. Electrochem. Soc.* **1997**, *144*, 3392.
11. Gordon C.M.; McLean, A.J. Photoelectron Transfer From Excited-state Ruthenium(II) Tris(bipyridyl) to Methylviologen in an Ionic Liquid. *Chem. Commun.* **2000**, *15*, 1395.
12. Boulaire, V.L.; Gree, R. Wittig Reactions in the Ionic Solvent [bmim][BF₄]. *Chem. Commun.* **2000**, *21*, 2195.
13. Lee, C.W. Diels-Alder Reactions in Chloroaluminate Ionic Liquids: Acceleration and Selectivity Enhancement. *Tetrahedron Lett.* **1999**, *40*, 2461-2464.
14. Adams, C.J.; Earle, M.J.; Hamill, J.; Lok, C.M.; Roberts, G.; Seddon, K.R. *World Patent WO 9807680*, **1998**.
15. Mendelson, W.L.; Spainhour, C.B.; Jones, S.S.; Lamb, B.L.; Wert, K.L. Intramolecular Friedel-Crafts Alkylations. II. An Efficient Synthesis of Biologically Active 1,2,3,4-Tetrahydroisoquinolines. *Tetrahedron Lett.* **1980**, *21*, 1393-1396.
16. Boon, J.A.; Levisky, J.A.; Pflug, J.L.; Wilkes, J.S. Friedel-Crafts Reactions in Ambient-Temperature Molten Salts. *J. Org. Chem.* **1986**, *51*, 480-483.
17. Holbrey, J.D.; Seddon, K.R. Ionic Liquids. *Clean Products and Processes*, **1999**, *1*, 223-236.
18. Chen, D.C.; Wang, L.S. Solubilities of Petroleum Ether, Heptane, Phosphorus Trichloride, and Benzene with the [Triethylamine Hydrochloride]-*x*[AlCl₃] Ionic Liquid. *J. Chem. Eng. Data*, **2005**, *50*, 616-618.
19. Wang, L.S.; Kang, H.B.; Wang, Z.W. Green Synthesis of Dichlorophenylphosphine Sulfide Using Chloroaluminate Ionic Liquids as a Catalyst. *Phosphorus Sulfur Silicon*, **2007**, *182*, 227-236.

20. Greco, C.C.; Fawzy, S.; Lieh-Jiun, S. *US Patent 5824832*, **1998**.
21. Mei, J.; Li, S.P.; Wang, X.B. *A Handbook of Methods for Analyzing General Chemical Products*; Chemical Industrial Press: Beijing. **1999**.
22. Wang, Z.W.; Wang, L.S. Friedel-Crafts Phosphylation of Benzene Catalyzed by [trEHAm]Cl- x AlCl₃ Ionic Liquids. *Appl. Catal. A: Gen.* **2004**, *262*, 101-104.

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