An Engineering-Purpose Preparation Strategy for Ammonium-Type Ionic Liquid with High Purity

Xiaoqi Sun, Yang Ji, Yu Liu, Ji Chen, and Deqian Li
State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, Changchun 130022, P.R. China

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A new strategy for preparing ammonium-type ionic liquid (IL) by acid/base neutralization reaction was proposed. The method contributed to preparing hydroxide-based ammonium IL and resulting task specific ionic liquid (TSIL) with high purity using a low-costly and environment-friendly synthetic route. Halide contamination in the prepared ILs could be markedly decreased than those prepared by well-established anion metathesis method. Moreover, some novel TSILs composed of cations and anions with big steric hindrances could be prepared by this method. Physicochemical properties of the bifunctional TSILs, i.e., density, water content, decomposition temperature, and munal solubility, were also studied in this article. © 2009 American Institute of Chemical Engineers *AIChE J,* 56: 989–996, 2010

Keywords: ammonium-type ionic liquid, acid/base neutralization synthetic route, high purity

Introduction

Ionic liquids (ILs) are a kind of booming "designer solvents." They are non-volatile, non-flammable, and possess wide electrochemical windows. Because of their unique advantages, the application of ILs have attracted considerable interest in many processes, such as reaction, catalysis, separation, and electrochemistry.[1–3] Since ever-increasing need for ILs in academic and industrial research, the preparation and purification of ILs are coming to be significant works. The common synthetic route of ILs was anion metathesis reaction, which was achieved by metathesis reactions between halide intermediates of ILs and appropriate acids or salts.[4–7] ILs prepared by anion metathesis were always contaminated by halide, the contaminations were detrimental to biology, synthesis, electrochemistry, catalysis, and spectroscopy.[8–10] To get IL with desired quality, some novel synthetic methods were studied for preparing halide-free ILs, such as using halide-free intermediates,[11–13] ring-opening reaction of alkylditriflates with *N*-alkylimidazoles,[14] extraction using dichloromethane,[15] quaternization of tertiary phosphines.[5] The improved methods aforementioned were always developed for imidazolium, pyrrolidinium, and phosphonium ILs.

Recently, the quaternary ammonium IL has attracted wide attention.[16,17] In the common four categories of ILs, i.e., imidazolium-type, pyrrolidinium-type, ammonium-type, and phosphonium-type,[18] ammonium-type IL possesses the lowest cost[19] and the least toxicity.[20] As a kind of important compounds, quaternary ammonium salts were widely used as phase-transfer catalyst, surfactant, and bactericide for a century. Quaternary ammoniums were conventionally synthesized by quaternizing tertiary amines.[21,22] Some quaternary ammoniums contained anion that could not be directly synthesized via quaternization, which could be prepared using a sequentially anion-exchange procedure between quaternary ammonium halide and acid[23] or salt[24] with corresponding anions. In the past decade, quaternary ammoniums have

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Correspondence concerning this article should be addressed to J. Chen at jchen@ciac.jl.cn

been further understood from the viewpoint of ILs in many fields, such as catalyst, electrochemistry, separation, lubricates, biochemistry, and synthesize. The booming "tailor-made" ammonium ILs might reveal considerable applying potentialities for some industrial processes. Accordingly, their purities seemed to be more important. To our knowledge, less study on preparing pure ammonium IL, especially bifunctional ammonium IL with low halide content, has been addressed. As a result, we studied herein a novel engineering-purpose acid/base neutralization strategy for preparing pure ammonium ILs. Acid/base neutralization using hydroxide-based IL and acid has been indicated to be an effective method for preparing halide-free ILs since there was no halide in the precursors. Some ILs were prepared using the method, for example, *N,N,N,N*-trialkyl-*N*-hexylammonium methanesulfonate,[25] 1-alkyl-3-methylimidazolium lactate,[26] 1-ethyl-3-methylimidazolium amino acid ILs,[27] tetrabutylphosphonium amino acid ILs,[28] and 1-ethyl-3-methylimidazolium benzoate.[29] Hydroxide-based ILs were a kind of alkaline ILs themselves; moreover, they were the important precursors in preparing some other ILs by acid/base neutralization reaction. The preparation of hydroxide-based IL could be achieved by ion exchange between halide IL precursor and silver hydroxide[25] or solid potassium hydroxide,[30] ion exchange resin,[25,27,31] and electrodialysis membrane.[29,32] In this study, we used another method to prepare quaternary onium hydroxides like elsewhere mentioned.[33] In contrast to the ion-exchange column or electrodialysis membrane, the preparation process concerned lower cost, shorter time, and less wastewater. Then, the ammonium hydroxide-based IL was used as precursor to prepare some novel bifunctional TSILs using acid/base neutralization.

Experimental

Chemicals

Tricaprylmethylammonium chloride (Aliquat 336) was purchased from ACROS. Bis(2,4,4-trimethylpentyl)phosphinic acid (86.5% purity, Cyanex272), bis(2,4,4-trimethylpentyl)monothiophosphinic acid (84% purity, Cyanex302) were kindly supplied by the CYTEC Canada Di-(2-ethylhexyl) phosphate (95% purity, P204), 2-ethylhexyl phosphoric acid mono(2-ethylhexyl) ester (93% purity, P507), sec-octylphenoxy acetic acid (92% purity, CA-12), and sec-nonylphenoxy acetic acid (98% purity, CA-100) were kindly supplied by Tianjin Xiandai Chemical Plant (China). Ethanol, propanol, isopropanol, nitric acid, sodium hydroxide, and sodium nitrate were purchased from Sinopharm Chemical Reagent. Acetone, ethanol, propanol, and isopropanol were distilled before use.

Procedure

The concentration of chloride ion was determined using ion chromatograph (Dionex ICS-1500). The content of [A336][OH] was determined by titration, using 0.1 mol/l HNO_3 solution, and bromothymol blue was used as the pH indicator. The reaction extents of [A336][CA-100], prepared by metathesis and acid/base neutralization reaction, were determined using HPLC at 205 nm, which was equipped with a pump (515 HPLC Pump, Waters), a UV detector (Waters 2487), and a SunFire C18 analytical column. The column temperature was kept at 33°C, eluent was methanol, and flow rate was 0.6 ml/min. ^1H and ^{13}C NMR spectra of the prepared ILs were obtained in pyridine-d5 with a Bruker AV 600 NMR spectrometer. The densities of TSILs were determined by gravimetric analysis, i.e., using 1 ml of each TSIL to determine the mass of that volume of liquid, every measurement was repeated five times and the average value was reported, all measurements were taken at 20°C. The water contents of TSILs were determined by Karl Fischer titration using a model WA-1C Electric Water Meter (Jiangsu Electric Analysis Instruments, China). Thermal stabilities were determined by differential scanning calorimetry using a Thermal Analysis Instrument (SDT 2960, TA Instruments, New Castle, DE). Measurements were conducted by heating the sample from 40°C to 600°C at a heating rate of 10°C/min under N_2 atmosphere. The mutual solubility tests of TSILs with some common solvents were conducted by KQ5200DE ultrasonic Instrument (Kunshan ultrasonic Instrument, China) at 140 W.

The preparation of TSIL

Anion Metathesis Reaction. [A336][NO_3]: 8.5 g (0.1 mol) of sodium nitrate was dissolved in 20 ml of DI water; 40.457 g (0.1 mol) of Aliquat 336 was dissolved in 50 ml of acetone and added dropwise into the aqueous-acetone mixture of sodium nitrate under vigorous magnetic stirring. The mixture was stirred for 1 h and left to settle. After a while, an aqueous layer formed at the bottom. The upper phase was poured into a vacuum rotatory evaporator (353 K, 20 mbar, 60 min) to remove residual water and acetone.

Then, 50 ml extra dry acetone was added. After sedimentation and subsequent filtration through a millipore 4.5 μm filter, vacuum was applied in a rotavapor (353 K, 20 mbar, 60 min). A clear, slightly yellowish liquid was obtained; the yield of [A336][NO_3] was 66.65%.

[A336][CA-100]: [A336][CA-100] was prepared by combining 50.975 g (0.126 mol) Aliquat 336 and 35.08 g (0.126 mol) CA-100 in the presence of 20% aqueous sodium hydroxide ($M_{NaOH} = 0.126$ mol). The mixture was heated to 55°C with vigorous agitation for 4 h, and washed three times with DI water (80 ml) to remove sodium chloride. Then, the product was poured into a vacuum rotatory evaporator (353 K, 20 mbar, 60 min) to remove residual water. A yellowish liquid was obtained.

Acid/Base Neutralization Reaction. [A336][OH]: Sodium alkoxide was prepared by combining 6.39 g (0.278 mol) sodium and 125 ml ethanol (propanol, isopropanol) for 3 h; 112.36 g (0.278 mol) Aliquat 336 was dissolved in 500 ml of ethanol (propanol, isopropanol), and added dropwise into the ethanol (propanol, isopropanol) solution containing sodium alkoxide. The solutions were stirred for 4 h at 50°C. The mixture was centrifuged at 8000 r/min for 10 min to remove the white precipitate of sodium chloride. Then, the filtrates were shaken with equal volume of DI water for half an hour to get [A336][OH] by the hydrolysis of [A336][OR]. The yield of [A336][OH] prepared by ethanol, propanol, and isopropanol were 66.25%, 59.4%, and 88.42%, respectively.

[A336][NO_3]: [A336][NO_3] was prepared by combining 250 ml [A336][OH] (0.12 mol/l) and 1.74 ml HNO_3 (15.69

mol/l) (mole ratio is 1.1:1). The mixture was vigorously agitated for 4 h at 50°C under reflux and left to settle. After a while, an aqueous layer formed at the bottom. The upper phase was poured into a vacuum rotatory evaporator (353 K, 20 mbar, 60 min) to remove residual water and isopropanol. The final yield of [A336][NO$_3$] was indicated to be 79.14%.

^{1}H NMR: 0.88 (t, J = 4 Hz, 9H), 1.27–1.36 (m, 42H), 1.66 (s, 6H), 3.19 (s, 3H), 3.33 (t, J = 8.0 Hz, 6H).

^{13}C NMR: 13.88, 22.17, 22.47, 25.66, 26.16, 27.21, 28.87, 29.23, 31.48, 31.67, 32.70, 48.23, 61.47.

[A336][CA-12]: [A336][CA-12] was prepared by combining 290 ml [A336][OH] (0.12 mol/l) and 11.02 g CA-12 (mole ratio is 1.1:1). The mixture was vigorously agitated for 12 h at 50°C under reflux and left to settle. After a while, an aqueous layer formed at the bottom. The upper phase was poured into a vacuum rotatory evaporator (353 K, 20 mbar, 60 min) to remove residual water and isopropanol. The final yield of [A336][CA-12] was indicated to be 71.57%.

^{1}H NMR: 0.664–0.710 (m, 3H), 0.719–0.7640 (m, 9H), 1.057–1.175 (m, 28H), 1.185–1.251 (m, 10H), 1.341–1.465 (m, 2H), 1.633–1.712 (m, 6H), 3.400 (s, 3H), 3.602–3.611 (m, 6H), 4.793–4.847 (m, 2H), 6.868–6.986 (m, 1H), 7.031–7.054 (m, 1H), 7.088 (s, 1H), 7.150–7.163 (m, 1H).

^{13}C NMR: 173.04, 128.70, 137.99, 126.73, 120.05, 115.45, 115.41, 70.36, 61.58 (3C), 48.38, 32.19, 32.04 (2C), 29.86, 29.84 (2C), 29.66 (2C), 29.61 (2C), 29.53 (2C), 29.46 (3C), 26.84 (5C), 23.04 (2C), 22.97 (2C), 22.72, 14.41, 14.38, 14.34.

[A336][CA-100]: [A336][CA-100] was prepared by combining 250 ml [A336][OH] (0.11 mol/l) and 6.96 g CA-100 (mole ratio is 1.1:1). The mixture was vigorously agitated for 12 h at 50°C under reflux and left to settle. After a while, an aqueous layer formed at the bottom. The upper phase was poured into a vacuum rotatory evaporator (353 K, 20 mbar, 60 min) to remove residual water and isopropanol. The final yield of [A336][CA-100] was indicated to be 78.69%.

^{1}H NMR: 0.86 (t, J = 1.2 Hz, 9H), 1.18 (m, 3H), 1.26 (m, 30H), 1.33 (m, 16H), 1.61 (m, 6H), 3.26 (s, 3H), 3.378–3.419 (t, J = 8.0 Hz, 6H), 4.44 (s,2H), 6.892 (d, J = 7.2 Hz, 2H), 7.125 (m, 2H).

^{13}C NMR: 13.81, 22.35, 26.11, 26.78, 27.46, 28.81, 29.03, 29.38, 31.62, 35.34, 41.31, 43.18, 48.47, 51.73, 54.03, 61.05, 62.04, 68.09, 113.84, 126.81, 139.06, 156.64, 173.12.

[A336][P204]: [A336][P204] was prepared by combining 190 ml [A336][OH] (0.11 mol/l) and 8 g P204 (mole ratio is 1.1:1). The mixture was vigorously agitated for 12 h at 50°C under reflux and left to settle. After a while, an aqueous layer formed at the bottom. The upper phase was poured into a vacuum rotatory evaporator (353 K, 20 mbar, 60 min) to remove residual water and isopropanol. The final yield of [A336][P204] was indicated to be 84.94%.

^{1}H NMR: 0.854–0.870 (m, 6H), 0.876–0.894 (m, 9H), 1.265–1.274 (m, 30H), 1.282–1.296 (m, 6H), 1.308–1.358 (m, 12H), 1.370–1.411 (m, 4H), 1.424–1.470 (m, 1H), 1.500–1.530 (m, 1H), 1.613–1.677 (m, 6H), 3.294 (s, 3H), 3.375–3.403 (t, J = 7.8 Hz, 6H), 3.711–3.745 (m, 4H).

^{13}C NMR: 10.66 (2C), 13.70, 13.74, 13.80, 22.11 (3C), 22.28 (3C), 22.33 (3C), 22.87 (3C), 23.06 (3C), 26.09 (2C), 28.77, 28.81 (2C), 28.91 (2C), 28.95, 29.12, 29.16, 29.85, 31.38, 31.54, 40.14, 48.59, 60.93, 67.32, 67.35 (2C).

[A336][P507]: [A336][P507] was prepared by combining 170 ml [A336][OH] (0.12 mol/l) and 6.25 g P507 (mole ratio is 1.1:1). The mixture was vigorously agitated for 12 h at 50°C under reflux and left to settle. After a while, an aqueous layer formed at the bottom. The upper phase was poured into a vacuum rotatory evaporator (353 K, 20 mbar, 60 min) to remove residual water and isopropanol. The final yield of [A336][P507] was indicated to be 73.62%.

^{1}H NMR: 0.822–0.847 (t, J = 8.4 Hz, 3H), 0.851–0.872 (t, J = 8.4 Hz, 3H), 0.875–0.894 (t, J = 6.6 Hz, 9H), 1.264 (s, 30H), 1.287–1.298 (m, 6H), 1.330–1.408 (m, 12H), 1.419–1.454 (m, 2H), 1.466–1.515 (m, 2H), 1.539–1.583 (m, 1H), 1.609–1.677 (m, 6H), 1.710–1.779 (m, 1H), 2.699 (s, 2H), 3.322 (s, 3H), 3.404–3.432 (t, J = 8.4 Hz, 6H), 3.672–3.705 (m, 2H).

^{13}C NMR: 65.87, 61.00 (3C), 48.82, 40.55, 34.80, 33.75, 31.65, 31.49 (2C), 30.0 (2C), 29.26, 29.22, 29.07 (2C), 29.02 (2C), 28.99 (2C), 28.87 (2C), 28.58 (2C), 26.42 (2C), 26.22 (2C), 23.26, 23.06, 22.46, 22.40, 22.21, 14.06, 13.95, 13.87, 13.83 (2C), 10.86, 10.25.

[A336][Cyanex 272]: [A336][Cyanex272] was prepared by combining 190 ml [A336][OH] (0.12 mol/l) and 7.14 g Cyanex272 (mole ratio is 1.1:1). The mixture was vigorously agitated for 12 h at 50°C under reflux and left to settle. After a while, an aqueous layer formed at the bottom. The upper phase was poured into a vacuum rotatory evaporator (353 K, 20 mbar, 60 min) to remove residual water and isopropanol. The final yield of [A336][Cyanex272] was indicated to be 81%.

^{1}H NMR: 0.86 (t, J = 1.2 Hz, 9H), 1.18 (s, 3H), 1.26 (s, 30H), 1.33 (s, 16H), 1.61 (s, 6H), 3.26 (s, 3H), 3.378–3.419 (t, J = 8.0 Hz, 6H), 4.44 (s, 2H), 6.892 (d, J = 7.2 Hz, 2H), 7.125 (m, 2H).

^{13}C NMR: 13.81, 22.35, 26.11, 26.78, 27.46, 28.81, 29.03, 29.38, 31.62, 35.34, 41.31, 43.18, 48.47, 51.73, 54.03, 61.05, 62.04, 68.09, 113.84, 126.81, 139.06, 156.64, 173.12.

[A336][Cyanex302]: [A336][Cyanex302] was prepared by combining 185 ml [A336][OH] (0.118 mol/l) and 7.23 g Cyanex 302 (mole ratio is 1.1:1). The mixture was vigorously agitated for 12 h at 50°C under reflux and left to settle. After a while, an aqueous layer formed at the bottom. The upper phase was poured into a vacuum rotatory evaporator (353 K, 20 mbar, 60 min) to remove residual water and isopropanol. The final yield of [A336][Cyanex 302] was indicated to be 78.69% (Figure 1).

^{1}H NMR: 0.729–0.766 (m, 9H), 0.922–0.968 (m, 18H), 1.115–1.919 (m, 30H), 1.298–1.347 (m, 4H), 1.370–1.415 (m, 6H), 1.535–1.641 (m, 2H), 1.738–1.749 (m, 6H), 1.724–2.034 (m, 4H). 3.457 (s, 3H), 3.662–3.672 (m, 6H).

^{13}C NMR: 14.35 (2C), 14.38, 22.80 (2C), 22.99 (2C), 23.03 (2C), 25.56, 25.63, 26.91 (3C), 29.52 (2C), 29.62 (2C), 29.67 (2C), 29.69 (2C), 29.79, 29.88, 30.03, 30.39, 30.77 (2C), 311.66 (2C), 32.06 (3C), 32.20 (2C), 48.47, 54.67, 54.73, 61.37 (3C).

Results and Discussion

Herein, a widely-used ammonium IL,[6] i.e., Aliquat 336 (A336), was used as precursor. As revealed in Figure 2,

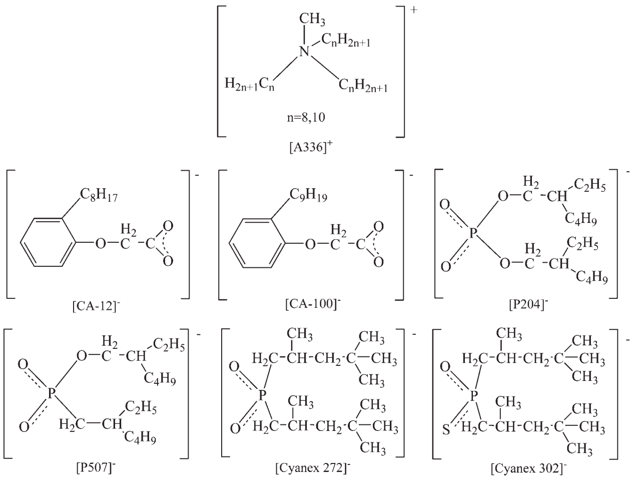

Figure 1. The prepared bifunctional TSILs.

sodium alkoxide was prepared by combining sodium, ethanol, propanol, and isopropanol, respectively. The sodium alkoxide was subsequently combined with A336 for preparing $[R_1R_2R_3R_4N]^+[OR]^-$ by anion exchange. Since $[R_1R_2R_3R_4N]^+[OR]^-$ had higher dissolving capacity in ethanol, propanol, and isopropanol than those of sodium ion and chloride ion, the sodium chloride precipitate could be easily removed from the solution by centrifugation. The $[R_1R_2R_3R_4N]^+[OR]^-$ was produced into quaternary ammonium hydroxide by hydrolysis. Yields of the $[R_1R_2R_3R_4N]^+[OH]^-$ prepared by ethanol, propanol, and isopropanol were indicated to be 66.25%, 59.4%, and 88.42%, respectively. The different yields could be attributed to the different alkalinity of $[R_1R_2R_3R_4N]^+[OR]^-$. Because isopropanol was secondary alcohol vs. ethanol and propanol were primary alcohol, the alkalinity of $[R_1R_2R_3R_4N]^+[OR]^-$ prepared by isopropanol was stronger than those prepared by ethanol and propanol. Consequently, the isopropanol-prepared $[R_1R_2R_3R_4N]^+[OR]^-$ had a better hydrolysis ability, which resulted in a better yield. Since isopropanol could bring higher yield than ethanol and propanol, isopropanol was chosen to make a further study. The regenerate isopropanol could be recovered from water by distillation[34] or membrane technology.[35] The prepared ammonium hydroxide was a strong base, it was prone to react with carbon dioxide in air. As a result, the separation and conservation of [A336][OH] from isopropanol and water would introduce unnecessary impurity and decrease yield. Because [A336][OH] was stable in isopropanol aqueous solution, it was conserved in to solution for further reaction. In addition, the solution could decrease high viscosities of the reactants effectively, which contributed to the following acid/base neutralization process.

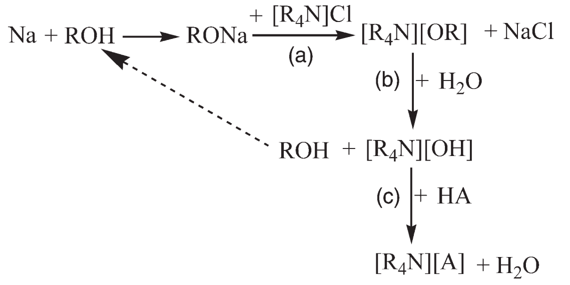

Figure 2. Synthetic route of ammonium IL by acid/base neutralization reaction.

(a) Anion exchange, (b) Hydrolysis, and (c) Acid/base neutralization.

The prepared [A336][OH] was subsequently combined with nitric acid to synthesize $[A336][NO_3]$. Although the proposed synthetic route concerned three processes, its overall yield of 79.14% vs. 66.65% of anion metathesis method indicated that the synthetic route was feasible. To confirm the validity of the proposed strategy, chloride ion concentrations in $[A336][NO_3]$ prepared by anion metathesis reaction, anion metathesis reaction with filtration by acetone and acid/base neutralization reaction were compared using ion chromatograph. As can be seen in Figure 3, 2 ml ILs prepared by the three methods were shaken with 5 ml DI water for six times, the chloride ion concentrations in wash water from the ILs prepared using anion metathesis reaction and anion metathesis reaction with filtration by acetone were quite higher than those prepared using acid/base neutralization reaction. Thus, a conclusion could be achieved that the halide content in $[A336][NO_3]$ prepared by acid/base neutralization reaction were much lower than those prepared by anion metathesis reaction even through a tedious filtration process. Actually, Ion chromatograph was quite sensitive for detecting halide.[36] Although there were still very few halide ions in the prepared IL, the synthetic route still seemed to be attractive for large scale preparation since its reactants seemed to be more cheap and available than halide-free intermediates.

TSILs contained specific functional groups in their cations and/or anions, which had been designed and synthesized for specific purposes such as catalysis, synthesis, and separation.

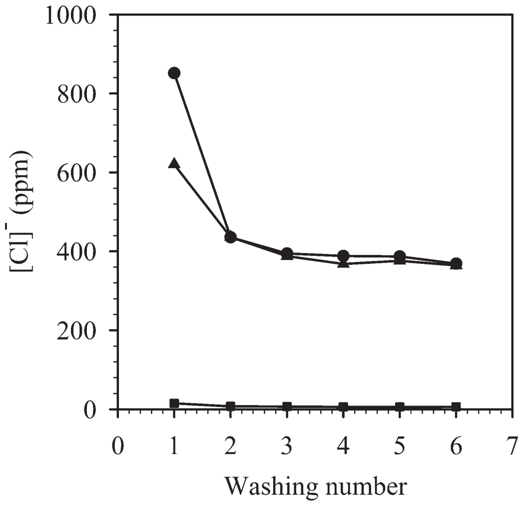

Figure 3. The chloride ion concentration in wash water of $[A336][NO_3]$ prepared using anion metathesis reaction(●), anion metathesis reaction with filtration by acetone(▲), and acid/base neutralization reaction(■).

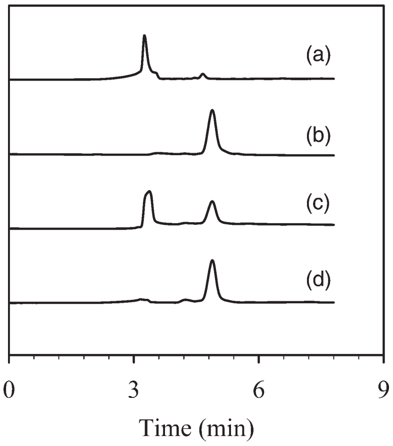

Figure 4. The liquid chromatogram of [A336][CA-100] prepared using anion metathesis reaction and acid/base neutralization reaction.

(a) Aliquat 336, (b) CA-100, (c) [A336][CA-100] prepared using anion metathesis reaction, and (d) [A336][CA-100] prepared using acid/base neutralization reaction.

Because TSILs acted as not only reaction medium but also reagent or catalyst,[37] their synthesis and purification seemed to be more important. Some macromolecular acids containing special functional groups were used to prepare TSILs, such as bis(2,4,4-trimethylpentyl)phosphinic acid,[5] heteropolyacid,[38] and amino acid.[28] Moreover, some of the prepared TSILs have been commercialized, such as trihexyl(tetradecyl)phosphonium bis2,4,4-trimethylpentylphosphinate (CyphosIL-104), which was indicated to be an effective extractant for lactic acid.[39] However, not all TSIL could be prepared by anion metathesis reaction. CA-100 was a carboxylic acid extractant, its physicochemical properties and extraction behaviors had been studied in our laboratory.[40] In this work, the [A336][CA-100] prepared by anion metathesis reaction and acid/base neutralization reaction were compared, and their reaction extents were investigated by HPLC. HPLC-UV-method was an effective method to investigate the purity of IL.[41] As revealed in Figure 4, the reaction extent of [A336][CA-100] prepared using anion metathesis reaction was not desirable and the residual Aliquat 336 was obvious. Actually, [A336][CA-100] was difficult to be prepared by anion metathesis since the big steric hindrances of $[A336]^+$ and $[CA\text{-}100]^-$. In contrast to anion metathesis reaction, the reaction extent of [A336][CA-100] prepared using acid/base neutralization reaction was satisfactory. In essence, "driving force" was crucial for a reaction that pushed reactants into product. The driving force of metathesis reaction was the removal of ions from solution by precipitate, and the reaction extent of metathesis was up to the efficiency of precipitate in solution. As for the preparation of [A336][CA-100] using anion metathesis, a full precipitation process of sodium chloride was difficult to be achieved because of the existence of water from aqueous sodium hydroxide during preparation. Unlike metathesis reaction, the driving force of acid/base neutralization reaction was the formation of stable water molecule. Obviously, the formation of water was easy than sodium chloride precipitation, i.e., the driving force of acid/base neutralization reaction was bigger than that of metathesis reaction. In addition, quaternary ammonium hydroxide ([A336][OH]) was a strong base itself, its alkalinity was equivalent to those of potassium hydroxide and sodium hydroxide. Undoubtedly, the strong base contributed to acid/base neutralization process.

As can be seen from Figures 4c, d, retention times of CA-100 and [A336][CA-100] were almost identical. The effect revealed a problem, i.e., it was difficult to purify the unreacted CA-100 from [A336][CA-100] because of their similar properties. To resolve the problem, molar ratio of [A336][OH] and CA-100 was set up according to 1.1:1 in the acid/base neutralization reaction. As a result, the CA-100 could be fully reacted. Because [A336][OH] was water-soluble, the excess base could be recycled by reusing the aqueous solution. From the angle of reaction extent, the higher driving force of acid/base neutralization reaction contributed not only higher yield but also higher purity.

The method mentioned in this study was not only suitable for preparing [A336][CA-100], but also some other bifunctional TSILs with big cations and anions, such as [tricaprylmethyl ammonium][s-octyl phenyloxy acetate] ([A336][CA-12]), [tricaprylmethyl ammonium][di-2-ethylhexylphosphinate] ([A336][P204]), [tricaprylmethyl ammonium][di-(2-ethylhexyl)orthophosphinate] ([A336][P507]), [tricaprylmethyl ammonium][bis(2,4,4-trimethylpentyl)phosphinate] ([A336][Cyanex272]), and [tricaprylmethyl ammonium][bis(2,4,4-trimethylpetyl)monothio phosphinate] ([A336][Cyanex302]) could also be prepared by the acid/base neutralization method. Since precursors of the TSILs, i.e., quaternary ammonium salt, phosphonic acid, and carboxylic acid were widely used in catalysis[42] and separation.[43,44] The novel bifunctional TSILs may reveal attractive application values for engineering processes. Such studies are under way in this laboratory. Before considering application of the novel TSILs in some engineering processes, a fundamental understanding must be established for their chemical and physical properties.

Table 1. Density and Water Content of the Dried (Water Equilibrated) TSILs (293 K)

	Dried		Water Equilibrated	
TSILs	Density (g/mL)	Water Content (ppm)	Density (g/mL)	Water Content (ppm)
[A336][P204]	1.019	967.2	0.987	10,296.8
[A336][P507]	1.042	576	1.007	8,760.8
[A336][CA-12]	1.021	876.8	0.959	10,348.8
[A336][CA-100]	0.979	420.8	0.975	9,448
[A336][Cyanex272]	–	378.4	0.987	13,956.8
[A336][Cyanex302]	–	461.6	0.993	5,518.4

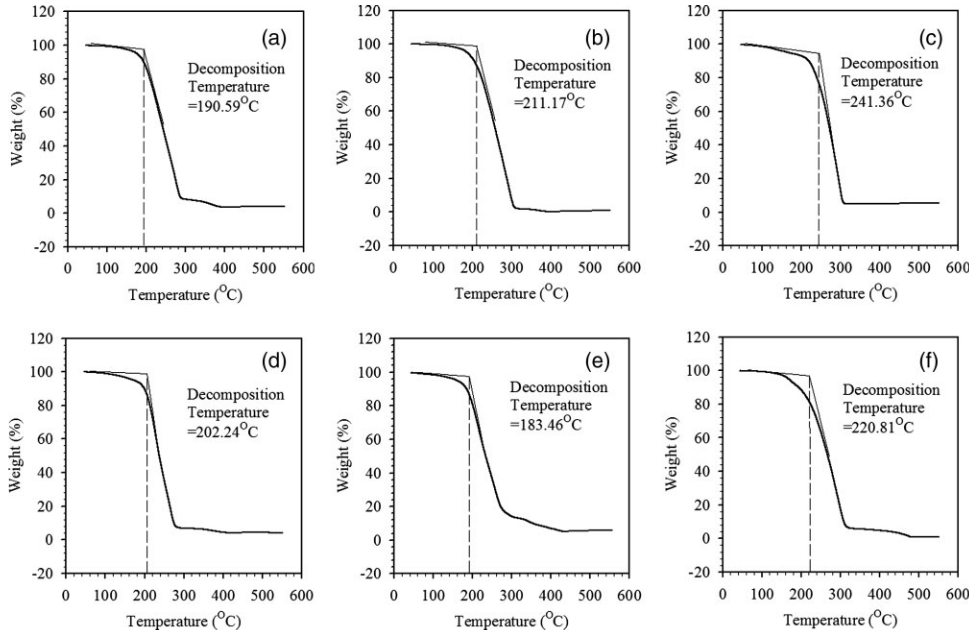

Figure 5. Thermogravimetric traces of the TSILs.

(a) [A336][CA-12], (b) [A336][CA-100], (c) [A336][P204], (d) [A336][P507], (e) [A336][Cyanex272], and (f) [A336][Cyanex302].

The presence of water may have an effect obviously on the physiochemical properties of TSIL. To study the TISLs' densities and water contents in the states of dried and saturated with water, 1 ml of each dried TSIL was equilibrated with 3 ml of water at 20°C, then densities and water contents of the TSILs were determined. As revealed in Table 1, water content of the TSILs could be obviously increased even by an order of magnitude after being saturated with water. The increase of water content might cause the densities of TSILs to be decreased. Moreover, viscosities of the TSILs could be evidently decreased as water content increased, for example, the state of [A336][Cyanex272] and [A336][Cyanex302] changed from waxy solid to viscous liquid after being equilibrated with water.

The results of thermogravimetric analysis, as depicted in Figure 5, revealed decomposition temperatures of the TSILs, which were [A336][Cyanex272] $<$ [A336][CA-12] $<$ [A336][P507] $<$ [A336][CA-100] $<$ [A336][Cyanex302] $<$ [A336][P204]. Since cations of the TSILs were all trialkylmethylammonium, thermal stability differences of the TSILs were mainly controlled by the combined anions. For instance, decomposition temperature of the TSIL containing bis(2,4,4-trimethylpentyl)phosphinate was found to be around 183°C, whereas a value of 241°C was observed for the case of di-2-ethylhexylphosphinate-containing IL. It was worth mentioning that the water and isopropanol used in preparation process were difficult to be thoroughly removed because of the bigger viscocities of the TSILs. The weight losses of TSILs before decomposition could be mainly attributed to the remanent water and isopropanol.

To apply the TSILs as solvents or reactants, it is necessary to acquire their miscibility with some common organic solvents. The prepared TSILs were tested for mutual solubilities in ethanol, acetone, heptane, toluene, dodecane, and chloroform at 293 K and atmospheric pressure. Every piece of 0.1 g TSILs and 0.5 ml organic solvents were ultrasonic mixed for half an hour. Then, the mixtures were settled for an hour, which was found to be enough for achieving a complete phase separation. As can be seen in Table 2, [A336][P204], [A336][P507], [A336][CA-12], and [A336][CA-100] have normally better mutual solubilities with the organic solvents than [A336][Cyanex272] and [A336][Cyanex302].

Table 2. Mutual Solubilities of the TSILs with Different Organic Solvents

Ionic Liquids	Ethanol	Acetone	Heptane	Toluene	Dodecane	Chloroform
[A336][P204]	Y	Y	Y	Y	Y	Y
[A336][P507]	Y	Y	Y	Y	Y	Y
[A336][CA-12]	Y	N	Y	Y	Y	P
[A336][CA-100]	Y	P	Y	Y	Y	P
[A336][Cyanex272]	Y	N	N	P	N	P
[A336][Cyanex302]	Y	P	P	P	P	P

Y, denotes totally soluble; P, partly soluble; N, insoluble.

Conclusions

In conclusion, a simple and efficient strategy for preparing pure ammonium IL was developed. The preparation method contained three procedures, i.e., anion exchange, hydrolysis, and acid/base neutralization. The isopropanol used was not only reactant but also effective solvent for removing sodium chloride, accordingly, [A336][OH] and [A336][NO_3] with very few chloride contamination could be prepared. In addition, driving force of the acid/base neutralization method was larger than that of general-used anion metathesis method, which contributed to prepare bifunctional TSIL with big steric hindrance that could not be prepared by anion metathesis. Some novel engineering-purpose bifunctional TSILs were prepared using the proposed synthetic route, such as [A336][CA-12], [A336][CA-100], [A336][P204], [A336][P507], [A336][Cyanex272], and [A336][Cyanex302]. Sodium chloride was the only by-product in the preparation processes. The low cost, mild condition, and environment-friendship make this preparation method to be attractive for scale-up purposes.

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Literature Cited

1. Rogers RD, Seddon KR. Ionic liquids-solvents of the future? *Science* 2003;302:792–793.
2. Plechkova NV, Seddon KR. Applications of ionic liquids in the chemical industry. *Chem Soc Rev*. 2008;1:123–150.
3. Sun XQ, Ji Y, Peng B, Chen J, Li DQ. Chitosan(chitin)/cellulose composite biosorbents prepared using ionic liquid for heavy metal ions adsorption. *AIChE J*. 2009;55:2062–2069.
4. Huddleston JG, Visser AE, Reichert WM, Willauer HD, Broker GA, Rogers RD. Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chem.* 2001;3:156–164.
5. Bradaric CJ, Downard A, Kennedy C, Robertson AJ, Zhou YH. Industrial preparation of phosphonium ionic liquids. *Green Chem.* 2003;5:143–152.
6. Mikkola JP, Virtanen P, Sjöholm R. Aliquat 336-a versatile and affordable cation source for an entirely new family of hydrophobic ionic liquids. *Green Chem.* 2006;8:250–255.
7. Ren W, Scurto AM. Global phase behavior of imidazolium ionic liquids and compressed 1,1,1,2-tetrafluoroethane (R-134a). *AIChE J*. 2009;55:486–493.
8. Seddon KR, Stark A, Torres MJ. Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. *Pure Appl Chem.* 2000;72:2275–2287.
9. Gallo V, Mastrorilli P, Nobile CF, Romanazzi G, Suranna GP. How does the presence of impurities change the performance of catalytic systems in ionic liquids? A case study: the Michael addition of acetylacetone to methyl vinyl ketone. *Dalton Trans.* 2002;23:4339–4342.
10. Mariotti AWA, Xie J, Abrahams BF, Bond AM, Wedd AG. Synthesis and voltammetry of [bmim]$_4$[α-$S_2W_{18}O_{62}$] and related compounds: rapid precipitation and dissolution of reduced surface films. *Inorg Chem.* 2007;46:2530–2540.
11. Holbrey JD, Reichert WM, Swatloski RP, Broker GA, Pitner WR, Seddon KR, Rogers RD. Efficient, halide free synthesis of new, low cost ionic liquids: 1,3-dialkylimidazolium salts containing methyl- and ethyl-sulfate anions. *Green Chem.* 2002;4:407–413.
12. Bridges NJ, Hines CC, Smiglak M, Rogers RD. An intermediate for the clean synthesis of ionic liquids: isolation and crystal structure of 1,3-dimethylimidazolium hydrogen carbonate monohydrate. *Chem Eur J*. 2007;13:5207–5212.
13. Cassol CC, Ebeling G, Ferrera B, Dupont J. A simple and practical method for the preparation and purity determination of halide-free imidazolium ionic liquids. *Adv Synth Catal*. 2006;348:243–248.
14. Leclercq L, Suisse I, Nowogrocki G, Niedercorn FA. Halide-free highly-pure imidazolium triflate ionic liquids: preparation and use in palladium-catalysed allylic alkylation. *Green Chem.* 2007;10:1097–1103.
15. Burrell AK, Del Sesto RE, Baker SN, McCleskey TM, Baker GA. The large scale synthesis of pure imidazolium and pyrrolidinium ionic liquids. *Green Chem.* 2007;9:449–454.
16. Pernak J, Smiglak M, Griffin ST, Hough WL, Wilson TB, Pernak A, Matejuk JZ, Fojutowski A, Kita K, Rogers RD. Long alkyl chain quaternary ammonium-based ionic liquids and potential applications. *Green Chem.* 2006;8:798–806.
17. Jiang H, Wang C, Li HR, Wang Y. Preparation of dialkoxypropanes in simple ammonium ionic liquids. *Green Chem.* 2006;8: 1076–1079.
18. Welton T. Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem Rev*. 1999;99:2071–2083.
19. Pwasserscheid P, Welton T. *Ionic Liquids in Synthesis*. New York: Wiley-VCH, 2002.
20. Couling DJ, Bernot RJ, Docherty KM, Dixona JK, Maginn EJ. Assessing the factors responsible for ionic liquid toxicity to aquatic organisms *via* quantitative structure-property relationship modeling. *Green Chem.* 2006;8:82–90.
21. Bottini AT, Dowden BF, VanEtten RL. On the stereochemistry of quaternization of amines. *J Am Chem Soc*. 1965;87:3250–3251.
22. Ruckenstein E, Chen XN. Covalent cross-linking of polymers through ionene formation and their thermal de-cross-linking. *Macromolecules.* 2000;33:8992–9001.
23. Moore FL. New liquid-liquid extraction method for the separation of Cerium(lV) from Berkelium(1V) and other elements. *Anal Chem.* 1969;41:1658–1661.
24. Maayan G, Fish RH, Neumann R. Polyfluorinated quaternary ammonium salts of polyoxometalate anions: fluorous biphasic oxidation catalysis with and without fluorous solvents. *Org Lett*. 2003;5:3547–3550.
25. Golding J, Forsyth S, MacFarlane DR, Forsyth M, Deacon GB. Methanesulfonate and p-toluenesulfonate salts of the N-methyl-N-alkylpyrrolidinium and quaternary ammonium cations: novel low cost ionic liquids. *Green Chem.* 2002;4:223–229.
26. Peng YQ, Li GY, Li JG, Yu SJ. Convenient synthesis of various ionic liquids from onium hydroxides and ammonium salts. *Tetrahedron Lett*. 2009;50:4286–4288.
27. Fukumoto K, Yoshizawa M, Ohno H. Room temperature ionic liquids from 20 natural amino acids. *J Am Chem Soc*. 2005;127: 2398–2399.
28. Zhang JM, Zhang SJ, Dong K, Zhang YQ, Shen YQ, Lv XM. Supported absorption of CO_2 by tetrabutylphosphonium amino acid ionic liquids. *Chem Eur J*. 2006;12:4021–4026.
29. Himmler S, König A, Wasserscheid P. Synthesis of [EMIM]OH *via* bipolar membrane electrodialysis-precursor production for the combinatorial synthesis of [EMIM]-based ionic liquids. *Green Chem.* 2007;9:935–942.
30. Ranu BC, Banerjee S. Ionic liquid as catalyst and reaction medium. The dramatic influence of a task-specific ionic liquid, [bmIm]OH, in michael addition of active methylene compounds to conjugated ketones, carboxylic esters, and nitriles. *Org Lett*. 2005;7: 3049–3052.
31. Ou GN, Zhu MX, She JR, Yuan YZ. Ionic liquid buffers: a new class of chemicals with potential for controlling pH in non-aqueous media. *Chem Commun*. 2006;44:4626–4628.
32. Wang TT, Yang WC. Factors affecting the current and the voltage efficiencies of the synthesis of quaternary ammonium hydroxides by electrolysis-electrodialysis. *Chem Eng J*. 2001;81:161–169.
33. He MS, Ke L, Hao YC, Yang Q, Feng Y. A method for preparing quaternary ammonium hydroxide from quaternary ammonium salt. *China Patent* 2004; CN1177803C.
34. Hoof VV, Abeele LVD, Buekenhoudt A, Dotremont C, Leysen R. Economic comparison between azeotropic distillation and different

hybrid systems combining distillation with pervaporation for the dehydration of isopropanol. *Sep Purif Technol*. 2004;37:33–49.

35. Zhang QG, Liu QL, Chen Y, Chen JH. Dehydration of isopropanol by novel poly(vinyl alcohol)-silicone hybrid membranes. *Ind Eng Chem Res*. 2007;46:913–920.
36. Villagrán G, Deetlefs M, Pitner WR, Hardacre C. Quantification of halide in ionic liquids using ion chromatography. *Anal Chem*. 2004;76:2118–2123.
37. Lee SG. Functionalized imidazolium salts for task-specific ionic liquids and their applications. *Chem Commun*. 2006;71:1049–1063.
38. Bourlinos AB, Raman K, Herrera R, Zhang Q, Archer LA, Giannelis EP. A liquid derivative of 12-tungstophosphoric acid with unusually high conductivity. *J Am Chem Soc*. 2004;126:15358–15359.
39. Marták J, Schlosser S. Extraction of lactic acid by phosphonium ionic liquids. *Sep Purif Technol*. 2007;57:483–494.
40. Wang YG, Xiong Y, Meng SL, Li DQ. Separation of yttrium from heavy lanthanide by CA-100 using the complexing agent. *Talanta*. 2004;63:239–243.
41. Stark A, Behrend P, Braun O, Müller A, Ranke J, Ondruschka B, Jastorff B. Purity specification methods for ionic liquids. *Green Chem*. 2008;10:1152–1161.
42. Naik SD, Doraiswamy LK. Phase transfer catalysis: chemistry and engineering. *AIChE J*. 1998;44:612–646.
43. Outokesh M, Mimura H, Niibori Y, Tanaka K. Equilibrium and kinetics of silver uptake by multinuclear alginate microcapsules comprising an ion exchanger matrix and Cyanex302 organophosphinic acid extractant. *Ind Eng Chem Res*. 2005;44:1922–1927.
44. Sun XB, Zhao JM, Meng SL, Li DQ. Synergistic extraction and separation of yttrium from heavy rare earths using mixture of *sec*-octylphenoxy acetic acid and bis(2,4,4-trimethylpentyl)phosphinic acid. *Anal Chim Acta*. 2005;533:83–88.

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