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Environmentally friendly and effective removal of Br− and Cl− impurities in hydrophilic ionic liquids by electrolysis and reaction

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Abstract

Environmentally friendly and effective removal of Br− and Cl− impurities in hydrophilic dialkylimdazolium or butylpyridinium ionic liquids was investigated and developed at room temperature to 80 °C and atomspheric pressure. Constant elelctrolysis was applied to oxidize Br− and Cl− to their corresponding Br_2 and Cl_2, then the BF_4^- and NO_3^- ions from HBF_4 and HNO_3 solution in the cathode zone move to anode zone through an anion exchange membrane and combine with dialkylimdazolium or butylpyridinium cation to form ionic liquids. The Br_2 and Cl_2 in electrolyzed ionic liquids are treated with ethylene to afford the corresponding 1,2-dibromo (or dichloro) ethane which could easily be removed by volatilisation under vacuum (ca. 10 mm Hg). Removal of Br− and Cl−impurities (0.94–4.47 wt%) from hydrophilic dialkyl imdazolium or butylpyridinium ionic liquids through electrolysis and ethylene treatment could be achieved at 0.06%–0.29% without any additional solvents and ionic liquid loss.
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1. Introduction

Room-temperature ionic liquids (RTILs or ILs) have recently been investigated for a wide range of potential applications, including electrolyte for dye-sensitized solar cell [1–3], Li battery [4–6], supercapacitor [7,8], lubricating materials [9], sensing materials [10,11] and optical materials [12,13] etc. besides conventional catalytic and synthetic applications [14]. Indeed, ILs are not environmentally benign solvents any more. In some areas such as high performance lubricating or optical materials, the purity of ILs must be highly required. However, most of the ILs cannot be purified directly either by distillation or by re-crystalliza-tion due to their very low vapour pressure and relatively lower melting points. The previous literatures [15–19]

showed that possible impurities in conventional ILs such as dialkyl imidazolium BF_4 and PF_6 were unreacted alkyl imidazole, alkyl halide, Br−, Cl−, water etc., in which Br−and Cl− were dominating impurities. Seddon et al. [15] showed that some physicochemical properties of ILs were highly dependent on the presence of Cl− impurities.

On the other hand, it has generally been accepted that ILs, such as popular dialkyl imidazolium ILs, could be green due to their outstanding characteristic of non-volatility: the conventional preparation processes of these ILs are, however, less environmentally friendly. For example, in order to remove Br− and Cl− impurities as low as possible from the dialkyl imidazolium hydrophobic ILs, large amount of water was generally used for washing away these impurities, and the loss of the ILs was also inevitably caused when the ILs were washed with water for several times. As to removing Br− and Cl− impurities from hydrophilic dialkyl imidazolium ILs, extraction of ILs with organic solvent from water containing the ILs were usually

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conducted, which even caused great loss of ILs due to the ILs partition between water and organic solvent, what is more, such process would consume large quantities of organic solvent. Metathesis with a silver salt would afford ILs with the lowest content of Br^- and Cl^-, but produces an equivalent molar of silver chloride, making this preparation method too expensive and environmentally unfriendly. In view of sustainable or green chemistry, such method of ILs preparation and purification is totally unacceptable particularly for the preparation of ILs on a large scale.

Since Br^- and Cl^- as electrochemical active species can be easily oxidized at proper oxidative potentials, the residual Br^- and Cl^- in ILs could be removed by electrolysis. Although Xiao and Johnson [20] demonstrated preliminarily or the removal of residue Cl^- from [BMIm]BF_4 by constant potential electrolysis, the practical effectiveness of such purification process is still doubtful. Herein we report a clean and practical method for removal of Br^- and Cl^- in hydrophilic dialkylimdazolium and butylpyridinium (BF_4^- and NO_3^- as anions) ILs through electrolysis in a divided cell, halogenation with ethylene and volatilisation under vacuum. The key innovation points of such purification process are: (1) The Br^- and Cl^- were oxidized to their corresponding Br_2 and Cl_2 in anode zone, and at same time the BF_4^- and NO_3^- ions from HBF_4 and HNO_3 solution in cathode zone move to anode zone through an anion exchange membrane and combine with dialkyl imidazolium cation to form ILs, thus establishing a whole electrochemical reaction. (2) The Br_2 and Cl_2 in electrolyzed ILs are treated with ethylene to afford the corresponding 1,2-dibromo (or dichloro) ethane, which could easily be removed by volatilisation under vacuum (*ca.* 10 mm Hg). Since this method could proceed without using any water or organic solvents and without causing any IL loss, and the produced 1,2-dibromo (or dichloro) ethane could be recovered as useful chemicals, such process of ILs preparation and purification would be environmentally friendly.

2. Experimental

All chemicals used in the experiments were of analytical grade and used without further purification. [EMIm]BF_4, [BMIm]BF_4, [BMIm]NO_3, and [BPy]BF_4 were prepared with two-step method with the corresponding dialkyl imidazolium bromide or chloride and *n*-butylpyridinium bromide salts according to the literatures [21,22]. The ILs were dried and degassed under vacuum (*ca.* 10 mm Hg) at 100 °C for 4 h prior to use. Anion exchange membrane was purchased from Zhejiang Qianqiu Environmental Water Treatment Ltd. (China).

The quantification of Br^- and Cl^- in the ILs using a METTLER TOLEDO SevenMuliti meter with Br^- and Cl^- ion selective electrodes was performed. To quantify Br^- and Cl^- concentration, ILs analyzed were diluted with purified water to 0.2 g/100 ml and then added with 2 ml ISA (ionic strength adjuster: 5 M $NaNO_3$ solution).

Electrochemical measurements for cyclic voltammetry were performed using a CHI660A electrochemical workstation (CH instruments, USA). Electrolysis was carried out in a conventional three-electrode electrochemical cell equipped with a chamber with which temperatures could be monitored and adjusted from room temperature to *ca.* 90 °C through a circular water bath system, and vacuum treating (*ca.* 1 mm Hg) and N_2 filling could also be implemented so as to minimize the influence of O_2 and H_2O during experiments. The working electrode was a glass carbon electrode (3-mm-diameter) and the auxiliary electrode was a platinum wire. The reference electrode is Ag/AgCl, of which porous glass frits was used to separate the internal solutions from the working solution and 3 M KCl solution.

The electrolysis and ethylene treatment equipments are shown in Figs. 1 and 2, which constant potential electrolysis was employed. The ILs (15 ml) and 20% HBF_4 aqueous solution (15 ml) or 20% HNO_3 aqueous solution (15 ml) were respectively charged into the anodic and cathodic compartment of the cell. 1.6 V (for ILs containing Br^-) at room temperature and 1.4 V at 80 °C (for ILs containing Cl^-) were applied to the electrolysis experiment respectively till the electrolysis current tended to zero, and typically the electrolysis time lasted for 12 h. During the electrolysis, the colour of the colourless ILs containing Br^- or Cl^- gradually turned into deep brown and light yellow, respectively, and at same time, H_2 bubbles derived from the oxidation of HBF_4 or HNO_3 aqueous solution were produced in cathode zone. After the electrolysis, ethylene treatment by bubbling ethylene (*ca.* 1–2 bubbles s^{-1}) into the electrolyzed ILs was conducted at 25 °C for the electrolyzed ILs containing Br_2 and 80 °C for the electrolyzed ILs containing Cl_2 at constant pressure for 0.5 h. Then the ILs containing 1,2-dibromo (or dichloro) ethane were degassed under vacuum (*ca.* 10 mm Hg) at 80 °C for
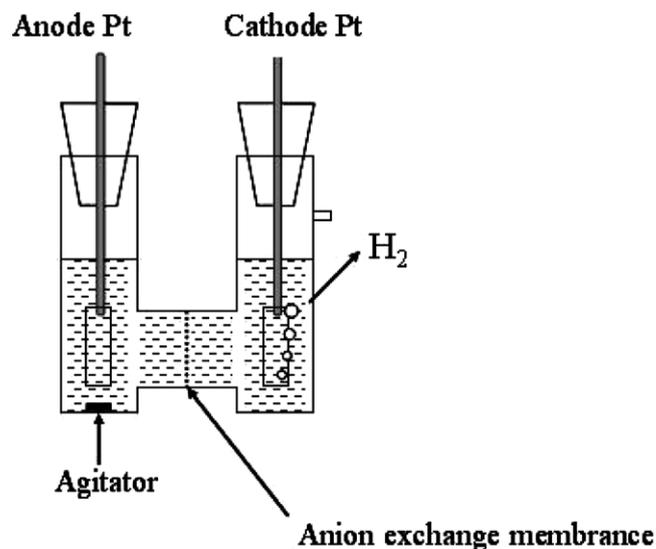

Fig. 1. The divided cell of electrolysis equipment.

1 ethylene gasbag
2 peristaltic pump
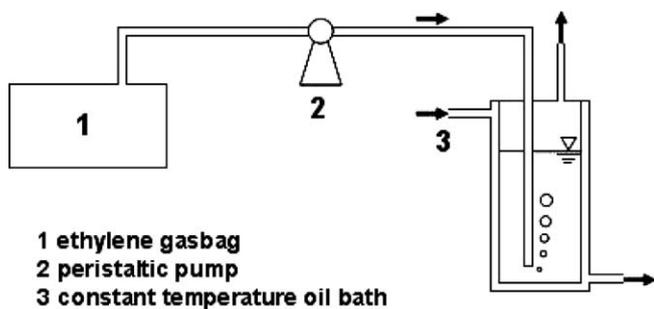3 constant temperature oil bath

Fig. 2. The ethylene treatment equipment.

3 h. If necessary, the procedures of electrolysis and ethylene treatment were repeated for the second or third times, *etc.*

The Raman spectra were performed with a Thermo Nicolet 5700 FT-Raman accessory spectroscopy meter, and UV–vis spectra were performed with an Agilent 8453 UV–vis spectrophotometer. Qualitative analyses after the electrolyzed ILs were treated with ethylene were conducted with a HP 6890/5973 GC–MS with a chemstation containing a NIST Mass Spectral Database.

3. Results and discussion

Dialkyl imidazolium and butylpyridinium ILs containing 2.96–4.47 wt% Br^- or 0.942–1.16 wt% Cl^- were tested. The electrochemical behaviour of Br^- (3.20 wt%) in [EMIm]BF_4 and Cl^- (1.16 wt%) in [BMIm]BF_4 was respectively measured with cyclic voltammetry at varied temperatures. Two oxidation waves, *ca.* 1.0 V and 1.4 V *vs.* Ag/AgCl (see Fig. 3A) at 25 °C were observed for [EMIm]BF_4 containing Br^-, the former is the oxidative wave of Br^- oxidized to Br_2, and the latter belongs to the oxidative wave of Br^- oxidized to Br_3^-. The irreversible single oxidative peak at *ca.* 1.7 V *vs.* Ag/AgCl at 25 °C was also observed for [BMIm]BF_4 containing Cl^- (see Fig. 3B), which is attributed to Cl^- oxidation to Cl_2. The above-mentioned electrochemical behaviours of Br^- and Cl^- in the dialkyl imidazolium ILs were consistent with the previous literatures [23–25]. This results indicated that Cl^- in the ILs was more difficult to be electrically oxidized at room temperature. The potential at which Cl^- could be electrically oxidized was, however, decreased to *ca.* 1.5 V (*vs.* Ag/AgCl) (see Fig. 4) when the temperature was increased to 80 °C, at which the viscosity of the IL would also be decreased markedly.

For [EMIm]BF_4 containing Br^-, when the electrolysis was started, the colour of the IL gradually turned from colourless into deep yellow, indicating that Br^- was oxidized into Br_2 at anode, and formation of H_2 bubbles was simultaneously observed in the cathode at 25 °C. In order to remove the produced Br_2 directly, an attempt was made to treat the deep yellow colour IL under vacuum (*ca.* 10 mm Hg), but was not successful. Raman analysis of the IL with deep yellow colour indicated that Br_3^- spices were formed since a strong adsorption occurred as *ca.*
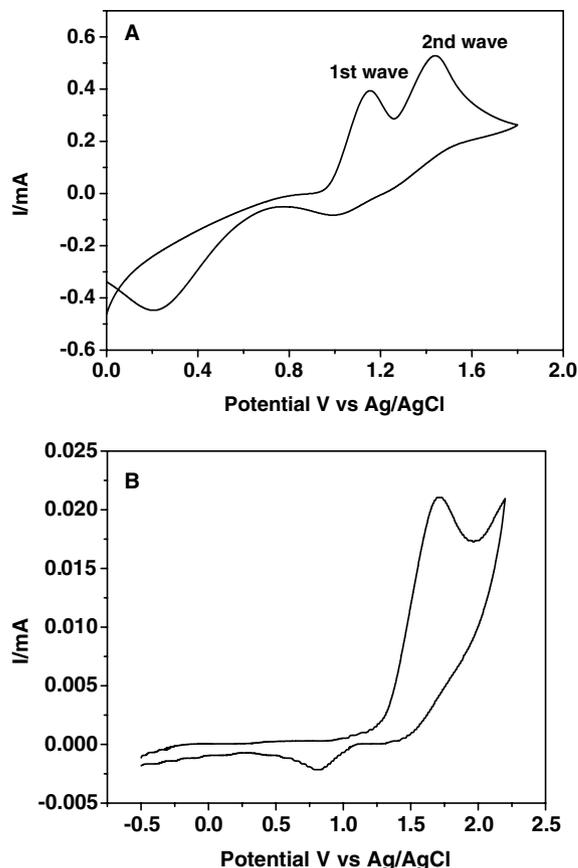

Fig. 3. Cyclic voltammograms of [EMIm]BF_4 containing 3.20 wt% Br^- (A) and [BMIm]BF_4 containing 1.16 wt% Cl^- (B) 3 mm-diameter-glass carbon working electrode; scan rate=50 mV s^{-1}.
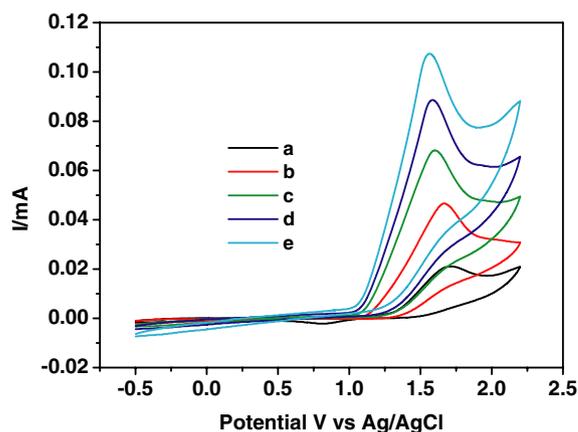

Fig. 4. Cyclic voltammograms of [BMIm]BF_4 containing 1.16 wt% Cl^- at (a) 25 °C, (b) 40 °C, (c) 60 °C, (d) 70 °C, and (e) 80 °C.

131 cm^{-1}, which should be attributed to the symmetric stretching vibration of Br_3^- [26] (see Fig. 5). This means that a reaction between the electrolyzed Br_2 and the existing Br^- occurred to form Br_3^- species, which were quite stable and well soluble in the IL. Since addition reaction of ethylene with Br_2 or Cl_2 could be occur relatively easily, an attempt was made to bubble ethylene at 25 °C to the ILs after electrolysis. After ethylene treatment, the result-

ing IL was extracted with diethyl ether for three times and the extractant was analysed with GC–MS and only 1,2-dibromoethane as product was detected. After the ethylene treatment, the resulted IL was further subjected to vacuum treatment so as to remove the produced 1,2-dibromoethane, and the Raman analysis of the IL treated with ethylene showed that such strong adsorption as *ca.* 131 cm^{-1} disappeared, indicating that ethylene reacted with Br$_3^-$ easily to produce 1,2-dibromoethane with high conversion and selectivity at room temperature, and 1,2-dibromoethane could easily be removed from the IL under vacuum (*ca.* 10 mm Hg) at room temperature.

For the removal of Cl$^-$ impurity from [BMIm]BF$_4$, initially, constant potential electrolysis at *ca.* 1.7 V and 25 °C was employed, but it was found that very lower electrolysis current through the electrodes was observed and the colour of [BMIm]BF$_4$ IL changed gradually from colourless to brown, indicating that IL itself may also be degraded simultaneously during oxidation of Cl$^-$, although the mechanism is still not clear at this stage. However, just as mentioned above, the potential for Cl$^-$ electrolysis could be reduced to 1.5 V(*vs.* Ag/AgCl) if the temperature of the electrolysis was increased to 80 °C. The colour of the [BMIm]BF$_4$ containing Cl$^-$ in anode gradually turned from colourless into light yellow during the electrolysis at 1.5 V and 80 °C, and a strong band (302 nm), which was slightly different from the absorbance of Cl$_3^-$ (267 nm) in [BMIm]PF$_6$, and haloaluminate ILs (320 nm) [27,28] of Cl$_3^-$, was clearly observed in electrolyzed [BMIm]BF$_4$ through UV–vis measurement (see Fig. 6). This may also mean that a reaction between the electrolyzed Cl$_2$ and the existing Cl$^-$ occurred to form Cl$_3^-$ species, and similarly, such Cl$_3^-$ species could not be removed with a simple volatilisation under vacuum. So, the procedure of bubbling ethylene to the ILs after electrolysis at 80 °C due to relatively slow reaction rate between ethylene and Cl$_2$, and then removing 1,2-chloroethane with vacuum at room temperature could be successfully conducted, which was confirmed with UV–vis measurement of
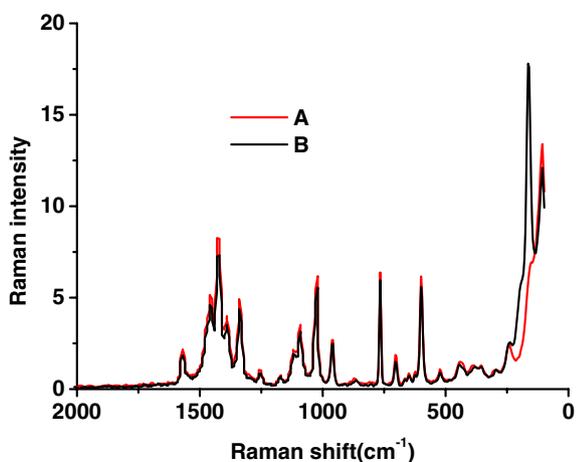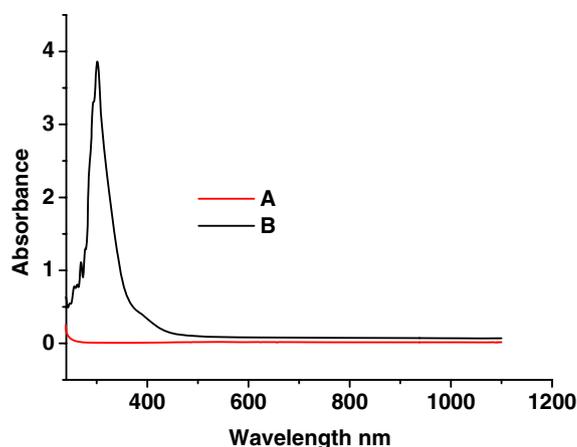

Fig. 6. UV–vis absorption spectra: (A) [BMIm]BF$_4$ before electrolysis in acetonitrile solution and (B) [BMIm]BF$_4$ after electrolysis in acetonitrile solution.

the IL treated with ethylene and then vacuum since such strong band (302 nm) of Cl$_3^-$ disappeared.

The results of cyclic voltammograms of [EMIm]BF$_4$ containing 3.20 wt% Br$^-$ before electrolysis, after the first electrolysis and ethylene treatment, and the second electrolysis and ethylene treatment (Fig. 7A and B) showed that ~0.8 wt% Br$^-$ still existed in IL after first electrolysis and ethylene treatment, Table 1, entry 1. So, the second electrolysis and ethylene treatment were carried out and residual Br$^-$ could be further reduced to 0.10% detected with ion selective electrode and nice CV curves were obtained, Fig. 7C. However, even with five times of electrolysis and ethylene treatment, there was still a very small amount of residual Br$^-$ (0.057 wt%) that could not be removed completely, entry 3. The initial content of Br$^-$ would slightly affect the removal efficiency, *i.e.* the higher the initial content of Br$^-$ in the IL, the higher the residual content of Br$^-$ in the treated IL, entries 4 and 5. For [BMIm]BF$_4$ and [BMIm]NO$_3$ ILs containing Cl$^-$, satisfactory results could also be obtained when two times of electrolysis and

Fig. 5. Raman spectra of [EMIm]BF$_4$ containing Br$^-$ before electrolysis (A) and after electrolysis (B).
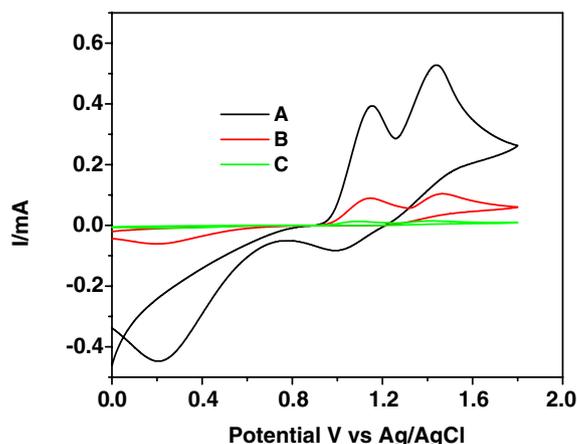

Fig. 7. Cyclic voltammograms of [EMIm]BF$_4$ containing 3.2 wt% Br$^-$: (A) before electrolysis, (B) after electrolysis and ethylene treatment, and (C) the second electrolysis and ethylene treatment, scan rate 50 mV s^{-1}, at a 3-mm-diameter glassy carbon working electrode.

Table 1
Comparison of halide concentration (wt%) in ILs before and after electrolysis

Entry	ILs and concentration of Br$^-$ (or Cl$^-$) impurities (wt%)	Times of electrolysis and ethylene treatment	The final concentration of Br$^-$ (or Cl$^-$) impurities after removing (wt%)
1	[EMIm]BF$_4$-Br 3.20	1	0.80
2	[EMIm]BF$_4$-Br 3.20	2	0.10
3	[EMIm]BF$_4$-Br 3.20	5	0.06
4	[EMIm]BF$_4$-Br 4.47	1	1.32
5	[EMIm]BF$_4$-Br 4.47	2	0.24
6	[BMIm]BF$_4$-Cl 1.16	2	0.10
7	[BMIm]NO$_3$-Cl 0.94	2	0.12
8	[Bpy]BF$_4$-Br 2.96	2	0.29
9	[BMIm]BF$_4$-Br 2.96	2	0.19

ethylene treatment were conducted at 1.5 V and 80 °C, entries 6 and 7.

In addition, variation of anions or cations of ILs had little effect on the removal results of Br$^-$ and Cl$^-$ impurities (entries 6–9) as long as the differences of the ILs viscosities were not too large.

4. Summary

In summary, removal of Br$^-$ and Cl$^-$ impurities (0.94–4.47 wt%) from hydrophilic dialkyl imidazolium or butylpyridinium ILs to 0.06–0.29 wt% through electrolysis and ethylene treatment could be achieved with an environmentally friendly method without additional solvent washing or extraction and IL loss. The electrolysis conditions could be further optimized, and such purification method could also be practical for ILs purification on a large scale and very important for precise characterizations of ILs properties.

Acknowledgement

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