Binary Ionic Liquid Mixtures as Electrolyte for Improving the Electro-Reduction of Nitrobenzene

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The binary composite ionic liquids mixtures composed of 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim][BF$_4$]) and 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim][PF$_6$]) were developed for reduction of nitrobenzene. ATR-IR spectroscopy was employed to achieve mixing behaviour of binary ionic liquids and significant change in the anion IR bands was observed. The electrochemical reduction of nitrobenzene was studied at platinum electrode in binary composite ionic liquids. Results indicated that the reduction reaction taken place in some binary composite ionic liquids demonstrated higher current densities with a more positive potential than in both single ionic liquids and the process was controlled by diffusion.

Keywords: Binary composite ionic liquids, ATR-IR spectroscopy, Nitrobenzene, Electrochemical reduction.

INTRODUCTION

Ionic liquids (ILs) are composed of organic cations and organic or inorganic anions, which are liquids at room temperature[1]. Ionic liquids have favorable properties, such as high solvent capacity, low volatility, and high chemical and thermal stability[2-5]. Furthermore, they also do not require addition of supporting electrolyte in electrochemical organic synthesis because of their high conductivity and it's possible to satisfy specific requirements by systematically tailoring the nature of one of their ions[6,7]. Due to these virtues mentioned above, the ionic liquids are widely applied in electrochemical fields[8-12]. In recent years, scientists have devoted to study the binary ionic liquids mixtures because it can expand the range of properties and versatility of this new class of solvents. For instance, some researches related to volumes, viscosities and transport properties of binary mixtures with a common ion have been reported[6,13-15]. Pinto *et al.*[16] found the mixtures of [C$_2$py][EtSO$_4$] and [C$_2$mim][NTf$_2$] had a higher absorption capacity than the one corresponding to the averaged capacities of the pure ionic liquids. Binary ionic liquids were used in gas chromatographic study[17] and in liquid-liquid extraction[18-20], which had distinct results about selectivity. However, most of researches merely focused on the properties of binary ionic liquids, studies on the application in electrochemical synthesis were seldom reported so far.

In this paper, we study binary ionic liquid mixtures including 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim][BF$_4$]) and 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim][PF$_6$]) for the electroreduction of nitrobenzene. Attenuated total reflection Fourier transform infrared was applied to gain further insight into this mixture. Comparing to that conducted in the neat ionic liquid, the reduction of nitrobenzene in binary mixtures exhibits a higher reductive current while the reductive potential shifts toward a positive direction. This indicates that the binary ionic liquid mixtures of 1-hexyl-3-methylimidazolium hexafluorophosphate and 1-hexyl-3-methylimidazolium tetrafluoroborate promote the electroreduction of nitrobenzene. Also this offers a method for the functionalization of ionic liquids in electrochemical field.

EXPERIMENTAL

N-Methyl imidazole, nitrobenzene and bromobutane, sodium tetrafluoroborate, magnesium sulfate, ether and other reagents are all of analytical reagent. Doubly distilled water was used in experiment. Room temperature ionic liquids 1-hexyl-3-methylimidazolium tetrafluoroborate and 1-hexyl-3-methylimidazolium hexafluorophosphate were prepared according to the procedure described[21,22]. Their ^{1}H NMR spectra are shown as follows: [hmim][BF$_4$]: ^{1}H NMR (DMSO, 500 MHz): δ = 0.86 (t, 3H); 1.27 (m, 6H); 1.78 (m, 2H); 3.85 (s, 3H); 4.15 (t, 2H); 7.70 (s, 1H); 7.77(s, 1H); 9.10(s, 1H). [hmim][PF$_6$]: ^{1}H NMR (DMSO, 500 MHz): δ = 0.87 (t, 3H); 1.27 (m, 6H); 1.77 (m, 2H); 3.85 (s, 3H); 4.15 (t, 2H); 7.70 (s, 1H); 7.77 (s, 1H); 9.10 (s, 1H).

A conductivity meter (DDS-11A, shanghai) was used to measure conductivities at temperature 303 K on the ionic liquid samples which were loaded in glass cells. ^{1}H NMR spectroscopic measurements were carried out with a AVANCE III 500 MHz NMR spectrometer. ATR-IR spectra were recorded on the range of 4000-600 cm^{-1} on Nicolet 670 FTIR spectrometer at ambient temperature.

Cyclic voltammetry and chronoamperometric experiment: Micro-platinum was used as the working electrode, which was first polished successively with finer grades of alumina powder (1.0, 0.3 and 0.05 μm) and then ultrasonically cleaned with ethanol, dilute nitric acid and distilled water. Cyclic voltammetric measurements were performed on CHI660C electrochemical workstation by using an undivided cell, in which a large area platinum foil and saturated calomel electrode was used as auxiliary electrode and reference electrode, respectively. Chronoamperometric experiment was also studied on CHI660C, the experimental transients were obtained by stepping the potential to the required value and measuring the current for 50 s.

RESULTS AND DISCUSSION

Conductivity measurements: The electrical conductivity is an important parameter for the electrolyte, which determines the internal resistance of the electrode, so the investigation on the electrical conductivity in the practical application is also very important. Fig. 1 plots the conductivity *vs.* [hmim][BF$_4$] volume fraction dependence of the (1-x) [hmim][PF$_6$]/(x) [hmim][BF$_4$] binary mixtures in the temperature 303 K. It is seen that the conductivity of [hmim][PF$_6$] is much smaller than [hmim][BF$_4$], so the conductivity of [hmim][BF$_4$] is better than [hmim][PF$_6$]; the conductivity of composite ionic liquids in between and with the increase [hmim][PF$_6$] volume decreases. Such a behaviour is similar to other binary mixtures[23].
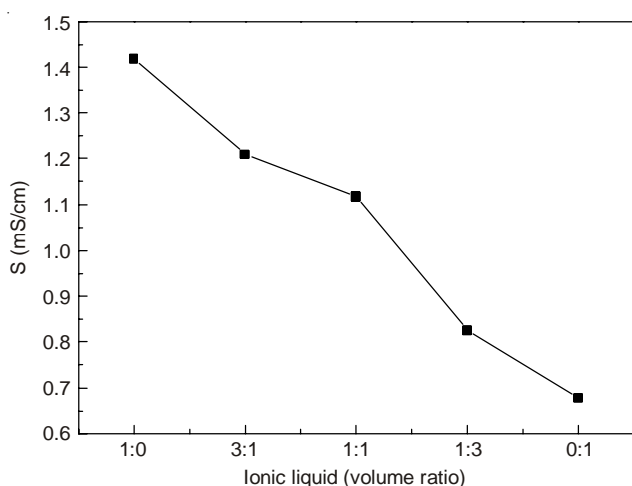

Fig. 1. Electric conductivity of different systems of ionic liquid. 1:0 means neat [hmim][BF$_4$], 0:1 means neat [hmim][PF$_6$], 3;1,1:1 and 1:3 mean volume ratios of binary ionic liquid.

ATR-IR spectroscopy: Attenuated total reflection Fourier transform infrared (ATR-FT-IR) spectroscopy is an efficient way to examine molecular structures of pure ionic liquids as well as the interaction between ionic liquids and water or ionic liquids and CO$_2$[24-26]. This technique has also been proved to

be efficient to research molecular structures of binary ionic liquids[27]. According to the reported paper, the main [BF$_4$]$^-$ band appears in the 1100-1000 cm^{-1} region[28,29] and the [PF$_6$]$^-$ band in the range of 900-800 cm^{-1} corresponds mainly to P-F stretching modes[24,30]. Mixtures of [hmim][BF$_4$]/[hmim][PF$_6$] were prepared with volume ratios of 1:0, 3:1, 1:1, and 1:3, 1:0. The influence of the mixing on some of the strong ionic liquid vibrational bands accessible in the mid-IR range is shown in Fig. 2. The wavenumber of [BF$_4$]$^-$ and [PF$_6$]$^-$ are change when in the binary ionic liquid, which indicates that the molecular environment of the anions is altered when changing the [BF$_4$]$^-$ and [PF$_6$]$^-$ ratio[27].
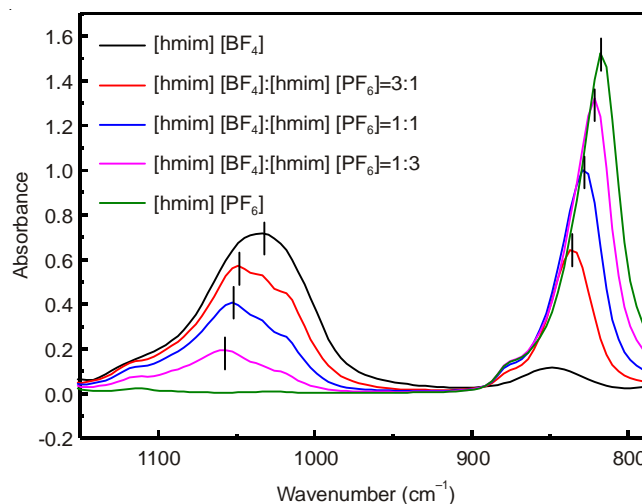

Fig. 2. Selected IR anion bands for [hmim][BF$_4$]/[hmim][PF$_6$] mixtures with volume ratios of 1:0, 3:1, 1:1, 1:3,0:1. 1:0 means neat [hmim][BF$_4$], 0:1 means neat [hmim][PF$_6$]

Electrochemical behaviours of nitrobenzene in binary ionic liquid: The cyclic voltammograms of nitrobenzene (0.1 mol L^{-1}) in different ratios of ionic liquids on a Pt electrode were carried out in an undivided cell with platinum as auxiliary electrode and a saturated calomel electrode as the reference electrode. As shown in Fig 3, the behaviours of all curves are similar. In different volume ratios of [hmim][BF$_4$] and [hmim][PF$_6$], peak current (I$_{PC}$) and peak potential of the curves are the highest when the volume ratios is 3:1. There may be the original system interactions and microscopic properties are destructed due to mixed system composed of ions are different from single ionic liquid, and the binary play a key role in improving electro-reduction of nitrobenzene. The results indicate that the mixture of ionic liquids could promote the electro-reduction of nitrobenzene. Due to the volume ratio of 3:1 shows the best in current and potential, which is chose for further study.

The cyclic voltammograms of nitrobenzene at different scan rates are shown in Fig. 4. As can be seen from Fig. 4, the plot of I$_{pc1}$ *vs.* v$^{1/2}$ gives a straight line at various scan rates ranging from 0.06-0.4 V s^{-1}. It suggested that the reduction of nitrobenzene in binary liquid ionic (3:1) is a diffusion-controlled process in the scan rate range tested[31]. Then the electrochemical reduction of nitrobenzene in binary ionic liquid was also carried out by chronoamperometry. The chronoamperograms were obtained for three nitrobenzene solutions
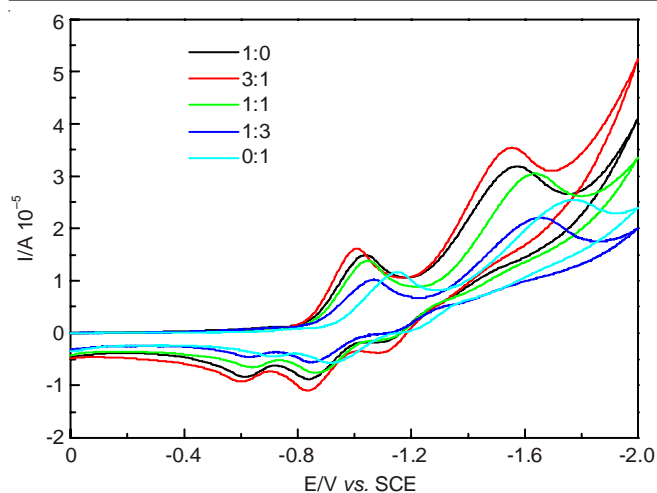
Fig. 3.   Cyclic voltammogram of nitrobenzene (0.01 mol L⁻¹) in various proportion of ionic liquids on Pt electrode at 100 mV s⁻¹, 1:0 means neat [hmim][BF₄], 0:1 means neat [hmim][PF₆]
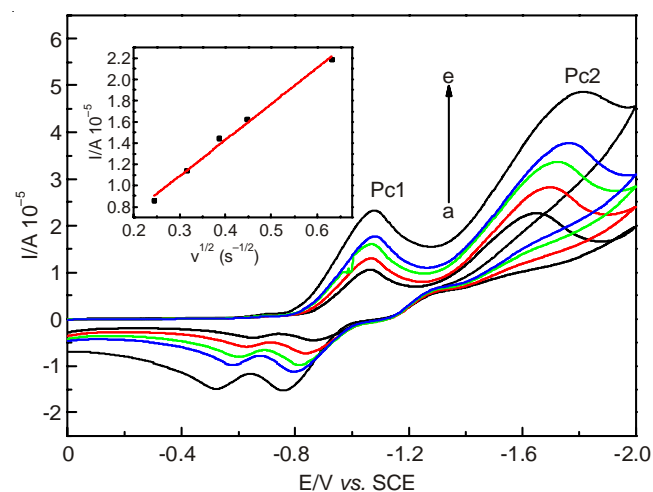

Fig. 4.   CV of the nitrobenzene in binary ionic liquid ($V_{[hmim][BF_4]}$:$V_{[hmim][PF_6]}$ = 3:1) at different scan rates (a→e) 0.06, 0.1, 0.15, 0.2 and 0.4 V s⁻¹. Inset shows the linear relationship between the peak currents (I_{pc1}) and the square roots of scan rates (0.06–0.4 V s⁻¹)

with various concentrations (0.05-0.2 mol L⁻¹) as shown in Fig. 5, which exhibits a good linear relationship at 20 s (Inset of Fig. 5A). Fig. 5. B depicts linear relationship of the experimental plots I $vs.$ t⁻¹/² for various concentrations of nitrobenzene at intermediate times (t = 0.8-1.4 s). Therefore, in order to obtain the diffusion coefficient D, we chose line b, according to Cottrell[32,33] eqn. 1:

$$i(t) = \frac{nFACD^{1/2}}{\pi^{1/2}t^{1/2}} \quad (1)$$

where n is the number of electrons transferred; D is the diffusion coefficient (cm₂ s⁻¹); c is the concentration (mol L⁻¹) of NB; A is the electrode area (0.00196 cm²). From Cottrell equation, D could be obtained from the slope, which was calculated as 7.11 × 10⁻⁸ cm² s⁻¹.

Conclusion

Binary mixtures of ionic liquid composed of 1-hexyl-3-methylimidazolium tetrafluoroborate and 1-hexyl-3-methyl-imidazolium were studied and used in the reduction of nitrobenzene on Pt electrode. ATR-IR measurement revealed
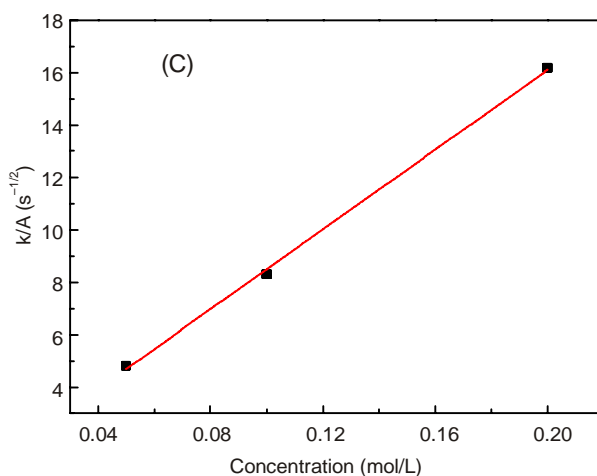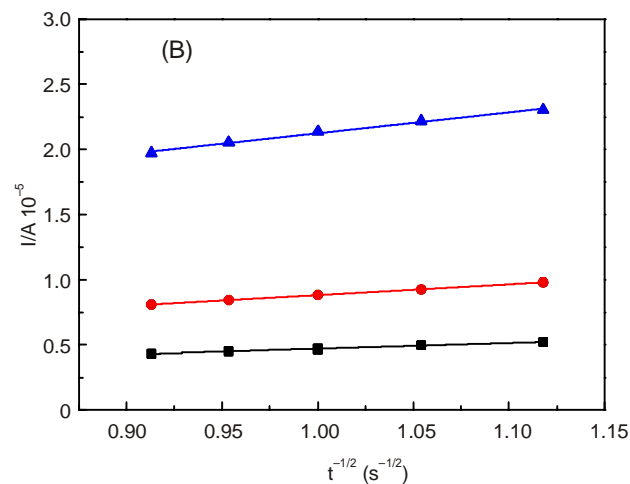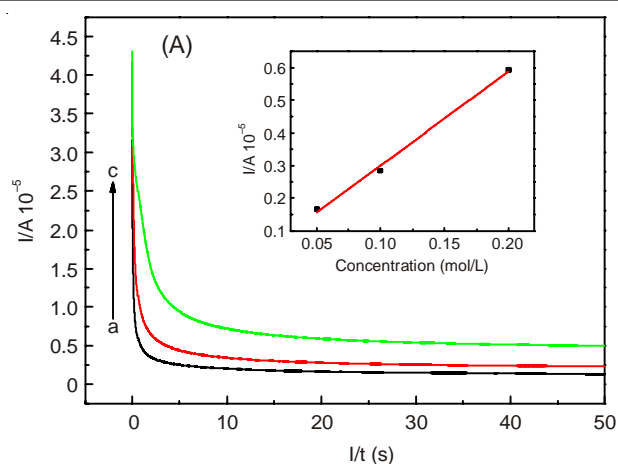

Fig. 5.   (A) Chronoamperograms of nitrobenzene in binary ionic liquid (a)-(c) of various concentrations of nitrobenzene: 0.05 mol L⁻¹, 0.1 mol L⁻¹, 0.2 mol L⁻¹, respectively. Inset (A) different chronoamperometric currents at 20 s $vs.$ the concentration of nitrobenzene. (B) and (C) The plots of I $vs.$ t⁻¹/² and The linear relationship of slope with concentration of nitrobenzene obtained from the chrono-amperograms, respectively

the change of chemical environment of [hmim][BF₄] and [hmim][PF₆]. The experiment showed that electro-reduction of nitrobenzene in some binary composite ionic liquids systems demonstrated higher current densities with a more positive potential than in neat ionic liquids, and the volume ratio of 3:1 shows the best in current and potential, and process was

controlled by diffusion, and the diffusion coefficient D was 7.11×10^{-8} cm^2 s^{-1}. These results turned out to be that binary ionic liquids could promote the electrochemical reduction of nitrobenzene and the idea of mixing different ionic liquids may also be enlightening for diversifying and maximizing the function of ionic liquids since the properties will not be the same being mixed.

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