

Electrochemical Behavior of Nitrobenzene in Binary Ionic Liquids OMImBF₄/BMImPF₆

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The binary ionic liquids([OMIm][BF₄]/[BMIm][PF₆]) were studied and applied to reduction of nitrobenzene for the first time. ATR-IR spectroscopy was used to demonstrate the variation of chemical environment of binary ionic liquids, and found that the anion IR bands have remarkable changes. Cyclic voltammetry and constant-potential electrolysis show that the reduction of nitrobenzene in binary ionic liquid (3:1) exhibit higher current density and more positive potential than that in the neat ionic liquid, and the conversion and selectivity of the product were also superior to that of single ionic liquid. The optimal results should be attributed to the changed chemical environment in binary ionic liquids and the effective interaction between binary ionic liquid and nitrobenzene. This provides a new method for functionalization of ionic liquids.

Keywords: Binary Ionic Liquids; Nitrobenzene; Electrochemical reduction; ATR-IR spectroscopy

1. INTRODUCTION

In recent years, room temperature ionic liquids as the green solvent are developed rapidly [1]. Ionic liquids have been widely used in electro-deposition, organic synthesis, lithium-ion batteries, electrochemical biosensors, electrochemical capacitors due to their peculiar physical and chemical properties, such as the low vapor pressure, stable thermal stability, wide electrochemical window, dissolving ability, etc [2-5]. Nowadays, scientists are paying an attention to research binary ionic liquids which can expand the properties and versatility of ionic liquids. A series of applications and fundamental studies of binary ionic liquid have appeared. For example, the volumetric, viscosities and transport properties of binary ionic liquids with a common ion have been studied [6-9]. Montanino

[10] reported binary ionic liquid mixtures: $(1-x)\text{PYR}_{14}\text{TFSI}-(x)\text{PYR}_{14}\text{IM}_{14}$ and found that may represent a practical method to obtain new electrolytic materials with enhanced properties for especial applications. Binary ionic liquids give gratifying results in both gas chromatographic [11] and liquid-liquid extraction [12-14]. The above results provide a feasible approach for functionalization of ionic liquids.

A lot of studies about the electro-reduction of nitrobenzene in binary ionic liquids have been reported. Chen [15] and Ma [16] found that the performances of nitrobenzene in composite ionic liquids were superior to that in single ionic liquid. Herein, to achieve functional development, we studied the binary ionic liquid $[\text{OMIm}][\text{BF}_4]/[\text{BMIm}][\text{PF}_6]$ for the first time, and attenuated total reflection fourier transform infrared was applied to gain further insight into these mixtures. Comparing with the results in the single ionic liquid, the reduction of nitrobenzene in binary ionic liquid (some ratios) exhibits a higher yield while the reductive potential shifts to positive direction. The results obtained here may provide practical supports for improving new solvents in electro-reduction of nitrocompounds.

2. EXPERIMENTAL SECTION

2.1 Chemicals

N-methyl imidazole, nitrobenzene, bromobutane, potassium hexafluorophosphate, magnesium sulfate, ether and other reagents are analytical reagent. Doubly distilled water was used in experiment. RTILs 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{BMIm}][\text{PF}_6]$) was prepared by the procedure described in earlier paper [17], 1-octyl-3-methylimidazolium tetrafluoroborate was purchased from Lanzhou institute of chemical physics.

Their ^1H NMR spectra are shown as follows:

BMImPF_6 : HNMR(DMSO, 500MHz): $\delta=0.90$ (t, 3H); 1.26 (m, 2H); 1.77 (m, 2H); 3.85 (s, 3H); 4.16 (t, 2H); 7.69 (s, 1H); 7.76 (s, 1H); 9.09 (s, 1H).

OMImBF_4 : HNMR(DMSO, 500MHz): $\delta=0.86$ (t, 3H); 1.26 (m, 10H); 1.77 (m, 2H); 3.85 (s, 3H); 4.15 (t, 2H); 7.68 (s, 1H); 7.75 (s, 1H); 9.07 (s, 1H).

2.2 Conductivity and viscosity measurements and ATR-IR spectroscopy

A conductivity meter (DDS-11A, shanghai) and a viscosity meter (DV2T, brookfield) was used to measure conductivity and viscosity of IL samples at temperature 303 K, respectively. ATR-IR spectra were recorded on the range of $4000-600\text{ cm}^{-1}$ on Nicolet 670 FTIR spectrometer at ambient temperature.

2.3 Calculation of the excess molar volumes

Density values of binary ionic liquids were measured and used to calculate the excess molar volumes with formula (1):

$$V_E = \frac{\chi_2 M_1 + (1-\chi_2) M_2}{\rho} - \frac{\chi M_1}{\rho_1} - \frac{(1-\chi_2) M_2}{\rho_2} \quad (1)$$

2.4 Cyclic voltammetry and constant potential electrolysis experiment

Cyclic voltammetric measurements were carried out on CHI660C electrochemical workstation by using an undivided cell with three-electrode system, in which micro-platinum was used as working electrode, a large area platinum foil and saturated calomel electrode was used as auxiliary electrode and reference electrode, respectively. Constant potential electrolysis was conducted in an undivided cell, and the cathode was platinum foil (1 cm×1 cm). A graphite rod was used as anode and a platinum wire served as reference electrode. Binary ionic liquids solution was employed as the electrolyte and the concentration of nitrobenzene was 0.05 mol·L⁻¹. The electrolyte was stirred by magnetic stirring apparatus and the temperature was controlled at 30 °C by an thermostat oil bath. Electrolysis product was extracted with ether, which was detected and analyzed by GC.

2.5 In situ FTIR experiments

Electrochemical in-situ FTIR experiments using special electrolytic cell with three electrodes system, working electrode is Pt electrode (6 mm diameter), auxiliary electrode is platinum black electrode, reference electrode is saturated calomel electrode. Infrared spectrometer equipped with liquid nitrogen cooling MCT-A detector, using CaF₂ infrared window piece (the diameter is 32 mm, and thickness is 2 mm). To acquire in situ FTIR data, two hundred interfereograms were collected at each potential at a resolution 8 cm⁻¹. The resulting spectrum recorded was defined as the potential-difference spectra, and was calculated by the following formula [18, 19]:

$$\frac{\Delta R}{R} = \frac{R(E_S) - R(E_R)}{R(E_R)} \quad (2)$$

Where $R(E_S)$ and $R(E_R)$ are single-beam spectra collected respectively at the sample potential (E_S) and the reference potential (E_R). In this paper, E_R was 0 mV because there was no reaction in this potential and no obvious changes could be observed on the FTIR spectra.

3. RESULTS AND DISCUSSION

3.1 Conductivity and viscosity

The conductivity and viscosity are primary properties for the organic electrolyte. The conductivity and viscosity of [OMim][BF₄], [BMim][PF₆], binary ionic liquids([OMim][BF₄]/[BMim][PF₆]) with various volume ratios are shown in Fig.1. It can be seen that conductivity of [OMim][BF₄] is much smaller than [BMim][PF₆], whereas, the viscosity is opposite. With increasing the volume of [BMim][PF₆], the conductivity of composite ionic liquids is increased, while the viscosity is decreased. The conductivity and viscosity of binary ionic liquids are between the two single ionic liquids.

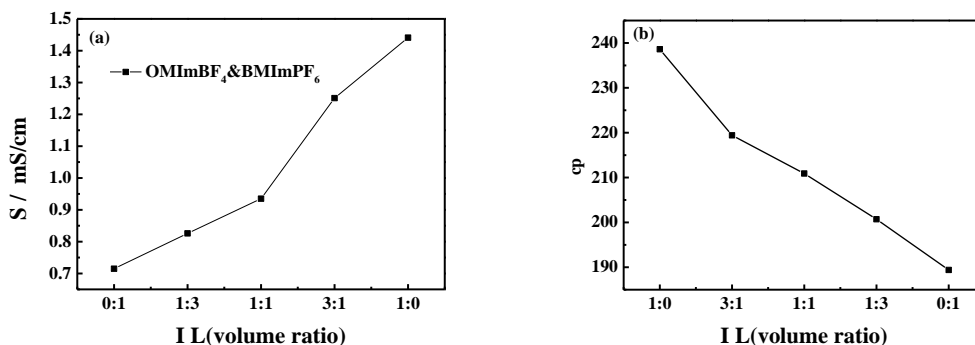


Figure 1. The electric-conductivity(a) and viscosity(b) of different volume ratios of [OMim][BF₄]/[BMim][PF₆] (1:0, 3:1, 1:1, 1:3 and 0:1)

3.2 The excess molar volume of binary ionic liquids

Table 1. Densities and excess molar volumes of [OMim][BF₄]/[BMIm][PF₆] mixtures

X[OMim][BF ₄]	ρ	V ^E
0.00	1.21	0.00
0.21	1.18	0.72
0.45	1.14	0.14
0.71	1.08	0.11
1.00	1.02	0.00

Table 1 shows that excess molar volume of binary system within the range of the mole fraction. According to the literature [20-22], V^E is related to the interaction, physical properties and structural characteristics of component of binary mixture. As can be seen from table 1, the excess molar volume of binary ionic liquids are all positive. The possible reasons should be: (1) for [OMim][BF₄]/[BMIm][PF₆] system, [OMim][BF₄] and [BMIm][PF₆] are both large molecules, so their steric hindrance effect are large; (2) heterogeneous intermolecular attraction is weak.

3.2 Spectroscopy measurements

3.2.1 Infrared Spectroscopy

The ATR-IR is an effective way to study the molecular structure of both neat ionic liquids and binary ionic liquids [23, 24]. Fig.2 shows that the influence of the mixing on bands of [BF₄]⁻ and [PF₆]⁻. According to previous literatures, the region of [BF₄]⁻ band is 1100-1000 cm⁻¹ [25, 26] and the [PF₆]⁻ band in the range of 900-800 cm⁻¹ [24, 27]. It can be seen from Fig. 2 that the [BF₄]⁻ and [PF₆]⁻ band of [OMim][BF₄]/[BMIm][PF₆] change obviously when altering the ratio of the two ionic liquids. These results indicate that the molecular environment of the anions is altered when changing the [BF₄]⁻ and [PF₆]⁻ ratio.

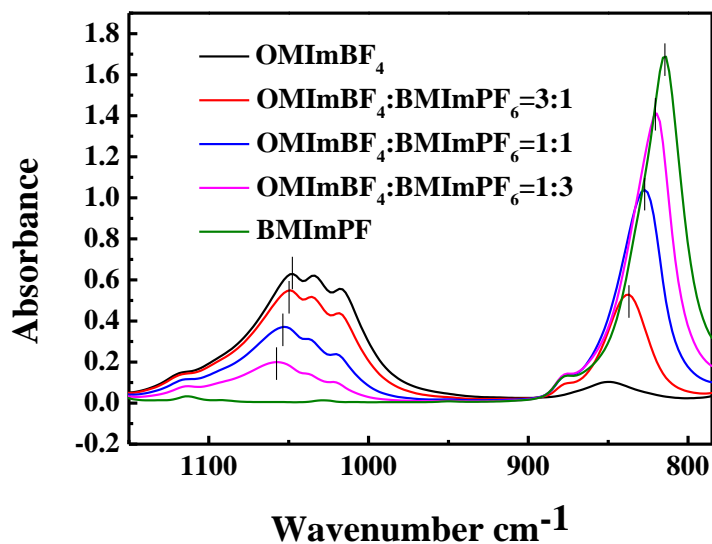


Figure 2. Selected IR anion bands for [OMIm][BF₄]/ [BMIm][PF₆] mixtures with volume ratios of 1:0, 3:1, 1:1, 1:3 and 0:1.

3.3 Electrochemical behaviors of nitrobenzene

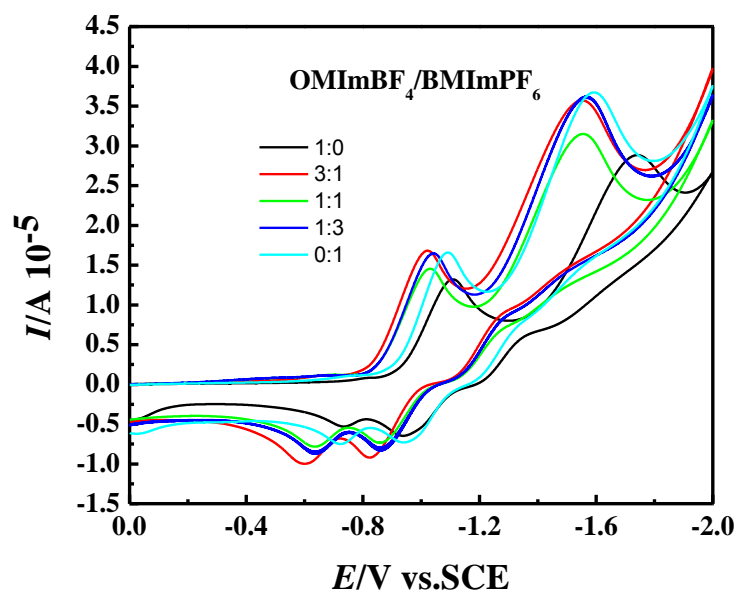


Figure 3. CV curves of nitrobenzene in different ionic liquids. ($v = 100 \text{ mV/s}$, $C_{\text{nitrobenzene}} = 0.1 \text{ mol/L}$, and $T = 303\text{K}$)

The cyclic voltammograms of nitrobenzene in binary ionic liquids with different volume ratios are shown in Fig. 3. It can be seen that, each CV curve has two reduction peaks, and the shape of all curves keeps similar. However, the reduction current densities of nitrobenzene in binary mixtures (certain ratios) of ionic liquids are slightly higher than that in both neat ionic liquids, and the potentials

are more positive at the first peak, and it shows some difference with in [BMim][Tf₂N]/[BMim][BF₄] [15]. It may be due to the difference of structure and volume between their cations and anions. Comparing each curve, the volume ratio of 3:1 shows the best in current and potential, which is chosen to study in detail. Electro-reduction of nitrobenzene in binary ionic liquids are superior to both single ionic liquids, which suggests that binary ionic liquids can improve electro-reduction of nitrobenzene. It may be due to the microscopic molecular environment changes.

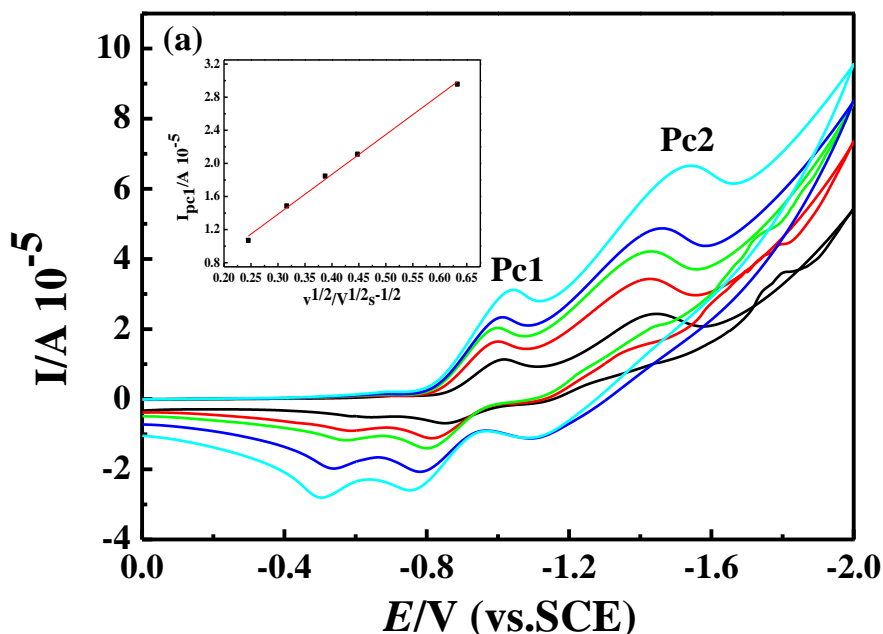


Figure 4. CV of the binary ionic liquids containing 0.1 mol·L⁻¹ nitrobenzene at different scan rates (0.06, 0.1, 0.15, 0.2, 0.4 V·s⁻¹). Inset shows the linear relationship between the peak currents and the square roots of scan rates (0.06–0.4 V·s⁻¹).

Fig. 4 shows cyclic voltammograms of nitrobenzene in binary ionic liquids (volume ratio=3:1) at different scan rates. The reduction current rises with increasing the scan rate. As shown in Fig. 4, a plot of I_{pc1} vs. $v^{1/2}$ presents a straight line at different scan rates in the range of 0.06 to 0.4 V·s⁻¹, which suggests that the electro-reduction of nitrobenzene in this binary ionic liquid is limited by diffusion-controlled process. Based on diffusion-controlled process, the chronoamperograms were obtained for a series of nitrobenzene solutions with various concentrations (0.015–0.10 mol·L⁻¹) as presented in Fig. 5a, Fig. 5b and Fig. 5c shows 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, the diffusion coefficient D is obtained from the Cottrell equation (Eq. (3)) [28,29].

$$i(t) = \frac{nFACD^{1/2}}{\pi^{1/2}t^{1/2}} \quad (3)$$

Where n is the electrons transfer number, D is the diffusion coefficient (cm²·s⁻¹), c is the concentration (mol·L⁻¹, we chose line c) of nitrobenzene, A is the electrode area (0.00196 cm²). Hence, D is 8.53×10^{-7} cm²·s⁻¹ by calculated from the Cottrell equation.

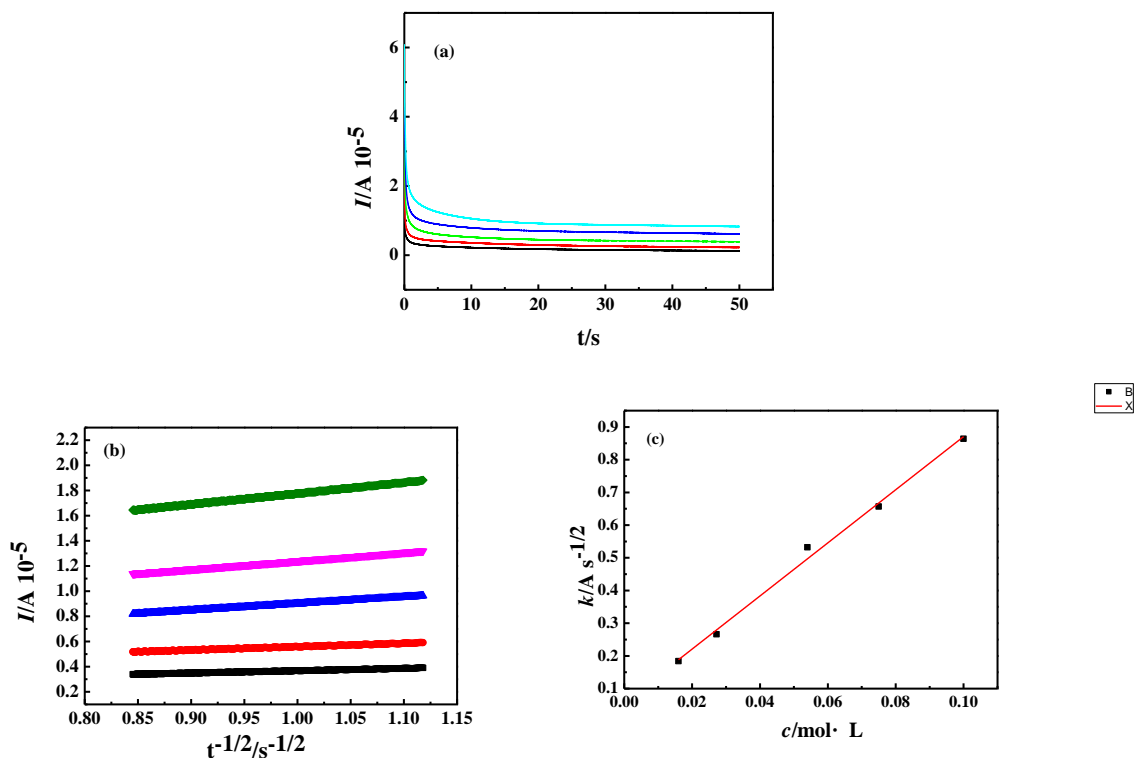


Figure 5. (a) Chronoamperograms of nitrobenzene in binary ionic liquid (a)–(c) of various concentrations of nitrobenzene: (a) $0.015 \text{ mol}\cdot\text{L}^{-1}$; (b) $0.026 \text{ mol}\cdot\text{L}^{-1}$; (c) $0.054 \text{ mol}\cdot\text{L}^{-1}$; (d) $0.075 \text{ mol}\cdot\text{L}^{-1}$; (e) $0.1 \text{ mol}\cdot\text{L}^{-1}$, respectively. (b) and (c) The plots of I vs. $t^{-1/2}$ and the linear relationship of slope with concentration of nitrobenzene obtained from the chronoamperograms, respectively.

The reductive behaviors of nitrobenzene in binary ionic liquid are better than that in single ionic liquid (Fig. 4). However, the yield and selective of reduction products are also the main factor to determine the performance of electroreduction. So the preparative constant-potential electrolysis experiments were carried out in solution of binary mixture and single ionic liquid at -1.6 V and $30 \text{ }^\circ\text{C}$. The product was detected by GC and GC-MS. The results of GC-MS present that the main reduction product is azobenzen ($m/z:182,152,105,77,51$) in binary ionic liquid and both single ionic liquid. Moreover, the conversion of nitrobenzene in binary system (92%) is higher than in OMImBF₄ (85%) and BMImPF₆ (87%). The selectivity of azobenzen is 91% in binary ionic liquid, the selectivity of azobenzen is 49% in OMImBF₄ and the selectivity of azobenzen is 69% in BMImPF₆, respectively.

In situ FTIR spectra was carried out to investigate the electrochemical reduction of nitrobenzene on Pt electrode in binary ionic liquid. Fig. 6 presents a series of in situ FTIR spectra obtained during electro-reduction of nitrobenzene on Pt at various potentials. When the sample potentials are more positive than -800 mV , no drastically changes could be observed on the FTIR spectra (Fig.8). At -1000 mV , the spectra exhibits two characteristic positive-going bands at 1524 cm^{-1} and 1348 cm^{-1} , which are related to asymmetric stretching vibration of nitryl ($\nu_{as}(-\text{NO}_2)$), and symmetric stretching vibration of nitryl ($\nu_s(-\text{NO}_2)$) of nitrobenzene. At the same time, four negative-going bands are observed. Bands at 1300 cm^{-1} , 1405 cm^{-1} and 1665 cm^{-1} and 1216 cm^{-1} are attributed to stretching

vibration of ν (N(O)=N) of azoxybenzene, stretching vibration of ν (N=O) of nitrosobenzene, stretching vibration of ν (-N=N-) of azobenzene and stretching vibration of Carbon-hydrogen bonds (ν (-C-N-)) of aniline[30], respectively.

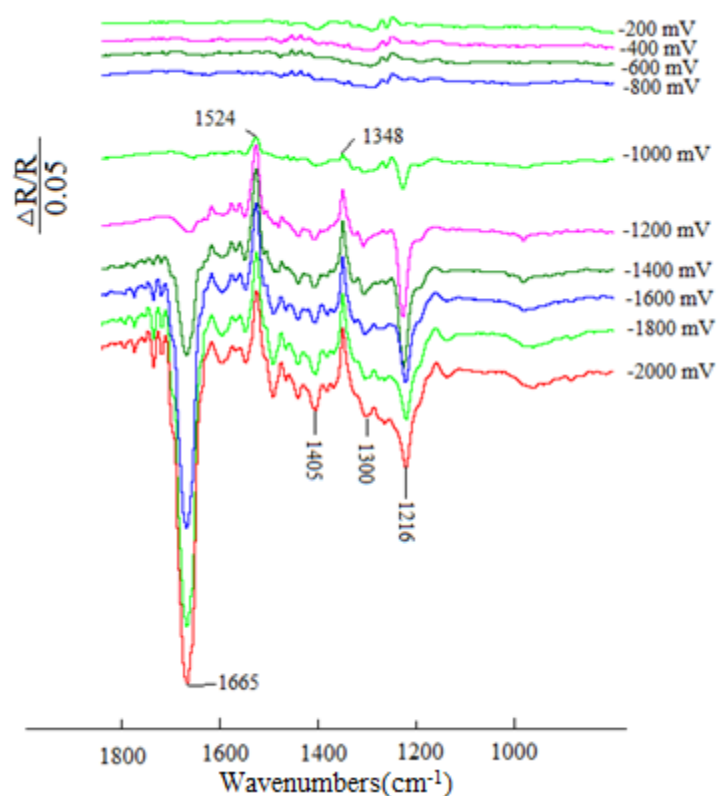


Figure 6. In-situ FTIRs collected during electro-reduction of nitrobenzene on Pt electrode in binary mixtures of ionic liquids. The potential was stepped from 0 mV to -2000 mV, reference potential: 0 mV, the spectral resolution is 8 cm^{-1} . The concentration of nitrobenzene is $0.05\text{ mol}\cdot\text{L}^{-1}$.

4. CONCLUSION

Binary ionic liquid mixtures were studied and used as electrolyte in electro-reduction of nitrobenzene. The experimental results present that electro-reduction of nitrobenzene in binary ionic liquids (some ratios) was superior to that in neat ionic liquids, and the volume ratio of 3:1 shows the best in current and potential. Cyclic voltammetry shows that electro-reduction process of nitrobenzene in OMIImBF₄/BMIImPF₆ under diffusion controlled and the diffusion coefficient is $8.53\times 10^{-7}\text{ cm}^2\cdot\text{s}^{-1}$. The constant-potential electrolysis results present that a better selectivity (91%) in binary ionic liquids. These results suggest that binary ionic liquids can play a key role to improve the electrochemical reduction of nitrobenzene. The results also suggested that and the mixtures of ILs may be also an effective way to achieve the function of ionic liquid because the characteristics change after ionic liquids are mixed.

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