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Infrared spectroscopic study on chemical and phase equilibrium in triethylammonium acetate

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Protic ionic liquid (PIL) triethylammonium acetate was prepared by mixing equimolar amounts of acetic acid and triethylamine, and then studied using the combination of the Attenuated Total Reflection Fourier Transform Infrared spectroscopy, *in-situ* infrared spectroscopy, pH, and conductivity titration measurements. It was found that the equimolar synthesized triethylammonium acetate was separated into two layers, which suggesting that there were both chemical and phase equilibrium in this solution. Molecular species could be directly observed in the IR spectra over the range of 1200–1800 cm^{-1} and also checked by ^{1}H NMR. Based on analysis, the upper layer was rich in amine with little acid and PIL, and the down layer was rich in PIL with residual acetic acid and amine. And single PIL-rich layer could be separated into two layers again when the mole ratio of newly added triethyamine to the theoretical produced triethylammonium acetate reached 0.12.

chemical equilibrium, phase equilibrium, triethylammonium acetate, IR spectroscopy

1 Introduction

Protic ionic liquids (PILs), which were classified as “poor” ionic liquids [1, 2], were rendered one of the most attractive ionic liquids as their widely uses [3–5] ranging from batteries [6], fuel cells [7, 8], double-layer capacitors [9, 10], catalysis [11–16], and solvent [17, 18]. A fraction of the researchers approved of the presenting of neutral acid and base species due to a chemical equilibrium (eq. (1)) [19–21] in PILs through different techniques. For example the neutral formic acid was believed to be exsting in the *N*-methyl-2-hydroxyethylammonium formate according to the faster diffusion obtained for the anion than the cation ($D^{-}>D^{+}$) [22]. And one kind neutral ion pair “molecules” held together through a strong hydrogen bond [23] was found in $[\{(CH_3)_2N\}_2CNH_2]Cl$ by Raman spectroscopy and quantum mechanical calculations [24].

$$\mathrm{AH(bronsted\ \ acid) + B(bronsted\ \ base) \leftrightarrow [BH]^{+} + A^{-}} \tag{1}$$

In case the equilibrium constant is very large, there will be little non-negligible amount of neutral molecular species in the PIL, however, when the equilibrium constant is not very large, the PIL contains not only ionic but also neutral species to form a complex system. MacFarlane and Seddon [25] discussed the question of “Is the PILs true ionic liquids or liquid mixture?”, and the equilibrium in PILs caught much attention by many researchers [26–31].

In the investigation of the equilibrium, the NMR measurement (^{1}H NMR, ^{13}C NMR, ^{15}N NMR) [27, 28, 32] is the commonly used technique, as the ^{13}C, ^{1}H chemical shifts, relaxation times, and diffusion coefficients, can be used to study the interaction between cation and anion [33]. Originally, NMR spectroscopy was adopted to distinguish the neutral and ionized proton in the study of the ionic pairs,

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molecules, and aggregation components in ILs. Especially, after Tokuda *et al.* [29, 34–36] successfully proposed the $\Lambda_{\rm imp}/\Lambda_{\rm NMR}$ ratio to describe the ionicity of APILs (aprotic ionic liquids), many researchers tried to apply NMR spectroscopy to investigate the properties and equilibrium in ILs. Tubbs *et al.*, for instance, applied ^{1}H NMR spectroscopy to explore the chemical equilibrium and thermodynamic properties in imidazolium based ILs [37]. However, in ammonium-based PILs, since one proton belonging to the acid in the PIL may transfer fast between the acid and the amine, only an average signal of the protons was observed in the spectra as reported by Nuthakki *et al.* [27] due to the fact that the lifetime of ion-pairs (20×10^{-14} s) was too short to monitor on a 10^{-11}–10^{-9} s timescale NMR spectroscopy [12, 29]. Even in ^{15}N NMR spectra, which exhibits a high polarity and is much more sensitive than the ^{13}C or ^{1}H NMR, also only one moved resonance was observed in the study of diethanolamine samples with different acetic acid concentrations [32]. In other words, it is impossible to figure out two different chemical shifts belonged to the neutral and ionized nitrogen to describe the chemical equilibrium directly by NMR spectroscopy. Besides this, Raman [38], IR, [39–41] and viscosity compared to ionic conductivity measurement (the classic Walden rule) [42–45] have also been used to investigate the equilibrium, but little specific quantitative data has been ever got. Furthermore, IR spectroscopy was usually used to investigate the general interactions that exist in ILs at molecular level [46–49]. For example, Shimomura *et al.* [50] applied ATR-IR spectroscopy to study the effect of the alkyl-chain length on the mixing state of imidazolium-based ionic liquid-methanol solutions. And the thermal stability of *N*-alkyl-*N*-alkyl-pyrrolidinium imides was also investigated by FT-IR spectroscopy [51]. Mashkovsky *et al.* [52, 53] studied the hydrogen bonding in triethylammonium salts by IR spectroscopy. And Wulf *et al.* [54] reported that both IR and NMR spectroscopic properties reflected a similar type of electronic perturbation caused by hydrogen bonding, but take place on different timescales. Compared to a 10^{-11}–10^{-9} s timescale NMR spectroscopy, IR spectroscopy is more suited to investigate the equilibrium as the lifetime of ion-pairs is 20×10^{-14} s.

In this paper, IR spectroscopy is chosen to investigate the equilibrium of triethylammonium acetate. We present the direct evidence of the existence of molecular species in triethylammnium acetate by IR spectroscopy rather than NMR spectroscopy to note that there is a chemical equilibrium as eq. (2) in the PIL.

$$\mathrm{NX} + \mathrm{HAc} \Leftrightarrow [\mathrm{NX^{+}H}][\mathrm{Ac^{-}}] \qquad (2)$$

And the results obtained from IR spectroscopy, *in-situ* IR spectroscopy, pH, and conductivity titration measurements indicate that there are both chemical and phase equilibrium in the equimolar synthesized solution.

2 Experimental

2.1 Synthesis and characterization

Triethylammonium acetate was synthesized by equimolar amounts of acid and base. The acetic acid (anhydrous, GR$\geqslant$99.8%, Aladdin) was added very slowly while stirring to triethylamine (anhydrous, GR$\geqslant$99.0%, Aladdin) contained in a round-bottom flask over water at room temperature. And then the mixture was stirring continuously at 25 °C for 5 h. However, further purity measurements were not applied on the equimolar synthesized solution, as we believed that there were no impurities existing in the reactants, even the residual neutral ones were considered as molecular species to maintain the well-known chemical equilibrium. The purpose of protecting the structure and properties of the equimolar synthesized solution could give us a chance to investigate the true contents of the PIL. The water content was checked by Carl-Fischer titration, 659 ppm.

It is interesting to find that the equimolar synthesized solution is separated into two layers (Figure 1). The down layer is recognized as the PIL-rich layer and the upper layer as amine-rich layer by ^{1}H NMR method.

The PIL-rich layer was characterized by NMR (^{1}H NMR and ^{13}C NMR) spectra (500 MHz, $\mathrm{CDCl_3}$, TMS) [55], DSC-TG (from room temperature to 500 °C at a cooling and heating rate of 10 °C/min in nitrogen flow on NETZSCH STA 409 PG/PC), and MS (used ESI as the ion source type by positive and negative ion polarity respectively for cation and anion) (Supporting Information).

2.2 Conductivity measurements

The conductivity of any solution depends not only on the number of charge carriers but also on their mobility. The ionic conductivity measurements of the PIL-rich layer were conducted on a Model DDS-307 conductometer with a DJS-10C type platinum black electrode at 25 °C. The cell constant was determined by calibration using an aqueous

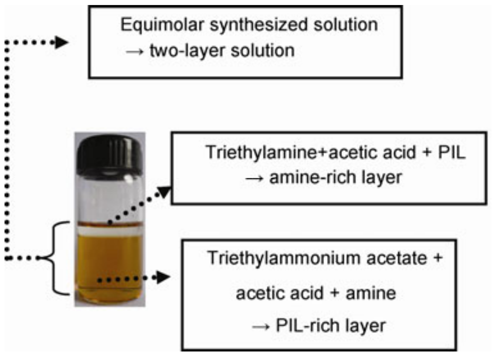

Figure 1 The picture of two-layer solution with three components. The upper layer is recognized as amine-rich layer and the down one is PIL-rich layer.

0.01 M KCl solution. In the process of conductivity titrations, the solutions were being equilibrated for 2 h before each measurement.

2.3 pH measurements

The pH measurements of the solution were conducted on a portable acidity meter PHB-2 with composite electrode at 25 °C, which was purchased from Hangzhou Leici analytical instrument company. In the process of pH titrations, the solutions were being equilibrated for 2 h before each measurement.

2.4 IR measurements

Infrared spectroscopy experiments were performed on a Nicolet FT-IR/Nexus 470 spectrometer in the attenuated total reflection mode at 25 °C. A small droplet of the PIL-rich layer was placed on top of Ge crystal. Spectra were obtained in the range of 4000–600 cm^{-1} at a resolution of 4 cm^{-1}, and accumulated for over 32 scans. Besides this, *in situ* Fourier transform infrared spectroscopy (BRUKER OPTIK GmbH, Matrix-MX) was used to explore the effect of the addition of triethylamine to single PIL-rich layer and two-layer solution (equimolar synthesized solution).

3 Results and discussion

3.1 Both chemical and phase equilibrium exist in two-layer solution

The equimolar synthesized solution surprises us as it is separated into two layers, and called two-layer solution, as shown in Figure 1. With the purpose to identify the components of those two layers, ^1H NMR spectroscopy was adopted to check the two layers compared to material triethylamine. The results are listed in Table 1, which indicates that both layers include triethylammonium acetate (PIL), triethylamine, and acetic acid. The upper layer is rich in amine with little acid and PIL, and the down layer is rich in PIL with residual acetic acid and amine. Furthermore, the single upper layer could stay stable as the two-layer solution was separated, and the single PIL-rich layer stay stable in a short period and would be separated into two layers again after a long period.

To confirm the characteristic absorption peaks of the PIL-rich layer, we conducted IR spectroscopy measurements on sodium acetate, acetic acid, sodium chloride, and the PIL-rich layer. Figure 2 shows the absorption spectra of HAc, NaAc/H_2O, and NH_4Cl/H_2O in the range of 1000–1800 cm^{-1}, with typical COO^- and N^+-H bands in the range of 1350–1450 cm^{-1}, COO^- 1500–1600 cm^{-1}, and significant COOH modes in the range of 1680–1750 cm^{-1} with C–O (1200–1300 cm^{-1}). According to Lange's Handbook of Chemistry and the IR results got from acetic and ammonium salts, peaks in Figure 3(a) of the PIL layer can be observed associated with: (1) ionic peaks: the peaks in the range of 1350–1450 cm^{-1} are attributed to both COO^- and N^+-H, and in 1500–1600 cm^{-1} is assigned to COO^-. (2) molecular peaks: significant COOH modes in the range of 1680–1750 cm^{-1}, and one peak in the rang of 1200–1300 cm^{-1} could be assigned to the C–O vibration in the COOH. The molecular and ionic species of the PIL-rich layer are directly observed in the IR spectra, suggesting that there is indeed a chemical equilibrium (eq. (2)) in it. And the distinct two-layer solution illustrates that there is also a phase equilibrium in the two-layer solution. In a word, the equimolar synthesized solution exhibits a distinct phenomenon: two-layer, three components, and there are both chemical and phase equilibrium in it.

Why is the equimolar synthesized solution separated into two layers as shown in Figure 1? This is probably attributed to the spatial structure of triethyammonium (with three alkyl around the nitrogen atoms), which makes it difficult for the proton transferring to produce triethylammonium acetate, and the amount of the produced PIL exceeds the dissolvability of neutral molecular species to the PIL. Figure 3(b) describes that the area of molecular species (C–O and COOH) is much larger than that of ionic species (COO^- and N^+–H), indicating that the amount of molecular species is much larger than ionic ones, and this could also attribute to the two separated layers phenomenon.

MacFarlane and Seddon [25] reported that below 1% of neutral species one could consider PILs as "pure" ILs. And Lopes *et al.* [21] concluded that the term "PIL" should definitely be replaced by the term "PIL solution". In other words, the PIL-rich layer could be recognized as PIL solution. As a result, both chemical and phase equilibrium existing in the two-layer solution. The structure and properties of that need further investigation.

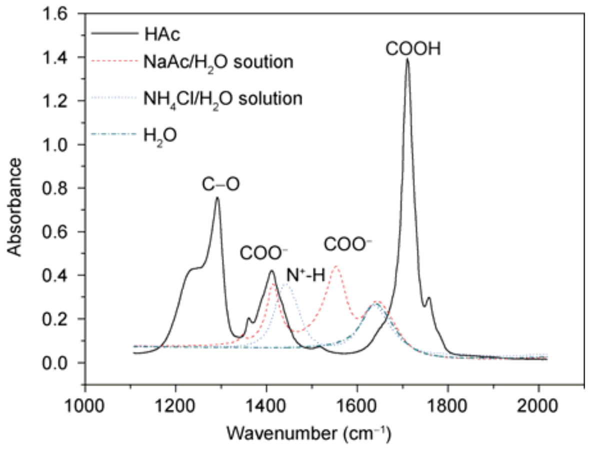

Figure 2 The IR spectra of HAc, NaAc/H_2O, NH_4Cl/H_2O, and H_2O in the range of 1000–1800 cm^{-1}.

Table 1 The ^{1}H NMR results of upper layer and down layer of the two-layer solution compared to triethylamine

PIL	^{1}H NMR chemical shifts
Triethylamine	0.99–1.03(CH$_3$, 9H) 2.48–2.53(CH$_2$, 6H)
Upper layer	0.99–1.03(CH$_3$, 9H 2.48–2.53(CH$_2$, 6H)
Down layer	1.22–1.25(CH$_3$, 9H), 2.00(CH$_3$, 3H), 2.97–3.02(CH$_2$, 6H), 10.8(H)

3.2 The equilibrium in the single PIL-rich layer compared to the two-layer solution

Conductivity and pH measurements as macroscopic techniques were used to monitor the movements of equilibrium during the process of single PIL-rich layer which was taken out of the two-layer solution changed into a new two-layer solution, along with triethylamine added. And all the measurements were focused on the PIL-rich layer. The conductivity could reflect the amount of moveable ions and the pH could give information about the change in the concentration of $[H]^+$ in that solution, and both of that are useful for investigation of equilibrium. The results were shown in Figure 4.

As shown in Figure 4(a), the addition of triethylamine causes the conductivity of the PIL-rich layer decrease firstly due to the fact that ionic species is diluted when the amine is added. Furthermore, triethylammonium acetate is not easily produced as the spatial structure of cation, let alone adding amine into the PIL-rich layer. All of this could attribute to the decrease of the conductivity before 0.16 mole ratio. Then adding amine to the PIL-rich layer continually causes the conductivity increase as a result of the single PIL-rich layer started to stratify. In other words, along with adding the amine, the single PIL-rich layer gradually separates into two layers again, and redundant amine goes to the new upper amine-rich layer, leading to the increase of the conductivity (after mole ratio 0.16, Figure 4), and the decrease of pH (mole ratio between 0.12–0.16, Figure 4). Furthermore, the two-layer phenomenon was observed during the experiment when the mole ratio of triethylamine to theoretical triethylammonium acetate (*n*(N222):*n*(theoretical N222HAc)) reached 0.12. After stratification, we still measured the conductivity and pH of PIL-rich layer to ex-

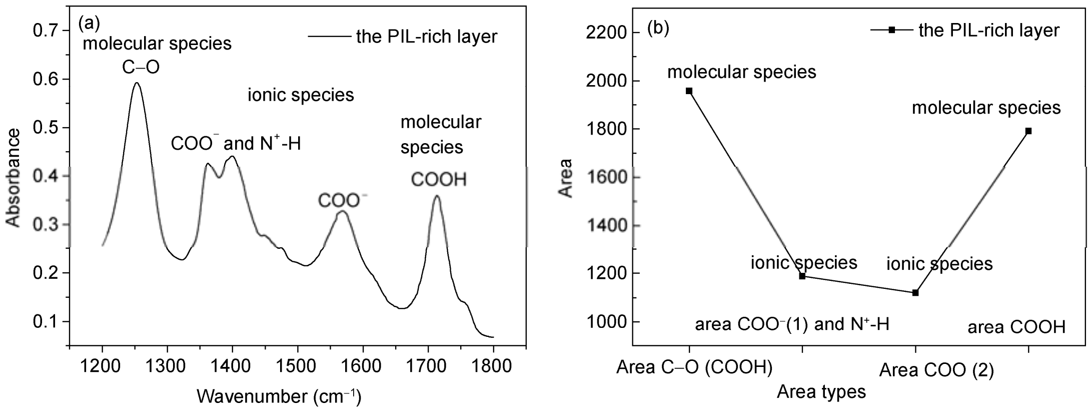

Figure 3 The attenuated total reflection (ATR) FTIR spectra and peak area of the PIL-rich layer in the range of 1200–1800 cm^{-1}. (a) The IR spectra with typical COO$^-$ and N$^+$-H bands in the range of 1350–1450 cm^{-1}, COO$^-$ 1500–1600 cm^{-1}, and significant COOH modes in the range of 1680–1750 cm^{-1} with C–O (1200–1300 cm^{-1}), (b) the area of the four typical peaks diagram. The area of molecular species is much larger than the ionic ones, indicating there is much more molecular species than ionic ones in the PIL-rich layer.

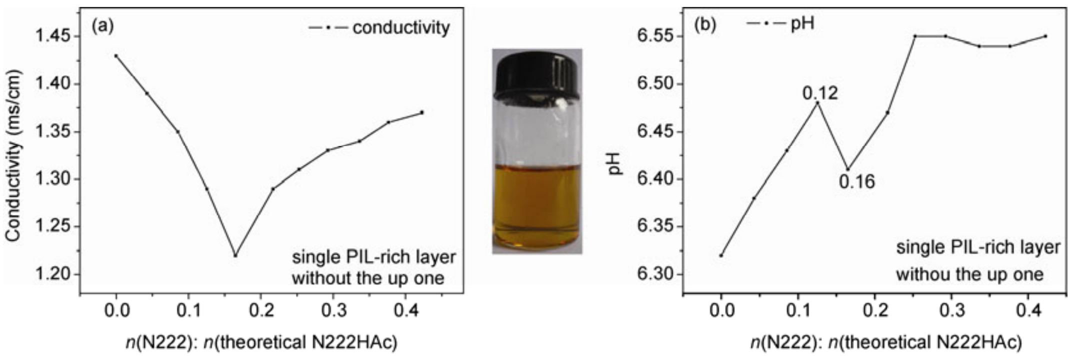

Figure 4 The conductivity and pH titration diagrams of PIL-rich layer separated out from two-layer solution along with the amine was added into the single layer (N222: $(CH_3CH_2)_3N$, N222HAc: $[(CH_3CH_2)_3NH][CH_3COO]$, the molar amount of theoretical N222HAc is calculated by the mole of raw material amine and acid: 0.5 mole amine mixed with 0.5 mole acid produce 0.5 mole PIL).

plore the equilibria in the solution. All the results demonstrated that at the first inflection point in Figure 4(b), the molecular amine was separated out from the previous single PIL-rich solution, and then the single layer gradually reached a new two-layer solution.

In-situ IR spectroscopy was used to explore equilibrium in both two-layer solution and single PIL-rich layer, along with triethylamine added into those solution, and the results are shown in Figure 5. In the two-layer solution, the trend of changes in the area of COOH of the amine-rich layer which was calculated by the IR auto-software is shown in Figure 5(a). It changes as "N" letter with two inflection points at 0.12 and 0.16. Before 0.12, the amount of acetic acid in the amine-rich layer increases along with the added amine as the dominant effect of phase equilibrium. Triethylammonium acetate is produced between 0.12 and 0.16 due to the chemical equilibrium. After 0.16 mole ratio, the effect of phase equilibrium on the two-layer solution makes the amount of acetic acid in the amine-rich layer increase again.

The properties of equilibria in single PIL-rich layer are quite different from the above mentioned two-layer solution with both chemical and phase equilibrium, which is demonstrated by the opposite trend of changes in the area of COOH of the two in Figure 5(b,c). In Figure 5(b), there is a significant increase in the area of COOH following the increased mole ratio of *n*(N222):*n*(theoretical N222HAc), which provides valuable insight into the fact that the amount of acetic acid may increase. In Figure 5(c) the area of COOH decreases along with the increase of *n*(N222):*n*(theoretical N222HAc) without the effect of the amine-rich layer. This is because the addition of N222 causes the right shift of the chemical equilibrium to produce PIL, reflecting the area of COOH decreases. In other words, eliminating the amine-rich layer, the single PIL-rich layer has a normal chemical equilibrium property. But in the two-layer solution, there is a balance between the chemical and phase equilibrium, which makes this solution quite distinctive. And in the process, the phase equilibrium plays a more important role. The competition between the chemical and phase equilibrium could be the key point, and this needs further investigation.

All the IR spectroscopy, conductivity, and pH titrations results tell us that the equimolar synthesized triethylammonium acetate solution is a two-layer solution with three components-PIL, amine, and acetic acid, existing both chemical and phase equilibrium. Therefore, we could not get the expected PIL by equimolar acid and amine. The down layer of the solution could be recognized as PIL solution according to MacFarlane and Seddon [24], and the PIL solution will be separated into two layers again when the amount of added amine reaches *n*(N222):*n*(theoretical N222HAc) of 0.12.

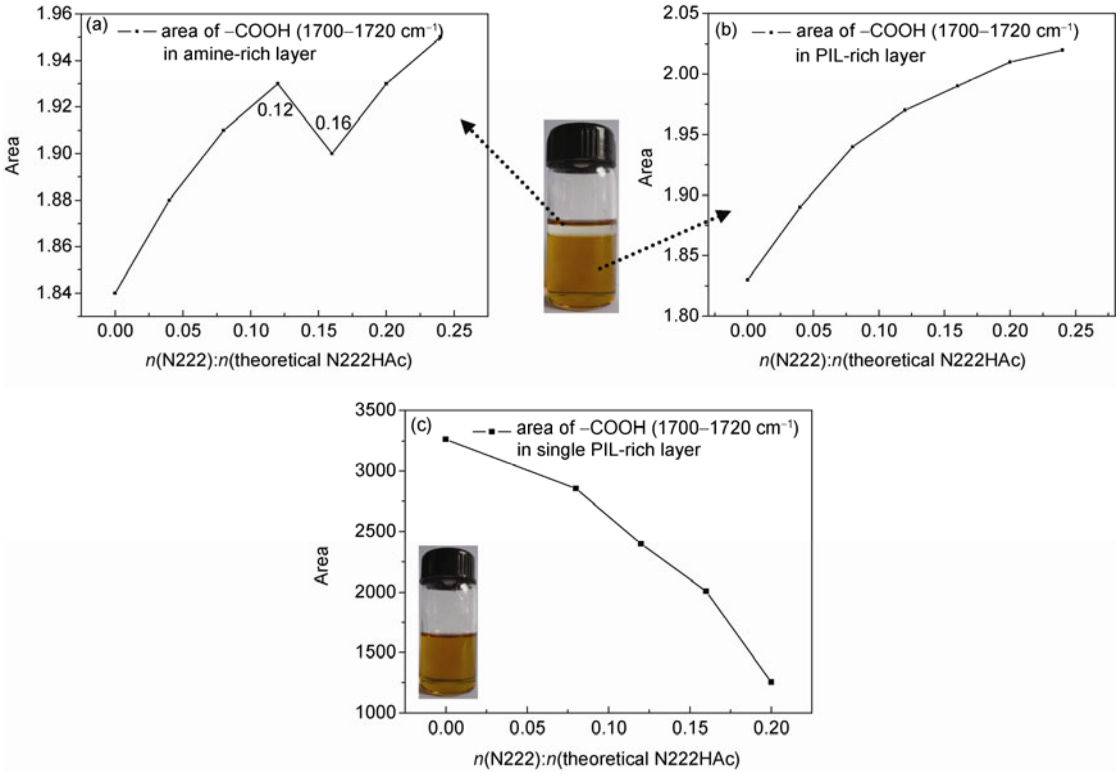

Figure 5 The relative area change of COOH peak by *in-situ* IR spectroscopy at various ratios of *n*(N222):*n*(theoretical N222HAc) in two-layer solution and single PIL-rich layer (N222: $(CH_3CH_2)_3N$, N222HAc: $[(CH_3CH_2)_3NH][CH_3COO]$, the molar amount of theoretical N222HAc is calculated by the mole of raw material amine and acid: 0.5 mole amine is mixed with 0.5 mole acid to produce 0.5 mole PIL).

4 Conclusions

In this work, we propose that there are both chemical and phase equilibrium in equimolar synthesized triethylammonium acetate solution by IR spectroscopy, *in-situ* IR spectroscopy, pH, and conductivity titrations measurements. And this equimolar synthesized triethylammonium acetate solution is composed of three components (PIL, acid, and amine) and separated into amine- and PIL-rich layers. Along with the addition of triethylamine into the two-layer solution and single PIL-rich layer, respectively, we could only get triethylammonium acetate solution, and in the single PIL-rich layer when the mole ratio of *n*(N222): *n*(theoretical N222HAc) reached 0.12, the single PIL-rich layer could be separated into two layers again to rebuild a new stable solution including both chemical and phase equilibrium. IR spectroscopy is an effective tool to investigate the equilibrium in PILs. And the quantitative and qualitative relationship between the chemical and phase equilibrium in this system need further investigation in the future. This could help us to synthesize purer trialkylammonium acetate at featured ratio of amine and acetate acid rather than equimolar.

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