Theoretical study of intermolecular interactions in protic ionic liquids: a single ion pair picture

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Abstract. Protic ionic liquids are made via intermolecular transfer between cation and anion. This research employs theoretical calculation to gain understanding of the intermolecular interactions at single-ion-pair level and their consequences to the macroscopic properties of the ionic liquids. The protic ionic liquids used in this study are ethylammonium nitrate (EAN), propylammonium nitrate (PAN), and butylammonium nitrate (BAN). Molecular structures of ions and ion pair of each liquid are optimized using the density functional theory. The ion pair binding energies and infrared spectra of optimized structures are investigated. Infrared spectra of separated cation and anion are compared with cation-anion ion pair to specify the vibrational band shifts due to intermolecular interactions. The infrared-spectra show the hydrogen-bond stretching modes in the far-infrared region at the wavenumber between 108-252 cm⁻¹ and the red shifts of four vibrational bands due to intermolecular interactions between the ions. Three vibrational band shifts are mainly due to Coulomb force, and the other shift is caused by combination of intermolecular interactions. Moreover, the energy calculations show that the binding energy decreases as the alkyl chain length increases.

1. Introduction
Ionic liquids (ILs) are room temperature liquids comprising entirely of cations and anions [1-3]. They have several properties that are of technological interest, for example, extremely low vapor pressure, high ionic strength, high thermal and chemical stability etc [4-6]. As a result, they are promising to be used in a wide range of applications such as electrolyte for electrochemical energy storage devices, electrotunable lubricants, and gating of semiconducting and superconducting electronic devices [2-3,7-8]. ILs can be classified in two large groups, protic ionic liquids (PILs) and aprotic ionic liquids
(APILs). Proton transfer reactions from Brønsted acid to Brønsted base are keys to distinguish PILs from APILs [9]. This mechanism also results in special intermolecular interactions, such as hydrogen bonds, between cation and anion besides Coulomb interactions. Forming and breaking of such interactions usually occur at a very short time scale in the order of picosecond. To have a clear and solid interpretation for experimental results of such fast interaction dynamics usually requires computational molecular calculations [10].

Generally, most of IL research performed the calculation based on cluster of molecules to understand interaction complexity, which can be computationally expensive [11-13]. For example, from our experience, density functional theory (DFT) based calculation for a cluster of only 4 molecules of water using a computer that has 4 core processors and 4GB of RAM took computational time of 3 hours. Similar calculation in IL systems will take much longer time due to stronger and more complex interactions. Quick and simple calculation approach would be advantageous for a preliminary study prior to full calculation. A single ion pair calculation is one way to observe interactions from a building block level. Although it may not provide a complete picture, still it is able to capture major molecular characteristics and behaviour with shorter computational time.

In this research, we focus on computational calculation of single ion pair of three PILs; ethylammonium nitrate (EAN), propylammonium nitrate (PAN), and butylammonium nitrate (BAN), using DFT method. The role of intermolecular interactions on infrared (IR) spectra as well as binding energy are investigated based on comparison between IR spectra of separated ions and ion pairs. From this method, we expect to get information about formation of ion pairs in vibrational peaks of far-IR region. The results are also compared with the results from published experiments and calculations using similar computational technique. Based on our findings, we have shown that single ion pair calculation can give a lot of meaningful information of molecular interactions and is suitable to be used as a preliminary study prior to complete calculation of larger IL systems.

2. Methodology

Single ion pair of three PILs, EAN, PAN, and BAN, were calculated computationally to investigate the intermolecular interactions between cation and anion. The ion structures of these three PILs are shown in figure 1. These liquids were chosen since they have many properties similar to water, for example, they can form a similar hydrogen-bonded network, which is one of the important intermolecular interactions that can affect thermophysical properties of the ILs [9]. Optimization of the molecular structures of cations, anions, and ion pairs to their ground state energy was done with the DFT method of the Gaussian09 program [14]. The aug-cc-pVTZ basis set with B3LYP functional were used in this calculation. Based on publication by Boese in 2015, the set of 16 hydrogen-bonded complexes were calculated using DFT method with B3LYP functional and several basis sets [15]. He showed that the aug-cc-pVTZ basis set is one of the appropriate basis sets for the systems containing hydrogen bonds because it yielded an RMS error of about 1 kJ/mol. Furthermore, the energies, the vibrational modes, and the IR spectra of the ions’ optimized structures were investigated. Vibrational bands and band shifting were considered by comparing IR spectra of cation and anion in each PIL with its ion pair.

Figure 1. Molecular structures of ethylammonium cation (EA⁺), propylammonium cation (PA⁺), butylammonium cation (BA⁺), and nitrate anion (NO₃⁻) [16].
In addition, the ion pair binding energy $\Delta E$ was calculated as [17]

$$\Delta E = E_{\text{PIL}} - E_{\text{Cation}} - E_{\text{Anion}},$$  

(1)

where $E_{\text{PIL}}$, $E_{\text{Cation}}$, and $E_{\text{Anion}}$ are the energies of ion pair, cation, and anion calculated using DFT method, respectively. The ion pair binding energies of each PIL were compared to obtain the strength of intermolecular interactions.

3. Results and discussion
The optimized molecular structures and their IR spectra of PILs were obtained from Gaussian09 calculation. Several absorption peaks appear on the IR spectra according to vibrational modes of ions. The peak assignments of cations, anions, and ion pairs of each PIL are summarized in table 1, with the optimized molecular structures presented in figure 2.

There are some interesting vibrational bands labelled with roman superscripts in table 1. The vibrational band I in the far-IR region of each ion pair has been attributed to stretching modes of the hydrogen bond $\text{N} - \text{H} \cdots \text{O}$ as shown in figure 2. This band appears only on ion pair spectra and does not exist on the spectra of separated cations and anions. This result is in line with the experimental and theoretical results reported by Fumino et al in 2007 [11]. This provides a convincing evidence of the formation of hydrogen bond between the hydrogen atom in cation and the oxygen atom in anion from the $\text{O} - \text{H}$ bond for each PIL.

| Assignment                  | Table 1. The peak assignments of cations, anions, and ion pairs of each PIL. |
|-----------------------------|--------------------------------------------------------------------------------|
| Wavenumber (cm$^{-1}$)      | NO$_3^-$ | EA$^+$ | PA$^+$ | BA$^+$ | EAN | PAN | BAN |
| N–H⋯O Stretching$^I$        | 217.43   | 198.59 | 251.48 |
| C–C–C Bending               | 254.31   | 286.78 | 303.29 | 396.06 |
| N–C–C Bending               | 372.27   | 370.15 | 349.18 | 358.49 |
| H–N–H Torsional             | 461.49   | 472.09 | 464.76 |
| O–N–O Bending$^I$           | 707.01   | 663.45 | 663.87 | 663.94 |
| O–N–O Bending$^I$           | 706.60   | 691.82 | 692.30 | 692.67 |
| NO$_3^-$ Pyramidal$^IV$     | 843.66   | 802.65 | 802.91 | 802.91 |
| N–O Stretching$^V$          | 1364.26  | 1364.92| 1364.18| 1364.18|
| CH$_3$ Pyramidal            | 1434.84  | 1436.68| 1428.31| 1417.65| 1419.98| 1418.90|
| H–C–H Bending               | 1513.61  | 1517.54| 1519.19| 1509.32| 1513.31| 1514.73|
| H–N–H Bending               | 1666.12  | 1667.03| 1666.17| 1651.28| 1648.74| 1651.41|
| C–H Stretching              | 3087.66  | 3079.51| 3080.70| 3046.39| 3039.11| 3038.35|
| N–H Stretching              | 3393.39  | 3394.57| 3394.91| 3471.35| 3472.94| 3472.53|
| N–H Stretching              | 3468.98  | 3470.58| 3471.52| 3544.78| 3546.53| 3545.80|

Figure 2. Optimized molecular structures and stretching modes of the hydrogen bond between cation and anion in vibrational band I of (a) EAN, (b) PAN, and (c) BAN.
Moreover, when the ion pairs are formed, intermolecular interactions between the cation and the anion can be complex due to many interactions, such as Coulomb force, hydrogen bond, and dispersion force. This can be observed from the shifting of vibrational bands in the mid-IR region [13,18]. From table 1, the vibrational bands II and III refer to the bending modes of the NO$_3^-$, On the spectrum of a single anion, these vibrational bands have slightly different wavenumbers (707.01 cm$^{-1}$ and 706.60 cm$^{-1}$). These wavenumbers shift to lower values when the ion pair is formed with the band shift of about 15 cm$^{-1}$ and 43 cm$^{-1}$, respectively. Band red shifting can also be observed with the vibrational bands IV and V. These bands are assigned to the pyramidal mode and the stretching mode of the NO$_3^-$, having shifted values about 40 cm$^{-1}$ and 50 cm$^{-1}$, respectively. The vibrational bands III, IV, and V have been observed in the experimental and theoretical spectra done by Bodo et al in 2012 [12]. However, the vibrational band II does not appear in their research. It could be that this band is suppressed in the force field of liquid clusters. The illustration of vibrational modes II, III, IV, and V are presented in figure 3.

![Figure 3. Bending modes (II III), pyramidal mode (IV), and stretching mode (V) of the nitrate anion.](image)

Band red shifting has been reported as caused by the existence of interactions between ions [18]. However, it is not a simple task to conclude which interaction contributes to band shifting and to what extent. In our systems, electrostatic forces and hydrogen bonds are the two major intermolecular interactions. To separate them, we also did simulations by systematically replacing the cations with electroneutral ethylamine, propylamine, and butylamine, whose molecular structures are similar to EA$^+$, PA$^+$, and BA$^+$. In these cases, the attractive Coulomb force has been switched off while the other interactions, such as hydrogen bond, are still allowed to form. The IR spectra in figure 4 clearly shows that the vibrational bands II, III, and IV do not undergo red shifting like ion pairs, meaning that such the red shifting of these vibrational bands in case of the three PILs is mainly caused by the Coulomb force rather than other interactions. However, the red shifting of the vibrational band V appears with smaller band shift (about 15 cm$^{-1}$). Therefore, the red shifting of the vibrational band V is potentially caused by both Coulomb force and other interactions. In terms of shift magnitude, the changes in wavenumbers of each vibrational band are similar for all PILs, indicating that the shifting of vibrational modes of the anion does not depend on the alkyl chain length of the cations.

The result of each band shifting can also be supported by the simulation results of the molecular pairs of NO$_3^-$ with water (H$_2$O) and hydronium ion (H$_3$O$^+$). It is found that shifting of the NO$_3^-$ bands paired with the electroneutral H$_2$O in figure 4 is similar to the shifting in the cases of ethylamine, propylamine, and butylamine, while the bands of NO$_3^-$ paired with the H$_3$O$^+$ shift the same way as in the case of the ion pairs EAN, PAN, and BAN. These further indicate that Coulomb interaction has more influence on NO$_3^-$ band shifting than the size of the molecule as shown by shifting caused by H$_3$O$^+$, whose molecular dimension is smaller than all PIL cations.

In addition to IR spectrum, we also calculate the binding energy of each ion pair as shown in table 2. This binding energy represents the strength of total interaction between ions. From our results, we found the magnitude of the binding energy is in the same order of electrostatic interaction, meaning that Coulomb forces have a major contribution to the overall interaction. In addition, we found that the intermolecular interaction strength decreases with an increasing of the alkyl chain length agreeing with the results reported in literature [19]. With this result in mind, the alkyl chain length has an effect on the ion pair interaction strength and the conclusion about the interaction strength cannot be made solely by looking at the spectral red shifting alone.
Figure 4. IR spectra of each compound and PIL.

Table 2. Energies of ion pair $E_{\text{PIL}}$, cation $E_{\text{Cation}}$, anion $E_{\text{Anion}}$, and binding energy $\Delta E$ of PIL.

| PIL  | $E_{\text{Cation}}$ (kJ/mol) | $E_{\text{Anion}}$ (kJ/mol) | $E_{\text{PIL}}$ (kJ/mol) | $\Delta E$ (kJ/mol) |
|------|-------------------------------|------------------------------|-------------------------|------------------|
| [EAN] | −356004.92                   | −736404.83                   | −1092900.14              | −490.39          |
| [PAN] | −459266.46                   | −736404.83                   | −1196156.46              | −485.17          |
| [BAN] | −562525.37                   | −736404.83                   | −1299412.09              | −481.89          |

4. Conclusion
The single ion and ion pair of three PILs were used to investigate the IR spectra and binding energies using DFT molecular computational calculations. From the results, an evidence of hydrogen bond formation between cation and anion is found as shown by the stretching mode absorption band in far-IR region around 108-252 cm$^{-1}$. In addition, intermolecular interactions also result in the red shifting of 4 vibrational bands of anion in mid-IR region. By switching off electrostatic interactions systematically, we show that the shifting of vibrational bands corresponding to bending and pyramidal modes of nitrate ion are caused mainly by the Coulomb force, while the shifting of stretching frequency of nitrate ion is caused by combination of intermolecular interactions. The strength of intermolecular interactions between ions has also been studied from the binding energy, which is found to decrease with increasing of the alkyl chain length. The calculation method based on single ion pair in this work can be used as a preliminary investigation of PILs having more complex molecular structure in the future work.

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