Volume 1 | Number 1 | Jan 2013 | Pages 1–100

PCCP

Physical Chemistry Chemical Physics
www.rsc.org/pccp

ROYAL SOCIETY OF CHEMISTRY

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

A table of contents entry
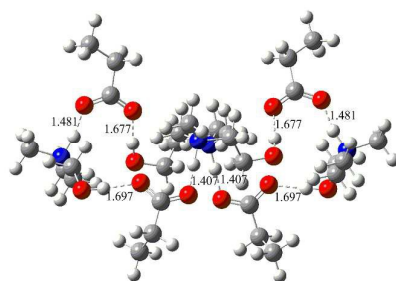
DMCEAP and DMEOAP are composed of neutral and ionized species in liquid phase through the experimental spectroscopy and DFT calculations.

ARTICLE TYPE

Experimental and Theoretical Studies on Compositions, Structures, IR and NMR Spectra of Functionalized Protic Ionic Liquid

Yingna Cui,[a] Jingmei Yin,[a] Changping Li,[*][a] Shenmin Li ,[*][a] Ailing Wang,[a] Guang Yang,[a] Yingping Jia[a]

The compositions and structures of amine-based functionalized protic ionic liquids (PILs), namely, N, N-dimethyl (cyanoethyl) ammonium propionate (DMCEAP) and N, N-dimethyl (hydroxyethyl) ammonium propionate(DMEOAP) have been investigated systematically by IR, ^{1}H NMR spectroscopy and the density functional theory (DFT) calculations. Analysis of the IR spectra suggests that both of DMCEAP
10 and DMEOAP are composed of neutral and ionized species in liquid phase, the former one mainly exists in the state of precursor molecules, and the latter mainly in ion-pairs. The ratio of precursor molecules to ion-pairs in the liquid phase depends on the type of precursors, especially the functional groups of cations. ^{1}H NMR spectra indicates that there is a dynamic equilibrium between neutral and ionized species, probably, some intermediates are formed in the PILs. The DFT calculations have been carried out
15 to reveal the conformation, and obtain the corresponding IR and ^{1}H NMR spectra of the neutral and ionized species, so that the theoretical support to the experiment results can be provided. The present study will help to understand the properties of PILs and provide a guide for further applications of PILs.

1. Introduction

20 In recent years, ionic liquids (ILs) have been used in a variety of applications due to their designable properties.[1-8] Among the existing ILs, protic ionic liquids (PILs), prepared through proton exchange between BrØnsted acid and BrØnsted base,[9] are an important subset of ILs. PILs have the lower boiling point than
25 traditional ILs, thus can be recycled by vacuum distillation.[10] Meanwhile, PILs have some unique properties, such as low cost, low viscosity, easy synthesis, easy recyclability, and good biocompatibility.[11] It has been widely utilized in many fields, such as organic synthesis,[12-14] extraction and separation,[10,15]
30 membrane fuel cells.[16,17]

As a large number of PILs have been prepared and applied, however, the questions on the compositions and structures of PILs remain controversial due to the proton transfer process of PILs is in a dynamic equilibrium. The uncertainty of structures
35 limits the further applications of PILs. Rebelo *et al.* found that a protic ionic liquid, [BH]$^+$X$^-$, consisted of isolated neutral molecules, B and HX, in the gas phase.[18] However, the ion clusters have also been discovered in the PILs. Ludwig *et al.* detected that ionic aggregates existed in ethyl ammonium nitrate,
40 and the stability of aggregate could be comprehended by the formation of a compact hydrogen-bond network.[19] In addition, Li *et al.*[20] and Mu *et al.*[21] confirmed that both molecular aggregates and ion aggregates may coexist in the gas phase for some PILs, and that the gas phase structure depends on the acidity and
45 basicity of the corresponding acid and base. Presently, there are still few reports on the compositions and structures of PILs in the liquid state. However, it can be of great significance because most of the PILs exist in the liquid state for practical applications. Rogers *et al.* found that proton transfer occurred frequently

50 between the acid and base species in the liquid state, resulting in the neutral and ionized species being present.[22-24] Theoretically, it is easy to obtain information on PILs composition if one knows what extent can the proton transfer. One efficient way to estimate the extent of a proton transfer in electrolyte is to measure the pKa
55 values of the acids and bases. Angell *et al.* considered that PILs with ΔpKa^{aq} (pKa(base)–pKa(acid)) >10 was required to ensure sufficient proton transfer to produce highly ionized PILs.[25] However, Stoimenovski *et al* proved that using this criterion to estimate ΔpKa for proton transfer is not always correct. Their
60 investigation indicated that for the specific PILs consisting of simple primary and tertiary amine cations with acetic acid anion, there is a clear distinction of degree of proton transfer, although all the amines have similar pKa value.[26] Another way to investigate the compositions of PILs is using spectrometric
65 techniques. Various spectra, such as NMR, IR, Raman spectra have been applied to obtain structural information of PILs.[27-32] For example, Li *et al.* applied ATR-IR to study the chemical and phase equilibrium in triethylammonium acetate,[29] Burrell *et al.* applied ^{15}N NMR to distinguish between neutral and ionized
70 amine bases in PILs.[32] Both of these groups obtained ideal experimental results, which indicate that spectroscopy is a simple but an effective approach for the study of the compositions of PILs.

Meanwhile, quantum chemical (QM) calculation, as an efficient
75 and indispensable approach, has been applied to simulate the exact microscopic structural of PILs.[19, 33, 34] Moreover, IR, NMR, Raman or EI-MS spectrum combined with the QM calculations have also been used to analyze PILs.[21, 35, 36] The combination of spectroscopy and QM calculations provide a powerful and
80 reliable method for the research of the compositions and structures of PILs.

Presently, functionalized amine-based PILs have drawn more and

more attention than simple primary or secondary amine-based PILs. Functionalized amine-based PILs can realize special functionality by introducing some functional groups, thus make them have more applications. Recently, we presented a new method for removing DBT from fuels by using functionalized PILs and high desulfurization efficiency was achieved.[10] However, more information on the compositions and structures of functionalized PILs is important to optimize the design of the new PILs and increase the desulfurization efficiency further. Obviously, a sound knowledge of the relationship between properties and structures will be beneficial to the application of full "accurate design" of PILs.

In this work, we investigated the compositions and structures of two functionalized PILs, namely, N, N-dimethyl (cyanoethyl) ammonium propionate (DMCEAP) and N, N-dimethyl(hydroxyethyl) ammonium propionate (DMEOAP) (Fig. 1), using experimental methods combined with quantum chemical calculations. These two PILs have better performance in desulfurization process. Particularly, both of them are tertiary amines with a functional group, without labile proton on the nitrogen center, which have not been investigated systematically in the previous literatures. FT-IR spectroscopy and ^{1}H NMR spectroscopy of PILs were used to analyze the composition of PILs. Then their conductivity is investigated to confirm their existing states. Finally, the microstructures of PILs are studied by the quantum chemical calculations further.
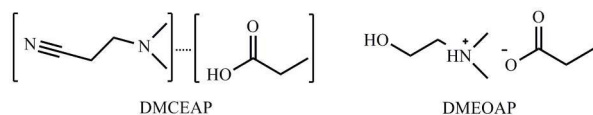

Fig. 1 Structures of PILs investigated in this work.

2. Experimentals

2.1 Chemicals and instruments

All chemicals were purchased from Shanghai crystal pure reagent Co., Ltd (Aladdin), which were used with further purification and drying. FT-IR analyses were carried out on a Nicolet IS-10 using a single reflection ATR cell. ^{1}H NMR spectra were recorded on a Bruker Ascend 500 spectrometer with the pure PILs samples. The pure liquid samples are characterized directly to avoid the disrupting of proton transfer by deuterated solvents. First, the ^{1}H NMR spectrum of CDCl$_3$ contained tetramethylsilane (TMS) was scanned, the chemical shift of hydrogen atoms in TMS was set at 0, that is, TMS was used as external standard to calibrate the chemical shift. Then, the value of calibration parameter SR was recorded to calibrate the hydrogen atoms of pure liquid samples with the same value of SR. Finally, the ^{1}H NMR spectra of PIL and precursors were scanned without the shimming and locks procedures, and the SR value were copied to the spectra of PILs and precursors. The ^{1}H NMR spectra of PILs and precursors were got. The water contents are determined before determination of the properties by a Cou-Lo Aquamax Karl Fischer moisture meter (v.10.06). The conductivity was carried out on an MP522 conductivity instrument with the cell constants of 1 cm^{-1} (the cell was calibrated with the KCl aqueous solution) in the temperature range of 283.15 to 333.15K and the uncertainties were estimated to be ± 1 %.

2.2 Synthesis of the PILs

The two PILs were prepared according to the procedure described previously. [10] Synthesis process was carried out under an inert atmosphere (N$_2$). Raw materials were purified before use. Amine was placed in a 250 mL round-bottomed flask equipped with a stirrer and cooled using an ice bath for 30 min. Acid was added dropwise using a dropping funnel. Care was taken to keep the reaction mixture cool because the reaction is very exothermic. After the addition was completed, the mixture was stirred for 24 h. Then, the PILs were removed from the reaction flask and stored under N$_2$ until use for further experiments. The water content were 210×10^{-6} and 260×10^{-6} (mass fraction) for DMCEAP and DMEOAP, respectively. No impurity was found in PIL from the ^{1}H NMR.

2.3 Computational methods

The geometries, vibrational frequencies and ^{1}H NMR chemical shifts of neutral and ionized species were calculated by the Gaussian 03 program package with the density functional theory (DFT) method. [37] The B3LYP functional as a typical hybrid-functional of DFT was used with a basis set of 6-311++G**. [21, 33] Taking into account the liquid state of PILs, the default PCM media model was used to calculate solvent effects.

3.Results and disccussions

3.1 IR spectra analysis

IR spectra of the PILs are recorded at room temperature as shown in Fig. 2. For comparison, the IR spectra of parent acid and base molecules are also given. It can be seen that a new broad peak appears in both of the spectra of DMCEAP and DMEOAP by comparing the spectra of their precursors, with the stretching vibration of carbonyl at 1716 cm^{-1} remaining. Since the new peak of DMCEAP appears at 1574 cm^{-1}, it is reasonable to assign it to a stretching vibration of a carboxylate ion group. For DMEOAP, a similar phenomenon was also found. A new peak attributed to the stretching vibration of carboxylate group appears at 1574 cm^{-1}. At the same time, the stretching vibration of carbonyl remains at 1716 cm^{-1}. A coexistence of the vibrational modes of carboxylate ion group and carbonyl group in both of the DMCEAP and DMEOAP samples suggests that both the molecular and ionic species present in the two PILs with equilibrium of hydrogen transfer between those two species. Moreover, the absorption intensities of carbonyl and carboxylate ions vibrational spectra maybe used to find out the extent of hydrogen transfer. As can be seen in Fig. 2 that the carbonyl intensity of DMCEAP is much stronger than that of DMEOAP. Furthermore, the carboxylate ions intensity of DMEOAP is stronger than that of DMCEAP, which implies that the number of ions in DMEOAP is bigger than that in DECEAP. That is, the dynamic equilibrium of proton transfer of DMEOAP tends to exist as the ionic species, while the proton transfers of DMCEAP as the molecular species.
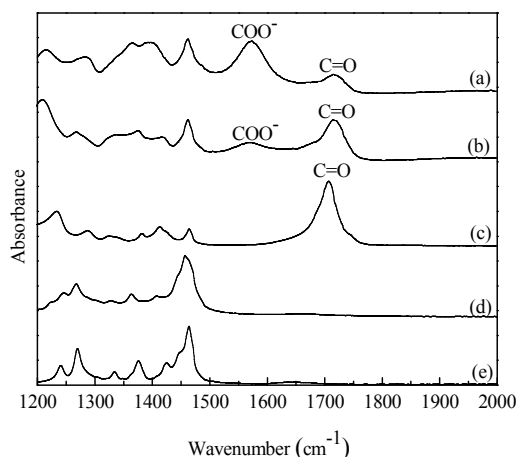
Fig. 2 IR spectra of PILs and their precursors at room temperature. Spectra (a), (b), (c), (d), and (e) were recorded for neat DMEOAP, DMCEAP, CH_3CH_2COOH, $HOCH_2CH_2N(CH_3)_2$, and NCCH$_2$CH$_2$N(CH$_3$)$_2$ liquids at room temperature, respectively.

3.2 ^{1}H NMR spectra analysis

In order to give new evidence to verify the compositions of the PILs suggested by the IR spectra above, we also characterized the two PILs, propionic acid and N,N-dimethyl ethanolamineby ^{1}H NMR spectra, which is shown in Fig. 3. The pure liquid samples are characterized directly to avoid disrupting the proton transfer by solvents. TMS was used as external standard to calibrate the chemical shift. Since those active hydrogens are most likely to take part in the hydrogen transfer process, the ^{1}H NMR shifts were used to distinguish between the transferred and non-transferred hydrogen of the PILs. It is indicated that the peak of hydrogen in the carboxyl group of DMCEAP appears at 13.40, slightly larger than that of the hydrogen in the carboxyl group of propionic acid(12.52), which shows that the hydrogen proton is mainly on the carboxyl, i.e. DMCEAP mainly exists in the state of precursor molecule. In the meantime, the slight shifting to the low magnetic field indicates that a small amount of amine cations are formed due to proton transfer from acid to base. The results are in good agreement with that was obtained by IR. However, the chemical shifts of the hydrogen atoms in amine cations group and the hydrogen atoms in hydroxyl group of DMEOAP are clearly distinguishable from the hydrogen in the carboxyl group of DMCEAP. The chemical shifts of the two hydrogen protons are both 9.85, which is larger than those hydroxyl groups (5.67) in common and much smaller than that in carboxyl group of propionic acid (12.52). The reason will be discussed in the following computational analysis section.
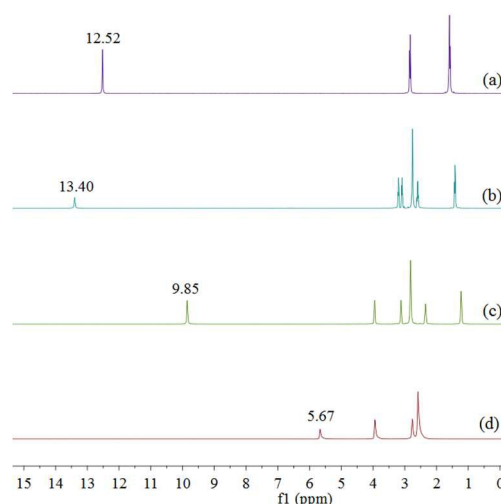

Fig. 3 ^{1}H NMR spectra of PILs at room temperature. Spectra (a), (b), (c), and (d) were recorded for neat CH_3CH_2COOH, DMCEAP, DMEOAP, and $HOCH_2CH_2N(CH_3)_2$ liquids at room temperature, respectively.

3.3 Conductivity analysis

In order to verify further the compositions of the PILs, their conductivity were also analyzed. As can be seen from table 1, the conductivity of the ionic liquids increases with increasing temperature, which implies the content of free ions in the sample increases with increasing temperature, i.e. more neutral molecules lose hydrogen become ions. Meanwhile, the conductivity of DMEOAP is higher than that of DMCEAP at the same temperature. This can be attributed to more free ions existing in DMEOAP than those in DMCEAP, which is consistent with the results of the above IR and NMR experiments. The presence of a large number of neutral molecules is an important reason for the low conductivity and easy decomposition of DMCEAP.

Table1 Experimental values of conductivity for DMCEAP and DMEOAP under atmospheric pressure

T (K)	DMCEAP Conductivity(10^{-3}S·m^{-1})	DMEOAP Conductivity/(10^{-3}S·m^{-1})
283.15	2.35	5.80
288.15	2.85	7.50
293.15	3.40	9.49
298.15	4.00	11.79
303.15	4.63	14.39
308.15	5.34	17.31
313.15	6.06	20.40
318.15	6.81	24.10
323.15	7.62	27.70
328.15	8.42	31.70
333.15	9.27	36.00

3.4 Computational analysis

The above analysis of IR, NMR spectra and conductivity suggests that neutral and ionized species coexist in the PILs of DMCEAP and DMEOAP in liquid phase. The degrees of proton transfer are different for the two PILs, which results in DMCEAP mainly exists in the state of molecules, and DMEOAP in the state of

ionic aggregates. However, only the evidence of hydrogen bond formation in the PILs was provided. There is no direct evidence on the structures of PILs. Contrast to those experimental conclusions induced actually, a quantum chemical calculation, a deduction theoretical method, can be used to optimize the structure and simulate experimental spectra, thus providing an effective and forceful guidance for the justification of experimental evidence. Generally, simplified model are often designed and applied for the chemical calculation, we are no exception.

An optimized structure of DMCEAP in the form of molecular is shown in Fig. 4, and the vibrational frequencies, ^{1}H NMR shifts corresponding to this stable structure are listed in Table 2-3, respectively. The optimized structure shows a hydrogen bond interaction between carboxyl hydrogen atom and the tertiary amine nitrogen atom, in which the H donor is the precursor of propionate acid molecule, and the H acceptor is the precursor of tertiary amine base molecule. The length of the hydrogen bond is 1.775 Å and the angle of ∠NHO is 168.12°. It is almost a linear hydrogen bond indicating a strong hydrogen bond formed. None of stable structure of DMCEAP in the form of an ion-pair can be obtained by an optimization of geometrical parameters if a similar hydrogen bond pattern is kept. The results indicate that the nitrogen atom has not the ability to attract hydrogen atom to form amine cation, due to the larger electro negativity of the oxygen atom than that of the nitrogen atom. Actually, an ion-pair form of DMCEAP can be optimized without hydrogen bonds pattern, in which an active H in tertiary amine group is in the opposite direction from the C=O bond. Moreover, the energy of the ion-pair is 112.90 kJ/mol higher than that of the molecular pair, which suggests that DMCEAP is more stable in the molecular pair.

A comparison of the calculated vibrational frequencies and the ^{1}HNMR shifts of DMCEAP in one molecular pair with the observed IR and ^{1}HNMR spectra are also made. The results indicated the simulated IR and ^{1}HNMR spectrum of the optimized structure satisfactorily reproduce the experimental spectra. Particularly, the difference of the ^{1}HNMR shift for each characterized hydrogen atom between the simulation and observation is less than 1.6. The extent to which the calculated spectrum meets the observed ones depends on the computing models from which we choose. It should be noted that the modeling structure we used is only one pair of molecules or ions, which is quite different from the liquid sample. Therefore, the better agreement of simulated NMR spectra with the observation indicates the effect of the long distance interaction of the surrounding on the shifts is small, on the contrary, for IR spectra, the effect is large relatively.

In addition, the calculated frequency value of ion-pair, 1600 cm^{-1}, assigned to the carboxyl group vibration in DMCEAP, is 116 cm^{-1} lower than that of observed C=O vibration. The mismatch means ion-pair model for DMCEAP is not a suitable candidate to justify the observed spectra, in another word, the liquid DMCEAP is not in the form of ion-pairs.
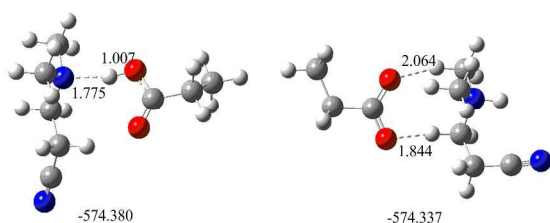
Table 2 Observed and calculated wavenumber of DMCEAP with Band Assignment

Assignments	IR spectrum (cm^{-1})	DFT calculations (cm^{-1})
ν(O-H)	-	3010
ν(C≡N)	2249	2352
ν(C=O)	1716	1761
δ(O-H)	1464	1468
ν(C-O)+δ(O-H)	1374	1315
ν(C-O)	1210	1254
δ(O-H)	920	1082

Table 3 Observed and calculated ^{1}HNMR of DMCEAP

H	DFT calculations	Experiment
CH_3-CH$_2$-	1.22	1.42
CH$_3$-CH_2-	2.17	2.60
-$COOH$	11.84	13.40
$(CH_3)_2$N-	2.20	2.76
N-CH_2-	2.63	3.07
-CH_2-CN	3.25	3.20

The same computing procedure is also applied to DMEOAP. In the case of one pair of molecules or ion-pair model, the optimized results of DMEOAP are similar to those of DMCEAP(Fig.5). Since there is no hydrogen bond formed in the ion-pair, the energy is higher than that of molecular pair with one hydrogen bond formed. Moreover, the calculated vibrational frequency cannot be mapped observed IR spectra. For example, since there is a dangling hydroxyl group, the frequency value of OH mode is 3852 cm^{-1}, which is about 600cm^{-1} larger than the maximum observed frequency. The result implies ion-pair is less stable than the molecular pair, which is not in agreement with the experimental observations in the liquid phase. In order to search for more stable ionized structure of DMEOAP, we attempt to model an aggregate of the ion-pairs. The optimized structure of dimer and tetramer of ion-pair are shown in Fig.6.The nuclear coordinates of optimized dimer and tetramer have been listed in supporting information Table S1-2. In the dimer, it can be seen that there are four hydrogen bonds formed by two oxygen atoms from two carboxyl group. Each oxygen atoms form two types of hydrogen bond, one is N-H···O, and the other is O-H···O. However, in the tetramer, all of the oxygen atoms from carboxyl group can be formed hydrogen bond, and the hydrogen bond types are the same as the dimer. We assume the hydrogen bond is benefit to lower the energy of a system, thus the larger the number of hydrogen bond there is, the more stable the system is. As a result, the energy of a dimer of DMEOAP is 215.29KJ/mol lower than the energy sum of two ion-pairs, the energy of a tetramer of DMEOAP is 31.51KJ/mol lower than the energy sum of two dimers. The results show that with the increasing of ion-pair, the energy of DMEOAP is decreased, that is, ion aggregates may coexist in the DMEOAP.
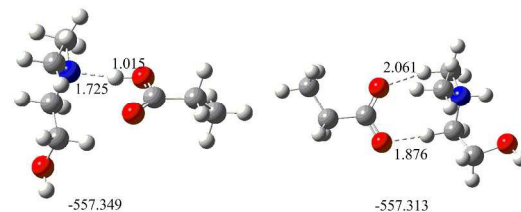

Fig. 4 Optimized structure of molecular pair and ion-pair of DMCEAP.

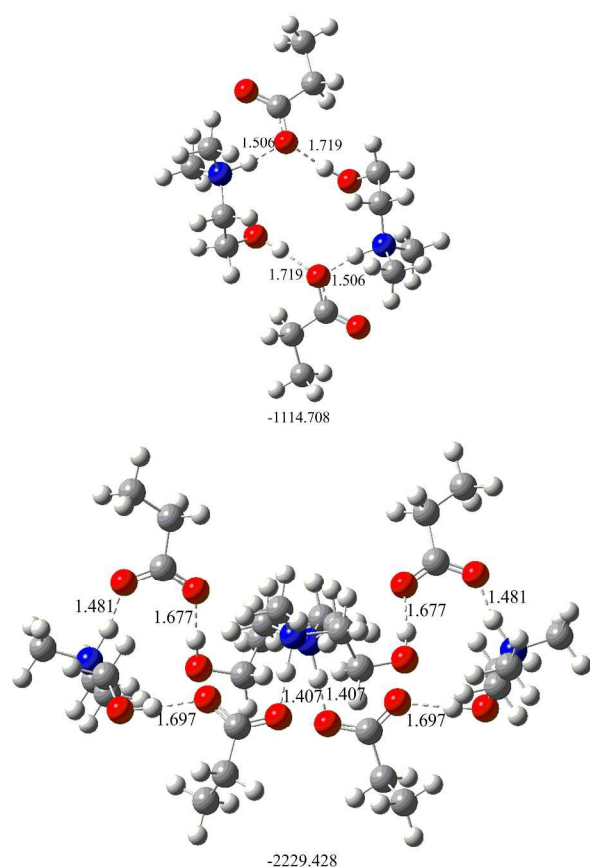**Fig. 5** Optimized structure of molecular pair and ion-pair of DMEOAP.

Fig. 6 Optimized structure of dimer and tetramer of DMEOAP.

The calculated vibrational frequencies and ¹H NMR shifts of the DMEOAP in ionic aggregate together with the observed IR and ¹H NMR spectra were list in Table 4-5. The calculated vibrational frequency values agree well with the experimental spectra except the modes of ν(O-H) and ν(N-H), which are attributed to the rapid proton exchange between the active H in OH and NH. However, the deviation between the calculated and observed spectra could not be reduced to a reasonable accuracy by changing functional or enlarging basis sets. The probable reason would be that the movement of the proton exchange is affected dramatically by the liquid surrounding, and the present simple cluster model cannot afford the complicated system of PILs in the liquid phase. This assumption is partly supported by enlarging the calculated model, as can be seen, the deviation is smaller for the tetramer, comparing with that of the dimmer.

A comparison of the calculated ¹H NMR shifts with the observed ones shows that most of the difference of shifts is within 1, which implies the computing model is reliable. The big deviations of ¹H NMR shifts also related to the active H. On the one hand, due to the intrinsic NMR time scale (10^{-9}-10^{-10} s) is slower than the survival time of ion-pair (20×10^{-14} s), [29] the NMR cannot distinguish a fast moving H atom from a precursor BrØnsted acid to a precursor BrØnsted bases, resulting in only the average peak of hydrogen protons obtained. That is, the NMR cannot differentiate the hydrogen atom in molecular or ion. On the other hand, the rapid proton exchange between the active H in OH and NH represents the average peak. Contrast to experiments, theoretical calculations based on a particular conformation, can obtain two H shifts. To average over these two H shifts, the dimer model get a value of 11.59, while the tetramer get a value of

12.16, which are closed to the observed value of 9.85. The errors between theory and experiment may be caused by the smaller calculation model. Meanwhile, the intermediates formed in the proton transfer are also ignored. As the cation and anion in each system form more than one hydrogen bond, an orderly hydrogen bond network may exist in DMEOAP. According to the structure of tetramer, a larger piece of ionic aggregates maybe formed. As ionic aggregates get bigger and more complex, the real structure of DMEOAP in liquid phase will be discovered. The calculation of more complex system is under way.

Table 4 Observed and calculated wavenumber ofDMEOAP with Band Assignment

Assign-ments	IR spectrum (cm⁻¹)	DFT calculations of dimers(cm⁻¹)	DFT calculations of tetramres(cm⁻¹)
ν(O-H)	3213	3344 3327	3323 3322 3245 3245
ν(N-H)	2478	2135 2112	2149 2146
ν(COO⁻)	1574	1645 1643 1629	1573 1565
ν(C-O)	1074	1121 1119	1084
δ(O-H)	774	862 830	884 883 877 876

Table 5 Observed and calculated ¹HNMR of DMEOAP

H	Experiment	DFT calculations of dimers	DFT calculations of tetramres
CH₃-CH₂-	1.23	0.90	1.02
CH₃-*CH₂*-	2.35	2.26	2.13
-*OH*	9.85	7.38	7.76
-*NH*	9.85	15.81	16.55
(*CH₃*)₂N-	2.82	2.83	2.64
N-*CH₂*-	3.12	2.79	2.78
-*CH₂*-OH	3.95	3.91	3.89

4. Conclusions

The compositions and structures of two functionalized amine-based protic ionic liquids (PILs) are studied by experimental observations and DFT calculations. The IR, ¹H NMR spectra and conductivity experiments indicated that ions and molecules coexist in the PILs. The relative amount of ions and molecules were determined by BrØnsted bases and acids. The composition and structures of PILs were strongly influenced by the functional groups of BrØnsted bases. DMCEAP mainly exists in the state of molecules; the ionic aggregates dominate in the DMEOAP. Some intermediates are more likely to form in the proton transfer process of the PILs. Fortunately, the DFT calculations results agreed well with experimental results. A hydrogen bond is formed between carboxyl hydrogen atom and the tertiary amine nitrogen atom in DMCEAP, and a large piece of ionic aggregates exists in DMEOAP. From the optimized structures of the ions and molecules, it was shown that hydrogen bond was important to the stabilization of PILs. The study provided useful

information for designing various functional PILs for a wide application prospects.

Notes and references

a Department of Chemical Engineering, Dalian University, Dalian, China Fax: 86-411-87403646;Tel: 86-411-87403646; E-mail:

changpingli@dicp.ac.cn

Fax: 86-411-87402449; Tel: 86-411-87403949; E-mail:

lishenmin@dlu.edu.cn

*To whom correspondence should be addressed

1   R. D. Rogers and K. R. Seddon, *Science*, 2003, **302,** 792-793.

2   M. J. Earle, J. M. Esperanca, M. A. Gilea, J. N. C. Lopes, L. P. Rebelo, J. W. Magee, K. R. Seddon and J. A. Widegren, *Nature*, 2006, **439**, 831-834.

3   P. S. Kulkarni and C. A. M Afonsoac, *Green Chem.*, 2010, **12**, 1139-1149.

4   R. Ferraz, L. C. Branco, I. M. Marrucho, J. M. M. Araújo, L. P. N Rebelo, M. N. da Ponte, C. Prudêncio, J. P. Noronha and Ž. Petrovski, *Med. Chem. Commun.*, 2012, **3**, 494-497.

5   H. Olivier-Bourbigou, L. Magna and D. Morvan, *Appl. Catal. A: General*, 2010, **373**, 1-56.

6   E. J. García-Suárez, S. G. Khokarale, O. N. van Buu, R. Fehrmann and A. Riisager, *Green Chem.*, 2014, **16**, 161-166.

7   J. C. Shi, Y. Yang, N. N. Wang, Z. X. Song, H. Y. Gao, Y. M. Xia, W. Li and H. J. Wang, *Catal. Commun.*, 2013, **42**, 89-92.

8   T. Vogl, S. Menne and A. Balducci, *Phys. Chem. Chem. Phys.*, 2014, **16**, 25014-25023.

9   T. L. Greaves and C. J. Drummond, *Chem. Rev.*, 2008, **108**, 206-237.

10   Z. Li, C. P. Li, Y. S. Chi, A. L. Wang, Z. D. Zhang, H. X. Li, Q. S. Liu and U. Welz-Biermann, *Energy Fuels*, 2012, **26**, 3723-3727.

11   D. Seth, S. Sarkar and N. Sarkar, *J. Phys. Chem. B*, 2008, **112**, 2629-2636.

12   H.Veisi, A. A. Manesh, N. Khankhania and R.Ghorbani-Vagheib, *RSC Adv.*, 2014, **4**, 25057-25062.

13   E. Janus, I. Goc-Maciejewska, M. Łożyński and J. Pernak, *Tetrahedron Lett.*, 2006, **47**, 4079-4083.

14   T. L. Greaves and C. J. Drummond, *Chem. Rev.*, 2008, **108**, 206-237.

15   Y. S. Chi, Z. D. Zhang, C. P. Li, Q. S. Liu, P. F. Yan and U. Welz-Biermann, *Green Chem.*, 2011, **13**, 666-670.

16   A. K. Mishra, T. Kuila, D. -Y. Kim, N. H. Kim and J. H. Lee, *J. Mater. Chem.*, 2012, **22**, 24366-24372.

17   Md. A. B. H. Susan, A. Noda, S. Mitsushima and M. Watanabe, *Chem. Commun.*, 2003, **8**, 938-939.

18   J. P. Leal, J. M. S. S. Esperanca, M. E. Minas da Piedade, J. N. C. Lopes, L. P. N. Rebelo and K. R. Seddon, *J. Phys. Chem. A*, 2007, **111**, 6176-6182.

19   R. A. Ludwig, *J. Phys. Chem. B,* 2009, **113**, 15419-15422.

20   X. Zhu, Y. Wang and H. R. Li, *Phys. Chem. Chem. Phys.,*2011, **13**, 17445-17448.

21   X. F. Sun, S.Y. Liu, A. Khan, C. Zhao, C. Y. Yan and T. C. Mu, *New J. Chem.*,2014, **38**, 3449-3456.

22   S. P. Kelley, A. Narita, J. D. Holbrey, K. D. Green, W. M. Reichert and R. D. Rogers, *Cryst. Growth Des.*, 2013, **13**, 965-975.

23   K. Bica, J. Shamshina, W. L. Hough, D. R. MacFarlaned and R. D. Rogers, *Chem. Commun.*, 2011, **47**, 2267-2269.

24   H. Wang, G. Gurau, J. Shamshina, O. A. Cojocaru, J. Janikowski, D. R. MacFarlane, J. H. Davis and R. D. Rogers, *Chem. Sci.*, 2014, **5**, 3449-3456.

25   M. Yoshizawa, W. Xu and C. A. Angell, *J. Am. Chem. Soc.*, 2003, **125**, 1541l-15419.

26   J. Stoimenovski, E. I. Izgorodina and D. R. MacFarlane, *Phys. Chem. Chem. Phys.*, 2010, **12**, 10341-10347.

27   B. Nuthakki, T. L. Greaves, I. Krodkiewska, A. Weerawardena, M. I. Burgar, R. J. Mulder and C. J. Drummond, *Aust. J. Chem.*, 2007, **60**, 21-28.

28   M. Horikawa, N. Akai, A. Kawai and K. Shibuya,*J. Phys. Chem. A*, 2014, **118**, 3280-3287.

29   Y. Q. Lv, Y. Guo, X. Y. Luo and H. R. Li, *SChina-Chem.*, 2012, **55**, 1688-1694.

30   R. W. Berg, J. N. C. Lopes, R. Ferreira, L. P. N. Rebelo, K. R. Seddon and A. A. Tomaszowska, *J. Phys. Chem. A*, 2010, **114**, 10834-10841.

31   J. W. Blanchard, J. -P. Belieres, T. M. Alam, J. L. Yarger and G. P. Holland, *J. Phys. Chem. Lett.*, 2011, **2**, 1077-1081.

32   G. L. Burrell, I. M. Burgar, F. Separovicc and N. F. Dunlopd, *Phys. Chem. Chem. Phys.*, 2010, **12**, 1571-1577.

33   L. Zhang, H. R. Li, Y. Wang and X. B. Hu, *J. Phys. Chem. B*, 2007, **111**, 11016-11020.

34   Q. Hayes, S. Imberyi, G. G. Warr and R. Alkin, *Angew. Chem.*, 2013, **125**, 4721-4725.

35   E. Bodo, S. Mangialardo, F. Ramondo, F. Ceccacci and P. Postorino, *J. Phys. Chem. B*, 2012, **116**, 13878-13888.

36   K. Fumino, A. Wulfa and R. Ludwig, *Phys. Chem. Chem. Phys.*, 2009, **11**, 8790-8794.

37   M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03, revision C.02*, Gaussian, Inc., Wallingford, CT, 2004.