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COMMUNICATION

Do all the protic ionic liquids exist as molecular aggregates in the gas phase?

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According to an EI-MS study of 1,1,3,3-tetramethylguanidium-based protic ionic liquids (PILs), it has been concluded that not all PILs exist as molecular aggregates in the gas phase. The detection of both ions of *m/z* 115.0 and *m/z* 116.0 for the 1,1,3,3-tetramethylguanidinium trifluoromethylsulfonate (TMGS) protic ionic liquid indicates that both the molecular and ionic aggregates co-exist in the gas phase, which is to say that the TMGS may also evaporate *via* the ionic aggregates just like aprotic ionic liquids. Furthermore, investigation on triethylamine-based and 1-methylimidazole-based PILs confirmed that the gas phase structure of PILs depends on both the acidity and basicity of the corresponding acid and base.

Introduction

In recent years, ionic liquids (ILs) have received considerable attention due to their unique properties, such as non-flammability, thermal stability, high conductivity, and excellent solubility. Thus they are considered to be very promising replacements for traditional volatile organic solvents and playing important roles in catalysis,[1] synthesis,[2] separations,[3] and nano-materials.[4] In addition, ILs have been widely regarded as the "green solvents", due to their negligible vapor pressure.[5] However, very recently, the general belief that ILs exert no measurable vapor pressure was shown to be erroneous. It has been demonstrated that some ILs are volatile, and they can be distilled at low pressure without decomposition.[6] Despite all recent reports on their stable thermal evaporation,[7] the nature of the species that are present in the gas phase has remained controversial. Vaghjiani *et al.*[8] demonstrated the presence of intact ion pairs in the gas phase using mass spectrometry. Jones *et al.*,[9] Rebelo *et al.*,[10] and Ballone *et al.*[11] have revealed that the vapor phase of aprotic ILs consists of ion pairs, with no detectable concentration of either free ions or larger clusters. Dai *et al.*[12] indicated that the IL vapors consist of ion pairs based on the direct UV-spectroscopic measurements. Leone *et al.*[13] obtained isolated ion pairs of a hypergolic ionic liquid using aerosol particle vaporization as a source. However, supra-molecules or ion clusters have been suggested to exist in the gas phase of the aprotic ILs by earlier mass spectrometric studies[14] and also the recent atmospheric-pressure thermal desorption ionization experiments,[15] atmospheric-pressure chemical ionization mass spectrometry experiments,[16a] and the electrospray ionization mass spectrometry.[17]

Protic ionic liquids (PILs) are a subset of ionic liquids formed by the equimolar mixing of a Brønsted acid and a Brønsted base, and they have been categorized as poor ionic liquids.[18] The proton transfer mechanism has been uncovered during the evaporation of the PILs.[10,19] For example, a typical protic ionic liquid, 1-methylimidazoium ethanoate, has been confirmed to exist as neutral molecules in the gas phase.[10] However, there is also substantial disagreement over the nature of species of PILs that are present in the gas phase. In the experiments of Rebelo *et al.*, in the PILs $[BH]^+X^-$ there appears to be no association between the acidic HX and basic B molecules. They suggested that protic ILs exist as fully dissociated neutral molecules in the vapor phase.[10] However, in recent works by Ludwig, Eberlin, and Dupont *et al.*, the ion clusters have also been detected in the PILs.[16]

In this paper, the electron ionization mass spectrometry (EI-MS) experiments have been carried out to investigate the gas phase structures of 1,1,3,3-tetramethylguanidinium-based PILs including 1,1,3,3-tetramethylguanidinium lactate (TMGL), 1,1,3,3-tetramethylguanidinium formate (TMGF), 1,1,3,3-tetramethylguanidinium trifluoroacetate (TMGA), and 1,1,3,3-tetramethylguanidinium trifluoromethylsulfonate (TMGS); triethylamine-based PILs including triethylammonium lactate (N222L), triethylammonium formate (N222F), triethylammonium trifluoroacetate (N222A), and triethylammonium trifluoromethylsulfonate (N222S); and 1-methylimidazole-based PILs including 1-methylimidazolium lactate (MimL), 1-methylimidazolium formate (MimF), 1-methylimidazolium trifluoroacetate (MimA), and 1-methylimidazolium trifluoromethylsulfonate (MimS). The EI-MS results of these PILs clearly illustrate that the gas phase structure of the PILs depends on both the acidity and basicity of the acid and base corresponding to the anion and cation.

Experiments

Synthesis of the protic ionic liquids

TMG-based PILs are synthesized according to the literature.[20] N222 and Mim-based PILs are synthesized as follows.

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N222A. The synthesis of the ionic liquid was carried out in a 100 ml round-bottomed flask, which was immersed in a water-bath and fitted with a reflux condenser. In a typical reaction, trifluoroacetic acid (28.8 g, 0.25 mol) was dropped into the diethylamine (15.0 g, 0.25 mol) at 25 °C for 2 hours (the dropping of the trifluoroacetic acid should be slow to avoid temperature runaway). After the addition, the reaction mixtures were stirred for an additional period of 2 hours at 60 °C to ensure that the reaction had proceeded to completion. The impurities were removed by extraction using ether for several times and then heating the residue at 80 °C in high vacuum (5 mmHg) until the weight of the residue remained constant. The yield of N222A was 95% (41.6 g). ^{1}H NMR δ (500 MHz, $CDCl_3$): 12.75 (s, 1H, NH), 8.48 (s, H, CH), 3.16 (m, 6H, CH_2), 1.35 (t, 9H, CH_3).

The following PILs were synthesized similarly to N222A.

N222L. 22.5 g (0.25 mol) of lactic acid, and 15.0 g (0.25 mol) of triethylamine, and the product N222L was obtained as a colorless or pale yellow liquid. Yield: 96%. ^{1}H NMR δ (500 MHz, $CDCl_3$): 8.53 (s, 1H, NH), 4.72 (s, 1H, OH), 3.80 (s, 1H, CH), 2.80 (m, 6H, CH_2), 1.10 (s, 3H, CH_3), 1.01 (t, 9H, CH_3).

N222F. 11.5 g (0.25 mol) of formic acid, and 15.0 g (0.25 mol) of triethylamine, and the product N222F was obtained as a colorless liquid. Yield: 90%. ^{1}H NMR δ (500 MHz, $CDCl_3$): 12.65 (s, 1H, NH), 3.21 (m, 6H, CH_2), 1.39 (t, 9H, CH_3).

N222S. 37.5 g (0.25 mol) of trifluoromethylsulfonic acid, and 15.0 g (0.25 mol) of triethylamine, and the product N222S was obtained as a white solid. Yield: 97%. ^{1}H NMR δ (500 MHz, $CDCl_3$): 3.18 (m, 6H, CH_2), 1.36 (t, 9H, CH_3).

MimL. 22.5 g (0.25 mol) of lactic acid, and 20.5 g (0.25 mol) of 1-methylimidazole, and the product MimL was obtained as a colorless or pale yellow liquid. Yield: 96%. ^{1}H NMR δ (500 MHz, $CDCl_3$): 8.77 (s, 1H, NH), 7.95 (s, 1H, CH), 7.23 (s, H, CH), 7.01 (s, H, CH), 3.76 (s, 3H, CH_3), 1.45 (s, 3H, CH_3).

MimF. 11.5 g (0.25 mol) of formic acid, and 20.5 g (0.25 mol) of 1-methylimidazole, and the product MimF was obtained as a colorless liquid. Yield: 90%. ^{1}H NMR δ (500 MHz, $CDCl_3$): 13.88 (s, 1H, NH), 8.42 (s, 1H, CH), 8.01 (s, H, OH), 7.15 (s, H, CH), 7.06 (s, H, CH), 3.80 (s, 3H, CH_3).

MimA. 28.8 g (0.25 mol) of trifluoroacetic acid, and 20.5 g (0.25 mol) of 1-methylimidazole, and the product MimA was obtained as a colorless liquid. Yield: 90%. ^{1}H NMR δ (500 MHz, $CDCl_3$): 12.67 (s, 1H, NH), 8.95 (s, 1H, CH), 7.38 (s, H, CH), 7.16 (s, H, CH), 3.96 (s, 3H, CH_3).

MimS. 37.5 g (0.25 mol) of trifluoromethylsulfonic acid, and 20.5 g (0.25 mol) of 1-methylimidazole, and the product MimS was obtained as a white solid. Yield: 97%. ^{1}H NMR δ (500 MHz, $CDCl_3$): 10.53 (s, 1H, NH), 8.46 (s, 1H, CH), 7.31 (s, 2H, CH), 3.81 (s, 3H, CH_3).

EI-MS spectra

The EI-MS spectra were obtained from a Thermofisher DSQ instrument and collected at 70 eV, all the samples were dissolved in chloroform.

Results and discussion

The EI-MS spectra of the TMG-based PILs are depicted in Fig. 1. The peak corresponding to the ionized molecules of m/z 115.0 is observed in TMGL, TMGF, and TMGA respectively. The ion of m/z 116.0 is also present. However, in the spectra of TMGL, TMGF, and TMGA, the ions m/z 116.0 : 115.0 ratio are 4.88%, 5.86%, and 6.05%, respectively, indicating that the m/z 116.0 might be the isotopic peak. This shows that the TMGL, TMGF, and TMGA PILs exist mainly as molecular

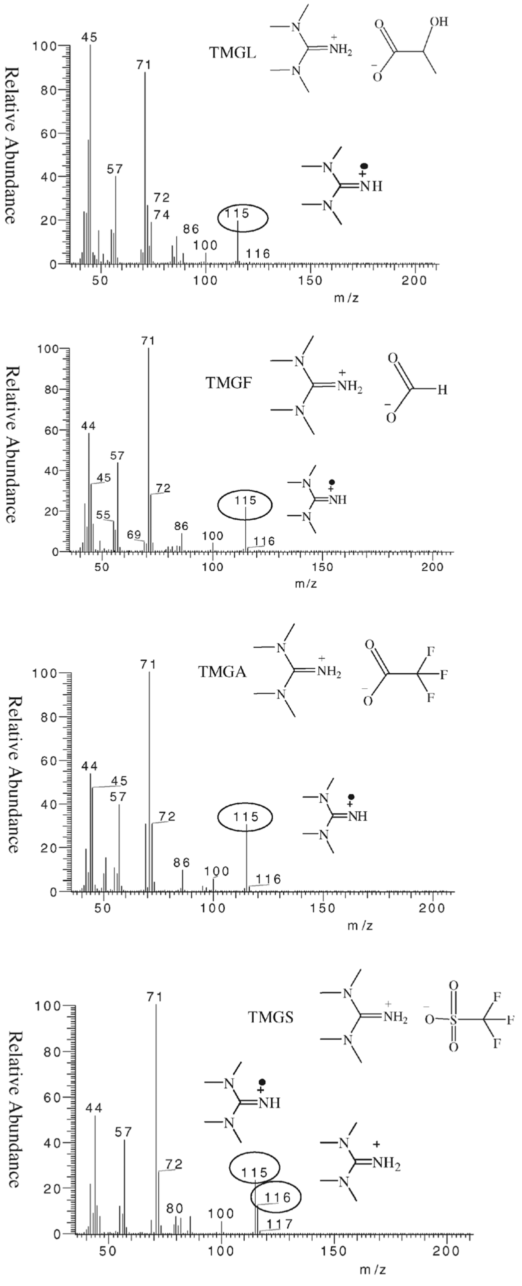

Fig. 1 The EI-MS spectra of the TMG-based ILs.

aggregates in the gas phase and the vaporization of these PILs involves a proton transfer mechanism with formation of two volatile neutral molecules. Actually it has been previously demonstrated that no charged species or ionic pairs were detected in the gas phase of 1,1,3,3-tetramethylguanidinium chloride and a proton transfer led to the formation of the neutral acid and base precursors.[21]

Compared with the above three kinds of PILs, in the case of TMGS, the m/z 116.0 : 115.0 ratio is 71.5 : 100.0, hence it is apparently not an isotopic peak. To eliminate the effect of the chemical ionization, we increased the concentration of the samples and re-measured their EI-MS spectra. If the peak m/z 116 is formed by the chemical ionization, the intensity of m/z 116 would increase with the increasing of the amount of TMGS. However, it was found that the intensity of m/z 116 decreased from 71.50 to 63.06 when we increased the TMGS concentration (one times higher than the former). This indicates that the peak m/z 116 is not caused by the chemical ionization. Besides, no significant changes have been found in EI-MS spectra of other three kinds of PILs when their concentration changed. Therefore the ion peak of m/z 116.0 corresponds to the $[TMG]^+$ cation, which strongly indicates the presence of the ionic aggregates in the gas phase of TMGS. In general belief, PILs evaporate *via* the neutral products of the proton transfer, while the aprotic ionic liquids evaporate *via* ion pairs (cation–anion).[6] The detection of both ions peak of m/z 115 and 116 indicates that the molecular and ionic aggregates co-exist in TMGS and the TMGS may also evaporate *via* ion pairs.

To examine the effect of various cations, the triethylamine and 1-methylimidazole-based PILs were synthesized and investigated. Similar to 1,1,3,3-tetramethylguanidinium (pK_a = 13.6), triethylamine is also a strong base (pK_a = 10.6), but Mim is a weak base (pK_a = 7.4). The EI-MS spectra of these two kinds of PILs are shown in Fig. 2 and 3. According to Fig. 2, the peak corresponding to the ionized molecules of m/z 101.0 is observed in N222L, N222F, N222A, and N222S, respectively. The peak corresponding to the N222 cation of m/z = 102.0 is present in spectra of N222S (the m/z 102.0 : 101.0 ratio is 44.5 : 13.8), but absent in the spectra of N222L, N222F, and N222A. This reveals that equilibrium between the ion aggregates and molecular aggregates exists in the gas phase of N222S. In addition, molecular aggregates may dominate in the gas phase of N222L, N222F, and N222A. Furthermore, as shown in Fig. 3, the peak corresponding to the Mim cation of m/z = 83 is relatively weaker. The m/z 83.0 : 82.0 ratio is 5.4 : 100.0 even in the MimS, which indicates that molecular aggregates may be the primary formation existing in the gas phase of the Mim-based PILs.

To our knowledge, the basicity of the cations and the acidity of the anions may significantly affect the gas phase structure of the PILs. 1,1,3,3-Tetramethylguanidinium and triethylamine are strong bases and are relatively easier to be protonated than 1-methylimidazole (a relatively weaker base). The acidity indices (pK_a) for lactic acid, formic acid, trifluoroacetic acid, and trifluoromethylsulfonic acid are 3.86, 3.75, 0.23, and <-1, respectively. This suggests that the trifluoromethylsulfonic acid is the strongest acid among the four acids mentioned above and the deprotonation of trifluoromethylsulfonic acid is easier than that of the other three acids. Therefore, the TMGS and N222S are combinations of a strong Brønsted base and a strong Brønsted acid, and proton transfer from cations to anions may not be so easy in these kinds of PILs, which may explain the co-existence of molecular and ionic aggregates in the gas phase of these PILs.

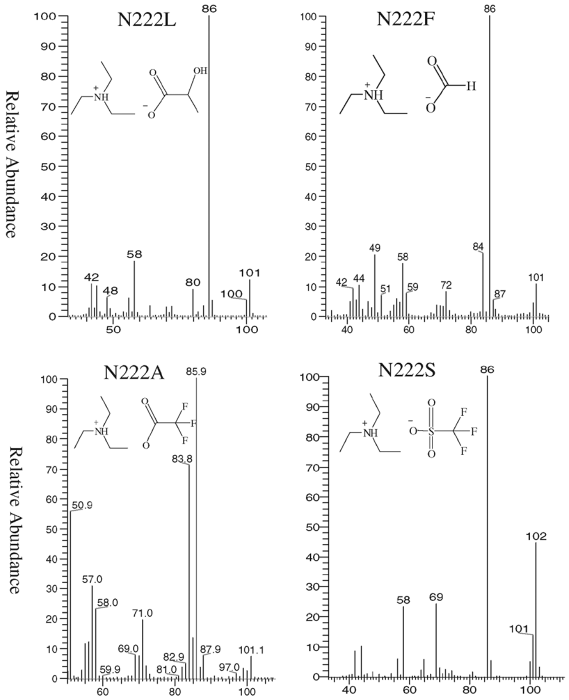

Fig. 2 The EI-MS spectra of the N222-based ILs.

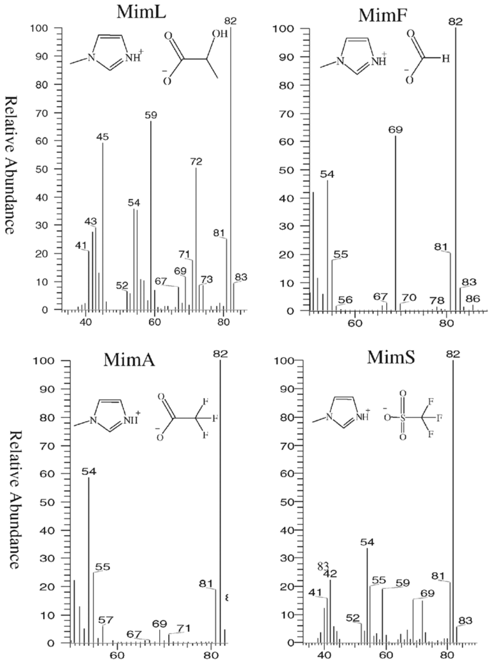

Fig. 3 The EI-MS spectra of the Mim-based ILs.

Conclusion

In conclusion, both molecular aggregates and ionic aggregates may co-exist in the gas phase for TMGS protic ionic liquid, and this finding shows that some PILs may also evaporate *via* both ion-pairs form and neutral molecules. To examine the effect of different cations, the triethylamine and 1-methylimidazole-based PILs were synthesized and investigated. Similar phenomena have also been found in the strong Brønsted base triethylamine-based PILs, but no evidence proved the presence of ionic aggregates in the weak Brønsted base 1-methylimidazole-based PILs. Further analysis of the pK_a values suggested that the gas phase structure of the PILs is governed by both the acidity and basicity of the acid and base corresponding to the anion and cation. The results will help us to extensively understand the behavior of vaporized PILs and offer us some valuable information for the design of PILs. More experiments are underway in our laboratory to explore the structure characters of other PILs.

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