Tetraalkylammonium amino acids as functionalized ionic liquids of low viscosity†

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Four of nine tetraalkylammonium-based amino-acid ionic liquids prepared in this work show lower viscosities than all amino acid-based ionic liquids found in the literature and their reversible CO_2 absorption approaches 0.5 mol per mol ionic liquid.

Since Wilkes and Zaworotko[1] synthesized the air- and water-stable ionic liquid (IL) [emim]BF_4 (1-ethyl-3-methylimidazolium tetrafluoroborate), ILs have attracted considerable attention from the industrial and academic communities as 'green solvents'. The study of air- and moisture-stable ionic liquids has become the subject of an increasing number of scientific investigations documented in the literature.[2–5] Particularly, after Fukumoto *et al.*[6] succeeded in synthesizing ionic liquids from 20 natural amino acids in 2005, many amino acid-based ionic liquids have been prepared including amino acids as anions,[7,8] amino acids as cations[9] or amino acid derivatives.[10] These ILs are high-quality functionalized liquids that have chiral centers, biodegradable characteristics, and high biocompatibility. Thus, in the fields of industrial chemistry and pharmaceutical chemistry, amino acid-based ILs (AAILs) should provide a variety of applications, such as intermediates for peptide syntheses, chiral solvents, absorbents for acidic gases and other functional materials.

Although most of the AAILs found and prepared in the literature are liquids at room temperature, their uses as liquid materials or solvents are still limited due to their viscous nature. For example, AAILs containing 1-ethyl-3-methylimidazolium as a cation ([emim][amino acid] ILs) were obtained as liquids at room temperature, but the hydrogen bonding at the 2-position of the imidazolium cation ring with its amino acid anions caused these imidazolium-based AAILs to have a minimum viscosity as high as 486 mPa s at 25 °C.[6] Tetrabutylphosphonium-based AAILs ([TBP][amino acid]) were also found to be more viscous than 344 mPa s, even though their thermal stability was generally better than that of [emim][amino acid] ILs.[7] The AAILs that were prepared using amino acids as cations[8] or using amino acid derivatives were either solids or liquids of extremely high viscosity, up to 4180 mPa s at room temperature.[10] Until now, no AAILs that have viscosity lower than 200 mPa s at 25 °C have ever been reported in the literature. Since viscosity is one of the most important characteristics that determine the efficiencies of heat and mass transfer processes, AAILs of low viscosity are eagerly sought for use as process solvents. In this work, as part of the search for AAILs of low viscosity, novel AAILs using symmetric tetraalkylammonium ([TAA]) as cation are prepared. All these newly-prepared tetraalkylammonium-based AAILs are found to be liquid below 50 °C and two of them are liquids with viscosities lower than 140 mPa s. In particular, among them tetraethylammonium α-alanine ($[N_{2222}]$[L-Ala]) is found to be the AAIL that has the lowest known viscosity of 81 mPa s. This paper is the first to report the existence of AAILs of low viscosities, especially when symmetric tetraalkylammoniums are used as the cations of AAILs. The details of the preparation and characterization experiments can be seen in the ESI.†

Table 1 summarizes the properties of nine [TAA][amino acid] ILs obtained in this work. It is clearly shown that seven of the nine products are room temperature ILs and all products are ILs below 50 °C. $[N_{1111}]$[Ala] and $[N_{1111}]$[Val] showed only a melting point (T_m) near 40 °C, five AAILs showed only a glass transition temperature (T_g), and two species showed both a melting point and a glass transition temperature. As is known from the literature, ILs that consist of symmetric tetraalkylammonium cations (alkyl chain length not larger than C_4) and a conventional anion such as tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-) and bis(trifluoromethylsulfonyl)imide (Tf_2N^-) are solids and have high melting points. The [TAA][amino acid] ILs in this paper behave completely in contrast to the traditional [TAA] ILs that contain a common anion such as BF_4^-, PF_6^- or Tf_2N^-. This difference may be due to the symmetric property of the anion structure, that is, the more symmetric the anion structure the higher the melting point. The T_m values of $[N_{1111}][BF_4]$, $[N_{1111}][Tf_2N]$ and tetramethylammonium 2,2,2-trifluoro-*N*-(trifluoromethylsulfonyl)acetamide ($[N_{1111}]$[TSAC]) appear to be related to the relative anion symmetric property. The trend of the highest to lowest T_m values is $[N_{1111}][BF_4]$ (>300 °C)[11] > $[N_{1111}][Tf_2N]$ (133 °C)[12] > $[N_{1111}]$[TSAC] (64 °C),[13] which is

Table 1 Properties of tetraalkylammonium type amino acid ionic liquids

IL	T_g/°C	T_m/°C	T_{dec}/°C	ρ/g cm^{-3}	η/mPa s
$[N_{1111}]$[L-Ala]	ND	42	219	ND	NA
$[N_{2222}]$[L-Ala]	−80	ND	185	0.9984	81
$[N_{1111}]$[β-Ala]	−82	ND	193	1.0877	668
$[N_{2222}]$[β-Ala]	−85	ND	184	1.0133	132
$[N_{4444}]$[β-Ala]	−73	ND	180	0.9545	465
$[N_{1111}]$[Gly]	−68	ND	181	1.0887	304
$[N_{4444}]$[Gly]	−71	16	179	0.9406	214
$[N_{1111}]$[Val]	ND	40	223	ND	NA
$[N_{4444}]$[Val]	−69	25	185	0.9470	660

[a] ND: not detected. NA: Solid or glass at 25 °C.

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similar to the case of the highest to lowest degree of symmetry of anions BF_4^- > Tf_2N^- > $TSAC^-$. Therefore, the high degree of asymmetric structure of amino acids contributes to the low T_m values of tested [TAA][amino acid] ILs. In addition, it should be noted here that some of the [TAA][amino acid] ILs were semi-stable supercooled liquids. Methyl and longer alkyl chains are effective for suppressing crystallization of the corresponding salts due to configurational rotations.[7]

The [TAA][amino acid] ILs obtained are thermally stable up to 170 to 230 °C, temperatures a little lower than those of [emim][amino acid] ILs. For example, the decomposition temperature (T_{dec}, onset) of an [emim][amino acid] was around 220 °C,[6] while the T_{dec} values of seven new [TAA][amino acid] ILs were in the range of 170 to 200 °C. Additionally, it is found that cations appear to play a more significant role than anions in determining the thermal stability of the [TAA][amino acid] ILs. The [N_{1111}] cation enables the [TAA][amino acid] to have a higher T_{dec}, in comparison to [N_{2222}] and [N_{4444}] AAILs, whereas the [N_{4444}] cation has little effect on the T_{dec} value relative to [N_{2222}] cation. Changing the anion from Val to Gly, β-Ala or L-Ala, all with the [N_{2222}] cation, made little difference to the thermal stability. In fact, the ionized amino acids are slightly basic and the mechanism of decomposition is probably related to a Hoffmann elimination reaction as discussed by MacFarlane *et al.*[14]

The T_g values of most [TAA][amino acid] ILs were about 10 °C lower than those of phosphonium-based ILs.[7] For instance, the T_g values of [N_{4444}][Val] and tetrabutylphosphonium valine ([TBP][Val]) were −69 and −59 °C, respectively. This tendency of T_g is attributed to the cation structure. Particularly, the ammonium has both a smaller molecular volume and a smaller molecular weight than phosphonium, so the alkyl chain of the TAA cation can move more flexibly than that of a phosphonium cation. In addition, [N_{2222}][α-Ala] had a higher T_g value than [N_{2222}][β-Ala]. The high T_g value of [N_{2222}][α-Ala] should be related to its anion structure; that is, a shorter distance between the anion and cation leads to a higher attracting ability and a higher glass transition temperature.

[TAA][amino acid] ILs had lower density than traditional ILs as shown in Table 1. It is clear that increasing the length of the alkyl chain in the cation decreases the density of [TAA][amino acid] ILs. This trend is consistent with that of other kinds of ILs, such as imidazolium-based ILs.

The viscosity, as also summarized in Table 1, was measured using a cone-plate viscometer (HAAKE Rheostress 600). It was found that some [TAA][amino acid] ILs had much lower viscosities than those of any of the AAILs reported in the literature. Although [emim][Gly] had the lowest viscosity (486 mPa s at 25 °C)[6] among the [emim][amino acid] ILs and [TBP][Ala] had the lowest viscosity (344 mPa s at 25 °C)[7] among the [TBP][amino acid] ILs, the four [TAA][amino acid] ILs ([N_{2222}][Ala], [N_{2222}][β-Ala], [N_{1111}][Gly] and [N_{4444}][Gly]) in this work had even lower viscosity than [emim][Gly] and [TBP][Ala]. In particular, the viscosity of [N_{2222}][Ala] was about 6 times lower than that of [emim][Gly] and 4 times lower than that of [TBP][Ala]. The [emim] cation has protons at the 2, 4 and 5 positions that contribute to hydrogen bonding and the hydrogen bonding becomes the reason for the high viscosity as well as for the high T_g value. In addition, since the [N_{2222}] has a much smaller molecular weight as well as a shorter and more flexible alkyl chain than the [TBP], the viscosity of [N_{2222}][Ala] is lower than that of [TBP][Ala]. Among the [TAA][amino acid] ILs obtained, the viscosities of the α-Ala and β-Ala AAILs were reduced by changing the counter cation from [N_{1111}] or [N_{4444}] to [N_{2222}]. This fact is attributed to the cation structure. As the viscosity of ILs generally decreases with decreasing molecular weight of the ion, the [N_{2222}][amino acid] ILs are less viscous than the [N_{4444}][amino acid] ILs. However, although [N_{1111}][amino acid] ILs have a smaller molecular weight than [N_{2222}][amino acid] ILs, the ethyl chain is more flexible than the methyl chain. Thus, the flexible structure of the cation becomes the main effect, resulting in a much lower viscosity of [N_{2222}][amino acid] ILs than [N_{1111}][amino acid] ILs.

Besides the flexible property of the cation, the symmetric structure of the anion also apparently influences the viscosity of [TAA][amino acid] ILs. The relationship of anion structure and [TAA][amino acid] viscosity is consistent with that of the T_m value and anion structure. In the same way, the symmetric structure of the anion brings a high viscosity value which has been proved in a previous report.[13] In this paper, the low viscous AAILs were composed of small amino acid anions of simple structure. It is generally thought that the amino acid anions containing functional groups such as carboxyl, hydroxy and a second amino group may lead to high viscosity because of hydrogen bonding and other additional interaction forces among ions. Additionally, as a general rule, symmetric cations usually bring high viscosity of aliphatic ammonium-based ILs.[12,15] Therefore, AAILs composed of asymmetric cations (such as [N_{1112}], [N_{1113}] *etc.*) and small amino acid anions of simple structure may be expected to have lower viscosity than the AAILs reported in this paper; this needs further experimental examination.

The absorption of CO_2 (99.99%, purchased from Nanjing Gas Supply Inc.) into [N_{2222}][Ala] and [N_{2222}][β-Ala] was carried out at ambient pressure and at 40.0 °C, according to the standard procedure reported in the literature.[16] The results, presented in Fig. 1, suggested that the absorption equilibria could all be reached within 60 min, much shorter than the time used in the case of [TBP][Gly] (≈ 200 min) as reported by Zhang *et al.*[16] Analysis shows that this is primarily due to the effect of viscosity on the mass transfer of CO_2. The absorbed CO_2 was extruded from the [TAA][amino acid] upon heating at 50 °C for 4 h under vacuum (≈ 0.1 KPa). The recovered ionic liquids had been repeatedly recycled for CO_2 uptake (four cycles) with no observed loss of

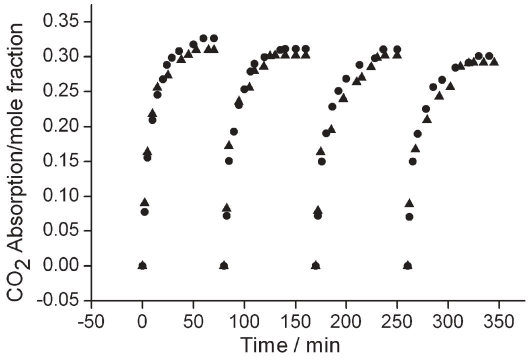

Fig. 1 Cycles of CO_2 absorption of [TAA][amino acid]. ● [N_{2222}][β-Ala] and ▲ [N_{2222}][L-Ala].

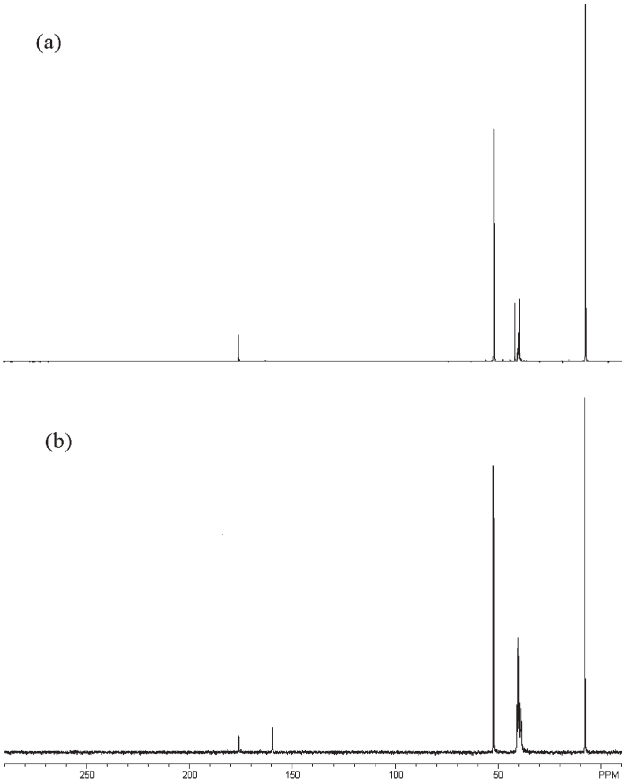

Fig. 2 ^{13}C NMR spectra (300 MHz) of the [N_{2222}][β-Ala] (a) and CO_2-absorbed [N_{2222}][β-Ala] (b) in DMSO.

absorption rate and absorption capacity. As for the fact that the absorption capacity in the first cycle was about 8% larger than those in the other three cycles, the result should be attributed to the incomplete desorption of CO_2 during the regeneration of the used AAILs since an absolute vacuum is not achieved. The mol uptake of CO_2 per mol of [TAA][amino acid] during the tested exposure period, as also shown in Fig. 1, approached 0.5 (equivalent to 0.32 mol fraction of CO_2 in ILs), consistent with the mechanism proposed by Davis Jr *et al.*[17] that one mol of 1-butyl-2-propylamineimidazole tetrafluoroborate ([(NH_2)pmim][BF_4]) can absorb half of one mol of CO_2. It was also observed that the viscosity was low and the liquid could be stirred with great ease at the beginning of the absorption. However, the viscosity finally became very high and the transparent liquid was cloudy at the end of absorption, which implied the formation of ammonium carbamate species.

The sequestration of CO_2 by the [TAA][amino acid] ILs *via* its fixation to become an ammonium carbamate is of great interest and can be elucidated from the comparison of NMR spectra of gas-free and gas-treated materials. The comparison of the ^{13}C NMR (300 MHz, DMSO) spectra of CO_2-free [N_{2222}][β-Ala] and CO_2-absorbed [N_{2222}][β-Ala], as given in Fig. 2, showed a notable new resonance at δ = 159.779 ppm, that is attributable to carbamate carbonyl carbon. The other features of the spectrum are generally the same as those of the starting CO_2-free ILs. These results illustrate that the chemical interaction between CO_2 and [TAA][amino acid] is similar to that of standard sequestering amines such as monoethanolamine (MEA) and diisopropanolamine (DIPA). Molten salts and NH_2-terminated ILs of low viscosity are of great scientific significance for acidic gas separation. Within this context, it is believed that AAILs of low viscosity in this work can be designed for the processing of acidic gas separation.

In conclusion, nine new AAILs were prepared by coupling tetraalkylammonium cations with amino-acid anions. All nine AAILs were found to be liquid below 50 °C. The AAILs with [N_{2222}] cation yielded low viscosity, especially [N_{2222}][L-Ala], the least viscous AAIL ever found and the least viscous IL based on a symmetric [TAA] cation. Although the thermal stability is not improved over typical AAILs, such as [emim][amino acid] and [TBP][amino acid], these newly synthesized AAILs are the first simple amine-functionalized ILs of low viscosity. Meanwhile, the CO_2 absorption capacity of two AAILs was investigated and the same absorption mechanism as that of the [(NH_2)pmim][BF_4] ILs was found. As these new ILs are halogen-free and have relatively low viscosity, it is expected that such new compounds will prove useful in further studies centered on the transfer processing, the chiral solvents and the selective sequestration and transport of acidic gases using [TAA][amino acid] ILs.

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