Low viscosity amino acid ionic liquids with asymmetric tetraalkylammonium cations for fast absorption of CO_2

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Fifteen novel amino acid ionic liquids (AAILs) were prepared by the combination of several tetraalkylammonium cations with four amino acid anions ([Gly], [L-Ala], [β-Ala] and [Val]). The asymmetry of the tetraalkylammonium cations is shown to have a significant influence on the viscosity of the ionic liquids composed of amino acid anions, especially for the four triethylbutylammonium ($[N_{2224}]$)-based ionic liquids that have viscosities of lower than 60 mPa s, with the lowest being only 29 mPa s. The low viscosity tetraalkylammonium-based AAILs are further demonstrated to improve apparently the reaction and mass transfer rates of CO_2 in the ionic liquids.

Ionic liquids (ILs) or molten salts have attracted much attention from industrial and academic communities as novel solvents or liquid materials for green chemistry.[1] ILs have mostly been designed using a series of cationic derivatives, such as imidazolium,[2,3] phosphonium,[4,5] and cyclic or non-cyclic quaternary ammonium,[6–8] due to their easy and convenient chemical modification. Among these cations, 1-ethyl-3-methylimidazolium (EMI) is found to more frequently form low viscosity, low melting ILs with various anions,[9] primarily owing to its flat chemical configuration, unsaturated nature and extended charge distribution. However, imidazolium-based ILs are fairly expensive and not readily available, which limits their large-scale applications in industry. In contrast, TAAs are cheap, readily available and widely used as mediums or phase-transfer catalysts in chemical synthesis. Because of this, it is a good step to use TAA as the potential cationic component for a variety of ILs. However, it is regrettable that most cheaply and readily available TAA salts with total carbon number less than 16 melt at temperatures far above room temperature,[10,11] *i.e.*, above 100 °C. Till now, only a fraction of those TAA salts formed with several expensive anions, such as $[Tf_2N]$[12] and [TSAC],[13] have been found to be ionic liquids of low melting points, not to mention the fact that the TAA-based ILs still have high viscosities. As the viscosity of ILs is one of the most important transport properties that determine their real applications in industry, new and readily available anions for the preparation of TAA-based ILs of low cost and viscosity are eagerly required.

After Fukumoto *et al.*[14] reported for the first time ILs composed of imidazolium cations and amino acid (AA) anions in 2005, amino acids have been used to act as a platform for the preparation of functionalized ILs, such as AAs as anions,[14–16] AAs as cations[17] or using AA derivatives.[18] In 2006, Ohno *et al.*[15] succeeded in synthesizing amino acid-based ionic liquids (AAILs) from phosphonium cation and found that these tetrabutylphosphonium-based (TBP or $[P_{4444}]$) AAILs were even less viscous than $[P_{666\ (14)}][Tf_2N]$ (450 mPa s at 25 °C).[19] Zhang *et al.*[16] also prepared [TBP][amino acid]s and indicated that this type of AAILs still had viscosities larger than 200 mPa s and had to be supported on porous silica gel for reversible CO_2 absorption. In a preliminary investigation, our group has reported that four of nine AAILs prepared from a symmetric tetraalkylammonium cation ($[N_{nnnn}]$, n = 1 to 4) are shown to have lower viscosities than the AAILs mentioned above. In particular, tetraethylammonium α-alanine ($[N_{2222}]$[L-Ala]) is found to have the lowest viscosity among all nine reported [TAA][amino acid]s, down to 81 mPa s,[20] which is over 4 times less viscous than tetrapentylammonium bis(trifluoromethylsulfonyl)imide ($[TPA][Tf_2N]$) (430 mPa s at 25 °C).[21] It is evident from our preliminary investigation that a combination of AAs with tetraalkylammonium cations may give ionic compounds with desirable properties, especially low viscosity. Since AAILs are multifunctionalized (with amino and carboxyl groups and chiral center), biodegradable and of high biological activity, they are expected to have potential use as green solvents for a wide variety of applications such as reactions and separations of chemical, biological, and pharmaceutical substances. However, since real industrial applications usually require ILs with additional features, such as low cost and low viscosity, it is of particular interest and critical importance to discover more TAA-based AAILs of low cost and viscosity.

Herein, as a continuation of our research, fifteen novel AAILs were prepared by coupling five tetraalkylammonium cations ($[N_{2222}]$, $[N_{4444}]$, $[N_{2221}]$, $[N_{1114}]$ and $[N_{2224}]$) with four amino acid anions ([Gly], [L-Ala], [β-Ala] and [Val]). Our emphasis was put on how the asymmetry of TAA cations and AA anions influences the properties of the AAILs, especially the viscosity. In addition, the low viscosity AAILs prepared were further demonstrated to improve apparently the absorption rate of CO_2.

Experimental

Trimethylbutylammonium chloride ($[N_{1114}][Cl]$, white solid) and triethylmethylammonium chloride ($[N_{2221}][Cl]$, white solid), both with a minimum purity of 99.5%, were purchased from Jintan Chemical Research Institute (Jiangsu, China).

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Anion exchange resin −711 (Cl) of analytical grade, as well as tetraethylammonium hydroxide and tetrabutylammonium hydroxide of electronic grade, was produced by Nanjing Chem. Industry Corporation (Nanjing, China). Other reagents such as triethylamine ($(C_2H_5)_3N$), butyl bromide (C_4H_9Br), glycine, L-alanine, β-alanine, valine and ethanol were of analytical grade and used without any further purification.

In the experiments, the synthesis of AAILs with symmetric tetraalkylammonium cations followed the procedure described in our previous work.[20] As for the preparation of AAILs with asymmetric tetraalkylammonium cations, a three-step procedure was adopted: the halide precursor (if not available) was synthesized in the first step followed by the anion exchange and neutralization. Triethylbutylammonium bromide ($[N_{2224}][Br]$) was prepared *via* the alkylation of $(C_2H_5)_3N$ (35.0 g) with C_4H_9Br (47.5 g) in ethanol (100 ml) under reflux and vigorous stirring for 12 h. The solvent and unreacted components were removed by rotary evaporation, and $[N_{2224}][Br]$ (80 g) white solid was obtained after being dried at 60 °C under vacuum for 24 h.

The tetraalkylammonium hydroxides ($[N_{2224}][OH]$, $[N_{1114}][OH]$, $[N_{2221}][OH]$) were obtained by anion exchange. All aqueous solutions were prepared with deionized water, and anion exchange resin −711 (Cl-type) was pretreated with hydrochloric acid (2 M) before use. The resin was transformed from Cl-type into OH-type by passing NaOH solution (5 M, 10 ml/min) through the resin column (l = 100 cm, r = 3 cm) until Cl^- could not be detected with $AgNO_3$–HNO_3 solution. As the resin (OH-type) is not stable at temperatures higher than 40 °C, NaOH solution must be used after it is cooled. Excess NaOH solution was washed off using deionized water. Tetraalkylammonium halide solution (2 M) was then loaded into the column, and transformed into tetraalkylammonium hydroxide ($[N_{2224}][OH]$, $[N_{1114}][OH]$, or $[N_{2221}][OH]$) solution. The OH^- concentrations of the resulting solutions were determined using titration with HCl solution. The tetraalkylammonium hydroxide solutions were then reacted with a slight excess of amino acid through neutralization at room temperature for 3 h. Water was evaporated to generate a residual solution that contained the required ionic liquid. After being further dried at 60 °C under vacuum, the residue was diluted with ethanol to precipitate the excess amino acids. After filtration, the ethanol was removed by evaporation. Finally, the products were dried at 60 °C under vacuum for 2 days before being used for differential scanning calorimetry (DSC, Perkin-Elmer DSC 7), thermogravimetric analysis (Perkin-Elmer TG/DTA, 2010), viscosity (HAAKE Rheostress 600) and density (DMA 5000 density meter) measurements. ^1H NMR spectroscopy (Varian XL-300) and elemental analysis (Elementar Vario EL) were performed to determine the structure of the ammonium amino acids. The amount of water was measured to be less than 0.05 w/w% using Karl Fisher coulometric titration (Brinkmann Metrohm 756 KF Coulometer) for all the AAILs.

Table 1 Properties of tetraalkylammonium-based amino acid ionic liquids prepared in this work

IL	T_g/°C	T_m/°C	T_{dec}/°C	ρ/g cm^{-3}	η/mPa s
$[N_{1114}]$[Gly]	−93	ND[a]	176	0.989	158
$[N_{1114}]$[L-Ala]	−92	ND[a]	175	0.969	62
$[N_{1114}]$[β-Ala]	−84	ND[a]	175	0.990	283
$[N_{1114}]$[Val]	−100	ND[a]	177	NA[b]	NA[b]
$[N_{2222}]$[Gly]	−79	14	180	1.064	129
$[N_{2222}]$[Val]	−78	22	186	1.006	163
$[N_{4444}]$[L-Ala]	−76	ND[a]	177	0.958	210
$[N_{2221}]$[Gly]	−87	ND[a]	182	1.051	151
$[N_{2221}]$[L-Ala]	−93	ND[a]	179	0.994	84
$[N_{2221}]$[β-Ala]	−94	ND[a]	178	1.008	171
$[N_{2221}]$[Val]	−95	ND[a]	180	0.973	244
$[N_{2224}]$[Gly]	−89	ND[a]	173	0.957	38
$[N_{2224}]$[L-Ala]	−92	5	176	0.940	29
$[N_{2224}]$[β-Ala]	−88	8	174	0.948	44
$[N_{2224}]$[Val]	−88	10	175	0.939	59

NA = not available.[a] The data at 30 °C. [b] The data are from Yaws.[33]

Table 1 summarizes the properties of fifteen [TAA][amino acid]s prepared in this work, three of them with symmetric TAA ($[N_{nnnn}]$) and twelve species with asymmetric TAA ($[N_{1114}]$, $[N_{2221}]$, $[N_{2224}]$). The colors of these fifteen AAILs are shown in Fig. 1, twelve of them being colorless or of light color while the other three are yellowish. All AAILs should be colorless in nature, and the yellow color may result from slight oxidation of the amino group during the removal of water and ethanol from the samples at high temperature.

As shown in Table 1, the melting points (T_m) of fifteen products are lowered to room temperature or below and all these AAILs show a glass transition temperature. Five of these AAILs have a melting point whilst no melting events for the remaining ten are detectable in the temperature range scanned. In contrast to the findings that ILs containing TAA cations are usually solids and have high melting points, all fifteen TAA-based products are ILs with melting points of lower than 30 °C. From the comparison of all AAILs that have a detectable value (see Table 1 of this paper and Table 1 in our previous paper)[20] it is apparent the AAILs having an asymmetric TAA cation ($[N_{2224}]$) melt at a temperature of 10 to 30 °C lower than those having symmetric [TAA] cations ($[N_{nnnn}]$, n = 1, 2, 4) no matter which amino acids are assigned to be the counter ions. All these observations may be due to the alkyl chain length and symmetry of the cation, that is, the longer the alkyl and the more asymmetric the cation, the lower the melting point. For example, the trend of the highest to lowest T_m values is $[N_{1111}]$[Val] (40 °C) > $[N_{4444}]$[Val] (25 °C) ≈ $[N_{2222}]$[Val] (22 °C) > $[N_{2224}]$[Val] (10 °C), which

Fig. 1 Prepared tetraalkylammonium-based amino acid ionic liquids. Above (left to right): $[N_{4444}]$[L-Ala], $[N_{2222}]$[Gly], $[N_{2222}]$[Val], $[N_{2224}]$[Val], $[N_{2224}]$[Gly], $[N_{2224}]$[L-Ala], $[N_{2224}]$[β-Ala]. Below (left to right): $[N_{1114}]$[Gly], $[N_{1114}]$[β-Ala], $[N_{1114}]$[L-Ala], $[N_{1114}]$[Val], $[N_{2221}]$[Gly], $[N_{2221}]$[β-Ala], $[N_{2221}]$[L-Ala], $[N_{2221}]$[Val].

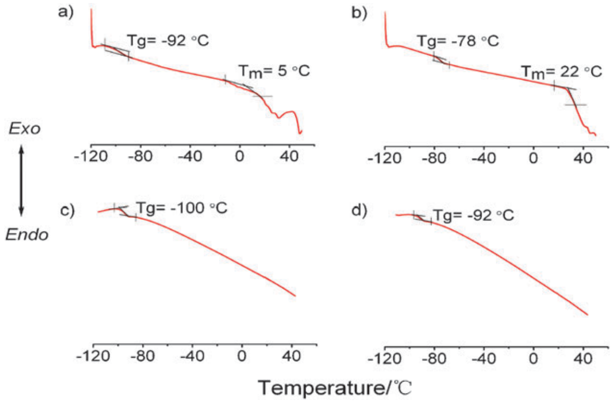


Fig. 2 Representative DSC traces at a heating rate of 10 °C/min. (a) $[N_{2224}]$-L-Ala: melting point (T_m) and glass transition (T_g); (b) $[N_{2222}]$Val: melting point (T_m) and glass transition (T_g); (c) $[N_{2221}]$-L-Ala: single glass transition (T_g); (d) $[N_{1114}]$-L-Ala: only glass transition(T_g).

is similar to the case of the lowest to highest degree of alkyl chain length and asymmetry of cations $[N_{1111}] < [N_{4444}] \approx [N_{2222}] < [N_{2224}]$. The T_g values of AAILs having asymmetric TAA cations are also found to be 10 to 20 °C lower than those having symmetric tetraalkylammonium cations, which can also be explained in terms of the symmetry and flexibility degree of the cations. Fig. 2 shows the DSC graphs of four ionic liquids ($[N_{2224}]$-L-Ala, $[N_{2222}]$Val, $[N_{2221}]$-L-Ala and $[N_{1114}]$-L-Ala) as examples to represent two types of phase transitions observed in all the 15 AAILs in the work. In addition, [TAA][amino acid]s are shown to have lower density than traditional ILs (such as imidazolium-based ILs[22]), with their values ranging from 0.94 to 1.1 g cm^{-3}. It is also evident from Table 1 that large and asymmetric TAA cations usually generate AAILs of low densities.

The [TAA][amino acid]s obtained in this work are thermally stable up to 170 to 190 °C as shown in Table 1 and exemplifed in Fig. 3. The T_{dec} values are generally found to decrease with increasing size and asymmetry of the cation, and $[N_{2224}]$ and $[N_{1114}]$ represent two cations of lower thermal stability. Changing the anion from Val to Gly, β-Ala or L-Ala, all with the same cation ($[N_{2224}]$, $[N_{2221}]$ or $[N_{1114}]$), made little difference to the thermal stability, indicating that cations appear to play a more significant role than anions. In fact, since the amino acid anions are slightly basic, TAA cations of larger size and asymmetry undergo easier β-elimination,[21] leading to lower thermal stability.

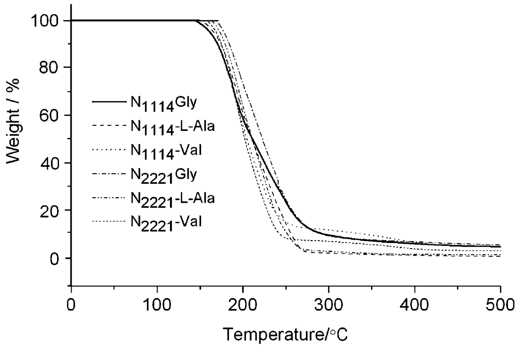


Fig. 3 Thermogravimetric analysis traces of six AAILs.

The viscosities of $[N_{2224}]$, $[N_{1114}]$ or $[N_{2221}]$[amino acid]s at 25 °C are found to be much lower than those of [emim][amino acid]s[14] and [TBP][amino acid]s.[15] Among the AAILs in Table 1, all $[N_{2224}]$[amino acid]s, containing Gly, Val, L-Ala or β-Ala, show the lowest viscosities in comparison to the symmetric [TAA]-based AAILs and other asymmetric [TAA]-based AAILs. In particular, the viscosity of $[N_{2224}]$[L-Ala] is 29 mPa s, only about 1/3 of the viscosity of $[N_{2222}]$[L-Ala] (81 mPa s at 25 °C).[14] It is even less viscous than many conventional ILs, such as ethylmethylimidazolium bis(trifluoromethanesulfonyl)-amide ([emim]$[Tf_2N]$, 34 mPa s at 25 °C)[22] and ethylmethyl-imidazolium trifluoromethanesulfonate ([emim]$[CF_3SO_3]$, 45 mPa s at 25 °C).[22] In addition, although $[N_{2222}]$[L-Ala] has the lowest viscosity among the symmetric TAA-based AAILs,[20] the viscosities of $[N_{2221}]$[L-Ala] (84 mPa s) and $[N_{1114}]$[L-Ala] (62 mPa s) are also similar to or lower than that of $[N_{2222}]$[L-Ala], implying that the asymmetry of the cation does have a significant impact on the viscosity.

Besides the asymmetry of the cations, the molecular size and asymmetry of the anions also apparently influence the viscosity of [TAA][amino acid]s. It is seen in Table 1 that the viscosities of [TAA][amino acid]s generally decrease in the order of [Val] > [β-Ala] > [Gly] > [L-Ala], no matter which tetraalkyl-ammonium is used as the counter cation. Since the viscosity of ILs generally decreases with decreasing molecular weight of the anion, it is reasonable that the viscosity decreases in the order of [TAA][Val] > [TAA][β-Ala] > [TAA][Gly]. However, although [TAA][L-Ala] has the same molecular weight as [TAA][β-Ala], [L-Ala] is more asymmetric than [Gly] and [β-Ala], which accounts for the viscosity of [TAA][L-Ala] being least. The fact that L-Ala anion forms even less viscous ILs with TAA cations than β-Ala reveals the significant impact of anion asymmetry on the viscosity. It is concluded that a carefully selected combination of molecular size and asymmetry for both the TAA cations and amino acid anions is essential to reduce the viscosity of [TAA][amino acid]s.

In fact, both the five TAA cations and the four amino acid anions used in this work are among the simplest and most readily available species. Even though other amino acids of simple molecular structure, such as leucine ([Leu]), isoleucine ([Ile]), serine ([Ser]), cysteine ([Cys]) and methionine ([Met]), may also be used to form $[N_{2224}]$, $[N_{2221}]$ or $[N_{1114}]$-based AAILs of possible low viscosity, it is believed that the viscosities of these AAILs may not be lowered to the level of $[N_{2224}]$[Val], $[N_{2221}]$[Val] or $[N_{1114}]$[Val] primarily due to the larger molecular size or the additional presence of polar groups (such as –OH, –SH) in such amino acid anions. On the other hand, it is also believed that there is little possibility of obtaining low viscosity AAILs by using more complex TAAs of carbon number larger than $[N_{4444}]$. A possible way of preparing more AAILs of low viscosity is to use asymmetric TAA cations of carbon number not larger than 12, such as $[N_{1223}]$, $[N_{2225}]$, and $[N_{1224}]$. However, since such asymmetric TAA cations are not commercially available nowadays and have to be prepared in the laboratory, the search for more AAILs of low viscosity is quite time-consuming but well worth doing. Nevertheless, the four $[N_{2224}]$-based AAILs that utilize the four simplest and most readily available amino acids as the counter anions are of low cost and viscosity, and are thought to meet the criteria for engineering purposes that concern mass and heat transfer.

The global warming due to the increased atmospheric CO_2 concentration results primarily from the excessive consumption of fossil fuels and is becoming an important environmental issue today.[23–25] Carbon sequestration, which captures CO_2 from large point sources such as fuel gas, natural gas, water gas and waste gas from electrical power plants and stores it in geological formations, has been proposed as a solution to this problem. However, aqueous amines that are currently used most frequently in industry for large scale CO_2 capture suffer from many technical difficulties, *i.e.*, the uptake of water into the gas stream, high energy consumption during the regeneration of the absorbing solution, and the volatile loss of amine sequestering agent. As a result, innovative task-specific amino-terminated[26,27] or amino acid-based ionic liquids[16] were developed and proposed to be stable and non-volatile CO_2 absorbents[28] for the replacement of traditional aqueous amines. However, all these new ILs reported in the literature still have high viscosity, which disfavors the heat and mass transfer during the applications. Therefore, efficient separation of CO_2 using low viscosity [TAA][amino acid]s is not only a potential addition to economically viable sequestration efforts, but also a good system for the verification of enhanced CO_2 mass transfer benefiting from low viscosity.

The absorption of CO_2 (99.99%) into $[N_{2224}]$[L-Ala], $[N_{2224}]$[β-Ala], $[N_{2221}]$[L-Ala], $[N_{2222}]$[L-Ala], $[N_{2222}]$[β-Ala], diethanolamine (DEA), methyldiethanolamine (MDEA), and aqueous MDEA (51.28% w/w) was carried out at 40 °C and ambient pressure, according to the standard procedure reported in the literature.[16] The absorbed CO_2 is almost completely extruded from the CO_2-absorbed $[N_{2224}]$[L-Ala] upon heating at 60 °C for 4 h under vacuum (about 0.1 KPa). If the CO_2-saturated AAIL is heated at 110 °C at atmospheric pressure for an hour, more than 90% of the absorbed CO_2 can be released, which is similar to the case of the DEA–CO_2 system. The recovered $[N_{2224}]$[L-Ala] has been repeatedly recycled for CO_2 uptake (four cycles) as presented in Fig. 4, with no apparent losses of absorption rate and absorption capacity. The mole uptake of CO_2 per mole $[N_{2224}]$[L-Ala] is found to approach 0.5, equivalent to 0.326 mole fraction of CO_2 in the IL. All other AAILs tested for CO_2 absorption (such as $[N_{2224}]$[β-Ala], $[N_{2221}]$[L-Ala], $[N_{2222}]$[L-Ala], $[N_{2222}]$[β-Ala]) have an absorption capacity (around 0.325 mole fraction) similar to that of $[N_{2224}]$[L-Ala]. In fact, since all the AAILs in this work have an exposed amino group, they absorb CO_2 chemically *via* the reaction of CO_2 with the amino group to form ammonium carbamate so that their absorption capacities are close to that of DEA (0.33 mole fraction of CO_2 in DEA at 40 °C). The formation of ammonium carbamate has been evidenced from the ^{13}C NMR analysis both in our laboratory[20] and by the research group of Davis.[27] In addition, it is observed that the viscosities of AAILs are low and the liquids can be stirred easily at the beginning of the absorption. However, the transparent liquid of $[N_{2224}]$[L-Ala] becomes a cloudy paste at the end of absorption, and the CO_2-saturated $[N_{2224}]$[L-Ala] sample collected for analysis is found to have a viscosity of 1543 mPa s at 25 °C, additionally indicating the formation of ammonium carbamate species.

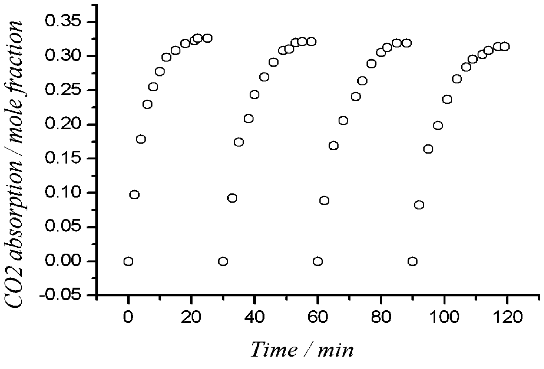


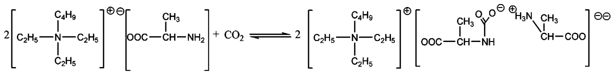
Fig. 4 Cycles of CO_2 absorption into $[N_{2224}]$[L-Ala] at 40 °C.

Even though DEA and AAILs have similar capacity in absorbing CO_2, the absorption rates of CO_2 in the AAILs and organic amines are quite different. The results in Fig. 4 demonstrate that the equilibrium of CO_2 absorption in $[N_{2224}]$[L-Ala] can be reached within 30 min, half the time required in the cases of $[N_{2222}]$[L-Ala] and $[N_{2222}]$[β-Ala] (≈60 min). As for the absorption of CO_2 in DEA, MDEA and aqueous MDEA solutions, the times required for reaching phase equilibrium are usually longer than several hours. In particular, $[N_{2224}]$[L-Ala] is observed to absorb CO_2 at a rate of 8 to 10 min to reach 90% of its saturated absorption capacity, vastly faster than that observed for other asymmetric [TAA][amino acid]s, symmetric [TAA][amino acid]s and organic amines (DEA, MDEA, aqueous MDEA). Analysis shows that this is primarily due to the effect of viscosity on the mass transfer of CO_2.

The CO_2 physical absorption mechanism was put forward by Brennecke and co-workers. They disclosed that CO_2 at high pressure exhibits intrinsic solubility in the "conventional" ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate.[29,30] The solubility of CO_2 in ionic liquids is dependent on their cations, anions, and substituents, and the anions play a major role. The interaction between CO_2 and imidazolium-type ionic liquid, attributed to the activity of H-2 in the imidazolium ring, accounts also for its higher solubility of CO_2.[31,32] However, in our work, the amino groups present in the AAILs can increase dramatically the CO_2 solubility up to 0.33 mole fraction of CO_2, consistent with the chemical mechanism proposed by Bates *et al.*[27] that one mole of 1-butyl-2-propylamineimidazole tetrafluoroborate ($[(NH_2)pmim][BF_4]$) can absorb half of one mole of CO_2. Therefore, the reaction between [TAA][amino acid] and CO_2 can be represented by Scheme 1, and the reaction rate (r) can be generally written as,

$$r = -dC/dt = KC \qquad (1)$$

where K is the apparent absorption reaction rate constant and C is the concentration of CO_2 in mol m^{-3}. Scheme 1 represents a pseudo-first order reaction for CO_2, since the concentrations of [TAA][amino acid]s can be regarded as a constant at the



Scheme 1 The reaction between $[N_{2224}]$[L-Ala] and CO_2.

beginning of the reaction. Thus, integrating eqn (1) leads to the following expression,

$$\ln(n - n_e)/(n_o - n_e) = Kt \qquad (2)$$

where n, n_o and n_e are the moles of CO_2 in the gas phase at times $t = t$, $t = 0$ (before absorption) and $t = \infty$ (after absorption), respectively.

Fig. 5 shows the plots of eqn (2) for CO_2 reacting with $[N_{2222}]$[L-Ala], $[N_{2222}]$[β-Ala], $[N_{2221}]$[L-Ala], $[N_{2224}]$[L-Ala], $[N_{2224}]$[β-Ala], MDEA, aqueous MDEA (51.28%), and DEA. The apparent reaction rate constants are calculated from the slopes of the plots and are summarized in Table 2. It is found that the trend of the highest to lowest apparent reaction rate constant is $[N_{2224}]$[L-Ala] ($0.36\ \mathrm{min}^{-1}$) > $[N_{2224}]$[β-Ala] ($0.28\ \mathrm{min}^{-1}$) > $[N_{2222}]$[L-Ala] ($0.21\ \mathrm{min}^{-1}$) ≈ $[N_{2221}]$[L-Ala] ($0.20\ \mathrm{min}^{-1}$) > $[N_{2222}]$[β-Ala] ($0.15\ \mathrm{min}^{-1}$) > DEA ($0.11\ \mathrm{min}^{-1}$) > aqueous MDEA (51.28%) ($0.066\ \mathrm{min}^{-1}$) > MDEA ($0.042\ \mathrm{min}^{-1}$). Particularly $[N_{2224}]$[L-Ala] has the highest apparent reaction rate constant, being about 2, 2, 3, and 6 times the values of the $[N_{2221}]$[L-Ala], $[N_{2222}]$[L-Ala], DEA and aqueous MDEA systems, respectively. It is also interesting to note that the apparent reaction rate constant decreases with increasing viscosity of the absorbent, no matter which AAILs or organic amines are used.

There is a close relationship between reaction rate constant and diffusivity. According to the Wilke–Chang equation and penetration theory in mass transfer,[34] the diffusivity (D_{AB}) of component A in liquid B is proportional to the reciprocal viscosity (η^{-1}) of liquid B, and the mass transfer coefficient (or reaction rate constant) is linearly dependent on the root square diffusivity ($D_{AB}{}^{0.5}$). The combination of the two theories implies that the product of K and $\eta^{0.5}$ is approximately a constant. The calculated values of $K{*}\eta^{0.5}$ for $[N_{2224}]$[L-Ala], $[N_{2224}]$[β-Ala], $[N_{2221}]$[L-Ala], $[N_{2221}]$[L-Ala], $[N_{2222}]$[β-Ala], DEA and MDEA systems, as also shown in Table 2, range from 0.029 to 0.036 $\mathrm{mPa}^{0.5}\ \mathrm{s}^{-1}$ and are fluctuant around an average value of 0.033, which agrees well with the theories. Since MDEA is a tertiary amine, its pure or aqueous solution absorbs CO_2 *via* a different mechanism that will not be discussed any further here.

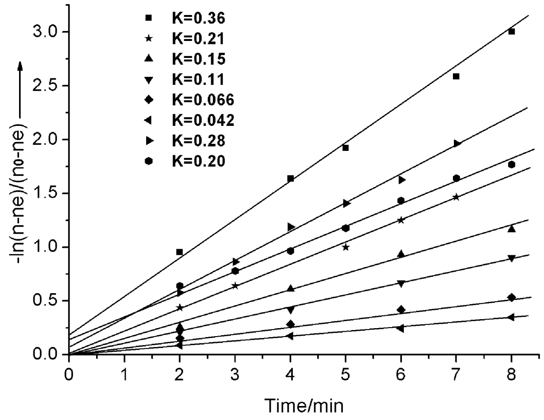


Fig. 5 Plots of CO_2 absorption at 40 °C as a function of time into $[N_{2224}]$[L-Ala] (■), $[N_{2224}]$[β-Ala] (▶), $[N_{2221}]$[L-Ala] (●), $[N_{2222}]$[L-Ala] (★), $[N_{2222}]$[β-Ala] (▲), DEA (▼), aqueous MDEA (51.28%) (◆), and MDEA (◀).

Table 2 Apparent reaction rate constants of CO_2 with AAILs and organic amines

Species	η/mPa s (25 °C)	K/min^{-1}	$K{*}\eta^{0.5}$/ $\mathrm{mPa}^{0.5}\ \mathrm{s}^{-1}$
$[N_{2224}]$[L-Ala]	29	0.36	0.032
$[N_{2224}]$[β-Ala]	44	0.28	0.031
$[N_{2221}]$[L-Ala]	84	0.20	0.030
$[N_{2222}]$[L-Ala]	81	0.21	0.031
$[N_{2222}]$[β-Ala]	132	0.15	0.029
DEA	$380^{a,b}$	0.11	0.036
MDEA	76^{b}	0.042	NA
Aqueous MDEA (51.28% w/w)	NA	0.066	NA

NA = not available.[a] The data at 30 °C. [b] The data are from Yaws.[33]

In summary, fifteen novel AAILs of low cost were prepared in our group by coupling symmetric and asymmetric tetraalkylammonium cations with four amino acid anions, and all these compounds are found to be liquids at room temperature. It is revealed that the four AAILs containing $[N_{2224}]$ cation yield dramatically low viscosity, especially $[N_{2224}]$[L-Ala] (29 mPa s), being the least viscous IL based on amino acids. A carefully selected combination of molecular size and asymmetry for both the TAA cations and amino acid anions is essential to reduce the viscosity of [TAA][amino acid]s. $[N_{2224}]$[L-Ala], as well as other AAILs of low viscosity, has been tested and verified to be of particular importance in enhancing the CO_2 mass transfer. Within this context, it is believed that AAILs of low viscosity and cost may open up a new road of amino-functionalized IL applications in large-scale acidic gas scrubbing processes.

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