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Novel ionic liquid analogs formed by triethylbutylammonium carboxylate-water mixtures for CO_2 absorption

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ABSTRACT

This work presents ten ionic liquid analogs of triethylbutylammonium carboxylate and water as CO_2 absorbents. The mixtures are liquids with relatively low viscosities at ambient temperature. The absorption experimental results have shown that each of them has fast absorption rate and large absorption capacity of CO_2.

1. Introduction

The removal of CO_2 from industrial flue gasses is now widely concerned because of the adverse effects such as global warming [1]. Various methods have been proposed, such as selective adsorption [2]/absorption [3,4] and membrane processes [5,6]. Although these methods have been successfully used in industries, they are still associated with energy consumption, corrosion and pollution problems [7]. In order to overcome such obstacles, many novel absorbents such as ionic liquids (ILs) [8], salt hydrates [9] and metal oxide complexes [10], have been developed to provide high CO_2 absorption capacity and thermal stability. However, such absorbents are strongly affected by the presence of water vapor in the gas stream so that the absorption capacity [11] and absorption mechanism [12] are much more different. Unfortunately, water is very common in flue gasses from fossil fuel combustion or other industrial gas streams [13]. Therefore, it is crucial to provide novel compounds which can absorb CO_2 in the presence of water.

In 1995, Quinn reported hydrated salts based on acetic acid and citrate acid, which showed good performance of CO_2 capture [9]. Inspired by his publication, ten novel ionic liquid analogs are prepared by coupling asymmetric triethylbutylammonium ($[N_{2224}]$) cation with carboxylate anion. It is found that each of them is in the liquid state at room temperature with a certain amount of water and can be detected only a glass transition temperature. The reason to define this type of compound as ionic liquid analogs is that the samples stay in the liquid state at a large temperature range just like the ILs though they are not composed entirely of ions. It is further proved that the $[N_{2224}]$[carboxylate]-nH_2O mixtures ($[N_{2224}]$[CA]-nH_2O) have high CO_2 absorption capacity and fast absorption rate of CO_2, which are very attractive for the capture and separation of acidic gasses in industrial applications.

2. Experimental section

2.1. Materials

Triethylamine ($(C_2H_5)_3N$), n-butyl bromide (C_4H_9Br), silver oxide (Ag_2O), and ethanol, obtained commercially from Sinopharm Chemical Reagent Co., Ltd (Nanjing, China), were of analytical grade and used without further purification. All carboxylate acids of analytical grade were purchased from Nanjing Chem. Co. (Nanjing, China) and used as received.

2.2. General procedure for $[N_{2224}]$[carboxylate]-nH_2O synthesis

Triethylbutylammonium bromide ($[N_{2224}]$[Br]) was prepared via the alkylation of $(C_2H_5)_3N$ (70.0 g) with C_4H_9Br (95.0 g) in ethanol (200 ml) under reflux and vigorous stirring for 12 h. The solvent and unreacted reactants were removed by rotary evaporation, $[N_{2224}]$[Br] (160 g) as white solid was obtained after being dried at 60 °C under vacuum ($\approx$0.1 kPa) for 24 h.

In the anion exchange reaction, Ag_2O was added in portions into $[N_{2224}]$[Br] solution, the mole ratio of Ag_2O to $[N_{2224}]$[Br] is 1:2, and stirred without air and light at room temperature for 6 h. After filtration, the $[OH^-]$ concentration of the resulting solution was

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determined from the titration with standard HCl solution. Then, the triethylbutylammonium hydroxide ([N_{2224}][OH]) solution reacted with a slight excess of carboxylate acid via neutralization at room temperature for 2 h. Water was evaporated to generate a residual solution that contained the [N_{2224}]-based samples. After being further dried at 60 °C under vacuum (≈0.1 kPa), the residue was extracted with diethyl ether for several times to remove the unreacted acid. The crude product was dissolved in the mixed solvent of dichloromethane with 2 vol.% methanol, and the solution was passed through a column filled with neutral silica. After the removal of the solvent by evaporation, the product was dried in a vacuum (≈0.1 kPa) oven at 80 °C for at least 5 days to remove water before the characterization experiments. If the samples were dried at other conditions (at 50 to 70 °C and for 1 to 3 d), triethylbutylammonium carboxylate ([N_{2224}][CA]) with different amount of water would be obtained [9]. The structures of the compounds are determined by the ^{1}H NMR spectroscopy (BRUKER DPX 300) and confirmed by the elemental analysis (Elementar Vario MICRO). Photos of the ten obtained samples can be found in Fig. 1 and details of characterization experiments were shown in Supplementary Data.

2.3. Water content measurement

The water contents in the samples were determined by Karl-Fisher Analysis (Metrohm 787 KF Titrino) and ^{1}H NMR spectroscopy (BRUKER DPX 300).

2.4. Physical properties measurement

The glass transition temperature (T_g) was recorded at the temperature range from −100 to 0 °C under N_2 atmosphere at the scan rate of 10 °C/min by different scanning calorimetry (Perkin-Elmer Diamond DSC), while melting temperature (T_m) was recorded at the temperature range from −20 °C to 50 °C by thermogravimetric analysis (Perkin-Elmer Pyris 1 TGA).

The temperatures of water loss (T_{loss}) and decomposition (T_{dec}) were determined at the scan rate of 10 °C/min under N_2 at the temperature range from room temperature to 500 °C by thermal analysis (TG) instrument (NETZSCH STA 449C). The details of DSC and TG spectrum can be seen in Supplementary Data.

The viscosity and density were measured by a cone-plate viscometer (HAAKE Rheostress 600, an uncertainty of ±1% in relation to the full scale) and a densitometer (DMA 5000 DENSITY METER, an uncertainty of $\pm 0.03\ \mathrm{kg \cdot m^{-3}}$).

2.5. CO_2 absorption experiment

The water content in the samples was adjusted to integral numbers by adding corresponding amount of fresh deionized water before the absorption experiments. The absorption of CO_2 (99.99%, from Nanjing Gas Supply Inc., China) into [N_{2224}][CA]-nH_2O was carried out at 25 °C and at the same initial CO_2 pressure of 0.1 MPa, according to the standard procedure [12]. The saturated samples were recovered by extruding CO_2 at 55 °C and under vacuum (0.1 kPa) for 4 h and repeated CO_2 absorptions into two typical samples were presented in Fig. 2.

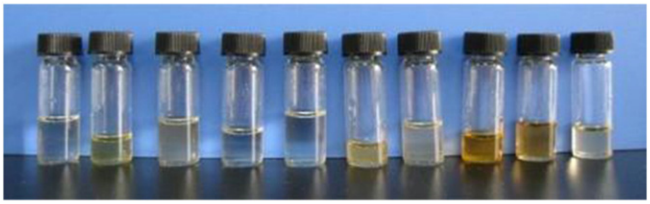

Fig. 1. [N_{2224}][CA]-nH_2O prepared in this work. Left to right: [N_{2224}][propionate]-0.5H_2O, [N_{2224}]$_2$[fumarate]-3.6H_2O, [N_{2224}]$_2$[malonate]-3.5H_2O, [N_{2224}][acetate]-1H_2O, [N_{2224}][butyrate]-0.5H_2O, [N_{2224}]$_2$[malate]-3H_2O, [N_{2224}]$_2$[succinate]-3H_2O, [N_{2224}]$_2$[phthalate]-2H_2O, [N_{2224}]$_3$[citrate]-2.5H_2O, [N_{2224}]$_2$[maleate]-2H_2O.

3. Results and discussion

3.1. The measurement of water content

As is known to all, carboxylate anions are highly hydrophilic and it is almost impossible to dry the samples completely as can be seen in Table 1. However, the evidences of FTIR and ^{1}H NMR analysis indicate that small amounts of water interact with the anions instead of being isolated molecules and form complexes with the [N_{2224}] salts. The DSC spectrum results suggest that the samples remain in the liquid state at a large range of temperature. Based on the phenomenon mentioned above, it is reasonable to regard [N_{2224}][CA]-nH_2O as ionic liquid analogs.

3.2. Physical properties

The important physical properties of all samples in this work are summarized in Table 1. It is obvious that only glass transition temperatures (T_g) can be detected ranging from −75 °C to −50 °C, and T_g increases generally with the number of carboxyl groups in the anion. For example, [N_{2224}]$_2$[phthalate]-2H_2O has the highest T_g value whereas the [N_{2224}][acetate]-1H_2O, [N_{2224}][propionate]-0.5H_2O and [N_{2224}][butyrate]-0.5H_2O have about 20 °C lower values. Those later three salts have almost identical T_g values, indicating that the length of alkyl chain in the mono-carboxylate anions has less effect on the T_g values. In contrast to [N_{2222}][acetate]-4H_2O that has a melting temperature at 45 °C [9], no melting temperatures were detected from −100 to 50 °C for all samples in this work, reflecting that the [N_{2224}] salts and water complexes were also eutectic liquid mixtures at the experimental temperature range.

The temperature of water loss (T_{loss}) is the temperature when the samples start to lose water and it is found that the values of T_{loss} are all above 100 °C and increase with the number of the functional groups in the anions. All [N_{2224}][CA]-nH_2O have the decomposition temperatures from 160 to 190 °C, which are a little lower than normal functional ionic liquids [14]. The fully ionized carboxylate anions are basic and triethylbutylammonium hydroxide was formed in the presence of water. So the mechanism of decomposition may relate to a Hoffman Elimination Reaction explained by MacFarlane [15]. From this respect, the reason for low thermal stability of the ILs may be the interaction of basic anions and cation in the presence of water.

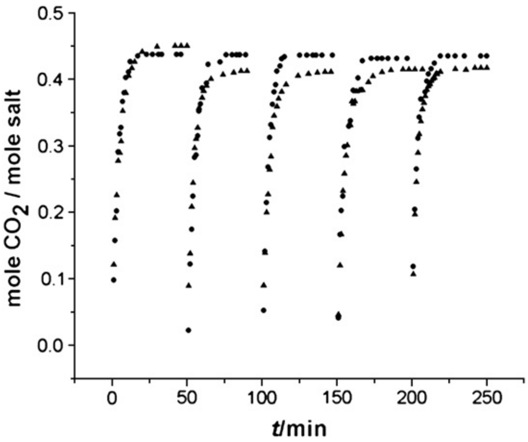

Fig. 2. Cycles of CO_2 absorption into [N_{2224}][CA]-nH_2O at 25 °C and at the same initial CO_2 pressure of 0.1 MPa. The saturated samples were recovered by extruding CO_2 at 55 °C and under vacuum (0.1 kPa) for 4 h. ● [N_{2224}][butyrate]-1H_2O and ▲ [N_{2224}][propionate]-1H_2O.

Table 1
Physical properties of $[N_{2224}]$ [carboxylate]-nH_2O.

Anion	T_g/°C	T_{loss}/°C	T_{dec}/°C	n	ρ/g·cm^{-3}	η/mPa·s
Acetate	−73	103	164	1	0.9981	79
Propionate	−74	107	162	0.5	0.9807	120
Butyrate	−74	101	161	0.5	0.9694	157
Malonate	−60	105	161	3.5	1.0393	509
Succinate	−57	111	162	3	1.0415	NA[1]
Phthalate	−49	113	161	2	1.0654	NA
Maleate	−60	110	156	2	1.0486	NA
Fumarate	−54	119	167	3.6	1.0477	NA
Malate	−55	117	187	3	1.0578	NA
Citrate	−52	125	190	2.5	1.0762	NA

[1] NA: higher than 3800 mPa·s at 25 °C.

The viscosities of all samples range from 79 mPa·s up to more than 3800 mPa·s (NA in Table 1) at 25 °C, depending on the anion types. $[N_{2224}]$[mono-carboxylate] water complexes are found to have viscosities lower than 160 mPa·s at 25 °C, primarily due to the lighter molecular weight of these anions. The reason for the high viscosities may be attributed to the multi-carbonyls in the anions which would enlarge the interactions between the ions. Relatively low viscosities make the $[N_{2224}]$[CA]-nH_2O attractive as industrial absorbents for CO_2 capture.

In addition, $[N_{2224}]$[CA]-nH_2O are of lower densities than traditional ILs. It is distinct that the densities of $[N_{2224}]$[CA]-nH_2O increase with a rise in the volume of the carboxylate anions, like the trend of other kinds of ILs, such as imidazolium-based ILs [16].

3.2.1. CO_2 absorption properties

In order to test the accuracy of the absorption apparatus, the solubility of CO_2 into 1 mol/L NaOH solution and [bmim]$[PF_6]$ was determined and compared with those in the references [17,18]. The experimental results have shown strong constancy that demonstrates the liability of the absorption apparatus in this work.

The absorption capacity is shown to reach 95% of the equilibrium value within 30 min which is even shorter than the amino acid ionic liquids [14]. $[N_{2224}]$[butyrate]-1H_2O had been recycled with no obvious loss of absorption capacity. However, the capacity of $[N_{2224}]$[propionate]-1H_2O in the later three cycles is 8% smaller than the first time. It may be reasoned that an absolute vacuum was not really achieved in the subsequent three cycles. Based on the absorption data in the first 30 s, the initial absorption rate constant (K/min^{-1}) was calculated and shown in Table 2. It is found that $[N_{2224}]$[CA]-nH_2O with the high CO_2 capacities usually has the large K values. Small K values may result from low CO_2 loadings or high viscosities. Nevertheless, all $[N_{2224}]$[CA]-nH_2O, which are comparable to the aqueous monoethanolamine (36 w/w%, $K = 0.24$ min^{-1}, results from our own experimental device), are also faster and more efficient CO_2 absorbents than methyldiethanolamine aqueous solutions (51.28 w/w%, $K = 0.066$ min^{-1}) [19] widely used in industrial processes [20].

Table 2
CO_2 absorption into $[N_{2224}]$[CA]-nH_2O at 25 °C and the same initial pressure of CO_2 (0.1 MPa).

Anion	n	P^*/kPa	Absorption capacity mol CO_2/mol compound	K/min^{-1}
Acetate	1	45	0.23	0.14
Propionate	1	46	0.39	0.33
Butyrate	1	44	0.45	0.22
Malonate	6	50	0.65	0.20
Succinate	6	61	0.57	0.09
Phthalate	6	50	0.66	0.17
Maleate	6	56	0.58	0.18
Fumarate	6	66	0.24	0.08
Malate	6	68	0.20	0.09
Citrate	10	66	0.38	0.08
L-Ala[13]	0	100	0.50	0.36
Citrate*[7]	10.1	100	0.48	NA[1]

[1] NA: not available. p^* is the partial pressure of CO_2 after absorption equilibrium.

$$RCOO^- \, nH_2O + CO_2 \rightleftharpoons HCO_3^- + RCOOH(n\text{-}1)H_2O$$

Scheme 1. Proposed reaction mechanism between $[N_{2224}]$[carboxylate]-nH_2O and CO_2.

The CO_2 absorption capacities of all $[N_{2224}]$[CA]-nH_2O at a certain equilibrium partial pressure of CO_2 are also summarized in Table 2. Generally speaking, all samples exhibit large CO_2 absorption capacities at relatively low partial pressures, i.e., one mole of $[N_{2224}]$[butyrate]-1H_2O (cheap) absorbs 0.45 mol of CO_2 at 25 °C and 44 kPa, which is comparable to the CO_2 absorption capacity of $[N_{2224}]$[L-Ala] (expensive). It can be found that the solubility of CO_2 into $[N_{2224}]$[mono-carboxylate]-nH_2O samples grows with the increasing length of the alkyl chain in the anion. The free volume between ions will increase if the alkyl chain in the anion is enlarged. However, for multi-carboxylate species, such a trend does not exist probably because the interactions between the carbonyl groups are strong enough to prevent the affinity with CO_2. In addition, the conformation of the anions affects not only the physical parameters but also the absorption capacity of CO_2. $[N_{2224}]_2$[fumarate]-6H_2O traps about 58% less CO_2 than $[N_{2224}]_2$[maleate]-6H_2O, which indicates that the trans-conformation favors strong intermolecular hydrogen bonds between anions rather than the combination with CO_2 [21]. The small difference in the absorption capacity between $[N_{2224}]_3$[citrate]-10H_2O and $[N_{2222}]_3$[citrate]-10.1H_2O [9] confirms the conclusion that the cation plays a less important role in determining the solubility of gasses into ILs [8].

The large CO_2 absorption capacities of the mixtures are resulted from the carboxylate anions which are conjugated bases of corresponding weak acids, being the main driving force for the chemical reaction. Scheme 1 was claimed by Quinn [9] and it was found to be suitable for our case from the results of ^{13}C NMR and ^1H NMR analysis for both CO_2-free and CO_2-treated samples (see Supplementary Data). The ^{13}C NMR spectrum detects a new resonance at 159.604 ppm, to be the bicarbonate carbonyl carbon [9] while other features of the spectrum stay the same. Correspondingly, there is an extra resonance signal at 2.084 ppm in the CO_2-saturated IL detected by ^1H NMR spectra.

4. Conclusion

From all aspects mentioned above, the ionic liquid analogs of $[N_{2224}]$[CA]-nH_2O are thought to be of significance for the industrial CO_2 capture due to the high absorption capacity, fast absorption rate and relatively low cost.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.molliq.2011.12.006.

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