Properties of aqueous amine based protic ionic liquids and its application for CO$_2$ quick capture

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ABSTRACT

Three kind of pure amines which have high solubility of CO$_2$ were used as absorbents hardly to be recovered. A series of aqueous ethoxyacetate anion-based protic ionic liquids (PILs) with three different amine cations were designed, and physical properties including measured density and viscosity were measured. Solubility of CO$_2$ in the three PILs solution, 90% [DMAPAH][EOAc], 90% [DEEDAH][EOAc] and 90% [DMEDAH][EOAc], were systematic determined at the range of 303.2–333.2 K under the pressure of 1.2 bar. Impressively, the solubility of CO$_2$ in 90% [DMAPAH][EOAc] reached up to 2.44 mol/kg, which showed more advantage than some traditional or functional ILs. The 90% [DMAPAH][EOAc] could be reused four times. Besides, the proposed mechanism was advised. Considering the advantages of high absorption capacity, low cost, easy regeneration including fast absorption rate, we believe the three PILs solution can be recommended as alternatives to some volatile organic amines to be applied in CO$_2$ capture.

1. Introduction

At least 97% of environmental scientists have an opinion that greenhouse gas emission (GHG) plays a key role for global climate change [1,2]. Fuel use, food production and agriculture are all sources of GHG. According to recent report by B Jacob group, direct emission for advanced coal power plants contribute CO$_2$ 850–1000 g/kWh, NO$_x$ 0.5–1.5 g/kWh, SO$_2$ 0.5–0.7 g/kWh and PM$_{2.5}$ g/kWh [3]. Hence, it is an urgent to find more efficient methods to reduce those GHG, especially CO$_2$ considering its huge emission. Currently, aqueous amines are common commercial absorbents to be widely used to remove CO$_2$ [4–9]. Primary amines often have more special affinity to CO$_2$ because they have higher basicity relative to secondary amines and tertiary amines. The binding energy of CO$_2$ to different amines decreases in the order: primary amine > secondary amine > tertiary amine studied by P Ratnasamy [10]. It is clear that primary amine may have more superiority than secondary amine and tertiary amine. Ethanolamine (MEA) is the benchmark absorbent of primary amine because of its outstanding advantages such as low price, high absorption capacity of CO$_2$ and higher reaction speed [11–13]. In general, CO$_2$ could direct react with MEA to form the carbamate complex and hardly to be recovered for next CO$_2$ capture cycle comparing with some recyclable absorbents. However, some shortcomings such as easy degradation, volatile organic compound and corrosion activity, should overcome [14].

Ionic liquids (ILs) which is a type of room temperature melt point salts with designable cations and anions are recognized as an kind of environmental friendly absorbent of CO$_2$ for some highlighted properties, for instance, neglected vapor pressure, stable chemical property, tunable structures et al [15,16]. Protic ionic liquids (PILs) are formed through the transfer of a proton from a BrØnsted acid to a BrØnsted base [17,18]. Compared with pure amines, PILs have a proton to form hydrogen bond avoiding non-negligible vapor pressure and decomposition of absorbent. If PILs are synthesized by stronger acid and/or stronger base in the case of aqueous solutions, the proton-transfer process can be improved [19,20]. D R MacFarlane et al. studied a series of diamino protic ILs, among that DEEDAH-formate and DMEDAH-acetate + water (1:1 by mol) could absorb 0.50 mol CO$_2$ of per mol ILs [21,22]. Y T Wu group found that cyano-containing PILs showed highly selective absorption of SO$_2$ from CO$_2$, ethoxyacetate anions would play role to capture SO$_2$ rather than tertiary amine cations [23]. Inspired by those pioneering works, we design three different amine-containing ILs solutions which may combine virtue of amine cations and ethoxyacetate anions. These PILs solutions are assumed to be excellent absorbents for CO$_2$ capture. The structures of three kinds of pure amine-containing PILs are listed in Scheme 1. It is found that pure [DMAPAH][EOAc] and [DEEDAH][EOAc] are solid at room temperature because of stronger ion-ion interactions. The mass fractions of water in those
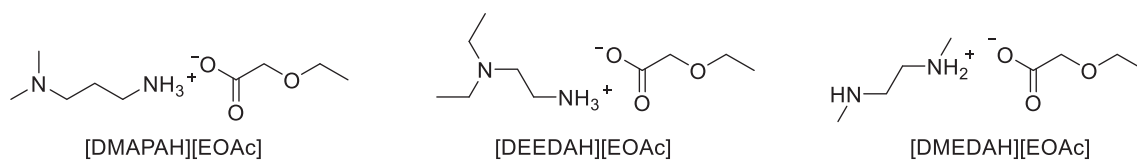
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Scheme 1. The structure of pure PILs.
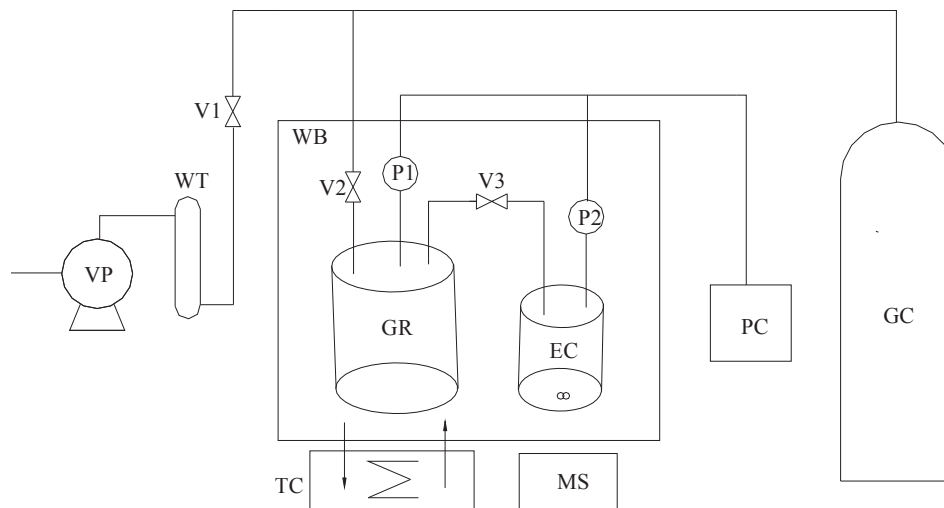
Scheme 2. Apparatus for the determination of gas solubility. (GC – gas cylinder; V_1, V_2, V_3, V_4 –valves; VP –vacuum pump; WT –washing tower; WB –water bath; TC –thermal controller; GR –gas reservior; EC –equilibrium cell; P –pressure transducer; MS –magnetic stirrer; NI –numerical instrument; PC – personal computer).

pure PILs are all no more than 200 ppm. 10% (wt) water is added into those pure PILs to get PILs solution. To prove the potential application of 90% PILs solution uptake CO_2, some properties are determined including density, viscosity and solubility of CO_2.

2. Experimental section

2.1. Materials and apparatus

CO_2 (99.99 mol%) were supplied from Nanjing Tianze Gas Co. (Nanjing, China). 3-(dimethylamino)-1-propylamine (AR grade, 99.5 wt %), N,N-diethylethylenediamine (AR grade, 99.5 wt%), N,N-dimethy-lethylenediamine, Ethanol amine (AR grade, 99 wt%) and ethoxyacetic acid (AR grade, 99.5 wt%) were purchased from Aladdin Chemical Reagent Co., and used without further purification.

The FTIR spectra were conducted on Bruker Tensor 27 FTIR instrument. ^1H and ^{13}C NMR spectra were measured on Bruker AVANCF 300 MHz spectrometer and 100 MHz spectrometer respectively, using Chloroform-d ($CDCl_3$) as a solvent with tetramethysilane (TMS) as internal standard. EI+-spectra were measured on a JOEL JMS-700 spectrometer. For ESI+-spectra a Bruker ApexQu FT-ICR-MS spectrometer was applied. The densities were determined using an Metler Toledo type automatic densitometer with a precision of 0.0001 g/cm^3. The apparatus was calibrated using distilled water. The viscosities were measured on a Brookfield LVDVII1Pro viscometer with an uncertainty of 61% in relation to the full scale. The pH was determined by Meter Toledo-pH (FE28) meter.

2.2. General procedures for determination of CO_2 absorption and kinetic

The apparatus for the determination of gas absorption in ILs is the same as that in our previous work. There are two 316 L stainless steel chambers whose volumes are 130.43 cm^3 (V_1) and 47.91 cm^3 (V_2), respectively. The bigger chamber, used as a gas reservoir, restores the gas before it goes into the smaller chamber through needle valve. The smaller chamber called as the equilibrium cell is equipped with a

magnetic stirrer. Both chambers are put in the water bath. The temperatures (T) are controlled by an automatic thermoregulatory with the uncertainty of $\pm$ 0.1 K. The pressures are monitored using two pressure transducers of $\pm$ 0.5% uncertainty. The pressure transducers are connected to a computer through an absolute pressure controller using RS 232 communication interface to record the pressure changes online. In a general procedure, a known mass of ILs was put into the equilibrium cell, and the air of the two chambers was evacuated. The residual pressure of the equilibrium cell was recorded to be P_0. The gas reservoir was fed to a pressure of P_1 from the cylinder. The needle valve was turned on to let some of gas be introduced to the equilibrium cell. When the two chambers remained constant for at least 1 h, absorption equilibrium was reached. The pressures of gas reservoir and equilibrium cell were denoted as P_1' and P_2 respectively. The partial pressure of the equilibrium cell was $P_g = P_2 - P_0$. The uptake of gas $n(P_g)$ was calculated by the following equation

$$n(P_g) = \rho_g(P_1, T)V_1 - \rho_g(P_1', T)V_1 - \rho_g(P_g, T)\left(V_2 - \frac{\omega}{\rho_{IL}}\right) \tag{1}$$

where $\rho_g(P_1, T)$ represents the density of gas in mol/cm^3 at $P_i (i = 1, g)$, ω is the weight of ILs and ρ_{IL} is the density of ILs in g/cm^3 at T. V_1 and V_2 represent the volumes in cm^3 of the two chambers, respectively.

In order to get solubility data at elevated pressures, more gas was introduced into the equilibrium cell to reach a new equilibrium. Duplicate experiments for each sample were run to obtain the averaged values of CO_2 solubility. The averaged reproducibility of the solubility data in this work was with 1% (see Scheme 2).

2.3. Synthesis of [DMAPAH][EOAc], [DEEDAH][EOAc] and [DMEDAH] [EOAc]

The PILs are synthesized according to reported literature through one step procedure [22]. As an example, the synthetic procedure of [DMAPA][EOAc] is described here. 5.10 g (0.05 mol) 3-(dimethyla-mino)-1-propylamine were dissolved in 50 ml ethanol in a 250 ml flask

with an ice bath, then 5.20 g (0.05 mol) ethoxyacetic acid in 50 ml ethanol is slowly drop wised. After 24 h of neutralization reaction, ethanol is removed by rotary evaporation and the product was subjected to vacuum drying for at least 48 h at 323.2 K. The [DEEDAH] [EOAc] and [DMEDAH][EOAc] are synthesized with the same procedure. 10 wt% deionized water is added into the pure PILs, then 90% [DMAPAH][EOAc], 90% [DEEDAH][EOAc] and 90% [DMEDAH] [EOAc] are produced. In this work these aqueous solutions of PILs are described on weight basis.

The spectra data of the pure PILs are given as follow:

[DMAPAH][EOAc]: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.56 (s, 3H), 3.83 (s, 2H), 3.53–3.46 (m, 2H), 3.01–2.95 (t, J = 6.3 Hz, 2H), 2.48–2.44 (m, 2H), 2.26–2.22 (m, z, 3H); ^{13}C NMR (16H), 1.83–1.75 (m, 2H), 1.21–1.15 (tt, J = 7.0, 1.8 H 00 MHz, CDCl$_3$) δ 176.3, 70.5, 65.9, 57.9, 45.0, 39.3, 24.4, 15.0. HRMS (EI+) Calcd for [C$_5$H$_{15}$N$_2$] (M$^+$): 103.12297, found 103.12352; HRMS (EI−) Calcd for [C$_4$H$_7$O$_3$] (M$^−$): 103.04007, found 103.03990. IR (ATR): ṽ 2974.5, 2869.0, 2822.0, 2777.3, 2148.1, 1590.6, 1463.4, 1421.6, 1403.5, 1319.7, 1262.1, 1219.1, 1177.1, 1118.4, 1075.0, 1039.7, 1013.1, 955.7, 934.2, 892.3, 855.5, 824.2, 752.1, 708.7, 604.6, 529.5, 471.1, 446.9, 405.8.

[DEEDAH][EOAc]: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.11 (s, 3H), 3.83 (s, 2H), 3.53–3.46 (q, J = 7.0 Hz, 2H), 2.92–2.88 (t, J = 6.2 Hz, 2H), 2.67–2.63 (t, J = 6.2 Hz, 2H), 2.58–2.51 (q, J = 7.1 Hz, 4H), 1.20–1.15 (t, J = 7.0 Hz, 3H), 1.01–0.96 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 176.5, 70.4, 66.0, 51.3, 50.2, 46.7, 46.5, 36.9, 14.9, 11.1. HRMS (EI+) Calcd for [C$_6$H$_{17}$N$_2$] (M$^+$): 117.13862, found 117.13912; HRMS (EI−) Calcd for [C$_4$H$_7$O$_3$] (M$^−$): 103.04007, found 103.03990. IR (ATR): ṽ 2972.2, 2934.4, 2875.0, 2138.1, 1587.9, 1471.5, 1450.2, 1421.2, 1403.5, 1319.4, 1205.7, 1175.8, 1188.6, 1074.5, 1032.9, 1012.6, 994.4, 934.3, 911.9, 892.1, 854.8, 767.6, 708.9, 602.7, 539.2, 418.2

[DMEDAH][EOAc]: ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.89 (s, 3H), 3.87 (m, 2H), 3.56–3.51 (m, 2H), 3.49 (s, 4H), 2.51(s, 6H), 1.22–1.18 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 176.8, 70.3, 66.0, 57.4, 47.3, 34.1, 18.3, 15.0. HRMS (EI+) Calcd for [C$_4$H$_{13}$N$_2$] (M$^+$): 89.10732, found 89.10746; HRMS (EI−) Calcd for [C$_4$H$_7$O$_3$] (M$^−$): 103.04007, found 103.03990. IR (ATR): ṽ 2974.3, 2934.5, 2855.0, 2803.3, 2466.7, 1601.9, 1450.1, 1425.4, 1367.2, 1175.4, 1122.9, 1077.3, 1037.2, 930.5, 893.2, 854.4, 793.2, 704.9, 608.1, 420.4.

The pH of 90% [DMAPAH][EOAc], 90% [DEEDAH][EOAc] and 90% [DMEDAH][EOAc] are 9.6, 8.7 and 9.4 respective.

3. Results and discussion

3.1. Physical property

3.1.1. Density of PILs

The density is one of basic physical properties to calculate gas solubility based on Eq. (2) for the process of absorption. Trends of densities of the three 90% PILs are measured in the temperature range of 303.2 K–333.2 K. The Eq. (2) where a and b are adjustable parameters was applied to linearly correlate between the temperature T and density ρ. The results are graphically shown in Fig. 1 and the related model parameters are shown in Table 1. The density data of three ILs could be fitted linear Eq. (2), because R^2 are all above 0.999. It can be seen that the density of three ILs are all above 0.9600 g/cm^3 with the ranking of 90% [DEEDAH][EOAc] < 90% [DMAPAH][EOAc] < 90% [DMEDAH][EOAc]. The 90% [DEEDAH][EOAc] has the lowest density and could be ascribed to its steric structure in comparison with the others.(see Fig. 2)

$$\rho = a + bT\,(K) \tag{2}$$

Density data provide a solution to deduce coefficient of the thermal expansion which could be calculated by the following Eq. (3), where α is the thermal expansion coefficient, V is the volume of ILs. The value of α is obtained from the experimental data of $ln\rho$ against T by the
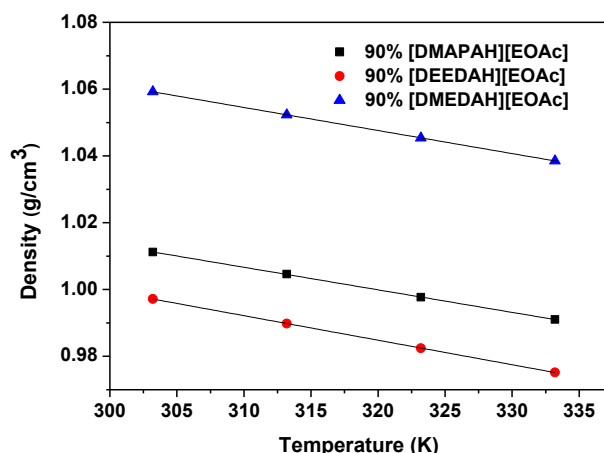

Fig. 1. Plot of density ρ vs temperature T of ILs.

empirical Eq. (4) where β is adjustable parameter. Therefore, the value of α is acquired from the fitting line, the result are summarized in Table 2, with the lowest for 90% [DMEDAH][EOAc] and the highest for 90% [DEEDAH][EOAc]. The obtained value of α is between 6.5×10^{-4} and 7.5×10^{-4} K^{-1}, which is same order of magnitude of other ILs, such as sulfonium [24], imidazolium [25] and pyridinium [26] based ILs. It seems that cation shows a lower impact on the thermal expansion coefficient than that reported for the anion replacement [27].

$$\alpha = -\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial ln\rho}{\partial T}\right)_p \tag{3}$$

$$ln\rho\ (\text{g·cm}^{-3}) = \beta - \alpha T\,(K) \tag{4}$$

The viscosities which play a crucial role during the process design of CO$_2$ capture [28,29]. Normally, the lower value of viscosity would be lower barrier for gas molecular transferring from gaseous phase to liquid phase. The viscosities are determined from 303.2 to 333.3 K and the relationship between viscosities and temperature are shown in Fig. 3. The viscosities of OA-ILs decrease non-linearly with the increase of temperature. The 90% [DEEDAH][EOAc] has the lowest value of viscosity than that of 90% [DMAPAH][EOAc] and 90% [DMEDAH] [EOAc].

The Arrhenius equation is common empirical equation to accurately fit the temperature-dependent viscosity of ILs when the cations present only a limited symmetry [30].

$$\eta = \eta_0 \exp(E_a/RT) \tag{5}$$

whereη is viscosity, cP; E_a is activation energy of viscous flow, J·mol^{-1}; T is temperature, K; R is universal gas law constant, J·K^{-1}·mol^{-1}; η_0 is viscosity at infinite temperature, cP.

Fitting results are summarized in Table 3. The activation energy of 90% [DMEDAH][EOAc] is close to that of 90% [DMAPAH][EOAc] and the value are 45.09 and 46.79 kJ·mol^{-1} respectively. 90% [DEEDAH] [EOAc] has the lowest activation energy data than that of the others. Higher value of activation energy indicates higher intermolecular resistance between the anions and cations.

3.2. Absorption of CO$_2$ with organic amines

Three kind of organic amines, 3-(dimethylamino)-1-propylamine (DMAPA), N,N-diethylethylenediamine (DEEDA) and N,N-dimethylethylenediamine (DMEDA), are often used in metal-organic framework (MOF) or membrane to enhance CO$_2$ capture [31,32]. However, there are no enough data about the capacity of CO$_2$ in these amines. Therefore, capacity of CO$_2$ in the three amines is measured as function of pressure at 303.2 K for this purpose (Fig. 4). With expectation, the

Table 1
The fitted data from the experiment value of ρ against *T*.

PILs solution	a/g·cm^{-3}	b/g·cm^{-3}·K^{-1}	R^2
90% [DMAPAH][EOAc]	1.2159 ± 0.0012	$-6.75 \times 10^{-4} \pm 3.87 \times 10^{-6}$	0.9999
90% [DEEDAH][EOAc]	1.2197 ± 0.0011	$-7.34 \times 10^{-4} \pm 3.46 \times 10^{-6}$	0.9993
90% [DMEDAH][EOAc]	1.2684 ± 0.0000	$-6.90 \times 10^{-4} \pm 4.02 \times 10^{-6}$	0.9999
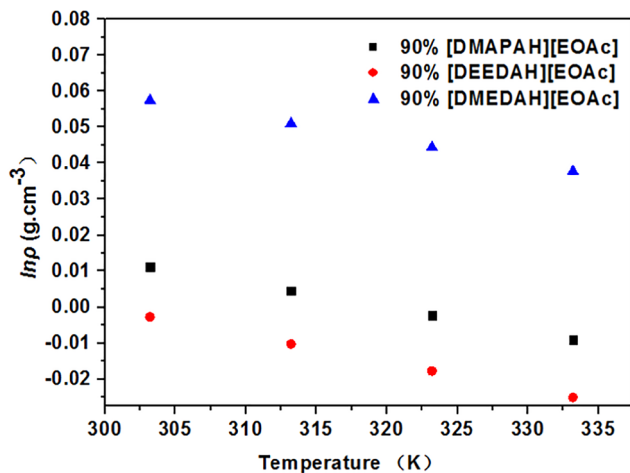
Fig. 2. Plot of density *lnρ* vs temperature *T* of the ionic liquids.
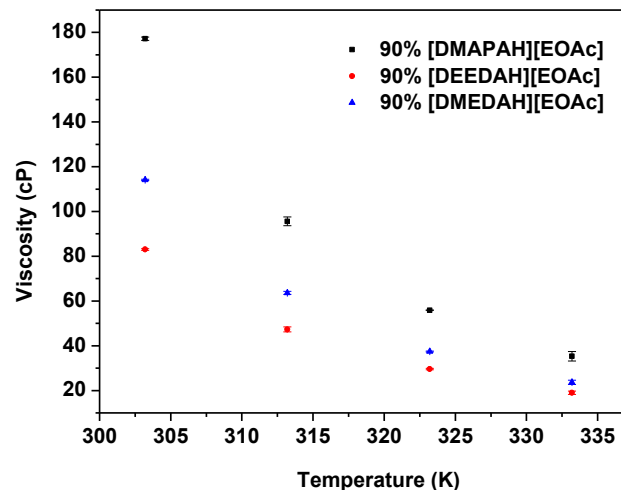
Fig. 3. Viscosity of PILs at different temperatures.

capacity of CO_2 of three amines increases with the increasing pressure. As can be seen, CO_2 absorption curves for DMEDA and DMAPA are very similar. It might be chemical absorption under the pressure of 0.15 bar. After that, there is nearly no obvious addition of absorption excluding physical absorption. For DEEDA two inflexions occurred under the pressure of 0.1 bar and 0.7 bar respectively. It would be explained that two active amine protons of DEEDA distribute dispersedly in comparison of DMEDA and DMAPA leading to hysteresis. The ranking of CO_2 capacity in three amines are DMEDA > DEEDA > DMAPA with the value of 11.24 mol/kg, 7.93 mol/kg and 5.91 mol/kg respectively. Obviously, all of three organic amines have highly superiority of CO_2 capacity than that of most of ILs which is about 1–3 mol/kg according to G K Cui's review [33]. Although CO_2 capacity for some special ILs have relative higher value, for instance, [MTBDH][TFE] [34], [AEMP] [Pro] [35] and [AEMP][Gly] [36] is 4.46 mol/kg, 5.96 mol/kg and 6.87 mol/kg respectively, which is far below that of DMEDA. However, after absorption of CO_2 all three organic amines convert into solid compounds and hardly to be reused again. That is the reason we designed the three PILs solutions which would play impressive role for CO_2 uptake. It is necessary to determine the CO_2 capacity of the three PILs solution, recyclability and mechanism in the following study.
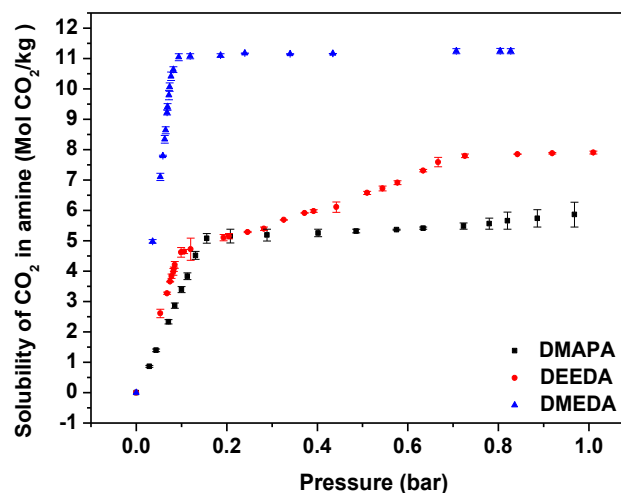
Table 3
Activation energy of PILs fitted by Arrhenius equation.

PILs	η_0/cP	E$_a$/J·mol^{-1}	R^2
90% [DMAPAH][EOAc]	1.53×10^{-6}	46.79×10^3	0.9988
90% [DEEDAH][EOAc]	4.39×10^{-6}	42.22×10^3	0.9987
90% [DMEDAH][EOAc]	1.94×10^{-6}	45.09×10^3	0.9995

Fig. 4. The capacity of CO_2 in different amines at 303.2 K.

3.3. Absorption of CO_2 with PILs

The solubility of CO_2 in the three aqueous solutions of PILs with different amines is shown in Fig. 5. Temperature and pressure are two crucial factors that influence the solubility of CO_2 in the ILs. As shown, the solubility of CO_2 increases with the increasing pressure and decreases with the increasing temperature as the majority of gases do in

Table 2
The fitting data from the experiment value of *lnρ* against *T*.

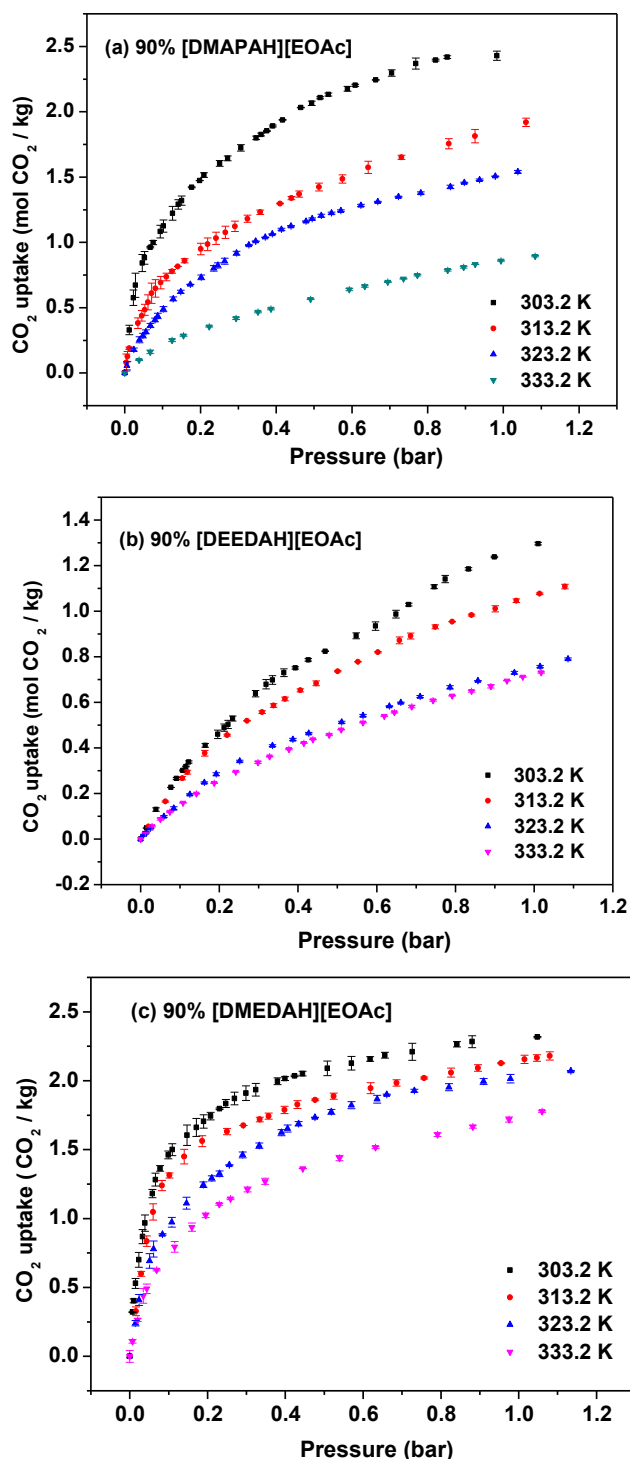| PILs solution	α/g·cm^{-3}	β/g·cm^{-3}·K^{-1}	R^2
90% [DMAPAH][EOAc]	$6.7428 \times 10^{-4} \pm 4.62 \times 10^{-6}$	0.21 ± 0.001	0.9998
90% [DEEDAH][EOAc]	$7.4430 \times 10^{-4} \pm 2.06 \times 10^{-6}$	0.22 ± 0.0006	0.9999
90% [DMEDAH][EOAc]	$6.5788 \times 10^{-4} \pm 1.37 \times 10^{-6}$	0.26 ± 0.0004	0.9999

Fig. 5. Absolute CO_2 solubility in 90% [DMAPAH][EOAc] (a) 90% [DEEDAH] [EOAc] (b) and 90% [DMEDAH][EOAc] (c) at different temperature.

the ILs. Using 90% [DMAPAH][EOAc] as an example, the solubility of CO_2 is 1.89 mol/kg at 313.2 K while it is 0.86 mol/kg at 333.2 K under the same pressure of 1.0 bar. The solubility of CO_2 is 0.95 mol/kg at the pressure of 0.2 bar while it is 1.42 mol/kg at the pressure of 0.5 bar at the same temperature of 313.2 K. The curve of 90% [DMEDAH][EOAc] showed that the CO_2 solubility increased steeply under the low pressure (0–0.2 bar), then leveled off in the high pressure (0.2–1.0 bar) (Fig. 5c). In low-pressure region, chemical absorption plays a dominating role leading to conspicuous increase of capacity CO_2 with the gradually increasing partial pressure. In high-pressure region, physical absorption

plays the leading role as most of common ILs has been done with CO_2. However, the curve of 90% [DMAPAH][EOAc] and 90% [DEEDAH] [EOAc] show similar tendency and there are no obvious inflexion as 90% [DMEDAH][EOAc]'s. Considering the effect of cations on the CO_2 capture, it is shown that the capacity of CO_2 in the PILs containing the same anions following the subsequent trend, [DMAPAH] > [DMEDAH] > [DEEDAH]. The result reveals cation from the stronger organic amine leads to the increase of capacity of CO_2 in the PIL solution, as uptake of CO_2 in 90% [DEEDAH][EOAc] solution with 1.30 mol/kg ILs are less than that of 90% [DMAPAH][EOAc] which is 2.44 mol/kg ILs at the temperature of 303.2 K under the pressure of 1 bar. It is found that 90% [DMEDAH][EOAc] whose cations comprise diamine group show competitive performance of CO_2 capture with 2.32 mol/kg ILs (T = 303.2 K, P = 1.05 bar), relative to 90% [DMAPAH][EOAc] containing cation of primary and tertiary amine groups. The capacity of CO_2 in the all three PILs solution decreased comparing with pure organic amines. The main difference between the PILs solution and organic amine is that the amine groups in the former are protonated while the latter are not, and react with CO_2 directly and quickly. Although CO_2 soluble capacity of PILs solution shows lower performance than that of amine, we still believe that these PILs solutions could be potential absorbents as we has discussed in above. In addition, PILs and its solution can be recovered at low temperature for CO_2 capture according to the study from the D R MacFarlane group [21].

In order to compare absorption of these three PILs solutions to other absorbents including reported PILs, functional ILs, traditional ILs and amines are summarized in Table 4. It has been seen that 90% [DMAPAH][EOAc] and 90% [DMEDAH][EOAc] displays superior

Table 4
Comparison of the solubility of CO_2 in functionalized ILs under 1 bar.

Entry	Absorbent	T/K	CO_2 uptake (mol/kg)	CO_2 uptake (%w/w)	Ref
1	90% [DMAPAH][EOAc]	303.2	2.44	9.7	This work
2	90% [DEEDAH][EOAc]	303.2	1.28	5.3	This work
3	90% [DMEDAH][EOAc]	303.2	2.32	9.3	This work
4	[DMAPAH][For][a] (70% wt)	308.2	2.50	9.9	[37]
5	[DMAPAH][F][b] (70% wt)	308.2	3.62	13.7	[37]
6	[DMAPAH][Ac][c]	293.2	1.87	7.4	[21]
7	[DMAPAH][For]	293.2	1.73	8.3	[22]
8	[DMEDAH][For]	293.2	2.83	12.3	[22]
9	[DEEDAH][For]	293.2	2.90	12.6	[21]
10	[DEEDAH][Ac][c]	293.2	1.70	7.4	[21]
11	[N$_{1111}$][Gly][d]	298.2	1.15	4.8	[38]
12	[N$_{1111}$][Gly]–H$_2$O (80% wt)	298.2	1.69	6.9	[38]
13	[N$_{2224}$][Ala][e]	313.2	∼1.95	7.9	[39]
14	[P$_{66614}$][3-Cl-PhO]	303.2	1.18	4.9	[40]
15	[P$_{4444}$][4-F-PhO]	313.2	2.27	9.1	[41]
16	[N$_{2224}$][Met][f]	313.2	0.73	3.1	[42]
17	[N$_{2224}$][Cro][g]	313.2	1.23	5.1	[42]
18	[Emim][Ac]	298.2	2.12	8.5	[43]
19	DEA (30% wt)	313.2	2.17	8.7	[7]
20	MDEA	303.2	2.07	8.4	[44]
21	[Bmim][Gly]–MDEA (5%)	303.2	2.20	8.8	[45]
22	[Bmim][PF$_6$]–DBU	296.2	1.72	7.0	[46]

[a] [For] represents formic acid anion.
[b] [F] represents hydrofluoric acid anion.
[c] [Ac] represents acetic acid anion.
[d] [Gly] represents glycine anion.
[e] [Ala] represents alanine anion.
[f] [Met] represents methacrylic acid anion.
[g] [Cro] represents crotonic acid anion.

performance on the capacity of CO_2 in comparison with functional ILs (entry 6–7, 10–17), common ILs (entry 18), traditional amines (entry 19–20), as well as ionic liquid mixed with amine absorbent (entry 21–22). Especially, MDEA and DEA are commonly employed for chemical capture of CO_2 in the industry. Even 90% [DEEDAH][EOAc] which is lowest CO_2 capture capacity among the three PILs shows some weak advantage than [N$_{1111}$][Gly] and [P$_{66614}$][3-Cl-PhO] (entry 11, 14).

It is noticed that the uptake of [DMAPAH][For] (70% wt) is 2.50 mol/kg, increased by 32% comparing with that of pure [DMAPAH][For] 1.87 mol/kg, implying the positive effect of water for CO_2 capture. In addition, it is noted that the CO_2 uptake of [DMAPAH] [For] Vs [DMEDAH][For] and [DEEDAH][For] vs [DEEDAH][Ac] are illustrated group effects in the different anions of ILs (entry 7–10). Thus, the above specifications point to the fact that both water content and ILs structures can take fundamental effect of CO_2 capacity in the ILs. So it is easy to understand the different CO_2 performance among the three PILs solutions we synthesized in comparison with other similar aqueous PILs (entry 4–5). It is well known that normal ILs often has higher viscosity and prices which hinder their wide application in the industry during the past decades. For instance, viscosity of [N$_{1111}$][Gly] is 304 cP at 298 K respectively, while that of 90% [DMAPAH][EOAc] is 244 cP which is fitted results from the Arrhenius equation at the same temperature. To prepare [N$_{1111}$][Gly], silver salt method through nucleophilic substitution of imidazole and anion exchange is often applied to get base [N$_{1111}$][OH] for neutralizing glycine where expensive materials are required [39,42]. As a contrast, pure [DMAPAH][EOAc], [DMEDAH][EOAc] and [DEEDAH][EOAc] in this work can be easily synthesized by one step through neutralizing of amine and ethoxyacetic acid. Hence, they are considered as attractive absorbents to others for CO_2 capture.

[DMAPAH][EOAc] and MEA mixtures with different water concentrations were prepared and determined for CO_2 capture at 313.2 K under the pressure of 1 bar. As shown in Fig. 6, with the increased water content from 10% to 30% in MEA the solubility of CO_2 decreased gradually. In the comparison of MEA solution's CO_2 capacity, the solubility of CO_2 in [DMAPAH][EOAc] initially increased when water concentration added from 10% to 20%, then solubility of CO_2 decreased when water content continued to increase from 20% to 30%. A similar situation has been found in [DMAPAH][formate] water mixtures [22]. The decreased absorption ability for aqueous [DMAPAH][EOAc] could be attributed to dilute active absorber and the increased absorption might be ascribe to the simultaneous formation of carbamate and bicarbonate species at some lower water concentration [22]. It was worth noticing that [DMAPAH][EOAc] with 20% water had more CO_2 capacity than that of MEA with 20% water.
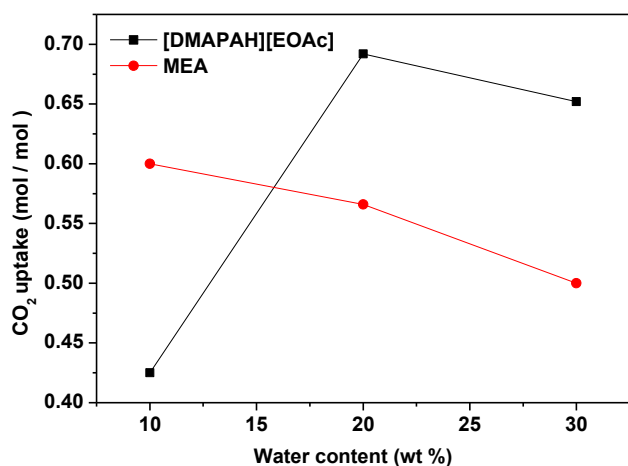

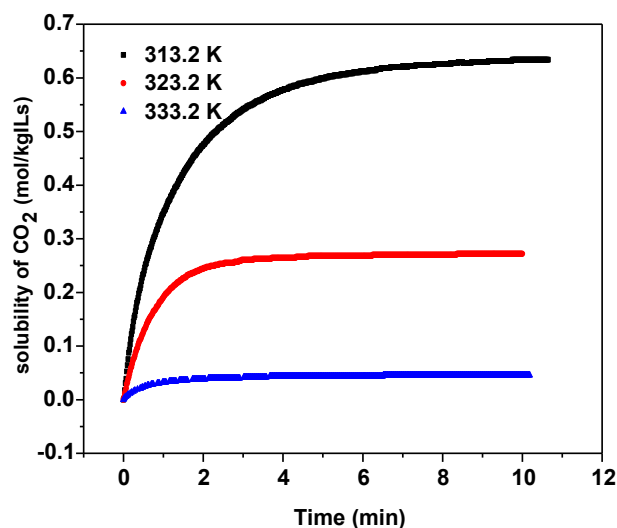**Fig. 6.** Effect of water content on CO_2 capture in [DMAPAH][EOAc] and MEA.

Fig. 7. Kinetic absorption of CO_2 in the 90% [DMAPAH][EOAc] solution at 313.2–333.2 K under 1 bar.

To obtain kinetic absorption of CO_2 in the absorbent at different temperatures, 1 g absorbent is put in the equilibrium cell. Next, vacuum the cell several times to make sure the residual pressure under the 15 bar. Before CO_2 in the gas reservoir is injected into the equilibrium cell to get about 1 bar gas, timer in the computer is set to record pressure one time per second lasted for at least 4 min until the absorption equilibrium arrives.

The absorption kinetics of CO_2 in 90% [DMAPAH][EOAc] solution was performed at $P_0 = 1$ bar, T = 313.2–333.2 K (Fig. 7). As can been seen that the CO_2 capacity of aqueous PILs decreased dramatically with the increase of temperature, the absorption equilibrium arrived following this order 333.3 K > 323.2 K > 313.2 K. It is found that 90% [DMAPAH][EOAc] solution capture CO_2 in a quite higher rate than [DMAPAH][F] (70% wt) which have more CO_2 capacity than ours according to the study [37]. For example, the absorption equilibrium for 90% [DMAPAH][EOAc] is arrived within 6 min while that for [DMAPAH][F] (70% wt) is about 50 min. According to previous study MDEA was mixed with ILs to pursue higher absorption rate for CO_2, equilibrium arrived at least 20 min [38]. The amount of absorbed CO_2 in 90% [DMAPAH][EOAc] is about 0.63 mol/kgILs, suggesting the advantages of 90% [DMAPAH][EOAc]. To further investigate absorption rate, the apparent absorption rate constant is introduced. The reaction rate equation is expressed by Eq. (6)

$$r = -\frac{dc_{Co_2}}{dt} = k \cdot c_{IL} \cdot c_{Co_2} \tag{6}$$

where c_{IL} is the concentration of PILs in solution, which is denoted to be a constant compared with the concentration of CO_2 (c_{Co_2}). For the isothermal absorption of gas, the follow Eq. (7) could be described the relationship between CO_2 partial pressure and time according to the Damping-Film Theory [47].

$$ln\frac{P_0 - P_e}{P - P_e} = ut \tag{7}$$

where P is partial pressure of CO_2 at time t, P_0 and P_e are the partial pressure at the beginning and the absorption equilibrium, respectively, u is apparent absorption rate constant as well as k. The Eq. (7) could be rewritten in form of n, which represents amount of CO_2, assuming that CO_2 is ideal gas.

$$ln\frac{n_0 - n_e}{n - n_e} = kt \tag{8}$$

Apparent absorption rate constant k is obtained from the slope of the plot of $ln\frac{n_0 - n_e}{n - n_e}$ Vs t (Fig. 8). The values of k are calculated by Eq. (8)
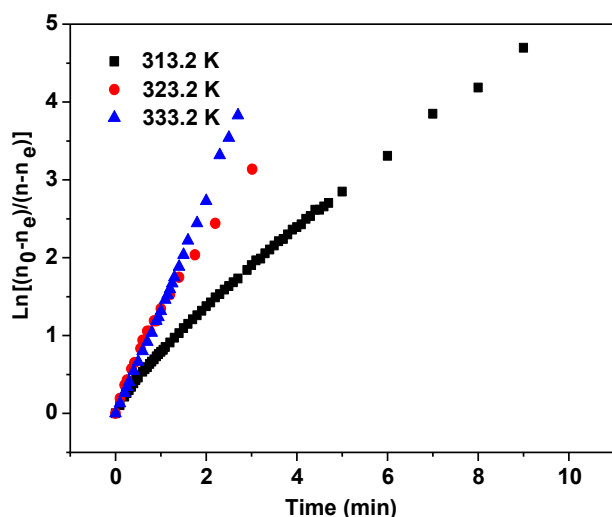
Fig. 8. The apparent absorption rate of 90% [DMAPAH][EOAc] solution at 313.2–333.2 K under 1 bar.

at 313.2 K, 323.2 K and 333.2 K, the results are summarized in Table 4. The value of k is 0.52 ± 0.006 at 313.2 K, which is two times of [DMAPAH][F] (70% wt) at 328.2 K. As can be seen the value of k at 333.2 K is highest which is nearly three times of that in 313.2 K.

The temperature dependency of the apparent absorption rate constant k is correlated with the Arrhenius equation as follow,

$$lnk = -\frac{E_a}{RT} + A \tag{9}$$

where E_a is the apparent reaction activation energy, T is the temperature, A is a constant. The activation energy E_a is obtained by linear fitting the plot lnk Vs $1/T$. As shown in Fig. 9, the linear relationship between lnk and $1/T$ are good, the value of R^2 is 0.9345. According to the slope (-5222) of the line, the value of E_a is 43.4 ± 7.9 kJ·mol^{-1} which is lower than that of [DMAPAH][F] (70% wt) illustrating easy desorption for next absorption cycle. Furthermore, it is comparable to the traditional absorbents (MEA, DEA and MDEA) with the value from 30 to 56 kJ·mol^{-1} [48], implying the superiority of 90% [DMAPAH][EOAc] (see Table 5).

3.4. The proposal mechanism of PILs solution for CO_2 capture

According to Donaldson and Nguyen's theory, tertiary amines including MDEA can't directly combine with CO_2 and the reaction
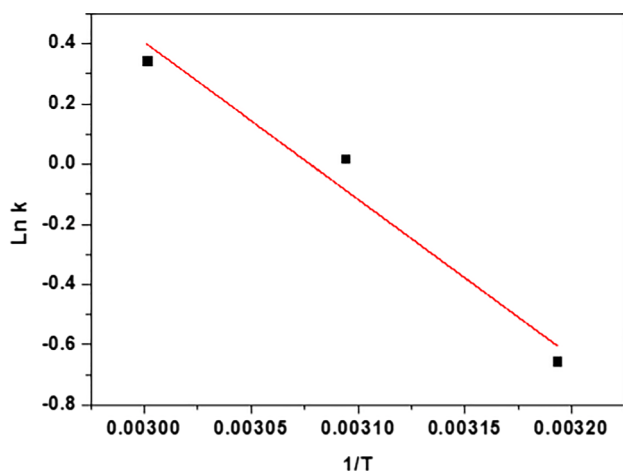

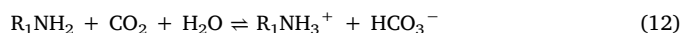**Fig. 9.** The linear fit of lnk Vs $1/T$.

Table 5
The apparent absorption rate constant k of 90% [DMAPAH][EOAc] solution at different temperatures.

Entry	T (K)	k (min^{-1})
1	313.2	0.52 ± 0.006
2	323.2	1.02 ± 0.032
3	333.2	1.42 ± 0.013

proceeds with a base-catalyzed CO_2 hydrolysis in a low absorption rate [49].

$$RN + CO_2 + H_2O \rightleftharpoons RNH^+ + HCO_3^- \tag{10}$$

For the [DMEDAH][EOAc] solution the potential mechanism could be proposed according to F Zhang's study [38]. The balance beween BrØnsted acid and BrØnsted base in PILs could be easily changed in the presence of water, the reaction are shown as following,

$$R_1NH_3^+R_2COO^- \rightleftharpoons R_1NH_2 + R_2COOH \tag{11}$$

$$R_1NH_2 + CO_2 + H_2O \rightleftharpoons R_1NH_3^+ + HCO_3^- \tag{12}$$

The zwitterion is obtained through the reaction of CO_2 with R_1NH_2,

$$R_1NH_2 + CO_2 \rightleftharpoons R_1NH_2^+COO^- \tag{13}$$

Then, the zwitterion could be deprotonated by base B including RNH_2, H_2O, OH^-, etc.

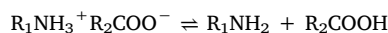$$R_1NH_2^+COO^- + B \rightleftharpoons R_1NHCOO^- + BH^+ \tag{14}$$
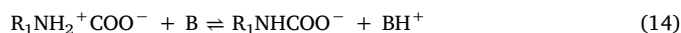
For the aqueous solution of PILs, the carbamate could be formed through the reaction between CO_2 and RNH_2, the CO_2 load is no more than 0.5 mol/mol PILs. The two steps of reaction is summarized as following,

$$2R_1NH_2 + CO_2 \rightleftharpoons R_1NHCOO^- + R_1NH_3^+ \tag{15}$$
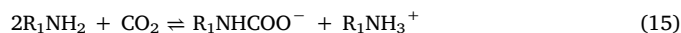
For the solution of [DMEDAH][EOAc] comprising tertiary amine group, the proton could be transferred from the $R_1NH_2^+COO^-$ to RN through intermolecular interaction.

$$R_1NH_2^+COO^- + RN \rightleftharpoons R_1NHCOO^- + RNH^+ \tag{16}$$

In the process of CO_2 capture, when the amines are produced, they could react quickly with CO_2 to form zwitterions and transfer proton to tertiary amine group through intermolecular way. The whole equilibrium reactions are suggested as follow,

$$R_1NH_3^+R_2COO^- \rightleftharpoons R_1NH_2 + R_2COOH$$

$$R_1NH_3^+ \rightleftharpoons R_1NH_2 + H^+ \tag{17}$$

$$CO_2 + H_2O \rightleftharpoons 2H^+ + CO_3^{2-} \tag{18}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{19}$$

$$RNH^+ \rightleftharpoons RN + H^+ \tag{20}$$

3.5. The recyclability of PILs solution

To test the recyclability and consistency of 90% [DMAPAH][EOAc], desorption of CO_2 is evaluated after 1.0 g 90% [DMAPAH][EOAc] is saturated by CO_2 in an airtight vessel at 303.2 K under the pressure of 1 bar. The CO_2-saturated 90% [DMAPAH][EOAc] is recovered by multiple evacuation of CO_2 through vacuuming the equilibrium cell about 10 Pa. Normally, higher temperature and lower pressure are necessary to remove CO_2 from the absorbents, here the latter is adopted to prevent the evaporation of water at the room temperature. The regenerated 90% [DMAPAH][EOAc] is recycled directly for the next time to measure the capacity of CO_2 without any treatment. The absorption-
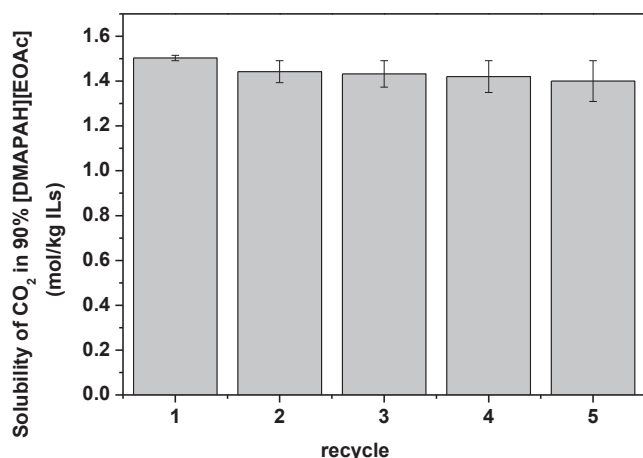
Fig. 10. The recyclability of 90% [DMAPAH][EOAc] at 303.2 K.

desorption is conducted five times, the results are shown in Fig. 10. The capacity of CO_2 for 90% [DMAPAH][EOAc] has slightly decreased compared with the above cycle. It might be lost trace water in the PILs solution which is necessary for CO_2 uptake during the vacuuming leading to loss of capacity. The results suggest that the absorption of CO_2 by 90% [DMAPAH][EOAc] is incredibly reversible.

4. Conclusion

In summary, [DMAPAH][EOAc], [DEEDAH][EOAc] and [DMEDAH][EOAc] were synthesized through one-step procedure and 10% water were added in the pure PILs to get high contents of PILs solution, 90% [DMAPAH][EOAc], 90% [DEEDAH][EOAc] and 90% [DMEDAH][EOAc]. The physical properties including density and viscosity were measured. To compare with pure amines for CO_2 uptake, the solubility of CO_2 in three PILs solutions was systematically determined from 303.2 K to 333.2 K under the pressure of 1.2 bar. The results illustrated that three PILs solution could efficiently capture CO_2 and showed their superiority to some absorbents. It is found that the solubility of CO_2 in the 90% [DMAPAH][EOAc] reached up to 2.44 mol/kg at 1 bar. Through the kinetic investigation, 90% [DMAPAH][EOAc] could capture CO_2 with quick rate, then apparent absorption rate constant k and activation energy E_a were also obtained from the dynamic data. The proposal mechanism of 90% [DMAPAH] [EOAc] was suggested. In addition, 90% [DMAPAH][EOAc] could be easily recycled four times and showed its stable consistency as an absorbent, while pure amines hardly recovered from solid state after CO_2 capture. Therefore, those three PILs solutions are expected as promising absorbents in the future.

CRediT authorship contribution statement

Liang Wei: Investigation, Writing - original draft. **Ruifeng Guo:** Investigation. **Yunqing Tang:** Data curation. **Jiamin Zhu:** Data curation. **Meiyang Liu:** Formal analysis. **Jianqiu Chen:** Conceptualization. **Yun Xu:** Conceptualization, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2020.116531.

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