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Reversible carbon dioxide capture at high temperatures by tetraethylenepentamine acetic acid and polyethylene glycol mixtures with high capacity and low viscosity

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ABSTRACT

Ionic liquids (ILs) are investigated in many studies to capture CO_2 in recent years. However, almost all of these studies carried out the absorption of CO_2 by ILs at relatively low temperatures (lower than 333.15K or even around the room temperature). Besides, the viscosity of ILs increases dramatically after absorbing CO_2 which could reduce the absorption efficiency significantly. Reversible and efficient absorption of CO_2 at high temperatures was investigated by IL of tetraethylenepentamine acetic acid ([TEPA]Ac) and polyethylene glycol 200 (PEG-200) mixtures with low viscosity. The results showed that the absorption capacity

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of [TEPA]Ac/PEG-200 mixtures achieved to 1.24 mol CO_2 per mole [TEPA]Ac at 353.15 K at ambient pressure (1.01 bar). The mixtures could be easily regenerated by bubbling dried N_2 through them. The addition of PEG-200 in the [TEPA]Ac could increase the efficiency of absorption and desorption significantly. Furthermore, the solubility data of CO_2 in the [TEPA]Ac/PEG-200 mixtures at T = (353.15, 368.15, 383.15, and 398.15) K under different pressures were measured and the solution enthalpy (ΔH_{sol}) and solution entropy (ΔS_{sol}) were calculated. Under all the conditions, the negative value of ΔH_{sol} indicated that the capture process is exothermic. The process of CO_2 capture described that using [TEPA]Ac/PEG-200 mixtures is a promising approach for CO_2 absorption with high reversibility and excellent absorption property at a relatively high temperature.

Keywords: Carbon capture, Ionic liquid, Tetraethylenepentamine acetic acid, Polyethylene glycol, High temperature, High capacity

1. Introduction

The emission of CO_2 from fossil fuel combustion causes serious effect to the environment and contributes to global warming and ocean acidification. Therefore, the concept of carbon capture and storage (CCS) has drawn considerable attention by the researchers during these years [1, 2]. The carbon capture technologies such as absorption, adsorption, and membrane gas separation technologies are developed and applied worldwide [3-8]. Physical absorbents, such as monoethanolamine (MEA), can absorb CO_2 at high partial pressures and low temperatures, which have been used industrially for many years. However, large energy consumption was consumed and partial decomposition occurred during regeneration process. Adsorption materials, such as carbon-based sorbents (e.g. carbon molecular sieves) and metal oxides (e.g. CaO, Li_2ZrO_3) have been used for CO_2 capture at high temperature (above 300□). For example, the CaO can capture CO_2 at 600-800□ with the mole ratio approach of 1.0 and regenerated at 800-850□. In addition, membrane is also a type of promising utilization of reversible material for CO_2 capture. The advantages of membrane absorption material are selective extraction of CO_2 from mixed gas streams and flexibility in their possible configurations in industrial plants. However, a common disadvantage of the membrane materials is their lack of stability under the application environment [7-10]. Therefore, seeking promising alternatives with low energy consumption and high stability to these solvents is desirable.

Ionic liquid (IL) is a promising material regarded as a kind of environmentally-friendly solvent which processes some superior properties, for example, wide liquid temperature range, low vapor pressure, high thermal and chemical stability, and excellent solvent power [11, 12]. Recently, there is a significant progress in the application of IL for CO_2 capturing.

Blanchard et al. [13] firstly reported that CO_2 could be absorbed by 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF_6] effectively, but the IL of [BMIM][PF_6] could not be dissolved in CO_2. After that, many researchers were engaged in the study of CO_2 capturing with ionic liquid [14, 15]. Bates et al. [16] synthesized a kind of IL by inducing a primary amine moiety and tetrafluoroborate anion to the structure of imidazolium cation and studied its property related to CO_2 absorption. Their results showed that the IL had a good effect on carbon absorption and molar absorption ratio of CO_2 to IL could approach 0.5. Galan Sanchez et al. [17] studied the absorption of CO_2 in different imidazolium-based ILs. They found out that the efficiency of CO_2 absorption increased significantly by attaching basic groups to the structure of the ILs. Gurkan et al. [18] reported that equimolar amount of CO_2 could be absorbed by the IL with amino acids anion. Zhang et al. [19] synthesized the phosphonium-based ILs with various amino acid anions for carbon capture. When the ILs were saturated with CO_2, the mole ratio of CO_2 to IL approached to 1.0.

Although ILs have many attractive superiorities for CO_2 capturing, they still have some drawbacks that need to be modified, such as promoting the absorption capacity and decreasing the viscosity [20, 21]. Furthermore, the capacity of CO_2 absorption by the present ILs declined dramatically when temperature elevated to 353.15 K [22]. Thus, their application for the CO_2 capture and storage was limited at low temperatures, being less than 333.15 K or even at room temperature [23, 24]. However, temperature of the flue gas is usually higher than room temperature and ranges from 353.15 K to 393.15 K. Therefore, designing new absorbents to capture CO_2 at higher temperatures (from 353.15 K to 393.15 K), with high absorption capacity, and high efficiency is required.

In the present work, a new type of IL-based adsorbent of tetraethylenepentamine acid ([TEPA]Ac) and [TEPA]Ac in polyethylene glycol (PEG) with average molecular weight of 200 g/mol (PEG-200) was studied for carbon capture. PEG-200 was mainly selected as a solvent to dissolve [TEPA]Ac in order to decrease the viscosity of the IL after absorbing CO_2. Also, PEG has other important advantages, such as nontoxic, biodegradable, nonvolatile, and cheap [25, 26]. In addition, the solubility of CO_2 in [TEPA]Ac/PEG-200 mixture at four temperatures under different pressures was also measured and the thermodynamic parameters were calculated by the thermodynamics theory and solubility data.

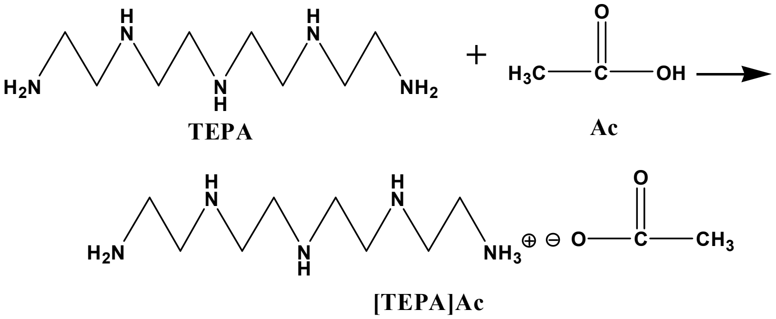
2. Materials and methods

2.1 Materials

CO_2 (99.999%) and N_2 (99.999%) were provided from Messer Gases Co. Ltd. (Guangzhou, China). Tetraethylenepentamine (TEPA) (≥ 99%) was supplied by Damao chemical reagent Co. Ltd. (Tianjin, China). Acetic acid (Ac) (≥ 99.5%) and polyethylene glycol (PEG-200, ≥ 99.5%) were purchased from Runjie chemical reagent Co. Ltd. (Tianjin, China).

2.2 Synthesis of [TEPA]Ac and the preparation of [TEPA]Ac/PEG-200 mixtures.

[TEPA]Ac was synthesized in following reaction:



The procedure included following steps: 1) 0.5 mol of TEPA and 150 mL of water were added into a 500 mL three-necked flask which was placed in an ice-water bath with a magnetic stirrer; 2) 0.5 mol of Ac was added dropwise from a pressure funnel to the flask over about 1.0 h. Then the reaction continued for 8 h at 298.15 K. 3) After that, the water was removed by a rotary evaporator and being dried under vacuum at 353.15 K for more than 48 h before use. After the drying process, the fractions of water were less than 0.5% which were determined by Karl Fischer titration.

The mixtures of [TEPA]Ac/PEG-200 were prepared with mass ratio of [TEPA]Ac to PEG-200 at 1:1, 1:2 and 1:3 by an analytical balance (AR224CN, OHAUS) with a precision of 0.1 mg. After mixing, the solutions were kept in the vacuum oven at 353.15 K for 48 hours to remove the volatile impurities and possible traces of water and then stored in a desiccator.

2.3 Absorption and desorption of CO_2

The process of absorption and desorption of CO_2 was carried out at ambient pressure. Figure 1 shows an experimental device for absorption and desorption of CO_2 by [TEPA]Ac. The temperature of an oil bath was controlled by a thermo controller. About 5.0 g of the [TEPA]Ac/PEG-200 mixture was loaded in the glass tube which was partly immersed in the oil bath at desired temperature, and then CO_2 was bubbled through the absorbent at the rate of 100 cm^3/min which was controlled by the gas rotameter.

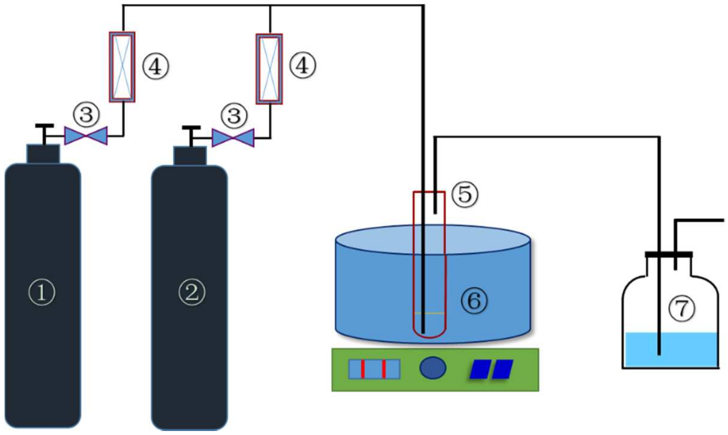


Fig. 1 Experimental device for CO_2 absorption and desorption by [TEPA]Ac: ① Cylinder

filled with pure N_2; ② Cylinder filled with pure CO_2; ③ Valves; ④ Flow meters; ⑤ Glass tube filled with [TEPA]Ac or [TEPA]Ac /PEG-200; ⑥ Oil baths; ⑦ NaOH aqueous solution for absorbing the exhaust CO_2.

The total weight of the glass tube including adsorbent and the needle was measured at regular intervals by an analytical balance (AR224CN, OHAUS). Then the absorbed CO_2 could be calculated through the weight increase of the glass tube. After that, dried N_2 was bubbled through the solution to regenerate the absorbent. The absorption of pure N_2 in [TEPA]Ac and [TEPA]Ac/PEG-200 mixtures at 353.15 K was also measured. The results showed that the content of N_2 absorbed by the [TEPA]Ac was less than 0.1%, which could be neglected during this study.

The viscosity of [TEPA]Ac/PEG-200 during the absorption of CO_2 was measured by a shear rate-controlled rheometer (Brookfield R/S plus) equipped with a shear vane (four blades with 20 mm in width and 40 mm in length).

2.4 Solubility of CO_2 in [TEPA]Ac/PEG-200 mixtures

CO_2 solubility measurement was performed on the basis of the isochoric saturation method [27]. Figure 2 shows the apparatus to measure CO_2 solubility. This device mainly consists of a CO_2 gas equilibrium cell (50 cm^3) with a magnetic stirrer, a gas reservoir (1000 cm^3), an oil bath and a pressure gauge (0-1.0 bar) with an accuracy of 0.0005 bar. The temperature of the oil bath was controlled by the thermo controller.

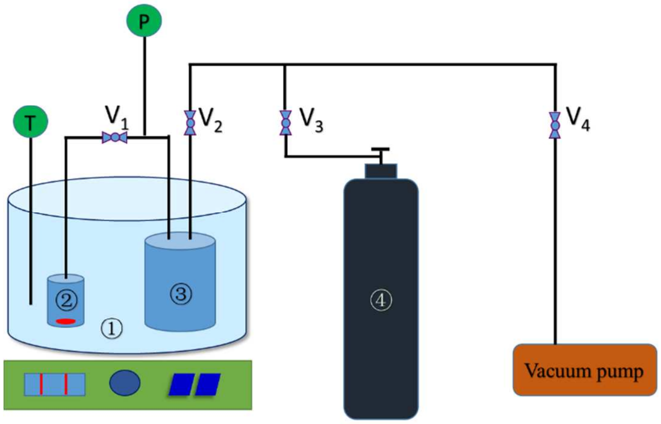


Fig. 2 Experimental device for measurement of CO_2 solubility. ① Oil bath; ② CO_2 gas equilibrium cell; ③ CO_2 gas reservoir; ④ Cylinder filled with pure CO_2; V1-V4, Valves; (P) Pressure transmitter; (T) Thermo controller.

In a typical experiment, about 5g of [TEPA]Ac/PEG-200 was loaded into the equilibrium cell and degassed at 298.15 K under vacuum for at least 1 h. The mass of the absorbent was determined by the electronic balance. At a fixed oil-bath temperature, the valve of V_3 was closed, V_1, V_2 and V_4 were opened and the whole system was evacuated to pressure p_1. Then V_1 and V_4 were closed and V_3 was opened. The gas reservoir was loaded with CO_2 from the gas cylinder until the pressure reached a scheduled value (P_2), which was closed to atmospheric pressure. After that, V_2 and V_3 were closed and V_1 was opened. Then CO_2 was charged into the equilibrium cell and began being dissolved by [TEPA]Ac/PEG-200 while stirring. It was assumed that equilibrium was reached after the pressure of the system had been constant for 3 h. The final pressure was recorded as p_3. The equilibrium partial pressure of CO_2 was obtained as (p_3–p_1). Then V_1 was closed and the mass of cell was determined. The total CO_2 amount in the equilibrium cell was easily obtained by the masses of cell with and without the charge of CO_2. Since the experiment was conducted at sub-atmospheric pressure and above the room temperature, the mass of gaseous CO_2 in the equilibrium cell could be calculated based on the ideal gas law. Therefore, the content of CO_2 in the absorbent could be calculated by deducting the mass of gaseous CO_2 from the total CO_2 amount.

In this work, the solubility of CO_2 in the [TEPA]Ac/PEG-200 mixtures with the mass ratio of [TEPA]Ac to PEG-200 at 1:1, 1:2 and 1:3 were measured at four temperatures (353.15 K, 368.15 K, 383.15 K, and 395.15 K). The amount of CO_2 absorbed in the absorbent can be calculated by the following equation,

$$n_{CO_2} = (m_2 - m_1) / 44 - (P_3 - P_1)(V_{cell} - V_{mixture}) / RT \qquad (1)$$

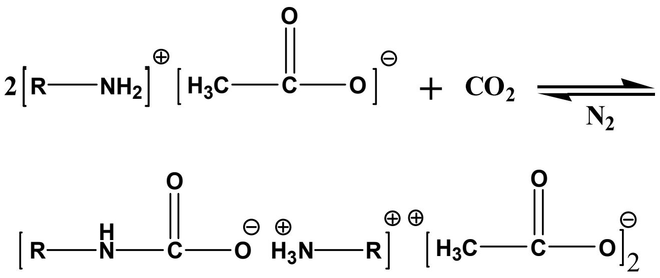
where V_{cell} is the volume of gas equilibrium cell; $V_{mixture}$ represents the volume of the [TEPA]Ac/PEG-200 mixture. The m_2 and m_1 are the mass of the cell containing [TEPA]Ac/PEG-200 before and after loading CO_2 into the cell, respectively. Besides, 44 is the molecular mass of CO_2.

The volume of [TEPA]Ac/PEG-200 mixtures increased about 3% after statured with CO_2. Therefore, the effect of expansion of [TEPA]Ac/PEG-200 mixtures on solubility calculation of CO_2 can be neglected.

3. Results and discussion

3.1 Absorption and desorption of CO_2

Based on the mechanism for the ILs with amine to capture CO_2 reported in some literatures [19, 28], it can be proposed that the process of CO_2 absorption and desorption in [TEPA]Ac should follow the mechanism as shown in Scheme 1.



Scheme 1 Mechanism on absorption and desorption of CO_2 by [TEPA]Ac

Figure 3 shows the results from experiments on absorption and desorption of CO_2 in/from [TEPA]Ac/PEG-200 mixtures with the mass ratio of 1:0, 1:1, 1:2, and 1:3. For the [TEPA]Ac/PEG-200 mixtures, the experiments were conducted at T = 353.15 K with CO_2 and N_2 of ambient pressure. For the pure [TEPA]Ac, the experiments were carried out at 383.15 K because the viscosity of [TEPA]Ac became very high (1550 mPa·s, Table 1) after absorbing CO_2 at T = 353.15 K. The content of PEG-200 has a strong effect on the CO_2 absorption rate (Fig. 3). The equilibrium absorption time was around 160 min for pure [TEPA]Ac. With the content of PEG-200 increased, the CO_2 absorption rate of [TEPA]Ac/PEG-200 mixtures increased dramatically even at a lower temperature (Figure 3). For example, the time required for CO_2 absorption up to saturation is about 85 min, 39 min, and 27 min at 353.15 K when the mass ratio of [TEPA]Ac to PEG-200 equals 1:1, 1:2, and 1:3, respectively.

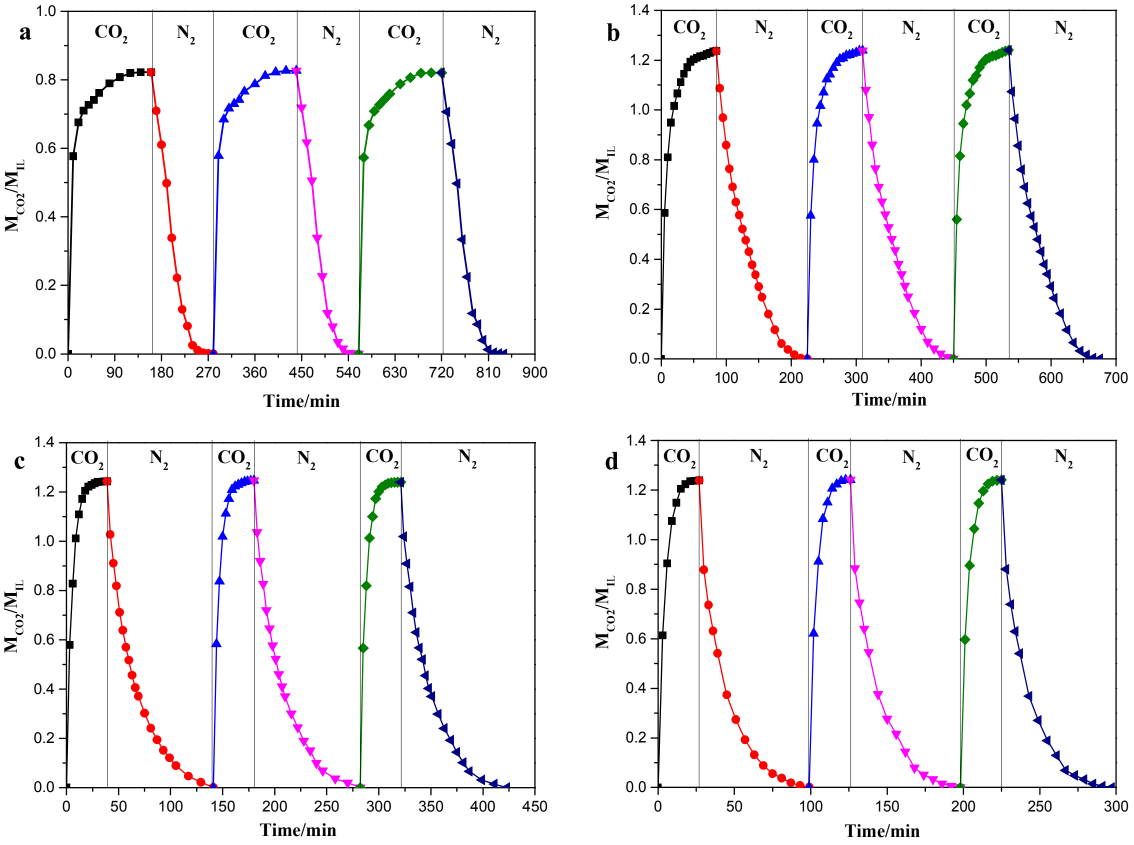


Fig. 3 Cycles of CO_2 absorption and desorption by [TEPA]Ac and [TEPA]Ac/PEG-200 mixtures: a)$W_{[TEPA]Ac}/W_{PEG-200}$ = 1 : 0 at T= 383.15 K; b) $W_{[TEPA]Ac}/W_{PEG-200}$ = 1 : 1 at T=353.15 K; c) $W_{[TEPA]Ac}/W_{PEG-200}$ = 1 : 2 at T=353.15 K; d) $W_{[TEPA]Ac}/W_{PEG-200}$ = 1 : 3 at T=353.15 K.

As shown in Figure 3, the capacities of [TEPA]Ac/PEG-200 mixtures are similar and the mole ratio of CO_2 to [TEPA]Ac is about 1.24 at 353.15 K, which is higher than other IL-based absorbents that reported by other authors even at a higher temperature (Table 1). Besides, the effect of PEG-200 content on the capacity of CO_2 absorption by [TEPA]Ac was not significant, which indicates that the contribution of PEG-200 to the absorption of CO_2 is very limited. The reason is that the CO_2 could hardly be absorbed by PEG-200 at ambient pressure

[29]. However, PEG-200 played the role as solvent for [TEPA]Ac and could increase the efficiency of CO_2 absorption significantly. In the desorption process, the absorbed CO_2 can be easily released by bubbling dried N_2 through the solution. Besides, the results for ten cycles of CO_2 absorption and desorption by [TEPA]Ac/PEG-200 mixture ($W_{[TEPA]Ac}/W_{PEG-200}$ = 1 : 3) are shown in Fig. 4. It can be seen that no observed loss of absorption capacity was found during the ten cycles, indicating that the absorbent can be completely regenerated.

Table 1. Comparisons of CO_2 capacity and viscosity of [TEPA]Ac/PEG-200 (mass ratio = 1:3) with IL-based absorbents around the ambient pressure.

Absorbents	Temperature, K	mol CO_2 /mol IL	Viscosity, mPa·s		Ref.
			Before absorption	After absorption	
[TEPA]Ac/PEG-200 (M^a = 3)	353.15	1.24^b	30	78	This work
[TEPA]Ac	353.15	1.24	130	1550	This work
$[P_{66614}]$[Ile]	353.15	----	97	1300	[30]
$[P_{66614}]$[Gly]	353.15	----	95	650	[30]
$[P_{66614}]$[Ile]	298.15	0.97^c	430	100000	[30]
$[P_{66614}]$[Ala]	298.15	0.66^c	450	53000	[30]
$[P_{66614}]$[Sar]	298.15	0.91^c	440	83000	[30]
$[P_{66614}]$[o-AA]	303.15	0.60	----	----	[31]
$[P_{66614}]$[o-AA]	343.15	0.16	----	----	[31]
$[P_{66614}]$[p-AA]	303.15	0.92	----	----	[31]

$[P_{66614}]$[p-AA]	343.15	0.41	----	----	[31]
[DETA]·Cl/EG (R^d = 4.0)	303.15	0.90	----	----	[32]
[DETA]·Cl/EG (R^d = 4.0)	323.15	0.71	----	----	[32]
[emim][2-CNPyr]	295.15	0.80	----	----	[33]
[emim][4-Triaz]	295.15	0.72	----	----	[33]
[emim][3-Triaz]	295.15	0.53	----	----	[33]

[a] M stands for mass ratio of PEG-200 to [TEPA]Ac.

[b] mol CO_2/mol [TEPA]Ac.

[c] Solubility of CO_2 was calculated by linear interpolation of the nearest experimental data points.

[d] R stands for mole ratio of EG to [DETA]·Cl.

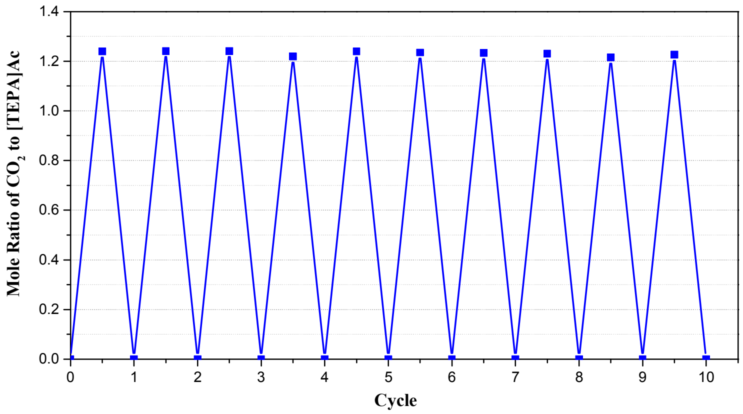


Fig. 4 Cycles of CO_2 absorption and desorption by [TEPA]Ac/PEG-200 mixture

($W_{[TEPA]Ac}/W_{PEG-200} = 1 : 3$)

3.2 Viscosity of the hybrid absorbent during the CO_2 absorption

Although [TEPA]Ac/PEG-200 has excellent properties, such as good circulation performance and high CO_2 capacity at high temperatures, the viscosity of IL will increase with absorbing CO_2 just as the other IL-based adsorbents [4, 30]. For example, the viscosity of $[P_{66614}]$[Ala] increased from 450 mPa·s to 53000 mPa·s after saturated with CO_2 (Table 1), which has a serious effect on the application of it for the capture of CO_2. Viscosity of [TEPA]Ac/PEG-200 (mass ratio = 1:3) after the CO_2 absorption at 353.15 K was measured, and the result is shown in Figure 5. The viscosity of [TEPA]Ac/PEG-200 mixture increased during the CO_2 absorption. The reason for increasing viscosity of [TEPA]Ac/PEG-200 after absorbing CO_2 is the formation of a hydrogen bond network during the CO_2 absorption by [TEPA]Ac [34]. The viscosity of [TEPA]Ac/PEG-200 (mass ratio = 1:3) before and after the CO_2 absorption was compared with other IL-based absorbents reported in the literatures (Table 1). It can be seen from Table 1, the viscosity of [TEPA]Ac/PEG-200 (mass ratio = 1:3) is just 78 mPa·s after saturation with CO_2, which is much lower than that of the other CO_2-saturated IL-based adsorbents.

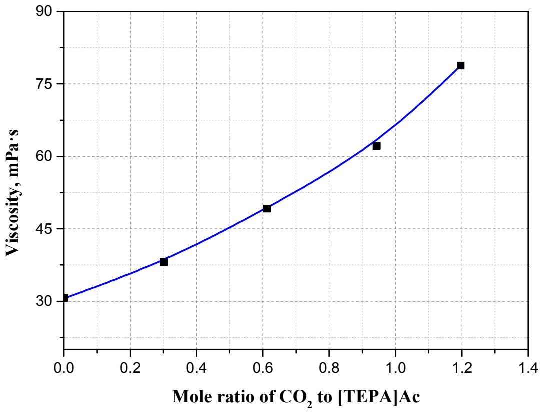


Fig. 5. Viscosity of [TEPA]Ac/PEG-200 (mass ratio = 1 : 3) during the absorption of CO_2 at 353.15 K

3.3 Solubility of CO_2 in [TEPA]Ac/PEG-200 mixtures

The study of solubility of CO_2 at equilibrium condition is very important and valuable for both fundamental research and practical applications of the [TEPA]Ac/PEG-200 mixtures. The results of the CO_2 solubility in the [TEPA]Ac/PEG-200 mixtures with different mass ratio and at four temperatures (353.15 K, 368.15 K, 383.15 K, and 395.15 K) were shown in Table 2. where x_1 and P represents the mole fraction of CO_2 in the absorbent and the equilibrium pressure, respectively.

Table 2 Mole ratio of CO_2 to [TEPA]Ac ($M_{CO_2}/M_{[TEPA]Ac}$) at different temperatures and pressures.

	$W_{IL}/W_{PEG-200}$=1 : 1			$W_{IL}/W_{PEG-200}$=1 : 2			$W_{IL}/W_{PEG-200}$=1 : 3		
T / K	P / bar	x_1^*	$M_{CO_2}/M_{[TEPA]Ac}$	P / bar	x_1^*	$M_{CO_2}/M_{[TEPA]Ac}$	P / bar	x_1^*	$M_{CO_2}/M_{[TEPA]Ac}$
353.15	0.0455	0.0373	0.0838	0.0195	0.0168	0.0585	0.0050	0.0087	0.0380
	0.2205	0.2889	0.6485	0.2095	0.1844	0.6435	0.1795	0.1352	0.5917
	0.4005	0.4251	0.9544	0.4185	0.2703	0.9435	0.4585	0.2266	0.9912
	0.6055	0.4878	1.0951	0.6055	0.3102	1.0825	0.6340	0.2512	1.0990
	0.8080	0.5350	1.2010	0.7505	0.3339	1.1652	0.8420	0.2754	1.2050
	1.0000	0.5523	1.2400	0.9560	0.3542	1.2361	0.9965	0.2846	1.2450
368.15	0.0585	0.0554	0.1243	0.0185	0.0196	0.0684	0.0185	0.0188	0.0821
	0.2850	0.2198	0.4935	0.3050	0.1487	0.5191	0.2470	0.1011	0.4421
	0.4285	0.3286	0.7376	0.4225	0.2077	0.7249	0.4620	0.1745	0.7634

	0.6165	0.3909	0.8775	0.5865	0.2444	0.8529	0.6320	0.1998	0.8741
	0.8055	0.4313	0.9682	0.7955	0.2744	0.9576	0.7855	0.2151	0.9411
	0.9890	0.4606	1.0341	0.9690	0.2926	1.0212	0.9950	0.2360	1.0326
383.15	0.1145	0.0524	0.1177	0.1025	0.0321	0.1121	0.1365	0.0360	0.1574
	0.2635	0.1328	0.2981	0.2155	0.0761	0.2655	0.3100	0.0841	0.3680
	0.4490	0.2355	0.5288	0.4230	0.1461	0.5099	0.4630	0.1262	0.5520
	0.6265	0.3087	0.6931	0.6755	0.2036	0.7106	0.6230	0.1579	0.6910
	0.8230	0.3491	0.7837	0.8145	0.2231	0.7758	0.7990	0.1770	0.7743
	0.9955	0.3648	0.8190	0.9990	0.2350	0.8200	0.9840	0.1867	0.8170
398.15	0.0385	0.0011	0.0025	0.0365	0.0006	0.0021	0.0250	0.0004	0.0018
	0.2315	0.0815	0.1830	0.2625	0.0559	0.1952	0.2215	0.0395	0.1730
	0.4360	0.1524	0.3421	0.4625	0.1035	0.3621	0.3950	0.0755	0.3302
	0.6170	0.1885	0.4231	0.5830	0.1182	0.4125	0.6040	0.0956	0.4181
	0.8040	0.2264	0.5082	0.7990	0.1447	0.5049	0.8105	0.1166	0.5100
	0.9895	0.2453	0.5506	0.9955	0.1581	0.5518	0.9845	0.1260	0.5512

* x_1, mole ratio of CO_2 to [TEPA]Ac/PEG-200 mixture

Figure 6 illustrates the isothermal solubility behavior of the [TEPA]Ac/PEG-200 mixtures at different temperatures. The solubility of CO_2 in the [TEPA]Ac/PEG-200 mixtures increased significantly with the increase of pressure. The CO_2 solubility is more sensitive to pressure in the low-pressure range. Also, it was shown that at each pressure, the solubility of CO_2 in the [TEPA]Ac/PEG-200 mixtures decreased with the increasing of temperature (Fig.

6).

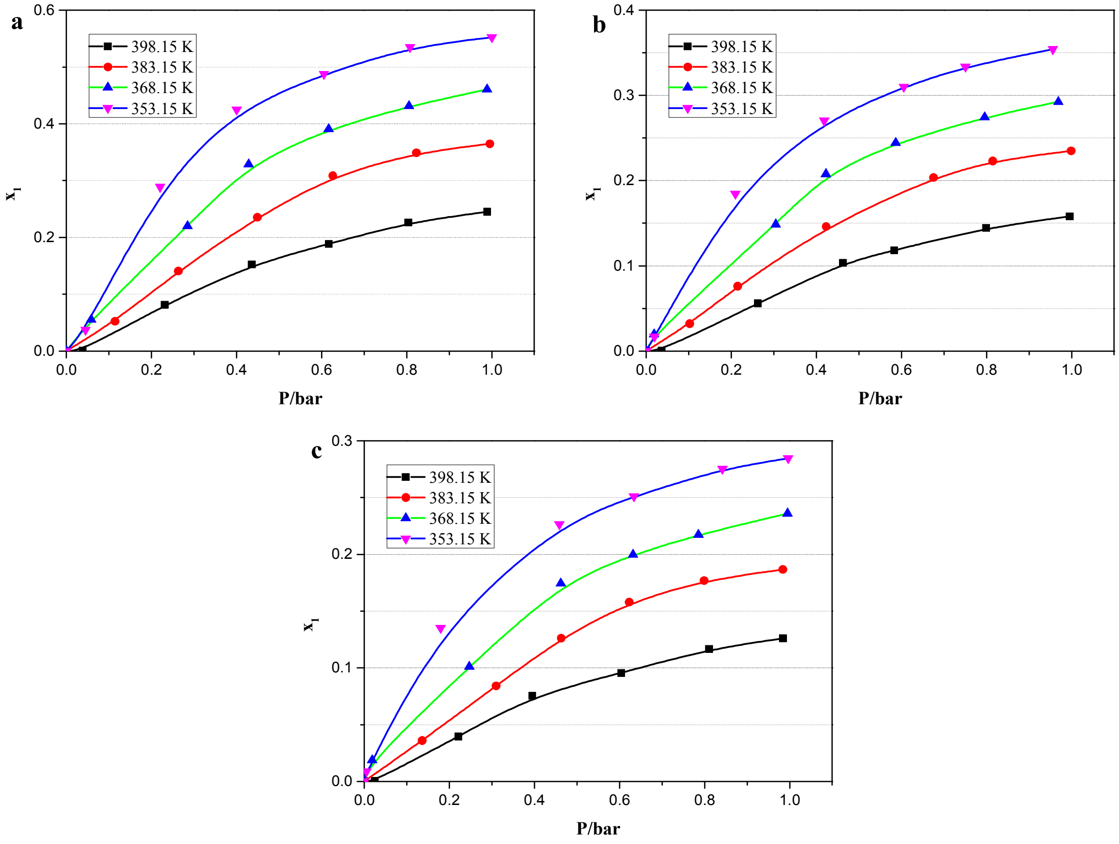


Fig. 6 Dependence of the solubility of CO_2 in the [TEPA]Ac/PEG-200 mixtures on temperature and pressure: a) $W_{[TEPA]Ac}$ /$W_{PEG-200}$ = 1 : 1; b) $W_{[TEPA]Ac}$ / $W_{PEG-200}$ = 1 : 2; c) $W_{[TEPA]Ac}$ /$W_{PEG-200}$ = 1 : 3 (x_1, mole ratio of CO_2 to [TEPA]Ac/PEG-200 mixture)

At the same temperature and pressure, the solubility of CO_2 in the [TEPA]Ac/PEG-200 mixtures decreased with the increase of the PEG-200 content. The reason is that the PEG-200 could hardly absorb CO_2 at each temperature and pressure which has been discussed above. Distribution of the molar ratio of CO_2 to [TEPA]Ac ($M_{CO_2}/M_{[TEPA]Ac}$) in the experiment at different [TEPA]Ac to PEG-200 mass ratios was shown in Figure 7 in order to describe clearly the role of [TEPA]Ac and PEG-200 for the CO_2 absorption. The effect of the mass ratio of [TEPA]Ac to PEG-200 on the $M_{CO_2}/M_{[TEPA]Ac}$ is very limited. Almost all amount of CO_2 was absorbed by [TEPA]Ac due to the strong interaction between the basic group of [TEPA]Ac and CO_2.

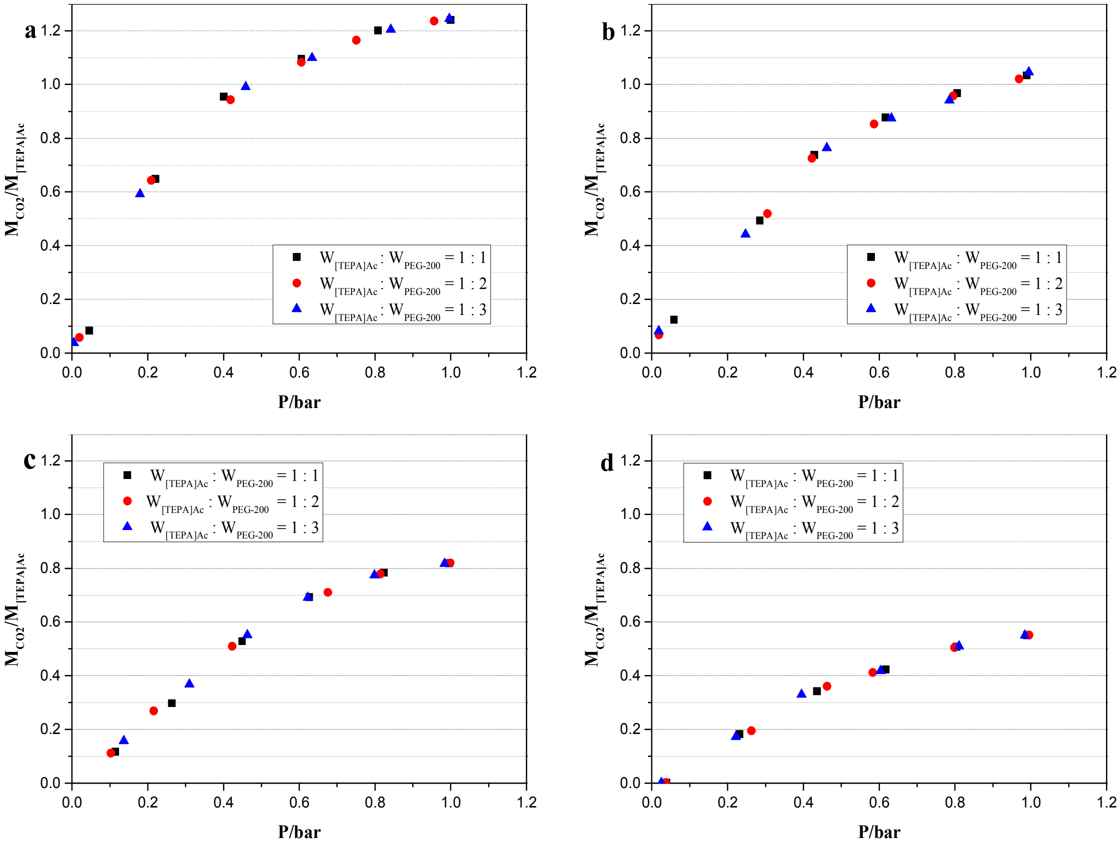


Fig. 7 The effect of temperature and pressure on the molar ratio of CO_2 to [TEPA]Ac (M_{CO_2} / $M_{[TEPA]Ac}$): a): T = 353.15 K; b) T = 368.15 K; c) T = 383.15 K; d) T = 398.15 K.

3.4 Enthalpy and entropy of solution

The strength of interaction between CO_2 and absorbent can be reflected by enthalpy (ΔH_{sol}), and the order degree changing of solution during the capture of CO_2 can be reflected by entropy (ΔS_{sol}), i.e. the ΔH_{sol} and ΔS_{sol} are important thermodynamic parameters for the investigated system. ΔH_{sol} and ΔS_{sol} can be calculated through the following equations [35]:

$$\frac{\Delta H_{sol}}{R} = \left(\frac{\partial \ln P}{\partial (1/T)}\right)_{x_1} \quad (2)$$

$$\frac{\Delta S_{sol}}{R} = -\left(\frac{\partial \ln P}{\partial T}\right)_{x_1} \quad (3)$$

where x_1 is the mole fraction of CO_2 in the [TEPA]Ac/PEG-200 mixtures, R is the molar gas constant. In the system investigated in this work, lnP had a linear relationship with 1/T and lnT at fixed x_1. For example, the dependence of $\ln P_1$ on 1/T at $x_1 = 0.055$ and $W_{IL}/W_{PEG\text{-}200} = 1:1$ was shown in Figure 8. The values of ΔH_{sol} and ΔS_{sol} at four fixed values of x_1 for each [TEPA]Ac/PEG-200 mixture were calculated and listed in Table 3.

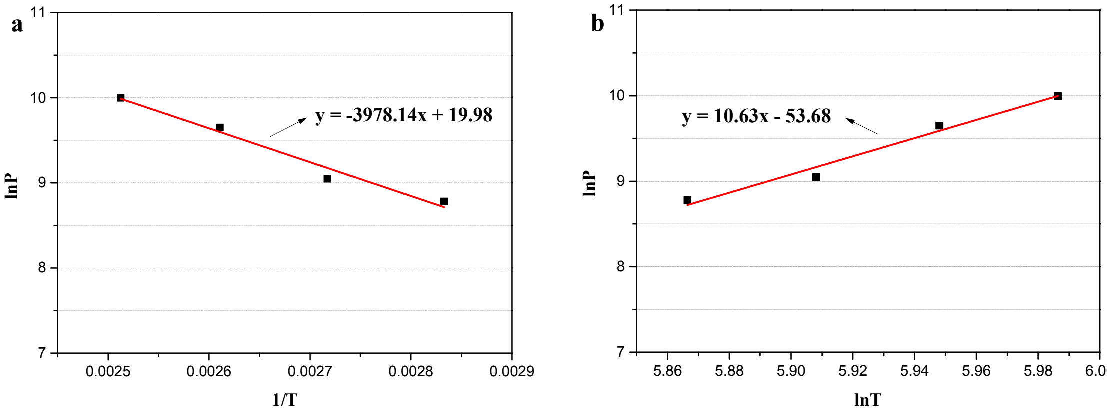


Fig. 8 Relationship between lnP and 1/T or lnT at $x_1 = 0.055$ for the [TEPA]Ac/PEG-200 mixture with the mass ratio of 1:1

Table 3 Enthalpy (kJ/mol) and entropy (J/K mol^{-1}) of solution of CO_2 in the [TEPA]Ac/PEG-200 mixtures (T = 353.15-395.15K)

$W_{[TEPA]Ac} / W_{PEG\text{-}200} = 1:1$	$W_{[TEPA]Ac} / W_{PEG\text{-}200} = 1:2$	$W_{[TEPA]Ac} / W_{PEG\text{-}200} = 1:3$

x_1^*	$-\Delta H_{sol}$	$-\Delta S_{sol}$	x_1^*	$-\Delta H_{sol}$	$-\Delta S_{sol}$	x_1^*	$-\Delta H_{sol}$	$-\Delta S_{sol}$
0.055	33.1	88.4	0.045	35.8	95.7	0.030	36.6	97.6
0.115	33.5	89.6	0.085	35.8	95.5	0.065	36.9	98.4
0.175	35.6	95.1	0.120	37.7	100.6	0.095	38.1	101.6
0.235	42.3	113.2	0.155	41.5	111.1	0.125	40.0	107.1

* x_1, mole fraction of CO_2 in the [TEPA]Ac/PEG-200 mixtures

Under all conditions, the ΔH_{sol} of absorbents has negative values indicating that a large amount of heat is released during the absorption process. This feature should be taken into consideration during the process of practical application. Also, the large negative values of ΔH_{sol} indicate that the interaction between the [TEPA]Ac/PEG-200 mixtures and CO_2 is quite strong. The ΔS_{sol} can reflect structure change of the absorbent before and after the CO_2 absorption. Thus, the negative values of ΔS_{sol} demonstrate that the structure of the [TEPA]Ac/PEG-200 mixtures has higher ordering degree after the absorption of CO_2.

4. Conclusions

The [TEPA]Ac/PEG-200 mixture is a new type of IL-based absorbent for CO_2 capture. It has excellent properties, such as good circulation performance and high CO_2 capacity at high temperatures. The main conclusions can be summarized as follow:

The [TEPA]Ac/PEG-200 mixtures have high CO_2 absorption capacity and the mole ratio of CO_2 to [TEPA]Ac can reach 1.24 at 353.15 K under the ambient pressure (1.01 bar). Moreover, the absorbents can absorb CO_2 effectively at a higher temperature indicating that they have potential application to capture CO_2 from flue gas in the industry.

The [TEPA]Ac/PEG-200 mixtures with CO_2 absorbed can be easily regenerated by bubbling N_2 through the absorbents. No observed loss of absorption capacity was found during ten absorption and desorption circulations, indicating that the absorbent can be completely regenerated.

The addition of PEG-200 increased significantly the CO_2 absorption efficiency of the absorbent.

The solubility of CO_2 in the [TEPA]Ac/PEG-200 mixtures decreased with increasing temperature or decreasing CO_2 partial pressure.

The CO_2 absorption in the [TEPA]Ac/PEG-200 mixtures is an exothermic process and the ordering degree of the absorbent structure increases during the CO_2 absorption.

Acknowledgements

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