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Investigation of the weak basic butyltriethylammonium acetylacetonate and polyethylene glycol mixture as a new efficient CO_2 absorption solvent

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ABSTRACT

Efficient and reversible absorption of CO_2 was investigated by weak basic ionic liquid of butyltriethylammonium acetylacetonate ($[N_{2224}][acac]$) and polyethylene glycol 200 (PEG-200) mixtures with different mass ratios. The results showed that $[N_{2224}][acac]$/PEG-200 mixtures possessed a maximum absorption capacity of 0.9 mol CO_2 per mole $[N_{2224}][acac]$ at $T = 298.15$ K under ambient pressure. The mixtures used could be easily regenerated by bubbling N_2 through the solutions without obvious loss of absorption performance. Furthermore, the solubility data of CO_2 in the mixtures at $T = (303.15, 318.15, \text{and } 333.15)$ K under different pressures were measured. The thermodynamic parameters of absorption enthalpy and absorption entropy were calculated with resulting negative values at each condition. The mixtures showed low absorption enthalpy for CO_2 capture. The addition of PEG-200 can accelerate absorption process. The CO_2 capture process described using $[N_{2224}][acac]$/PEG-200 mixtures is a promising method for CO_2 absorption with both good reversibility and high absorption capacity.

1. Introduction

Carbon dioxide (CO_2) capture and storage (CCS) have attracted worldwide attention in recent decades because of the environmental and economic threats posed by global warming and disastrous climate problems due to CO_2 emissions from fossil fuel combustion [1,2]. Up to now, many CO_2 capture technologies have been developed, including absorption, membrane, adsorption and any of their combination [3]. Currently, the absorption technology based on aqueous alkanolamine solutions seems to be the leading candidate in industrial applications [4,5]. Although the aqueous alkanolamine mixtures are highly effective for CO_2 removal, they have several inherent drawbacks such as intensive energy consumption and thermal decomposition in the regeneration section, solvent loss, and corrosion [6,7]. Therefore, searching for promising alternatives to these solvents is highly desirable.

In the past two decades, ionic liquids (ILs) have attracted considerable attention as designed solvents used for separation and reaction in the chemical industry [8,9]. Many ILs have been reported as promising mediums for CO_2 removal in natural gas sweetening or greenhouse gas control processes [10,11]. The intrinsic properties including non-volatility, high thermal stability, diversity, and tuneable chemistry, make ILs more attractive than common alkanolamine solutions [12].

Although ILs possess attractive advantages as absorbents for CO_2, they still have several shortcomings that need modification currently, such as the promotion of absorption capacity, reduction of energy consumption during the regeneration process, and decrease of viscosity. The physical absorbent of common ILs suffers from the relatively small absorption capacity within the low CO_2 pressure region [13,14]. Although NH_2-functionized ionic liquids (NH_2-ILs) can increase remarkably the absorption capacity, they have the obstacle of high viscosity, especially after the absorption of CO_2 [15–18]. The blended solvents of organic amine with common ILs or NH_2-ILs with low volatile organic solvents [19–22] can modify the viscosity, but the intensive energy consumption is still needed because of the strong chemical interaction between amino group and CO_2. Recently, Wang *et al.* [23] proposed a new strategy for CO_2 capture based on weak basic ILs composed of diverse phenolic anion and large cation of trihexyl(-tetradecyl) phosphonium, the results demonstrated that these ILs can capture equimolar CO_2 with low capture enthalpy. Interestingly, Huang *et al.* [24] designed several weak acidic task-specific ILs of dicarboxylic acid salts for SO_2 capture, the results were also satisfactory.

Herein, we also prepared a new weak basic IL of butyltriethylammonium acetylacetonate ($[N_{2224}][acac]$) and diluted it with polyethylene glycol 200 (PEG-200) to form $[N_{2224}][acac]$/PEG-200

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mixtures for CO_2 capture. In addition, the solubility of CO_2 at three temperatures under various pressures were determined and used to calculate the thermodynamic parameters. Excitingly, these mixtures have been found to be good CO_2 absorbents with high absorption capacity and low absorption enthalpy.

2. Experimental

2.1. Materials

The specifications of chemicals used are listed in table 1. All chemicals were obtained in the highest purity grade possible and used as received without further purification. The ^{1}H NMR spectra of [N_{2224}][acac] were recorded with a 300 MHz Bruker spectrometer in DMSO-d_6 and calibrated with the tetramethylsilane (TMS) as the internal reference. The pressure was determined using a pressure transmitter (Yeli Engineering Hangzhou, WMB2088, (0 to 200) kPa, with a precision of 0.25% full scale).

In a typical experiment, butyltriethylammonium bromide ([N_{2224}][Br]) was synthesized by alkylation of triethylamine (10.12 g, 100 mmol) with slightly excess 1-bromobutane (13.09 g, 125 mmol) under a nitrogen atmosphere and purified by re-crystallization in the mixed solvent of acetonitrile and ethyl acetate. The white solid of [N_{2224}][Br] obtained was converted to the ethanol solution of butyltriethylammonium hydroxide ([N_{2224}][OH]) using anion-exchange resin (201 * 7 (OH)). The concentration of OH^- in the ([N_{2224}][OH] + ethanol) mixture was titrated using standard HCl solution. The [N_{2224}][acac] was then prepared by the neutralization reaction of [N_{2224}][OH] with acetylacetone according to the literature method [11]. For example, equimolar acetylacetone was slowly added to the ethanol solution of [N_{2224}][OH], and the mixture was then stirred magnetically for 2 h at room temperature. Subsequently, ethanol and water were distilled off under reduced pressure to gain the concentrated [N_{2224}][acac] solution. Finally, the [N_{2224}][acac] as a light-yellow viscous liquid was obtained under vacuum at T = 338 K for more than 24 h to remove possible traces of water and volatile impurities. Thus, the bromide ion mass fraction was determined by the Mohr method with the result of $2.0 \cdot 10^{-3}$, while the Karl-Fischer analysis (SF-3 Karl-Fischer Titration, Zibo Zifen Instrument Co. Ltd.) indicated water mass fraction of $1.2 \cdot 10^{-3}$ in [N_{2224}][acac]. The total yield was 81.5%. ^{1}H NMR (DMSO-d_6): δ = 6.05 (s,1H), 3.20 to 3.31 (m,8H), 2.32 (s,3H), 1.73 (s,3H), 1.52 to 1.63 (m,2H), 1.21 to 1.36 (m,2H), 1.16 (t,9H), 0.92 (t,3H). The mass fraction purity of the [N_{2224}][acac] was 0.985 according to NMR spectra and titration analysis.

2.2. Apparatus and procedures to study the absorption of CO_2

In a typical CO_2 absorption experiment, about 4.0 g of the [N_{2224}][acac]/PEG-200 mixture was stored in the glass tube with an inner diameter of 8 mm and length of 120 mm. The glass tube was partly immersed in the thermostatic oil bath at the experimental temperature. Atmospheric CO_2 was bubbled into the mixture using a long stainless needle at a flow rate of 50 $cm^3 \cdot min^{-1}$. The total mass of the glass tube containing sample as well as needle was determined at regular intervals using an electronic balance (Mettler-Toledo AL204, with an uncertainty of $\pm 2 \cdot 10^{-4}$ g). The amount of CO_2 absorbed was calculated according to the difference of the total mass before and after CO_2 bubbling. The regeneration process was recorded with the same procedures by bubbling dried N_2 instead of CO_2 into the solution.

2.3. Apparatus and procedures to determine the solubility of CO_2

CO_2 solubility data were determined using a modified apparatus on the basis of our previous study [25] and illustrated in figure 1, mainly containing the equilibrium cell (EC,2) with a magnetic stirrer and a gas reservoir (GR,3). The volume of the EC (92.05 cm^3) was directly calibrated with double distilled water at room temperature using titration column, with the accuracy of 0.01 cm^3. The volume of the GR and the other parts of the system (640.01 cm^3) was determined using dried N_2 expansion method described in the literature [25]. The temperature of EC and GR was maintained at a certain value using thermostatic water bath with a precision of ±0.05 K. In a typical experiment, a desired amount of [N_{2224}][acac]/PEG-200 was loaded into the EC and degassed at T = 328 K under vacuum while stirring for at least 2 h. The mass of the mixture in the EC was determined by the weighing method using the electronic balance. At a specified water-bath temperature, V3 was closed, V1, V2 and V4, opened and the whole system was evacuated to pressure p_1. Then V1 and V4 were closed, V3 was opened, and GR was loaded with CO_2 from the gas cylinder until the pressure reached a scheduled value close to atmospheric pressure, recorded as p_2. V2 and V3

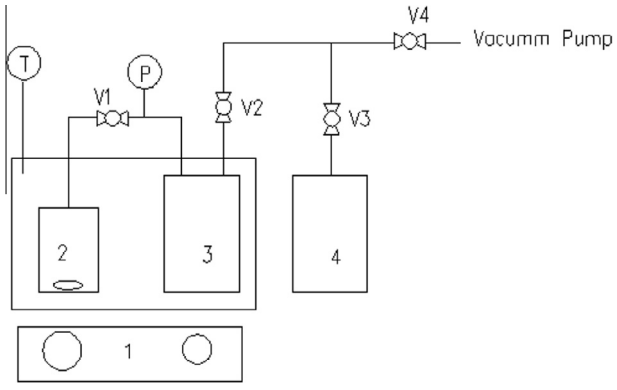

FIGURE 1. Schematic diagram of the CO_2 solubility apparatus. (1) Magnetic stirrer and warmer; (2) CO_2 gas equilibrium cell (EC); (3) CO_2 gas reservoir (GR); (4) CO_2 gas cylinder; V1–V4, stainless valve; (*T*) temperature controller; (*P*) pressure transmitter.

TABLE 1
Specifications of chemical reagents.

Chemical reagent	Source	Mass fraction purity (as received)
Triethylamine	Sinopharm chemical reagent Co., Ltd.	>0.999
1-Bromobutane	Sinopharm chemical reagent Co., Ltd.	>0.997
Acetylacetone	Sinopharm chemical reagent Co., Ltd.	>0.995
Polyethylene glycol-200	Beijing chemical reagent Co., Ltd.	>0.995
Anion-exchange resin (201 * 7 (OH))	Chemical Plant of Nankai University	
Carbon dioxide	Jingong Special Gas Co., Ltd.	>0.9995
Nitrogen	Jingong Special Gas Co., Ltd.	>0.9999
Acetonitrile	Sinopharm chemical reagent Co., Ltd.	>0.996
Ethyl acetate	Sinopharm chemical reagent Co., Ltd.	>0.997
Ethanol	Sinopharm chemical reagent Co., Ltd.	>0.995