



## Full Length Article

## Liquid-solid phase-change absorption of acidic gas by polyamine in nonaqueous organic solvent

Wenbo Zhao<sup>a,\*</sup>, Qian Zhao<sup>a</sup>, Zheng Zhang<sup>a</sup>, Jiaju Liu<sup>a</sup>, Rui Chen<sup>a</sup>, Yuan Chen<sup>a</sup>, Jian Chen<sup>b</sup><sup>a</sup> Faculty of Chemical Engineering, Kunming University of Science and Technology, Kunming 650500, China<sup>b</sup> State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

## ARTICLE INFO

## Keywords:

Liquid-solid phase-change capture  
Carbon dioxide  
Sulfur dioxide  
Diamine  
Sulfite  
Carbamate

## ABSTRACT

Acidic gas capture by traditional aqueous amine solution requires a plenty of energy for solvent regeneration. A phase-change capture system was considered to be a promising alternative because only the CO<sub>2</sub>-rich phase needs to be recovered and the CO<sub>2</sub>-lean phase can be reused directly without disposal, improving the energy utilization efficiency. Based on this principle, the phase-change absorption behavior of linear polyamines including ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine, tetraethylenepentamine, and cyclic diamines including piperazine (PZ) and triethylene diamine (DABCO) in organic solvents was investigated in the present work. The result indicated that polyamines could react with CO<sub>2</sub> to form carbamate precipitates except DABCO, which had no absorption effect. For the absorption of SO<sub>2</sub>, polyamines could react with SO<sub>2</sub> and water from air to form rare organic sulfites except DABCO, which merely absorbed two SO<sub>2</sub> molecules to form the electron transfer complex DABCO(SO<sub>2</sub>)<sub>2</sub>. The peculiar absorption behavior of DABCO for CO<sub>2</sub> and SO<sub>2</sub> implied that it is a highly selective phase-change desulfurizer for flue gas. The sequence of decomposition temperature for the CO<sub>2</sub> capture product was DETA-carbamate > EDA-carbamate > PZ-carbamate, while for the SO<sub>2</sub> capture product was [EDA<sub>2</sub>][SO<sub>3</sub>] > [PZH<sub>2</sub>][SO<sub>3</sub>]·H<sub>2</sub>O > DABCO(SO<sub>2</sub>)<sub>2</sub>.

## 1. Introduction

With the rapid development of economy and society, fossil fuels are extensively used in modern life. This causes the excessive emission of acidic gases such as CO<sub>2</sub> and SO<sub>2</sub>. The former is considered to be the major contributor to global warming and the latter could result in acid rain, disease, and corrosion of architectures. Up to now, many kinds of materials have been investigated to capture CO<sub>2</sub> and SO<sub>2</sub> such as calcium-based materials [1–3], room temperature ionic liquids [4], zeolites [5], carbon material [6], deep eutectic solvents [7] and metal-organic frameworks [8,9]. One commercial absorbent for acidic gases capture is aqueous amine solvents used within the absorber-stripper process [10,11]. While this process is effective and reliable for the removal of acid gas, it requires plenty of energy for solvent regeneration due to the evaporation and high thermal capacity of water [12].

In order to reduce the energy consumption during CO<sub>2</sub> removal, many materials and technologies have been proposed. Among them, phase-change solvents were considered to be promising for industrial application [13–15]. In the absorption process, these homogeneous solvents would react with CO<sub>2</sub> to form two immiscible phases: a CO<sub>2</sub>-rich phase and a CO<sub>2</sub>-lean phase. Only the former has to be sent to

stripper for regeneration and the latter could be reused directly, thus the total solvent regeneration energy required would be reduced greatly [16]. The phase-change solvent would undergo liquid-liquid or liquid-solid phase-change after the absorption of CO<sub>2</sub>.

IFP Energies nouvelles invented a DMX™ technique in which the DMX solvents would form two immiscible liquid phases under specific CO<sub>2</sub> loading or temperature conditions. The regeneration energy of this process (2.3 GJ/t CO<sub>2</sub>) is much lower than the process involving 30 wt % monoethanolamine (MEA) solution (3.7 GJ/t CO<sub>2</sub>) [17–19]. The blended amines solvent such as 2-(Diethylamino)ethanol and 3-(Methylamino)propylamine (or 1,4-Butanediamine) could also form two liquid phases upon CO<sub>2</sub> loading [20,21]. Li et al. [16] found L-alanine solution was a unique phase-change system among a series of amino acid aqueous solutions. In non-aqueous systems, some alkanolamine-alcohol mixtures separated into two liquid-liquid phases after the absorption of CO<sub>2</sub> [22]. In this work, MEA carbamate [HOC<sub>2</sub>H<sub>4</sub>NH<sub>3</sub>]<sup>+</sup>[HOC<sub>2</sub>H<sub>4</sub>NHCO<sub>2</sub>]<sup>-</sup> and diethanolamine (DEA) carbamate [(HOC<sub>2</sub>H<sub>4</sub>)<sub>2</sub>NH<sub>2</sub>]<sup>+</sup>[(HOC<sub>2</sub>H<sub>4</sub>)<sub>2</sub>NCO<sub>2</sub>]<sup>-</sup> were obtained from MEA/isoctanol and DEA/isoctanol solutions, respectively. Zhang et al. [23] proposed to use thermomorphic biphasic systems to capture CO<sub>2</sub>. In this process, the lipophilic amine solvent would undergo a liquid-liquid

\* Corresponding author.

E-mail address: [Wenshuixing@126.com](mailto:Wenshuixing@126.com) (W. Zhao).

phase-change phenomenon once the temperature was high enough during the regeneration process.

Liquid-solid phase-change absorption of CO<sub>2</sub> was also considered to be a promising alternative to conventional amine processes. According to Le Chatelier's principle, the CO<sub>2</sub> absorption equilibrium can be shifted by removing one product from the reaction, leading to improvement of absorption capacity. In aqueous system, alkali carbonates, ammonia, and amino acid salts with tertiary or sterically hindered secondary amino groups such as potassium proline and potassium sarcosine can react with CO<sub>2</sub> to form bicarbonate precipitates [24]. In contrast, amino acid salts with a primary amino group can react with CO<sub>2</sub> to form a carbamate ion and a zwitterion precipitate [25]. Regardless of the precipitate type, only a part of the CO<sub>2</sub> capture product would precipitate from solvent water due to solubility of the capture product. Some of product remains dissolved in the solution and cannot be sent to the stripper for regeneration [26,27].

Except common solvent water, room-temperature ionic liquids (RTIL) were also used as solvents for the liquid-solid phase-change capture of CO<sub>2</sub>. Commercial absorbents such as MEA, DEA and 2-amino-2-methyl-1-propanol (AMP) could react with CO<sub>2</sub> to form carbamates which consisted of [RNHCO<sub>2</sub>]<sup>-</sup> anions and [RNH<sub>3</sub>]<sup>+</sup> cations. They are a kind of ammonium salt that would precipitate from RTIL solvents such as 1-hexyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide. However, the high cost and viscosity of RTIL make it infeasible for real applications at present [28–30].

In order to circumvent the disadvantages of RTIL, organic solvent alcohols were tested for the liquid-solid phase-change capture of CO<sub>2</sub>. In the work of Barzagli et al. [31], an efficient process for CO<sub>2</sub> capture using AMP–alkanolamine blends, namely DEA, N-methyl-DEA, N-methyl-MEA, diisopropanolamine, in non-aqueous solvents were investigated. The solvents used were mixtures of ethylene glycol or 1,2-propanediol with either methanol or ethanol. The solid product was identified as the carbamate derivative of AMP, [(AMPH)(AMPCO<sub>2</sub>)]. In the work of Zheng et al. [32], triethylenetetramine dissolved in ethanol yielded a solid precipitate after absorption of CO<sub>2</sub>. In our previous work [33], we found that diethylenetriamine could absorb equimolar CO<sub>2</sub> to form a zwitterion compound with all kinds of organic solvent used. Some work about liquid-solid phase-change absorption of CO<sub>2</sub> with amine in organic solvent has been conducted at present. However, the research in this field is still segmented and scattered. In the present work, we systematically investigated the absorption behavior of linear polyamines including ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), and cyclic polyamines including piperazine (PZ) and triethylene diamine (DABCO) in organic solvent such as ethanol, diethylene glycol dimethyl ether (DGDE), N-methyl-pyrrolidone (NMP) and diethyl carbonate (DEC) as representatives of alcohols, ethers, ketones and esters, respectively.

Aqueous amines solutions were also employed to reduce SO<sub>2</sub> emissions. For instance, in the commercial Cansolv's process, a mixture of diamine and acid could capture SO<sub>2</sub> from flue gas. However, compared to phase-change absorption of CO<sub>2</sub>, far few studies related to the phase-change capture of SO<sub>2</sub> using amine as an absorbent have been reported. Only Shannon et al. [34] observed that some N-functionalized imidazoles would be converted from liquid to solid or gel after the absorption of SO<sub>2</sub>. In the present work, the same absorbent and organic solvents for CO<sub>2</sub> capture were utilized for the phase-change absorption of SO<sub>2</sub>. The composition and structure of capture product were studied by using powder X-ray diffraction (PXRD), FTIR, elemental analysis and single crystal XRD. Their thermostability was also determined by thermogravimetric analysis (TG).

## 2. Experimental

### 2.1. Materials

All chemicals in the present work were purchased from commercially available sources and used as received without further purification. Analytical reagent EDA (> 99%), DETA (> 99%), PZ (> 99%), DGDE (> 99%), NMP (> 99%) and DEC (> 98%) were purchased from Aladdin-Reagent Company in Shanghai. Ethanol (> 99.7%), TETA (> 98%) and TEPA (> 95%) were obtained from Chengdu Kelong Chemical Reagent Company. CO<sub>2</sub> (> 99.9%) and SO<sub>2</sub> (2%) was obtained from Kunming Shitouren Gases Co., Ltd.

### 2.2. Characterization

PXRD analysis was performed using a Rigaku D/max-A X-ray diffractometer with  $\lambda = 0.1541$  nm, Cu K $\alpha$  radiation in the  $2\theta$  range of 10–90° with the step of 0.02° at room temperature. FTIR spectra were recorded on a Bruker TENSOR27 Fourier-transform infrared spectrometer in the region 4000–400 cm<sup>-1</sup>. The CHNS contents of the precipitate were determined using an elemental analyzer (PerkinElmer 2400). Thermal stability was measured on a NETZSCH STA-449 F3 under a flow of nitrogen at a 5 K/min heating rate up to 523 K. Single crystal X-ray diffraction data were collected on a Bruker Apex II CCD diffractometer equipped with CCD area detector using graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were solved by direct methods with the SHELXTL 97 program. It was refined by a full-matrix least squares analysis using anisotropic thermal parameters for non-hydrogen atoms. All hydrogen atoms were calculated at idealized positions and refined with the riding models.

### 2.3. Absorption of CO<sub>2</sub> and SO<sub>2</sub>

The absorption experiment of CO<sub>2</sub> was carried out in a 250 mL three-necked flask at room temperature. In a typical process, 2 g absorbent and 8 g solvent were put into the flask and then pure CO<sub>2</sub> gas, which was first saturated by the corresponding solvent, was bubbled into the reactor at the flow rate of 100 mL/min with continued magnetic stirring. After the precipitate formed, the mixture of solid and liquid was separated by filtration. The solid was washed with solvent and dried in a vacuum oven to eliminate the influence of organic solvents. The equipment and procedure for the phase absorption of SO<sub>2</sub> were similar to that of CO<sub>2</sub>, except the SO<sub>2</sub> gas was diluted by 98% N<sub>2</sub>.

### 2.4. Preparation of single crystal

The single crystal suitable for the X-ray diffraction analysis was prepared by dissolving the solid powder in anhydrous ethanol and then evaporating the solution in a vacuum oven for a certain time at room temperature. Crystallographic data have been deposited in the Cambridge Crystallographic Data Center with CCDC reference numbers 1504431 and 1504432.

## 3. Results and discussion

### 3.1. CO<sub>2</sub> absorption

Precipitate formed immediately once CO<sub>2</sub> was bubbled into solution of EDA and organic solvent. In order to find out the structure of the precipitates, they were first characterized by PXRD, Fig. 1(a). In ethanol, only one type of EDA-carbamate <sup>+</sup>NH<sub>3</sub>C<sub>2</sub>H<sub>4</sub>NHCO<sub>2</sub><sup>-</sup>, whose Joint Committee on Powder Diffraction Standards (JCPDS) number is 34-1992, was formed, pattern B; while another type of EDA-carbamate, whose JCPDS number is 34-1993, was formed in NMP or DEC, patterns C and D. The pattern A indicated that both crystal forms of EDA-carbamate were yielded in DGDE. The difference between these two type

Download English Version:

<https://daneshyari.com/en/article/6473818>

Download Persian Version:

<https://daneshyari.com/article/6473818>

[Daneshyari.com](https://daneshyari.com)