Research Article

Measurement of CO_2 solubility in aqueous branched polyamine solutions

Abstract

In energy industry as petrochemicals and electricity generation, absorption technology is looked as the main one for CO_2 capture from flue gases. In this work, absorption solubility of CO_2 in aqueous solutions of four branched polyamines were determined at 313.15 K and 393.15 K using the constant-volume method combined with gas chromatography analysis. The relationship between molecular structure of these polyamines and absorption performance is discussed. It is found that the capture performance is affected by the number of amino groups, the carbon number between the amino groups and the chain length of polyamines. The corresponding values of CO_2 absorption heat were also estimated using the Gibbs-Helmholtz equation and were analyzed from the view of molecular conformation.

Keywords: CO_2 capture, absorption, branched polyamine, solubility

Jian Chen,[1] Ruilei Zhang,[2] Yanmei Yu,[1] Jianguo Mi[2]
[1]State Key Laboratory of Chemical Engineering, Tsinghua University, China
[2]State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, China

Correspondence: Jian Chen, State Key Laboratory of Chemical Engineering, Tsinghua University, China, Email cj-dce@tsinghua.edu.cn

Introduction

Global climate warming associated with increased emissions of CO_2 from anthropogenic sources have become one of the most critical worldwide issues of the current age. A multitude of technological advances[1–3] have been developed to reduce CO_2 emissions from combustion exhaust gases from petrochemicals and electricity generation. Nowadays amine-based aqueous solutions are the most commonly used absorbents for the absorption process.[4] In this case, finding new solvents that offer highly cyclic absorption capacity is important. Compared with monoamine solvents, polyamines solvents [5] are expected to have lower volatility along with higher CO_2 loading capacity and mass transfer rate. For example, diethylenetriamine (DETA) entails a higher mass transfer rate, [6] higher cyclic capacity,[7–9] and significant lower heat of absorption [10] than monoethanolamine (MEA). Tetraethylenepentamine (TEPA) shows outstanding potential for CO_2 absorption, and it can maintain a high absorption rate as well as cyclic absorption capacity.[11] One mole TEPA removes three times more CO_2 per cycle than 1.0 mole MEA. Cyclic absorption capacity is the solubility difference between absorption and desorption. These investigations reveal that polyamines make a good prospect for chemical absorption. Singh et al showed that an increase in chain length between the amine and different functional groups, result in

a decrease of absorption rate whereas, the absorption capacity was increased in most absorbents.[12,13] Machida et al.[14] observed that alkyl chain length between two amines has an important role in CO_2 solubility.[14] Although some fragment solubility data for polyamines have been reported in previous literature, the data for the polyamines in different structures are insufficient.

In this work, the vapor-liquid phase equilibria of CO_2 in aqueous solutions of four branched polyamines were measured at 313.15 K (absorption process) and 393.15 K (desorption process). Based on the solubility data, the corresponding absorption heats (ΔH_{abs}) were calculated to analyze the energy consumptions for CO_2 capture with these solutions.

Experimental section

a. Materials

CO_2 and N_2 with a volume fraction of 0.99999 were supplied by Millennium City Gas. The solvents used are listed in Table 1. The solution was prepared using ultrapure water, which was taken from the Center 120 FV-S ultrapure water machine. The resistivity of ultrapure water is 18.2 MΩ·cm at 298.15 K. All components were used without further purification.

Table 1 Chemicals used in this work

Component	Abbreviation	Molecular formula	CAS number	Purity (%)	Source
3,3'-Diamino-N-methyl- dipropylamine	DAMDPA	C7H19N3	105-83-9	>98	TCI Shanghai
N,N Dimethyldipropylenetriamine	DMDPTA	C8H21N3	10563-29-8	99	Sigma-Aldrich
N,N-Dimethyl-1,3 propanediamine	DMPDA	C5H14N2	109-55-7	99	Alfa Aesar
N,N,N',N'-Tetramethyl-trimethylenediamine	TMTMDA	C7H18N2	110-95-2	>98	TCI Shanghai

b. Apparatus and procedure

The constant-volume method, combined with gas chromatography analysis was used to measure the differing levels of solubility. A detailed description of the vapor–liquid equilibrium apparatus can be obtained from previous literature.[15,16] It is comprised of two stainless

steel tanks for buffer and reaction. Both tanks are equipped with temperature transducers (PT-100, Kunlunhaian Co.) and pressure transducers (JYB-KO-HAG, Kunlunhaian Co.). The accuracy of the temperature and pressure transducers is ±0.1 K and ±0.5%, respectively. In accordance with the Peng-Robinson (PR) equation, the precise amount of CO_2 in the gas phase was determined using its

volume, pressure, and temperature.[17] The principle of this method is to accomplish a known volume of gas with the known-volume polyamine solutions. The amount $n_{CO_2}^{all}$ of CO_2 gas introduced into the reaction tank was determined by the change in the buffer tank, before and after injection. After equilibrium was achieved at a constant temperature, the amount of CO_2 gas absorbed in the solutions $n_{CO_2}^{l}$ was equal to $n_{CO_2}^{all}$ subtracted by the amount of CO_2 in the vapor phase $n_{CO_2}^{g}$. The CO_2 solubility, α_{co_2}, in the liquid phase was defined as $n_{CO_2}^{l}$ divided by the mole number or mass of amine. The experimental error of CO_2 loading is ±8%.

At low partial pressure (<10 kPa), the pressure transducer error may have a greater impact on results. Therefore, the CO_2 partial pressure was obtained using gas chromatography (Agilent 7890). The gas phase is primarily composed of CO_2, with minor components of N_2, H_2O, and amine. The partial pressure of amine is small enough to be considered negligible. The partial pressure of water was calculated according to Raoult's law. Prior to the introduction of CO_2 into the reaction tank, the partial pressure of N_2 was calculated by subtracting H_2O partial pressure from total pressure. Correspondent to the increase in CO_2 amount, the solution's volume change remained negligible and the N_2 partial pressure was assumed constant. The apparatus was verified by determining the solution of CO_2 in 30 mass% MEA solution at T=313.15K and 393.15K. The results are compared with reported data.[18–20] Our results are agree with reported data.

Results and discussion

CO_2 solubility levels in aqueous solutions of four branched polyamines at 313.15 K and 393.15 K were measured using the constant-volume method combined with gas chromatography analysis, and the results are shown in (Figures 1–3). The concentration of amines were set to be 2.5M, which correspond to about 25% - 40% in weight percentage, which is the usual range used in CO_2 absorption processes. The measured corresponding solubility levels are expressed in two forms, both involving the mole number of CO_2; in one form, it is dissolved in per mole of amine, and in the second, per kilogram of amine. The relationship between solubility and molecular structure Table 2 can be also seen in Figures 1–3.
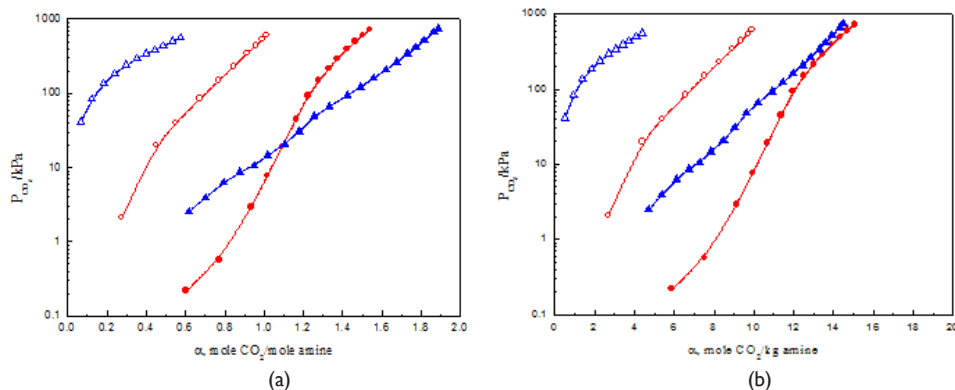

(a)

(b)

Figure 1 Solubility of CO_2 in 2.5 mol·L⁻¹ DMPDA, and TMTMDA solutions.

●: DMPDA 313.15 K; ○: DMPDA 393.15 K; ▲ TMTMDA 313.15 K; △ TMTMDA 393.15 K.
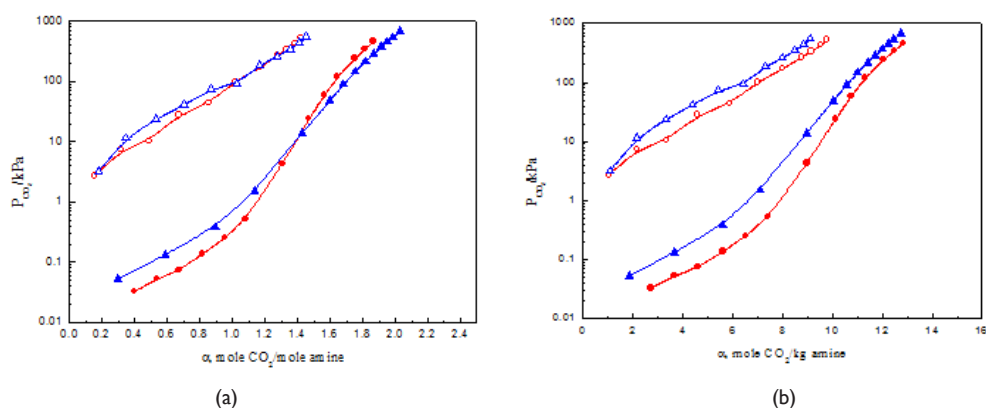

(a)

(b)

Figure 2 Solubility of CO_2 in 2.5 mol·L⁻¹ DAMDPA, and DMDPTA solutions.

● DAMDPA 313.15 K; ○ DAMDPA 393.15 K; ▲ DMDPTA 313.15 K; △ DMDPTA 393.15 K.

c. Relationship between the solubility and molecular structure.

i. Effects of different types of amino groups: DMPDA and TMTMDA all have two amino groups, though these groups are different in type. Figure 1 demonstrates that as the number of tertiary amino groups increases, cyclic absorption capacity also increases in the high CO_2 partial pressure region. The reaction mechanisms for tertiary and primary amines differ with each other. Theoretically, one

mole of CO_2 reacts with one mole of tertiary amines but with two moles of primary amines. In other words, tertiary amines have a higher CO_2 loading capacity than primary amines if CO_2 partial pressure is high enough. So at low temperatures, the absorption capacity can be enhanced by increasing the number of tertiary amino group. However, as shown by lines at 393.15K in Figure 1A, Figure 1b, the absorption capacity is reduced with the increasing number of tertiary amino groups at high temperatures, which means that bicarbonate-the product of tertiary amine is unstable and easily decomposes at high temperatures. DAMDPA and DMDPTA have three amino groups. Regarding DAMDPA and DMDPTA, the secondary and primary amines, respectively, of dipropylenetriamine are substituted by a tertiary amino group. So DAMDPA has two primary amino group and one tertiary amino group, while DMDPTA has one primary, one secondary and one tertiary amino group. The difference between them is a primary amino group compared with a secondary amino group. As shown in Figure 2. The solubility of CO_2 for DAMDPA is slightly higher than that for DMDPTA both at 313.15K and 393.15K in the lower pressure range. That means a primary amino group can absorb a little bit more CO_2 than a secondary amino group in the lower pressure range. Compare the results in Figure 2 with those in Figure 1, one can see that the difference of a tertiary amino group with a primary amino group is larger than the difference of a secondary amino group with a primary amino group.
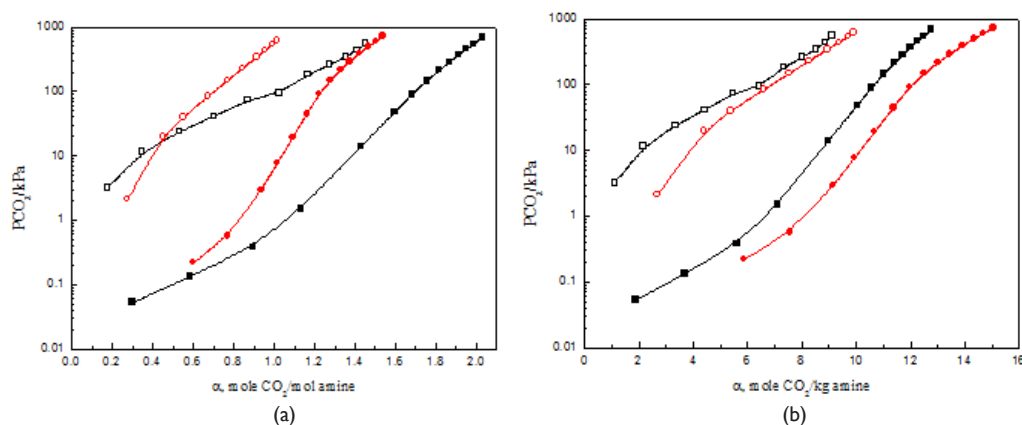

(a)   (b)

Figure 3 Solubility of CO_2 in 2.5 mol·L⁻¹ DMDPTA and DMPDA solutions.

■ DMDPTA 313.15 K; □ DMDPTA 393.15K; ● DMPDA 313.15K; ○ DMPDA 393.15K.

Table 2 Molecular Structure of Chemicals used in this work

Abbreviation	DMPDA	TMTMDA	DAMDPA	DMDPTA
Molecular Structure				

ii. Effects of the number of amino groups: The solubility levels per mole of amine and per kilogram of amine for DMDPTA and DMPDA are presented in Figure 3A, Figure 3b, respectively. A similar conclusion can be obtained regarding the two subfigures: DMDPTA has higher absorption capacity than DMPDA in unit of mole of CO_2/mol of amine, whereas the capacity is relatively lower in unit of mole of CO_2/kg of amine.

iii. CO_2 absorption heat: As one of the important properties, the absorption heat in the aqueous solution of amine can be estimated using the Gibbs-Helmholtz equation.[21] According to the equation, the absorption heat with different amine aqueous solutions can be calculated from the corresponding solubility data. Results are presented in Figure 4. There is not data for TMTMDA because of no data at the same loading at two temperatures. Values of the absorption heat for DAMDPA, DMPDA and DMDPTA are between -75 and -65 kJ/mol. The comparison of DAMDPA and DMDPTA, offers the conclusion that the absorption heat decreases with the secondary amino group compared that with the primary amino group. When the loading goes larger, the absorption heat decreases first for DMPDA because of DMPDA has only two amino group, while DAMDPA and DMDPTA have three amino group.
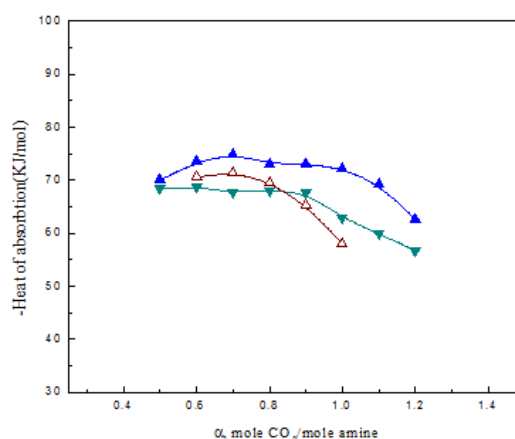

Figure 4 Heats of absorption of CO_2 with aqueous solutions of amines.

▲: DAMDPA; △: DMPDA; ▼: DMDPTA.

Conclusion

CO_2 solubility in aqueous solutions of four branched polyamines are measured and compared with each other. The cyclic absorption capacity increases with an increase in the relative amount of tertiary amino groups in the amines, while primary and secondary amines have similar absorption capacity. For polyamine containing three or more amino groups, the situation is more complex due to impact of the steric hindrance. The high theoretical absorption capacity of tertiary

amines, steric effects, and the instability of bicarbonates should be simultaneously accounted for the total results. As the number of amino groups increases, the ability to absorb CO$_2$ declines. The value of absorption heat is crucial for the energy consumption to desorb CO$_2$, and it decreases as alkyl groups on nitrogen atom increases.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest

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