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Equilibrium solubility of carbon dioxide in aqueous solutions of 3-amino-1-propanol, 4-amino-1-butanol and 5-amino-1-pentanol at low partial pressures

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ABSTRACT

Vapor liquid equilibrium (VLE) data of CO_2 solubility in aqueous amine solutions are essential for solving problems associated with flue gas purification. This work presents new VLE data of 3-amino-1-propanol, 4-amino-1-butanol and 5-amino-1-pentanol, respectively. An equilibrium cell, connected to a gas chromatograph was first utilized to measure the partial pressures of CO_2 over 2-amino-1-ethanol (MEA). The setup was validated against literature data and is capable of producing reliable and reproducible results. Measurements of CO_2 solubility in these primary alkanolamines at two different concentrations (5 molar and 30 wt%) were performed at a temperature of 40 °C. Results showed that these amines have higher CO_2 solubility than MEA, and we found that increasing the chain length increase the solubility of CO_2.

1. Introduction

One of the alternatives to mitigate the amount of carbon dioxide (CO_2) released into the atmosphere is by applying post combustion capture technology onto the power plants [1]. This technology is attractive as it requires less modification to the existing power plants and is thus potentially able to save the operators millions of dollars. Alkanolamine based solvent is currently the preferred method for CO_2 absorption at different partial pressures, and several commercially available amines have been utilized for this technology [2]. Alkanolamines can be classified into three classes depending on the numbers of hydrogen atoms bonded to the nitrogen atom in its amino group. The well-known 2-amino-1-ethanol (MEA), 2-2′-iminodiethanol (DEA) and 2-2′-methylimino-diethanol (MDEA) are examples of primary, secondary and tertiary alkanolamines, respectively.

Information on the solubility of CO_2 in the amine is required in order to evaluate a new solvent. Normally, this will involve measuring partial pressures of CO_2 during equilibrium at different CO_2 and amine concentrations. In industry, CO_2 is chemically absorbed into aqueous amine at a low temperature (approximately 40 °C) and desorbed at high temperature (varies in the range of 90–120 °C). Numerous studies on different types of alkanolamines have been performed to evaluate their suitability for CO_2 absorption. There are many vapor liquid equilibrium (VLE) data of MEA reported by the research groups of Mather and Svendsen over the past years [3–7]. MEA has attracted a lot of attention due to its high absorption rate, low cost, reasonable thermal stability and manageable degradation rates. However, its high desorption energy requirement due to its high enthalpy of reaction with CO_2 and the need for dilution steam have encouraged researchers to look for new and more energy efficient solvents. Sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP) have been proposed as potential candidates due to their high CO_2 absorption capacity; AMP leads to formation of bicarbonate due to instability of its carbamate complex. However, as reported by Hook, problems with precipitation formation and poor absorption rates at low CO_2 levels are some of the challenges needed to be overcome [8]. Mixtures of two or more amines have been reported to increase absorption rates and cyclic capacities. A mixture of MEA and MDEA may be able to save a significant amount of solvent regeneration cost as demonstrated by Idem et al. in their pilot plant studies, albeit, the fulfillment of this mixture is subject to chemical stability of the solvents [9]. Recently, there are reports on utilizing di- or tri-amines which may be able to react with more CO_2 molecules than ordinary amines [10]. A di-amine such as piperazine has been shown to increase the MDEA–CO_2 absorption rate, and the mixture enabling a maximum energy saving of 22% [11].

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List of symbols

VLE	Vapor liquid equilibrium
CO_2	Carbon dioxide
°C	Degree celsius
MEA	2-Amino-1-ethanol/ethanolamine/monoethanolamine
DEA	2-2′-Iminodiethanol/diethanolamine
MDEA	2-2′-Methyliminodiethanol/methyl diethanolamine
AMP	2-Amino-2-methyl-1-propanol
%	Percentage
^{13}C NMR	Carbon-13id=6#NMR
pK_a	Acid dissociation constant
3A1P	3-Amino-1-propanol
4A1B	4-Amino-1-butanol
5A1P	5-Amino-1-pentanol
g	Gram
MΩ cm	Resistivity unit
GC	Gas chromatograph
N_2	Nitrogen
mL	Milliliter
molar	Molarity unit (mole/Liter)
μm	Micrometer
u	Uncertainty
P	Pressure
T	Temperature
A	Area
rep	Repeatability
R^2	Level of confidence
wt%	Weight percentage
kPa	Kilopascal
α	Loading, mole of CO_2/mole of amine
P_{CO_2}	Partial pressure of CO_2
AAD	Average absolute deviation

To be able to effectively select new solvents, the chemical reactions involved between amine molecules and CO_2 needs to be understood. Yang et al. used a ^{13}C NMR technique to examine the effects of amines' chemical structures [12]. Previously, Singh and Versteeg presented the effects that different amines structures have on the CO_2 desorption rate and capacities [13]. Puxty et al. screened 76 different amines and found that the CO_2 absorption capacity for tertiary amines, which do not form stable carbamate complexes, is strongly dependent on pK_a values [14]. We have also illustrated that pK_a values may influence CO_2 loading capacity for sterically hindered amines [15]. Nevertheless, it is also important to collect CO_2-amine solubility data in the laboratory and these data can then be used for estimation and modeling purposes. This paper aims at studying the solubility of CO_2 in different alkanolamine solutions. We present new VLE data for three alkanolamines i.e., 3-amino-1-propanol (3A1P), 4-amino-1-butanol (4A1B) and 5-amino-1-pentanol (5A1P) at 40 °C and two different concentrations, at industrially relevant CO_2 loadings. The amines studied have different chemical structures and an insight into structural effect on the CO_2 absorption will be discussed in this paper.

2. Experimental

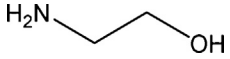
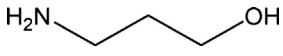
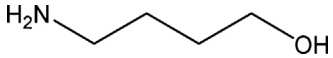
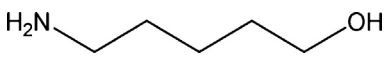
2.1. Chemicals and gases

Table 1 shows the details of the chemicals used in our VLE experiments. All of the chemicals were used as received, without any purification. A precision balance (Mettler Toledo XS-403S, accuracy ±0.001 g) was used to weigh the required amount of chemicals, and solutions were prepared using degassed deionized water (resistivity, 18.2 MΩ cm).

2.2. Measurement of CO_2 solubility

Fig. 1 depicts a schematic diagram of the experimental setup used for measuring CO_2 solubility in alkanolamines. There are two components involved: an in-house equilibrium cell and a gas chromatograph, GC. The equilibrium cell consists of three glass bottles (500 mL) connected in a closed loop system and placed in an insulated oven. During experiments, only one glass bottle was filled with known concentration of aqueous alkanolamines, whilst the remaining bottles were used to supply a sufficient amount of gas to the system to minimize pressure drop during gas sample injections into the GC. The equilibrium cell is designed to operate at temperatures up to 80 °C and is equipped with heating and cooling instruments. A temperature controller with two thermal elements, one inserted in the liquid and the other in the gas (West 6100 supplied by WEST Control Solutions), was used to obtain accurate readings of the temperatures during experiments (accuracy ±0.2 °C). A mass flow meter (SmartTrak 100 from Sierra Instruments) was used to establish a nominal gas mixture into the closed-loop system during experiments' start-up whilst continuous circulation of gases was achieved by using a pump. The pressure of the system was monitored using a pressure gauge, with an accuracy of ±0.02 bar. A magnetic stirrer and a frit were placed in the bottle containing alkanolamine solution to ensure complete mixing of CO_2 gas and the amine solution. Before the start of an

Table 1
Chemicals utilized for our experiments.

Chemical name	Structural formulae	Mole fraction purity	Source	Molecular weight (g/mole)
2-amino-1-ethanol		≥0.995	Merck	61.08
3-amino-1-propanol		≥0.99	Sigma–Aldrich	75.11
4-amino-1-butanol		0.98	Alfa Aesar	89.14
5-amino-1-pentanol		0.97	Alfa Aesar	103.16