SOLUBILITY OF CO$_2$ IN CHOLINE CHLORIDE-AMINE BASED DEEP EUTECTIC SOLVENTS

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Abstract - In this study, we report new measurements of the solubility of carbon dioxide in three types of deep eutectic solvents (DESs), (Choline chloride + Monoethanolamine, ChCl-MEA), (Choline chloride + Diethanolamine, ChCl-DEA) and (Choline chloride + Methyl diethanolamine, ChCl-MDEA), which was determined at three different ChCl:amine molar ratios of 1:6, 1:8 and 1:10. The selected amines represent the primary, secondary and tertiary amines, respectively. The CO$_2$ absorption was conducted with a solvent screening set-up (SSS) and the CO$_2$ loading was measured with an ‘Elementar’ total organic carbon (TOC) analyzer. The solubility experiments were performed based on the conditions of the absorber in the post-combustion capture process ($P_{CO2}$ = 15kPa and $T = 40^\circ$C). Results revealed that amine-based DESs have absorption capacity that is much higher than both 30wt% aqueous amine solutions and conventional DESs. The solubility of CO$_2$ was found to increase as the molar ratio of the amine in the DES increased. ChCl-MEA absorbed the highest quantity of CO$_2$ while ChCl-MDEA absorbed the least.

Keywords - Deep eutectic solvent, Amines, Solubility of CO$_2$, Choline chloride

I. INTRODUCTION

Post-combustion capture technology is one of the chief means of capturing carbon dioxide (CO$_2$) emanating from power plants. The big advantage of post-combustion capture technologies is that they are the most mature carbon capture techniques and they are easy to retrofit existing power plants. Post combustion carbon capture with aqueous amines is the most advanced because of their high absorption capability of CO$_2$ and high selectivity of CO$_2$ over N$_2$. However, the utilization of aqueous amines have brought with it some demerits like high regeneration energy, high cost, high vapor pressure, corrosion, fouling, foaming, instability etc.

This study seeks to alleviate the disadvantages encountered with conventional aqueous amines absorbents whilst maintaining their high absorption capacity with the utilization of novel solvents referred to as deep eutectic solvents. The idea of deep eutectic solvent was first described by Abbot et al. in 2003 [1]. Deep eutectic solvent (DES) is a solvent composed of a mixture of two or more components that forms a eutectic with melting point lower than that of individual components.

Although there are several studies that have been conducted in order to determine the solubility of CO$_2$ in different types of conventional DESs [2-8], there are little to no work that has been studied on the solubility of CO$_2$ in amine-based DESs [9-10]. Determination of the solubility of amine based DESs is particularly important because conventional DESs have lower solubility of CO$_2$ as compared to amine based DESs. Moreover, conventional DESs need to work at a pressure above 5 bars for (physical) absorption to be significant.

In this study, we report new measurements of the solubility of CO$_2$ in three types of amine based deep eutectic solvents, (ChCl-MEA), (ChCl-DEA) and (ChCl-MDEA), which was determined at three different molar ratios of 1:6, 1:8 and 1:10.

II. EXPERIMENT

2.1 Materials

Monoethanolamine (MEA≥99%), diethanolamine (DEA≥99%), methyl diethanolamine (MDEA≥99%), Choline chloride (2-hydroxyethyl-trimethylammonium) (≥98%) were all purchased from Sigma Aldrich and used without any further purification. Deionized water of purity more than 1 MΩ.cm was obtained using Purite’s PUREWATER 300.

2.2 Sample preparation

In this work, the method of preparation reported by Abbott et al. [1] was used. The proper quantities of salt and HBD were put in a well-sealed vial. The vial was then placed on a hot plate and stirred at around 80°C for about a few hours until a homogeneous colourless liquid is formed. This is a very good method for producing DESs, easy to follow and less expensive compared to the synthesis of ionic liquids whereby reactors are needed to carry out the syntheses reactions and further purification is required to purify the resulting ionic liquid.

2.3 Carbon dioxide solubility measurements

After the DES has been prepared, the CO$_2$ solubility experiment was conducted with the solvent screening experimental set-up and the CO$_2$ was analyzed with an ‘Elementar’ Total Organic Carbon (TOC) analyzer. The solvent screening set-up (S. S. S.) equipment is constituted of six glass reactors ($V = 250\text{mL} \pm 0.5$) which can be operated independently in
the temperature range from 298.15-423.15 K (±1K) and the pressure range of 0-6 bars (±0.01 bar). The tests were done at 313.15K with a mixing speed of 500 rpm. Moreover, to simulate the flue gas flow, a blend of CO2 and N2, with 15 vol% and 85 vol% respectively, is first fed to make-up vessel until a pressure of 2 bars is reached and then flown into the reactors at a flow rate of 15 L/h controlled by a mass flow controller. The pressure inside each reactors was kept at 1 bar during all the CO2 absorption experiment. The reaction of CO2 with the aqueous amine solution was complete when the equilibrium is reached i.e. when the flow of CO2 in is equal to the flow of CO2 out (Fig. 1). After the solvent has become saturated with CO2, the carbon loading in mole of CO2 per mole of solvent was obtained with the ‘Elementar’ total organic carbon (TOC) analyzer.

**III. RESULTS AND DISCUSSION**

### 3.1 Validation of the Solubility Method

The validation of experimental methods and procedures is of prime importance in empirical studies before further estimation is made with the experimental set-up. The solubility method for this study was validated with the experimental data of Kohl and Nielsen [11]. The CO2 loading for 30% weight of MEA obtained in this study agrees well with what is obtainable in the literature (Fig. 2). Hence, the solubility method was utilized for further study.

### 3.2 Effect of HBD and Molar Ratio on the Solubility of CO2

One significant benefit of amine based DESs over conventional DESs (Choline Chloride- Urea (ChCl-U), Choline Chloride-Glycerol (ChCl-G), Choline Chloride-Ethylene Glycol (ChCl-EG) etc.) is that amine based DESs have far higher solubility of CO2 compared to their conventional DESs counterparts (Fig. 3). Moreover, the solubility of amine based DESs is much higher than that of aqueous solutions of amines. For instance, the solubility of CO2 in ChCl-MEA 1:8 is almost 265% of that of 30% wt, aqueous MEA as compared to 12.3% of ChCl-Glycerol.

Absorption of CO2 in amine based DES can occur by both physical and chemical means. For the chemical absorption, the solubility of CO2 in primary, secondary and tertiary amines depends on the reaction steps in the equilibrium reaction mechanisms. For primary and secondary amines, the reaction proceeds in two steps without the need for water addition in order to obtain carbamate. However, for tertiary amines, the one step reaction would not proceed in the absence of water. The first step for the primary and secondary amines is bimolecular, second order and rate determining while the second step is instantaneous. The reaction steps for the mechanism are listed below for primary and secondary amine using $R_1R_2NH$ to represent both [14]:

**First stage:**

$$CO_2 + R_1R_2NH \rightleftharpoons R_1R_2NCOOH$$

**Second stage:**

$$R_1R_2NCOOH + R_1R_2NH \rightleftharpoons R_1R_2NCOO^- + R_1R_2NH_2^+$$

Amine based DESs have similar solubility of CO2 when compared with stand-alone amines. ChCl-MEA DESs have solubility of CO2 of around 265% of the solubility of CO2 in 30% weight MEA (Fig. 4). This solubility comes from both physical absorption and chemical absorption. The physical absorption is attributed to the ability of the choline chloride to form hydrogen bonds with the amines. The solubility of CO2 increased with increasing molar ratio of amine in the DES. This is reasonable because the more the
amine, the more the possibility of the formation of hydrogen bond network with the choline chloride.

Fig. 4 Effect of molar ratio on the solubility of CO2 in ChCl-MEA

The solubility of CO2 in 30% weight DEA is lower than that of 30% weight MEA. The same is true for their amine based DESs. ChCl-DEA DES has a lower solubility of CO2 than that of ChCl-MEA DES. This can be attributed to the higher viscosity of ChCl-DEA as compared to ChCl-MEA. This results in an extensive hydrogen bond network between each component in the DES, which in turn results in lower mobility of free species within the DESs. Another cause of lower solubility of CO2 is the other forces of interaction like van der Waal’s and electrostatic interactions, and small void volume. The solubility of CO2 in ChCl-DEA is around 163% of the solubility of 30% weight DEA aqueous solution (Fig. 5). Moreover, the solubility of CO2 increased with the increase of the molar ratio of DEA in the DES. This is reasonable because more DEA addition will lead to increased physical and chemical absorption of CO2.

Fig. 5 Effect of molar ratio on the solubility of CO2 in ChCl-DEA

For the chemical absorption of CO2, there is only one reaction step for the formation of carbamate with tertiary amines and that reaction step requires water [15]. The reaction would not proceed in the absence of water. This is why the solubility of CO2 in ChCl-MDEA is only around 16% of the solubility of CO2 in 30% weight MDEA (Fig. 6). Donaldson and Nguyen also suggested the mechanism in which tertiary alkanolamines cannot react directly with CO2. These amines have a base-catalytic effect in the hydration of CO2 [12]. This was also confirmed by Versteeg and Van Swaaij by the absorption of CO2 into a water free solution of MDEA and ethanol [13]. They concluded that CO2 was only physically absorbed and also agreed with the proposed reaction mechanism [14]. At higher pH values (pH =13), a direct reaction between CO2 and tertiary amine has been reported by Jørgensen and Faurholt [14]. However, the rate of this reaction can be neglected at lower pH values (pH < 11) [14], which is the case of MDEA. Versteeg and Swaaij [15] showed that the rate of absorption of CO2 into an MDEA-ethanol solution could be described as physical absorption, which was almost identical to absorption of N2O in the same solution. Hence, the 16% extra absorption of CO2 can be attributed to the physical absorption of CO2.

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R_1R_2R_3N + H_2O + \text{CO}_2 \rightleftharpoons R_1R_2R_3\text{NH}^+ + \text{HCO}_3^-
\]

The solubility of CO2 increased with the increase of MDEA molar ratio in the DES. This is reasonable because more MDEA addition will lead to increased physical absorption of CO2.

Fig. 6 Effect of molar ratio on the solubility of CO2 in ChCl-MDEA

CONCLUSION

In this study, we report new measurements of the solubility of CO2 in three types of amine based DESs, (ChCl-MEA), (ChCl-DEA) and (ChCl-MDEA), and at three different salt:amine molar ratios of 1:6, 1:8 and 1:10. Results revealed that amine-based DESs have absorption capacity that is much higher than stand-alone amine solvents and conventional DESs. The solubility of CO2 was found to increase as the molar ratio of the amine in the DES increased. ChCl-MEA absorbed the highest quantity of CO2 while ChCl-MDEA absorbed the least.

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