Betaine-based deep eutectic solvents with diol, acid and amine hydrogen bond donors for carbon dioxide absorption

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Abstract. Deep eutectic solvents (DESs) are known as alternative green solvents due to their ease of synthesis, availability, biodegradability and negligible volatility. DESs consisted of betaine as the hydrogen bond acceptor with 1,2-propanediol, levulinic acid and methyl diethanolamine (MDEA) as the hydrogen bond donors, were prepared in 1:3 and 1:6 molar ratios. The carbon dioxide solubilities in these DESs were determined using a volumetric apparatus at 313.15 K and 6 bar. The results show that CO2 solubilities in betaine-based DESs are higher than the reported CO2 solubilities in choline chloride-based DESs, for DESs having the same hydrogen bonding donor and an identical or similar composition. The viscosity and polarity of hydrogen bond donors affected the ability of deep eutectic solvent to absorb carbon dioxide. The betaine-MDEA deep eutectic solvent, with molar ratio of 1:6, has the highest absorption capacity of 0.0814 mol CO2/mol DES, measured at 313.15 K and 6 bar.

1 Introduction
The presence of carbon dioxide (CO2) reduces the calorific value of industrial gases and potentially freezes in the liquefaction processes. Natural gases in Indonesia contain varying amount of carbon dioxide up to 70%, while the required level of carbon dioxide in a sales gas must be below 3-5%. This requirement could be met using commonly used technology such as carbon dioxide absorption using alkanolamine solvents [1]. Carbon dioxide absorption is a mature technology. However, it still has deficiencies such as high operating costs for solvent regeneration, corrosion, solvent degradation, and amine emissions causing environmental and health effects [2,3]. Other methods such as adsorption, cryogenic distillation, and membrane technology also have been applied. However, carbon dioxide adsorption tends to have lower adsorption efficiency [4], cryogenic distillation requires high installation and operating costs [5], and membrane separation could suffer from large pressure drop and low selectivity that cause hydrocarbons to escape with carbon dioxide [6]. Uses of ionic liquids (ILs) have been explored due to their properties such as extremely low vapor pressures, wide liquid temperature range, and their ability to dissolve CO2. In spite of the advantages, ILs are still relatively expensive and their toxicities have hindered their industrial applications [7].

More recently, deep eutectic solvents (DESs) have been studied as substitutes for ILs as green solvents. A DES, in a strict sense, is a mixture of two or more components that possesses the lowest melting point temperature among all of the possible compositions. DESs consist of a hydrogen bond acceptor (HBA) molecule, usually a quaternary ammonium salt such as choline chloride, and one or more hydrogen bond donor (HBD) molecule such an amide or a carboxylic acid. These DESs are usually stable as liquids at room-temperature and has been used in diverse areas such as electrolytes in...
metal processing [8] and extraction of bioactive compounds [9]. DESs could be prepared from many readily available organic compounds making them suitable as ‘designer solvents’. They are also known as 'green solvents' since many HBAs and HBDs have low vapor pressures with excellent biocompatible and biodegradable properties [9].

DESs have been used as a potent absorbent for gases such as carbon dioxide, mainly with choline chloride as the HBA [10]. Garcia et al showed that choline chloride with propanediol DES has ability to absorb CO$_2$ [11]. Adeyemi et al. showed that amine based DES are better in absorbing CO$_2$ than other DES by 30% [12]. DESs are easy to prepare at high purity, low toxicity, and low cost. Betaine was chosen as the hydrogen bond acceptor because it is classified as a non-toxic quaternary ammonium salt and most of carbon dioxide absorption with DES research using choline chloride as HBA. Relatively low toxicity diol, acid and amine group are chosen to determine the best combination of betaine based DES for carbon dioxide absorption.

2 Materials and methods

2.1 Materials

The raw materials used in this study were empty analytical grade betaine anhydrous (>98%), Levulinic acid (>98%), 1,2-propanediol (>99.5%), MDEA (>98%) were purchased from Merck. High purity gases were used Helium (99.995%) and CO$_2$ (99.995%).

2.2 DES synthesis

Both HBA and HBD are put into 250 ml closed beaker glass, then heated and stirred at the same time using hot plates and magnetic stirrer. The temperature is set at 50°C for 90 minutes. After that, the DES was kept in a closed flask at room temperature for several days until it was homogeneous and ready to be used for absorption of carbon dioxide [3]. DES prepared in this work is shown in Table 1.

| Code  | HBA and HBD        | HBA to HBD mole ratio |
|-------|--------------------|-----------------------|
| MDEA-6| Betaine - MDEA     | 1:6                   |
| LEV-3 | Betaine - levulinic acid | 1:3               |
| LEV-6 | Betaine - levulinic acid | 1:6               |
| PRO-3 | Betaine - 1,2-propanediol | 1:3              |
| PRO-6 | Betaine - 1,2-propanediol | 1:6              |

2.3 Carbon dioxide absorption measurement

The carbon dioxide absorption capacity was measured using the volumetric method and the equipment used is shown in figure 1. Charging cell and measuring cells are made of SS 304 stainless steel and are connected by a stainless steel tube. The temperature of both cells was maintained using a HUBER circulating water bath, measured using type K thermocouples. Pressure was measured by a PTX DRUCK 1400 pressure transmitter. Pressure and temperature were recorded using the National Instrument data acquisition system.

The measurement procedure consists of measuring the volume of measuring cell followed by measuring the solubility of carbon dioxide in a DES. In both measurements, the equipment underwent degassing process to clean the equipment from impurities and accurately measured amount of DES was put into the charging cell. Degassing was done by heating the charging cell at 140 °C in vacuum by using a vacuum pump for 2 hours. The measuring cell volume was determined by charging helium gas into the charging cell and the initial pressure was recorded. Then, the valve between the charging cell and the measuring cell was opened to let helium gas fill both cells. Pressures and temperatures in both cells were recorded after equilibrium is reached, approximately in 15 minutes. The amount of
absorbed gas was calculated from pressure changes and compressibility factor (Z) obtained from the REFROP software version 8.

![Image of the CO2 absorption equipment]

**Figure 1.** Schematic of the CO2 absorption equipment.

The following equation provided the relationship between specific volume, Z, temperature, and pressure:

\[ V = \frac{n \cdot Z_{\text{He}} \cdot R \cdot T}{P} \]  

(1)

and the solubility of carbon dioxide in DES was calculated using the following equations:

\[ \text{CO}_2\text{absorbed} = \left( \frac{P_{\text{CC}}V_{\text{CC}}}{zRT_{\text{CC}}} \right)_i - \left( \frac{P_{\text{MC}}V_{\text{void}}}{zRT_{\text{MC}}} \right)_f + \left( \frac{P_{\text{MC}}V_{\text{void}}}{zRT_{\text{MC}}} \right)_f \]  

(2)

\[ x \cdot \text{CO}_2\text{terabsorp} = \frac{n_{\text{CO}_2}}{n_{\text{CO}_2} + n_{\text{DES}}} \]  

(3)

where CC, MC, void, i, and f, signify charging cell, measuring cell, system volume (excluding volume of charging and measuring cells), initial condition, and final condition after the valve is opened, respectively.

2.4 **Density of DESs**

The density measurement is carried out by using the Anton Paar densitometer, operated at constant temperatures of 20, 30, and 40 °C.

2.5 **Infrared spectra**

FTIR (Fourier Transform Infrared Spectroscopy) spectra of each DES were obtained an IR spectrophotometer, scanned in the wavenumber range of 500-4000 cm\(^{-1}\).

3 **Results and discussion**

3.1 **Density of DESs**

The density of the DESs decreases with increasing temperature as given in Table 2. The enhanced activity and molecular mobility, increased the molar volume and decreased the density of the solvents [13]. In general, densities of the DESs are greater than that of water, influenced by the molecular structure of the HBA and the HBD that form the DES. In addition, the molar ratio of the quaternary salt to HBD also affects the density.
Table 2. Density of DES used in this work.

| Code | Temperature (°C) | Density (g/cm³) |
|------|-----------------|----------------|
| MDEA-6 | 20.01 | 1.0645 |
| | 29.99 | 1.0575 |
| | 39.99 | 1.0503 |
| | 20.01 | 1.1569 |
| LEV-3 | 29.99 | 1.1497 |
| | 39.99 | 1.1425 |
| | 20.01 | 1.1518 |
| LEV-6 | 29.99 | 1.1439 |
| | 39.99 | 1.1360 |
| | 20.01 | 1.0825 |
| PRO-3 | 29.99 | 1.0759 |
| | 39.99 | 1.0694 |
| | 20.01 | 1.0632 |
| PRO-6 | 29.99 | 1.0563 |
| | 39.99 | 1.0493 |

3.2 Infrared spectra of DESs

IR spectra of MDEA-6, LEV-3 and LEV-6, PRO-3 and PRO-6 DESs are shown in figures 2, 3, and 4, respectively. Betaine-MDEA and betaine-1,2-propanediol DESs absorb infrared rays in the wavelength range of 3200-3600 cm⁻¹ due to the presence of the O-H (hydroxyl) group (figures 2 and 3).

![Figure 2. IR spectra of betaine-MDEA.](image)

In DES with higher diol to betaine mole ratio, the shape of the O-H curvature becomes deeper, indicating stronger O-H bonds. Another bond present in the alcohol-based DES is an in-plane C-O-H bond, seen in the wavelength range of 1370-1450 cm⁻¹ (figure 3). This bond is sharper, is not as wide as the O-H bonds, and seen in all types of alcohol-based DESs. As for Betaine-Levulinic C-H group (2920 cm⁻¹) and aliphatic ketone group (1200-1700 cm⁻¹) can be seen in IR spectra (figure 4).
3.3 Solubility of carbon dioxide in DES

The isothermal absorption of CO$_2$ was carried out at a temperature of 313.15 K and at pressures of up to 10 bar. For comparison purposes, CO$_2$ mole fraction absorbed in each DES was interpolated to absorption at 6 bar, assuming a linear dependence of absorption on pressure. The absorption capacity (in mol CO$_2$/mol DES) of the DESs tested are decreasing in the order: MDEA-6 (0.0814) > PRO-6 (0.0484) > PRO-3 (0.0422) > LEV-6 (0.0400) > LEV-3 (0.0311). The absorption of CO$_2$ in DESs increases when the pressure of absorption (partial gas pressure) is higher, following the Henry’s law for absorption at isothermal temperatures.

In addition to pressure, the physicochemical properties of DESs also affect their ability to absorb CO$_2$. These properties are the polarity and viscosity of DES which have important roles in the CO$_2$ absorption process [14]. Figure 5 shows that for DES with same HBA and HBD as the viscosity decreases, the ability of DES to absorb CO$_2$ is higher. This is because when the lower viscosity DES has more free volume, means the greater the amount of CO$_2$ that can be absorbed.

Carbon dioxide is a non-polar compound that has a tendency to bind to other non-polar compounds [15]. Figure 6 shows the relationship between polarity and the ability of DES to absorb CO$_2$. Betaine-1,2-propanediol (1:3) as the most non polar DES in this research is not the best DES in absorbing CO$_2$ This is because there are other factors that affect the ability to absorb CO$_2$ such as viscosity, HBD mol ratio and HBD functional group.

The mole ratio of HBD and the functional group of HBD also has an important effect on the ability of DES to absorb CO$_2$. As the HBD mole ratios become larger the DES tends to be more polar but the viscosity is lower. In this study, it is found that betaine-MDEA (1:6) has the highest ability to...
absorb CO₂ even though its viscosity and polarity is in the middle of other DESs. This is due to the acid-base reaction between MDEA, a basic amine, and an acidic CO₂ [16]. It is of interest to compare the CO₂ absorption capacity of betaine-based DESs with choline chloride-based DESs that have been reported so far. The comparative advantage of the betaine-based DESs is given in Table 3.

![Figure 5](image1.png)

**Figure 5.** The effect of viscosity on DES absorption solubility.

![Figure 6](image2.png)

**Figure 6.** The effect of polarity on DES absorption solubility.

| DES                    | HBA:HBD mole ratio | Solubility (S) mol CO₂/mol DES | T (K) | P (bar) | dS/dP (mol CO₂/mol DES/bar) | Source            |
|-----------------------|-------------------|--------------------------------|-------|---------|----------------------------|-------------------|
| Betaine-MDEA          | 1:6               | 0.0814                         | 313.5 | 6.0     | 0.0136                     | This work         |
| ChCl-MDEA             | 1:6               | 0.0754                         | 313.5 | 0.15    | 0.0176                     | [16]              |
| Betaine-levulinic acid| 1:3               | 0.0311                         | 313.5 | 6.0     | 0.0052                     | This work         |
| ChCl-levulinic acid   | 1:3               | 0.0274                         | 313.5 | 5.8     | 0.0045                     | [17]              |
| Betaine-1,2-propanediol| 1:3              | 0.0422                         | 313.5 | 6.0     | 0.0070                     | This work         |
| ChCl-1,2-propanediol  | 1:2               | 0.0204                         | 323.5 | 6.0     | 0.0032                     | [18]              |
Conclusion

Higher carbon dioxide solubility in betaine-based has been shown to be higher than in choline chloride-based deep eutectic solvents. Pressure, polarity, viscosity, and hydrogen-bonding donor functional groups affect the capacity of a DES in absorbing CO$_2$ under isothermal conditions. Based on the results of the five DESs tested, higher CO$_2$ absorption capacity can be achieved using a less viscous and more polar DES. Significantly higher CO$_2$ absorption capacity of 0.0814 mol CO$_2$/mol DES is achieved at equilibrium pressure of 6 bars using the betaine-MDEA in 1:6 molar ratio, due to the acid-base reaction between basic MDEA and acidic carbon dioxide.

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