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Natural Deep Eutectic Solvents (NADES) as Green Solvents for Carbon Dioxide Capture

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Abstract. This study was conducted to determine the effectiveness of Natural Deep Eutectic Solvent (NADES), consisting of choline chloride and a hydrogen bonding donor (HBD) compound, in terms of carbon dioxide absorption. Solubility of carbon dioxide in NADES was found to be influenced HBD compound used and choline chloride to HBD ratio, carbon dioxide pressure, and contact time. HBD and choline/HBD ratios used were 1,2-propanediol (1:2), glycerol (1:2), and malic acid (1:1). The carbon dioxide absorption measurement was conducted using an apparatus that utilizes the volumetric method. Absorption curves were obtained up to pressures of 30 bar, showing a linear relationship between the amount absorbed and the final pressure of carbon dioxide. The choline and 1,2-propanediol eutectic mixture absorbs the highest amount of carbon dioxide, approaching 0.1 mole-fraction at 3.0 MPa and 50°C. We found that NADES ability to absorb carbon dioxide correlates with its polarity as tested using Nile Red as a solvatochromic probe.

Keywords. Deep eutectic solvent, carbon dioxide, absorption, choline chloride

INTRODUCTION

Why capture CO_2

Concern about the global warming has driven the scientific community to develop processes for capturing carbon dioxide (CO_2) since this gas is considered responsible for the greenhouse phenomenon. The removal of CO_2 from natural gas or flue gas is a challenge due to the large volume of CO_2 source gases and lower CO_2 concentration. Various methods of carbon dioxide capture have been performed such as selective adsorption or absorption, membrane separation, and ionic liquid (IL) absorption; however, these methods still have drawbacks such as energy consumption, corrosion, and pollution problems. Various amine solutions have been widely used as solvents for chemical absorption CO_2. However, amine-based processes have the following drawbacks: high operational cost, solvent regeneration, and the tendency of amines to undergo thermal degradation.

Due to the toxicity and high cost of ILs, ionic solvents known as deep eutectic solvents (DES) having similar physical properties and behavior as ILs, have been developed in recent years. Mixing two or more pure solid in certain ratio would produce a liquid having a lower melting point than those of the individual DES components. Natural-based DES (NADES) can be formed by mixing a non-toxic quaternary ammonium salt such as choline chloride (ChCl), and low toxicity hydrogen bond donor (HBD) compounds such as urea, polyols, sugar, and organic acids. The eutectic point in NADES is due to the presence of hydrogen bonding between the chloride of choline chloride and the protons in HBDs. NADES are chosen in this study because these are promising solvents, just like ILs, but they are readily available at much low cost, easy to prepare in high purity, and have low toxicities. Choi et al[1] showed that NADES can be formed from natural-based chemicals and NADES are promising lower toxicity ILs. Choline chloride is considered GRAS (generally recognized as safe) and is known for its nutritional benefits, for example, as a supplement to lower cholesterol level. Many inexpensive, non-toxic, non-flammable, and biodegradable natural HBDs are available. Glycerols are produced from the hydrolysis of triglycerides found in fats and oils of vegetables and animals, which could be converted into 1,2 propanediol. Xylitol, a polyol, can be produced from hemicellulose extracted from cornhusks, sugar cane

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baggase, wheat straws, which is hydrolyzed into xylose and then hydrogenated into xylitol. Glucose that is known as grape sugar is a monosaccharide found in plants. Malic acid as dicarboxylic acid can be isolated from many fruits such as apples, grapes, and vegetables. These compounds are selected as HBD in this study.

Natural deep eutectic solvents (NADES)

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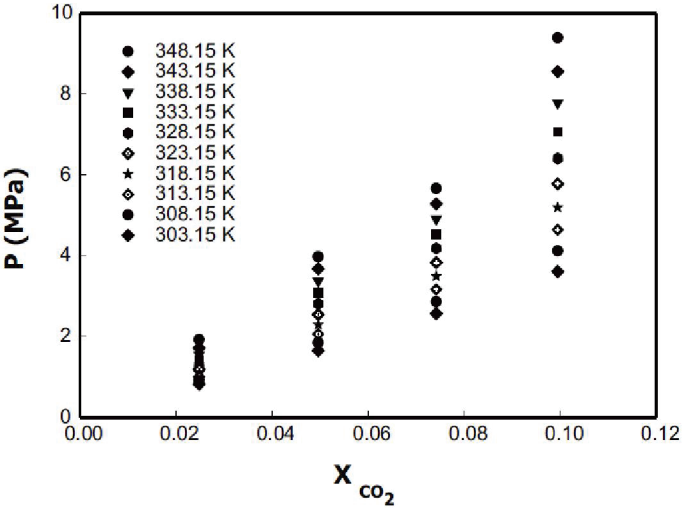

FIGURE 1. Bubble point of choline chloride-lactic acid (2:1 mole ratio).

MATERIALS

Analytical grade choline chloride (> 98%), malic acid (> 99%), glycerol (> 99%), 1,2-propanediol (> 99.5%), were purchased from Sigma Aldrich. High purity gases were used (Helium 99,995 % and CO_2 99,995 %).

METHODS

NADES Preparation

Both bond donor and acceptor of CO_2 put into a closed glass flask size 100 ml and stirred until homogeneous before it is heated. The temperature is set to be 80°C ± 0.1 K using a thermostatic oil bath with a temperature controller. When the solid mixture becomes a molten solution, a hot plate stirrer and a magnetic bar were used to fasten the NADES formation. After that, NADES settled at room temperature in a period of 1-7 days until ready to be used for CO_2 absorption stage. Three different NADES has been prepared for the isothermal absorption studies: malic acid-choline (MCh). 1,2-propanediol-choline (PCh), and glycerol-choline (GlyCh).

CO_2 Absorption Equipment Preparation

The isothermal absorption study was conducted based on the volumetric method. Variables measured by the volumetric method are pressure and temperature, while the volume of pressurized chambers is already known. When equilibrium is reached, the amount of the absorbed gas could be calculated from pressure changes that occur with the use of a CO_2 gas-specific equation of state. The amount of moles is calculated using the compressibility factor, Z obtained from REFROP software Version 8. Isothermal test equipment is shown Fig 2. The isothermal absorption test equipment, in principle, consists of two cylinders that cylinder charging (charging cell) and cylinder measurements (measuring cell) made of 304 stainless steel (SS 304). Both tubes were connected to a stainless steel tube, wherein the charging cell immersed in a fluid whose temperature is controlled by circulating thermal bath (HUBER) with an accuracy of 0.2°C and measuring cell is placed on a hotplate stirrer IKA brand. The pressure in both cylinders was measured by using a pressure transmitter with a measurement range of 0-40 bar absolute (PTX DRUCK 1400) with an accuracy of 0.15%. A type K thermocouple class is used to measure the temperature of the absorbate (CO_2) and the absorbent (NADES). Pressure and temperature data recorded by the data acquisition (National Instrument).

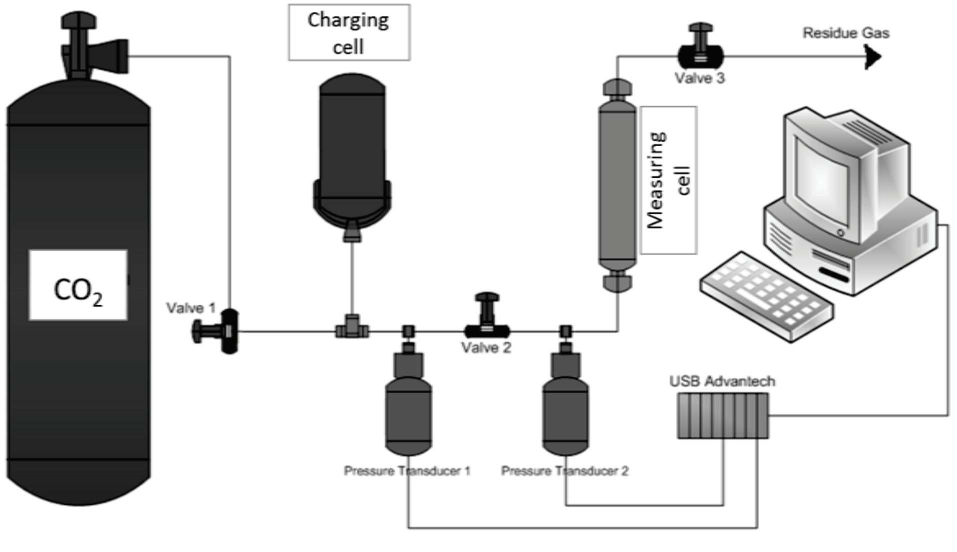

FIGURE 2. The schematic of CO_2 Absorption Equipment.

Charging cell volume is measured by weighing the empty and the water-filled charging cell filled with water to obtain the mass of water required to fill up the chamber, and, divide the mass of water by its density. The empty volume of the measuring cell is the total volume of empty space subtracted by the NADES added into the measuring cell. The temperature in the measuring cell and the charging cell conditioned at a temperature of 30°C using a circulating thermal bath. Helium gas is inserted into the charging cell by opening valve 1. The valve is closed again when the pressure in the charging cell has reached the desired pressure. Initial charging pressure cell noted, the data will be obtained by the number of moles of He contained in the charging cell.

By opening the gas valve 2, He goes into the cell and then measuring the pressure at the end of charging cell recorded and the number of moles of He that goes into the measuring cell calculated. Having reached equilibrium conditions, where the charging pressure measured in the cell is constant for about 15 minutes, the final pressure in the measuring cell is recorded, and the empty volume of the measuring cell calculated. This procedure is repeated several times.

RESULTS AND DISCUSSION

In principle, NADES manufacture is done by mixing the two chemicals and stirred at a temperature of 55°C during the period of 30 minutes to 2 hours. But not all NADES be formed under these conditions. If NADES formed of two solids, it must be stirred and heated at a temperature of 80-100°C[5]. In this study, a single HBA (choline chloride) and three HBD (malic acid, 1,2-propanediol, and glycerol) are used. Treatment for these three different HBD in the making and is described in the following table:

TABLE 1. NADES mixtures used.

Type of NADES	Molar Ratio	Code	Mixing time (min)	Mixing temperature (°C)	Time to reach stability (days)
ChCl – 1,2-Propanediol	1:2	DES-1	60	55	1
ChCl – Malic Acid	1:1	DES-2	90	80	14
ChCl – Glycerol	1:2	DES-3	60	55	7

NADES formation time varied in the range of 1-14 days is due to differences in the time required by each compound mixture to reach the eutectic point. The energy required to lower the melting point of the solid compounds such as malic acid (130°C) is greater than the energy to lower the melting point of 1,2-propanediol and glycerol were lower (-59 and 17.8°C, respectively). Therefore, in making any use of malic acid NADES that require time and temperature higher than the manufacture of other NADES[5].

Polarity of NADES

Nile Red dye produces different colors on NADES or ethanol solvent. The solubilization of Nile Red in different solvents was also required different times. Nile Red is very rapidly soluble in ethanol, giving off a strong pink color. In NADES, the color of Nile Red takes some time to be seen, especially the very viscous NADES of malic acid. In NADES based on 1,2-propanediol, the color change of Nile Red was rapid[6]. It is assumed that the viscosity inhibits the dissolution of Nile Red in NADES. Polarity is expressed in molar transition energy (ENR) were calculated from the absorption maximum of Nile Red dissolved in NADES. The ENR calculation formula is:

$$E_{NR}(kcal\ mol^{-1}) = 28591/\lambda_{max}$$

TABLE 2 shows the ENR values of the NADES used in this study. It can be seen that the addition of alkyl chain length on the causes that the smaller the value of ENR.

TABLE 2. Polarity of NADES

HBD	Λ (nm)	E_{NR} (kcal/mole)
Propanediol, 1:2	563	50,7
Glycerol, 1:2	575	49,6
Malic Acid, 1:1	608	46,9

The addition of hydroxyl groups increases the polarity value. At the eutectic mixture proportion of alcohol is replaced by salt ions, which had a rate greater polarity than the alcohol itself. In this study, chloride ions affect the polarity of the solvent. The addition of ChCl can cause a decrease in the hydrogen bond donors considering that chloride ions act as a compound that disrupt the structure[9].

FTIR

Based on the IR spectra shown that the malic acid OH groups can be seen in both solvents, either pure or NADES. However, noticeable changes in wavelength caused by the involvement of hydrogen bonding in the formation NADES. While the C=O groups on malic acid: choline chloride looks sharper because of the involvement of hydrogen bonding. As for 1,2-propanediol and glycerol, they do not have significant changes in the CH group, but the wavelength of visible differences in the OH group, both in the solution of 1,2-Propanediol: choline chloride and glycerol: choline chloride. This is due to the involvement of hydrogen bonding in the formation NADES[2].

DSC

NADES have T_g below -50°C without melting point, indicating that NADES are supermolecular complexes with a stable liquid state in a wide temperature range[5]. Conditions NADES liquid at low temperatures showed that NADES contribute to the life of plants at low temperatures. It is also proved that NADES can be used as a solvent at a temperature between 20-100°C. However, in this study the results obtained are not suitable due to an error in setting the temperature on the DSC instrument. Supposedly DSC curves were recorded in a temperature range of -50°C to 120°C at a rate of $10^{o}C^{min-1}$ by raising and lowering the heat using nitrogen. Final transition on the DSC chart is the degradation temperature, T_d. At this point in the heating cycle, individual bonds between atoms will begin to break the vibration until the end of each molecule decomposes into individual components. T_d may occur in endothermic or exothermic conditions. In NADES, T_d occurs in endothermic conditions.

Viscosity of NADES

The viscosity data of NADES used in this study determined using a Brookfield viscometer is given in TABLE 3. The data show that choline: 1,2-propanediol has the lowest viscosity compared with the two other compounds, namely 25 cp. NADES made of choline chloride: malic acid, which has the highest viscosity 446 cp. Viscosity decreases with increasing number of carbon chains and choline chloride. NADES made by the molar mass ratio, which means the greater the value of the molar mass of an HBD greater the choline chloride is needed. It can be explained that the decline in the strength of hydrogen bonds directly proportional to the decrease in the amount of choline chloride. Hydrogen bond formation causes more resistance to deformation of the structure. However, no specific measures to support this hypothesis and more research should be done on the strength of hydrogen bonds[2].

TABLE 3. Viscosity of NADES.

HBD	Λ (nm)	Viscosity (cp)
Propanediol, 1:2	563	25
Glycerol, 1:2	575	113
Malic Acid, 1:1	608	446

CO_2 Absorbed by NADES

FIGURE 3 shows that the 1,2-propanediol: choline chloride (2:1) absorb the most CO_2 compared with the other two mixtures: glycerol: choline chloride (2:1) and malic acid: choline chloride (1:1). It can be seen that the absorption capacity is linearly dependent on the pressure of the absorption process. The carbon dioxide absorption capacity of the NADES at a constant temperature will increase at higher pressures as stipulated by the Henry's law. The highest absorption capacity, given as the mole fraction of CO_2 in the NADES, is approximately 0.9 for the 1,2-propanediol/choline chloride mixture with molar ratio of 1:1 at 30°C.

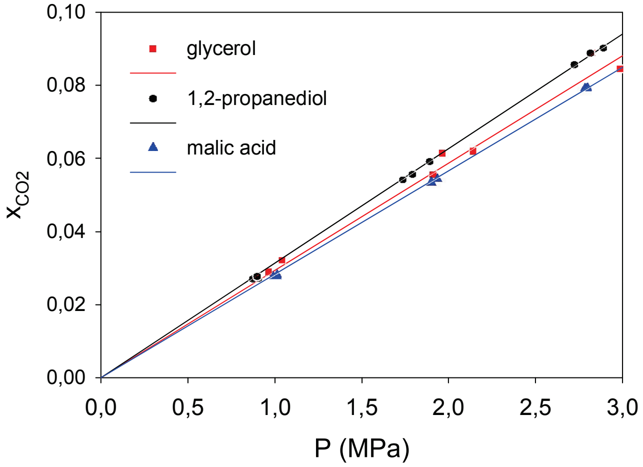

FIGURE 3. Mole-fraction of CO2 in NADES as a function of pressure.

NADES ability to absorb CO_2 is also influenced by the physicochemical, the polarity and viscosity. FIGURE 4 shows the relationship between the polarity and viscosity of NADES and the number of moles of CO_2 are absorbed at 30 bar. CO_2 is non-polar compound, and, non-polar compounds have a tendency to interact with non-polar compounds[7], but NADES a polar compound. It can be seen that malic acid: choline chloride (1:1) is the most polar solvent with the lowest CO_2 absorbing capabilities. While 1,2-propanediol: choline chloride (2:1) is the least polar compound and the highest CO_2 absorbing capabilities. Therefore, it can be concluded that the polarity affects the ability to absorb CO_2 NADES. The more polar NADES, the lower the ability of the solvent to absorb CO_2.

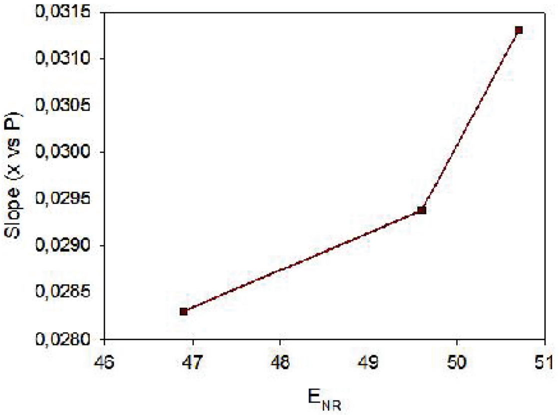

FIGURE 4. The plot of the slope obtained from absorption data correlated with the Nile Red solvatochromic polarity of NADES.

Based on several previous studies have reported that NADES have the ability to lower CO_2 absorption[8]. This limitation can be achieved by adding the amine group to form a chemical bond. Increased viscosity NADES cause considerable energy needed to absorb CO_2[9]. CO_2 reacts with an acid to form a carbamic group. Chemical absorption of CO_2 occurs and causes an increase in viscosity NADES anyway, but this can be reduced by reducing the number of available hydrogen on the anions on hydrogen bonding. Yu and Zhang[10] studied the intermolecular interactions and claimed that the NH2 hydrogen bonding can improve interaction between anions and cations in which it affects the viscosity NADES.

CONCLUSION

Solubility of CO_2 in NADES was found to be influenced HBD compound used and choline chloride to HBD ratio, CO_2 pressure, and contact time. HBD and choline/HBD ratios used were 1,2-propanediol (1:2), glycerol (1:2), and malic acid (1:1). Absorption curves obtained up to pressures of 30 bar, showed a linear relationship between the amount absorbed and the final pressure of CO_2. The choline and 1,2-propanediol eutectic mixture absorbs the highest amount of CO_2, approaching 0.1 mole-fraction at 3.0 MPa and 50°C. It is noted that NADES ability to absorb CO_2 correlates with its polarity as tested using Nile Red as a solvatochromic probe.

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