Carbon Dioxide Capture with Choline-Based DESs Solvents
Gabriela CIRIACO, Alain LEDOUX, Lionel ESTEL

Normandie Univ, INSA Rouen, Laboratoire de Sécurité des Procédés Chimiques LSPC, 76000 Rouen, France.
Gabriela.ciriaco_villegas@insa-rouen.fr alain.ledoux@insa-rouen.fr lionel.estel@insa-rouen.fr

Abstract
Deep eutectic solvents (DES) are an interesting alternative to conventional amines. Due to their biodegradability, lower toxicity and lower prices, DES are considered "more benign" sorbents for CO₂ capture than ionic liquids. To study the effect of water on the properties of choline chloride (ChCl)/glycerol mixtures (1:3 on a molar basis), the density and viscosity of ChCl/Gly with different water content (30%, 40% and 50%) were measured at temperature from 293.15 K to 333.15 K at atmospheric pressure, the CO₂ solubility in (ChCl/Gly) with water was determined from 293.15 K to 373.15 K and at pressure from 0.5 MPa to 3 MPa. The result shows the dramatically influence of water in the viscosity but not in the CO₂ solubility and Absorption.

Keywords
CO₂ capture, Solubility, Absorption, Deep eutectic solvent, Henry’s law equation.

1. Introduction

With 2Gt reduced by 2020 as a result of COVID-19, carbon dioxide still remains the most human emitted greenhouse gases in the world [1]. Climate change is accelerating at an alarming rate, and over the past 30 years, governments have met many times to affirm their desire to fight global warming together. For this reason, carbon dioxide capture and storage continue to receive a lot of attention to further reduce these emissions. Amine absorption is currently the most widely used technology for carbon dioxide capture[2]. Despite their high absorption capacity, these sorbents have some drawbacks such as degradation and high energy requirement for solvent regeneration [3] This process Lately, many researches explore the potential of ionic liquids (ILs) as alternatives to volatile amine absorbers, such as carbon dioxide (CO₂) capture. ILs possess unique properties such as extremely low vapor pressure, high thermal and chemical stability, non-flammability, high solvation capacity, and some exhibit large capacity for dissolving CO₂ [4]. Despite the great characteristics of ILs, they have not been widely developed due to their toxicity, low biodegradability and high prices. Deep eutectic solvents (DESs) have recently been considered as a new type of ionic liquids with improved synthesis and lower environmental impact.

DESs are eutectic mixtures of Lewis or Brønsted acids and bases that are characterized respectively by their ability to accept or donate electrons and accept or donate protons. Thus, interactions between the hydrogen bond acceptor (HBA) and the hydrogen bond donor (HBD) are mainly hydrogen bonds, although electrostatic forces and van der Waals interactions can also occur [5].

In this context, choline-based eutectic solvents represent a promising category of solvents for carbon dioxide separation. The main concern for the application of DESs is their high viscosity. High viscosity inhibits mass transfer between gas and DES [6], one method to address this problem is to form aqueous deep eutectic solvents. In this work Choline-Based DES have been synthesized at different water concentrations in order to decrease the viscosity. Li et al. studied the solubility of CO₂ at moderate pressures and temperatures which varied between 303.15 to 343.15 K, where the deep eutectic solvents are formed by choline chloride (ChCl) as hydrogen bond acceptor (HBA) and glycerol and ethylene glycol as hydrogen bond donors (HBDs)[7].This research is focused on evaluation of interesting thermodynamic properties of CO₂ in Choline chloride/Glycerol (ChCl/Gly) DES solutions at 1:3 molar ratio to study the aspects gas/liquid equilibrium and then the absorption kinetics at different CO₂ loadings.

The carbon dioxide solubility in the Choline-based DESs have been carried out at constant volume in a range of pressure and temperature determined. On the other hand, the study of the absorption kinetics has been performed in a stirred reactor (Lewis cell) where an efficient absorption of CO₂ is observed depending on the composition of the solvent. As such, our work focuses on investigating the effect of the decent of viscosity with the solubility of CO₂ and the kinetic absorption by varying the water content in the synthesized DESs with the aim of finding optimal operating conditions that lead to greater capture of CO₂ in the selected deep eutectic solvents.
2. Experimental section

Chemical

The cylinder of CO\(_2\) was purchased from Linde France s. a. with purity of 0.999, Choline chloride with purity of ≥ 0.98 and Glycerol with purity of 0.995 Abanicolain were purchased from SERVILAB, distilled water. All the chemicals were used as received without further purification.

DES preparation

The process for performing DES synthesis was similar to that described by Belal et al[8]. In general, ChCl/Gly was synthesized by the molar combination of 1:3, choline chloride as a hydrogen bond acceptor (HBA) and glycerol as a hydrogen bridge donor (HBD). The mixture was heated to 348.5 K for 4 hours under constant stirring of 450 rpm to obtain a homogeneous mixture without precipitate. Moisture from ChCl/Gly was removed by vacuum drying at 333.15 K overnight.

Density and viscosity measurement

The densities of solutions were measured by a high-precision vibrating tube densimeter (Anton Paar DMA 4100). The accuracy of temperature measurements is ± 0.02 K. It was calibrated using air and degassed deionized water. The viscosities of solutions were measured by the Anton Paar Lovis 2000 M/ME according to Hoeppler’s falling ball principle. The combinations of capillary/ball with different diameters (1.59 mm, 1.8 mm and 2.5 mm) can be selected to measure viscosities from 0.3 mPa·s to 1700 mPa·s. Calibration of viscosity was carried out using ultrapure water for the 1.59 mm capillary, oil N26 standard and oil N100 standard for the 1.8 mm and 2.5 mm capillaries respectively.

CO\(_2\) solubility experiment

CO\(_2\) solubility apparatus consists of a stainless-steel reactor with a capacity of 0.305 L (± 0.02 L). The cell is equipped with two sensors, one for temperature (T\(_\text{R}\)) and one for pressure (P\(_\text{R}\)). The reactor has an aluminum block heater that also serves as a support. A thermal fluid circulates through a conduit inside the reactor to control the temperature in the cell. A turbine type stirrer was used to stir the solution at about 600 rpm. The CO\(_2\) cylinder was connected to a stainless-steel buffer tank with a capacity of 0.168 L (±0.001 L). The buffer tank has two sensors, one for temperature (T\(_\text{s}\)) and one for pressure (P\(_\text{s}\)). A valve controlled the injection of CO\(_2\) from the buffer tank to the cell. All the temperatures and pressures measured during the experiments were recorded continuously using an acquisition system. The overall idea is to conduct the experiments with a solution of ChCl/Gly at 1:3 molar ratio with different mass concentration of water (30%, 40% and 50%). At the beginning of the experiment, a mass of about 200 g of solution is introduced into the reactor. Then a vacuum is made in the cell up to 1000 Pa. The temperature is maintained at 293.15 K, the mixture is stirred during the whole experiment at 600 rpm, once the temperature and pressure are stable CO\(_2\) is injected until a pressure of 0.5 MPa is reached in the reactor. When the pressure and temperature were stabilized, the temperature was raised from 293.15 K up to 373.15 K by step of 10 or 20 K. At each step, we considered that the equilibrium was reached when the pressure was constant. Several injections of CO\(_2\) were made for each solvent to determine the equilibrium pressure under the different operating conditions established. The temperature and pressure in the cell recorded during all the experiments.

Calculation of solubility

The mole fraction (x\(_{\text{CO}_2}\)) and the amount of solvent introduced can be described as follows:

\[
x_{\text{CO}_2} = \frac{n_{\text{CO}_2}^{\text{sol}}}{n_{\text{CO}_2}^{\text{sol}} + n_s}
\]

\[
n_s = \frac{m_s}{M_s}
\]

Where \(n_{\text{CO}_2}^{\text{sol}}\) correspond to the amount of CO\(_2\) absorbed in the solvent, \(n_s\) is the amount of solvent introduced in the cell, \(m_s\) denotes the mass of solvent injected in the cell and \(M_s\) is the molar mass of the solvent. The moles of CO\(_2\) absorbed in the solvent are calculated by a mass balance:

\[
n_{\text{CO}_2}^{\text{sol}} = n_{\text{CO}_2}^{\text{inj}} - n_{\text{CO}_2}^{\text{eq}}
\]
\( n_{CO_2}^{Eq} \) is the amount of CO\(_2\) at the equilibrium in the gas phase in the reactor and \( n_{CO_2}^{inj} \) is calculated by the difference of the amount of CO\(_2\) in the buffer tank before and after the injection. All the amounts of CO\(_2\) in the cell and in the buffer tank were calculated by using the Peng-Robinson equation of state [9]:

\[
P_{CO_2} = \frac{RT_r}{v - b} - \frac{\alpha(T_r)a}{v^2 + 2vb + b^2}
\]  

(4)

The Tr represents the temperature of the cell and \( v \) is the molar volume of CO\(_2\). \( a \) and \( b \) are two constants calculated with the following equations where \( \Omega_a = 0.457 \) and \( \Omega_b = 0.07780 \):

\[
a = \Omega_a \frac{R^2T_c^2}{P_c}
\]  

(5)

\[
b = \Omega_b \frac{RT_c}{P_c}
\]  

(6)

We assumed that liquids are ideal and follow the Raoult’s law to calculate the partial pressure of CO\(_2\) at each equilibrium in the cell:

\[
P_{CO_2} = P_{cell} - P_{liq}^s(1 - x_{CO_2})
\]  

(7)

Where \( P_{cell} \) represents the pressure measured in the cell by the transducer and \( P_{liq}^s \) corresponds to the saturated vapor pressure of the solvent calculated for each temperature in using the Antoine’s equation.

**Absorption experiment**

The reactor consists of two double walled Pyrex glass cylinders, stacked on top of each other. They are joined by a PTFE flange, with chicanes in the middle. The gas-liquid interface will be on the level of these chicanes. The outer hollow cylinder is connected to an oil bath with thermostat to regulate the temperature inside the cell. The double walled STR is equipped with 2 temperature sensors (one on the top for the gas, one on the bottom for the liquid) and one pressure sensor (on the top). Moreover, it is equipped with a Rushton stirrer, agitated by an electric motor, that is placed below the reactor. There is no mechanical connection between the motor and the stirrer. The agitation is magnetic.

The ChCl/Gly solution is prepared from pure liquid DES and distilled water. Both liquids are weighed to give a solution with a certain mass percentage. The solution with its bottle is weighed, its mass is \( m_0 \). Using the vacuum pump, a vacuum is created in the reactor, which is used to aspire the solution up to the level of the chicanes. With the stirrer turned on, the temperature and pressure in the reactor will eventually stabilize.

CO\(_2\) is introduced into the reservoir. Once temperature and pressure in the reservoir have stabilized a small injection is made into the reactor (injection time about 0.5 s). The pressure in the reactor may not exceed 2 bar since it is made from glass. The next injection can be made once the pressure in the reactor has stabilized again.

There is an automatic injection mode which injects small quantities of CO\(_2\) automatically. Weighing the liquid with its bottle before and after introduction into the reactor to find \( m_1 \), allows for the determination of the mass of the liquid now in the reactor (Equation (8)).

\[
m_L = m_0 - m_1
\]  

(8)

Pressure and temperature in the reactor and in the reservoir are constantly measured. Before injecting the CO\(_2\) into the cell, the amount in the reservoir needs to be calculated. Using the hypothesis that CO\(_2\) can be treated as an ideal gas at the given pressures, the ideal gas equation (Equation (9)) can be used.

\[
n_{CO_2} = \frac{P_{CO_2}V}{RT}
\]  

(9)

Upon injection, the pressure in the reservoir will sink, and the pressure in the cell will increase. The quantity of CO\(_2\) per injection can thus be calculated from the change of state within the reservoir (Equation (10)). The total quantity of gas injected is the sum of the previous injections (Equation (11)).
\[ \Delta n = \frac{V_R}{R} \left( \frac{p_0}{T_0} - \frac{p_1}{T_1} \right) \]  

(10)

\[ n_{CO_2, tot} = \sum_{i=1}^{n} \Delta n_i \]  

(11)

Within the reservoir the quantity of CO₂ in the gas phase can also be calculated using equation (9). In order to find the partial pressure of CO₂, the difference between the total and vapor pressure of the solvent is calculated (equation (12)) [10]. The latter is the pressure measured in the cell before introduction of CO₂.

\[ p_{CO_2} = p_{tot} - p_{vap, L} \]  

(12)

The volume of the gas phase in the reactor can be determined using the mass of the liquid introduced and its density, as in equation (13).

\[ V_G = V_{tot} - V_L = V_{tot} - \frac{m_L}{\rho_L} \]  

(13)

3. Results and discussion

Density and viscosity

The densities of \{ChCl/Gly\} were measured at temperatures from 293.15 K to 333.15 K at atmospheric pressure. The densities decrease linearly with increasing temperature at different water content as shown in Figure 1(a) where the dependence of density on DES concentration and temperature is observed. Density decreased with temperature and increased with DES concentration, as expected. Such is a typical behavior observed for the densities of many aqueous DES aqueous systems[11].

![Figure 1](https://example.com/figure1.png)

Figure 1. (a) Densities of \{ChCl/Gly 1:3\} at different wt% of water. Symbols: ⋆, 0 wt%; ●, 30 wt%; ■, 40 wt%; ▲, 50 wt%. (b) Viscosity of \{ChCl/Gly 1:3\} at different wt% of water. Symbols: ●, 30 wt%; ■, 40 wt%; ▲, 50 wt%.

The viscosities of \{ChCl/Gly 1:3\} were measured at temperatures from 293.15 K to 333.15 K and at atmospheric pressure. The results are illustrated in Figure 1(b) and Figure 2

The temperature effect on the viscosity of ChCl/Gly is significant. Viscosity decreases dramatically with temperature in pure DES. At low temperature DES is extremely viscous. For example, at 293.15 a viscosity of 520.8 mPa·s is observed when the temperature increases to 333.15 a viscosity is 58.47 mPa·s. Also, the viscosity of DES decreases dramatically with increasing water content. It is observed that at 293.15 K with a water content of 30 Wt%, the viscosity of DES goes from 520.8 mPa·s to 15.72 mPa·s, with increasing water content the viscosity continues to decrease but not as markedly as in pure DES as can be shown in Figure 1(b).

Abbott et al. [12] measured the viscosities of ChCl/Gly at 298.15 K, 303.15 K, 313.15 K, and 323.15 K with viscosity measurements of 320 mPa·s, 229 mPa·s, 169 mPa·s respectively. Viscosity measurements were compared with the literature, a slight discrepancy was found. The relative deviation of these measurements at these temperatures are 4%, 5% and 5.2 % respectively.
The values of the solubility of CO\textsubscript{2} in the DES (1 ChCl: 3 glycerol) with different content of water (30 wt%, 40 wt% and 50 wt%) were measured at temperatures (293.15–373.15) K at 10 or 20 K intervals and pressures (0.5-3) MPa. The experimental data are given in Figure 3, Table 1, and Table 2. Within the temperature and pressure ranges investigated in this work, the solubility of CO\textsubscript{2} increase with increasing water content.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>CO\textsubscript{2} Solubility (mol CO\textsubscript{2} kg\textsuperscript{-1} DES)</th>
<th>Pressure (MPa)</th>
<th>CO\textsubscript{2} Solubility (mol CO\textsubscript{2} kg\textsuperscript{-1} DES)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>0.008</td>
<td>0.015</td>
<td>0.018</td>
</tr>
<tr>
<td>303.15</td>
<td>0.007</td>
<td>0.021</td>
<td>0.016</td>
</tr>
<tr>
<td>313.15</td>
<td>0.006</td>
<td>0.022</td>
<td>0.015</td>
</tr>
<tr>
<td>323.15</td>
<td>0.005</td>
<td>0.023</td>
<td>0.014</td>
</tr>
<tr>
<td>333.15</td>
<td>0.004</td>
<td>0.024</td>
<td>0.013</td>
</tr>
<tr>
<td>343.15</td>
<td>0.003</td>
<td>0.025</td>
<td>0.012</td>
</tr>
</tbody>
</table>

**Figure 2. Viscosity of [ChCl/Gly 1:3] at different temperature. Symbols: ♦, this work; - , Abbott et al [12]**

**Figure 3. Pressure-solubility diagram for CO\textsubscript{2} in ChCl/Gly 30 wt%**

**Table 1. CO\textsubscript{2} solubility in DES 40 wt%**

<table>
<thead>
<tr>
<th>P\textsubscript{CO\textsubscript{2}} /MPa</th>
<th>(mol CO\textsubscript{2} kg\textsuperscript{-1} DES)</th>
<th>x\textsubscript{CO\textsubscript{2}}</th>
<th>P\textsubscript{CO\textsubscript{2}} /MPa</th>
<th>(mol CO\textsubscript{2} kg\textsuperscript{-1} DES)</th>
<th>x\textsubscript{CO\textsubscript{2}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>0.04</td>
<td>0.008</td>
<td>0.035</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>0.888</td>
<td>0.057</td>
<td>0.011</td>
<td>0.054</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td>1.038</td>
<td>0.090</td>
<td>0.018</td>
<td>1.4841</td>
<td>0.088</td>
<td>0.018</td>
</tr>
<tr>
<td>303.15</td>
<td>0.035</td>
<td>0.007</td>
<td>0.550</td>
<td>0.035</td>
<td>0.007</td>
</tr>
<tr>
<td>0.957</td>
<td>0.055</td>
<td>0.011</td>
<td>1.100</td>
<td>0.052</td>
<td>0.011</td>
</tr>
<tr>
<td>1.397</td>
<td>0.089</td>
<td>0.018</td>
<td>1.570</td>
<td>0.087</td>
<td>0.017</td>
</tr>
</tbody>
</table>

**Table 2. CO\textsubscript{2} solubility in DES 50 wt%**

<table>
<thead>
<tr>
<th>P\textsubscript{CO\textsubscript{2}} /MPa</th>
<th>(mol CO\textsubscript{2} kg\textsuperscript{-1} DES)</th>
<th>x\textsubscript{CO\textsubscript{2}}</th>
<th>P\textsubscript{CO\textsubscript{2}} /MPa</th>
<th>(mol CO\textsubscript{2} kg\textsuperscript{-1} DES)</th>
<th>x\textsubscript{CO\textsubscript{2}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>0.144</td>
<td>0.008</td>
<td>0.433</td>
<td>0.135</td>
<td>0.0076</td>
</tr>
<tr>
<td>0.818</td>
<td>0.305</td>
<td>0.0169</td>
<td>1.616</td>
<td>0.517</td>
<td>0.0287</td>
</tr>
<tr>
<td>1.508</td>
<td>0.532</td>
<td>0.0291</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>303.15</td>
<td>0.140</td>
<td>0.008</td>
<td>0.517</td>
<td>0.134</td>
<td>0.0075</td>
</tr>
<tr>
<td>0.886</td>
<td>0.297</td>
<td>0.016</td>
<td>1.043</td>
<td>0.287</td>
<td>0.0159</td>
</tr>
<tr>
<td>1.616</td>
<td>0.523</td>
<td>0.029</td>
<td>1.809</td>
<td>0.512</td>
<td>0.0280</td>
</tr>
</tbody>
</table>
The solubility of CO$_2$ is 0.008 when the percentage of water is 30% and increases to 0.0081 when the percentage of water is 50%. With increasing temperature, the CO$_2$ solubility decreases but the influence is low. For example, at 1.5 MPa and 50 wt% the solubilities are 0.0081, 0.0078 and 0.0076 when the temperatures are 293.15K, 303.15K and 313.15K respectively. The addition of water has an effect on the solubility of CO$_2$ in ChCl/Gly, significantly decreasing the viscosity of ChCl/Gly. The decrease in viscosity will improve heat and mass transfer but not significantly. Therefore, a balance between viscosity and gas solubility must be considered to capture CO$_2$ with high efficiency.

**Henry's constant**

In our range of temperature and pressure, the solubility of CO$_2$ is proportional to the pressure of the gas over the solvent, according to the Henry’s law:

$$P_{CO_2} = H_{CO_2} \times$$ (14)

The $H$ represents the Henry’s law constant. It refers to the slope of the line $P_{CO_2}$ to $x$. All the Henry’s law coefficients are plotted in Figure 4. For the system studied in this work, the vapor pressure of ChCl/Gly is negligible.

![Figure 4](image)

**Figure 4.** Henry’s constant of [CO$_2$] in [ChCl/Gly 1:3] at different wt% of water. Symbols: ●, 30 wt%; ■, 40 wt%; ▲, 50 wt%.

Henry's constant $H_{CO_2}(T)$ obtained at different temperatures are plotted in Figure 4 changes slightly with water content due to the slight increase in CO$_2$ solubility with increasing water content. For example, at 308.2 K, $H_{CO_2}(T)$ varies from 92.99 MPa to 74.29 MPa when the wt% changes from 30% to 40%.

**CO$_2$ absorption**

In the present study, the absorption capacities of various [ChCl/Gly] solutions have been inspected at different temperatures and concentrations. In order to make the results more easily comparable, the same molar concentrations were used for the different water content. Following the injection of CO$_2$ into the reactor, the measured pressure decreases over time, as the gas is absorbed into the liquid. Eventually, equilibrium is reached and the pressure remains constant, until the next injection. The higher the CO$_2$-load, the slower the absorption and the higher the pressure at equilibrium.

The normalized pressure in Figure 5., has been calculated using equation 15

$$P_{norm} = \frac{P - P_{\infty}}{P_0 - P_{\infty}}$$ (15)
Figure 5. Pressure during absorption (50 wt% ChCl-Gly, 40°C)

Figure 5 represents the normalized pressure during an injection. For each injection, the rate is faster at the beginning, since the driving force (difference between the CO₂ content between the liquid and gas phase) is higher. The initial CO₂ absorption rate is found by linear regression of the first 30 pressure time data points. Different numbers of points were examined, but in general the best results were obtained with the regression of the first 30 points. The absorption rate decreases as the CO₂ load increases. This is due to the saturation of the solution.

Figure 6. Initial Absorption Rate for different temperature of ChCl/Gly 50 wt %

According to the literature, the absorption of CO₂ in DESs made of choline chloride and glycerol is only due to physisorption[13]. The CO₂ absorption capacities measured for the ChCl/Gly DESs are clearly lower than the CO₂ absorption capacity reported in the literature for aqueous solutions of MEA at 30 wt%[14]. This might be due to the fact that the CO₂ absorption mechanism is different in both cases: CO₂ absorption in MEA solutions an absorption
with chemical reaction, whereas the CO₂ absorption in the DESs studied in this work is limited to physisorption only. As expected from the experimental results presented in Figure 4, they are quite consistent with the behavior of the other DESs in the literature. The value of $H_{\text{CO}_2}(T)$ increased with increasing temperature for all ChCl/Gly compositions and the value of $H_{\text{CO}_2}(T)$ decreased with increasing water content, reflecting an increase in CO₂ absorption. One trend observed in the experiments was the effect of temperature on the decrease in CO₂ absorption kinetic as temperature increases. This behavior agrees with the results reported in the literature for other DESs.

4. Conclusion

The effect of water on the density, viscosity, solubility CO₂ and CO₂ absorption in ChCl/Gly was studied. The densities and viscosities of ChCl/Gly were measured at different temperatures and atmospheric pressure, it was shown that both density and viscosity decrease with increasing temperature and water content. The water has a strong impact on the viscosity of (ChCl/Gly + H₂O). The solubilities of carbon dioxide were measured at different temperatures and pressures also with different water content (30 wt%, 40 wt%, 50 wt%). Where it was observed that the solubility decreases with increasing temperature and increases with increasing pressure. In spite of the different water contents used to carry out the experiments, water did not have a significant influence on the CO₂ solubility as it did on the decrease of viscosity. Considering the measurements of the ChCl/Gly experiment, it was found that the conditions for which the greatest solubility and maximum absorption kinetics were obtained were at 293.15 K with a water content of 50 wt%.

References


