Experimental Investigation of CO₂ Solubility in New Amine-Based Deep Eutectic Solvents

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Keywords:
CO₂ Absorption; Deep Eutectic; Energy; Environment; Greenhouse.

Highlights:
• The research aims to find the most suitable solvent for CO₂ capture in synthetic gas mixtures, comparing deep eutectic and standard solvents.
• It also examines the impact of factors like solvent temperature, concentration, and absorption duration on carbon dioxide capture.
• The ultimate goal is to improve the performance of the chosen solvent, determine optimal CO₂ capture working conditions, and calculate the reaction rate constant and reaction order for the chosen solvent.

Abstract: The growing concern about global warming and climate has raised the research field dedicated to finding solutions. One area that has received considerable attention is the exponential increase of carbon dioxide emissions from the atmosphere from the petroleum and gas industries. So, to solve this problem, researchers investigated new ways to collect CO₂ from the air depending on the fact that CO₂ is soluble in water because using aqueous amine absorbents to collect CO₂ has a lot of drawbacks, such as the need for tremendous energy to recycle the solvent and high operational costs. In this study, a specific type of deep eutectic solvent (DES), namely Choline chloride + monoethanolamine (ChCl-MEA), was used as a promising solvent in the CO₂ capture process. Solubility measurements were conducted at 1:6 molar ratios. The amines chosen are typical of basic amines. Experiment absorption data were investigated at various parameters, including a concentration range of 0–3 mol/L, temperatures ranging from 25 to 45 °C, and absorption durations ranging from 60 to 120 minutes, to get the best conditions for high-loading CO₂ uptake. The study found that amine-based DESs had a significantly greater absorption capacity than monoethanolamine-based and conventional DESs. The study examined what happened when water was added to a deep eutectic solvent made of choline chloride and monoethanolamine (ChCl-MEA DES). The most effective way to absorb CO₂ was physical absorption, which can hold 276.13 mol CO₂ per gram of DES at 1 bar and 29.025 °C when mixed with water. The deep eutectic was mixed with water to increase the absorption efficiency. 10 ml of aqueous solution (DESs + water) was taken. The combination of DES and water significantly increased CO₂’s low solubility. The modified Design-Expert model satisfactorily represents the experimental solubility of CO₂ in the solvent. The average percent differences between experimental and projected values were 10.7% and 6.8% for binary and ternary systems, respectively. The optimal conditions for maximum absorption rate were 29.025°C, 2.233 mol/L, and 101 minutes, with an absorption ratio of 0.0734 mol/kg.min and efficiency of absorption of 85.3% for solution DESs and water.
دراسة تجريبيّة لقابلية ذوبان ثاني أكسيد الكربون في المذيبات

العميقة سهلة الانصهار القائمة على الأمينات

محمد نوري جاسم، ثامر جاسم محمد، عبد المنعم عباس كريم

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الخلاصة
قد أدى القلق المتزايد بشأن ظاهرة التغير المناخي إلى تغيير المناخ بدوره إلى ظهور مجال بحثي مختص لإيجاد الحلول. أحد المجالات المحددة التي تحمل بأهميتها كبيرة هو الزائدة الهيدرولوجية في مجالات ثاني أكسيد الكربون في الغلاف الجوي. نقلت هذه المشكلة بحثنا إلى تطبيق قابلية ذوبان ثاني أكسيد الكربون. ونتقدم للآلة من المواد المذابة في الماء، وذلك لأن استخدام الأمينات في جمع ثاني أكسيد الكربون له الكثير من التراكمات، مثل الحاجة إلى إزالة المذيب، وارتفاع انبعاثات ثاني أكسيد الكربون في الغلاف الجوي من صناعات النفط والغاز. لذا، لحل هذه المشكلة، ومكنايس الاحتراق ثاني أكسيد الكربون نلاحظ أن قابلية ذوبان ثاني أكسيد الكربون من الماء مستخدمة سنة DE-Solvant MEA (DES)، كمصدر الأمين. مع إجراء احتجاز ثاني أكسيد الكربون مالي مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستدعى الأدوات المذابة بنسب مولية 0.2، إستديا...
capture [13]. However, CO₂ solubility data are scarce for DESs, prompting more studies to design novel gas absorbents. Recent research [14] presented a novel class of DESs with relatively high CO₂ uptake, accomplished using ethylenediamine (EDA) as a hydrogen-bond donor (HBD) and monoethanolamide hydrochloride as a hydrogen-bond acceptor (HBA), created by adding hydrochloric chloride (HCl) to monoethanolamine. This combination has the highest CO₂ loading value of any current DES. A similar study has indicated that DESs are viable replacements for standard monoethanolamine-based solvents utilized in cleaning technologies [5]. DES’s creation depends on the intensity of the interaction between its constituent parts. Fig. 1 illustrates the interaction between A and B. In theory, unlike perfect mixtures, these interactions result in a significant value of freezing point AT. The eutectic point is reached at a specific temperature when the amount of A to B is just right. At this time, the melting point, the depression seen in Fig. 1 [15], is detected. As seen in Table 1, DESs may be broadly categorized into four main groups. The cation indicated as CAT+ in the table in type III DES is commonly quaternary ammonium, phosphonium, or sulfonium salt. The anionic component, designated by the symbol x, forms hydrogen bonds with the protons of the RZ donor group [1]. Choline chloride is a popular quaternary ammonium salt due to its cost, accessibility, biodegradability, and low toxicity. Hydrogen bonding makes it easier for the chloride anion to interact with diverse proton donors [2,3].

![Fig. 1 T-X diagram for DES. Adopted from [8].](image)

### Table 1 General Formula for DES Classification, Adopted from [9].

<table>
<thead>
<tr>
<th>Type</th>
<th>General Formula</th>
<th>Terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I</td>
<td>Cat-X₂zMClₓ</td>
<td>M= Zn, Sn, Sn, Fe, Ga, In</td>
</tr>
<tr>
<td>Type II</td>
<td>Cat-X₂zMClₓ⁺RZ</td>
<td>M= Cr, Co, Cu, Ni, Fe</td>
</tr>
<tr>
<td>Type III</td>
<td>Cat-X₂zRZ</td>
<td>Z= CONH₂, COOH, OH</td>
</tr>
<tr>
<td>Type IV</td>
<td>MClₓ + RZ = MClₓ⁺z₁</td>
<td>M= Al, Zn and Z= CONH₂, OH</td>
</tr>
</tbody>
</table>

As previously stated, DES is synthesized by combining a hydrogen bond donor (HBD) with a hydrogen bond acceptor (HBA). Various combinations could provide desirable physicochemical qualities, such as conductivity, viscosity, polarity, and thermal properties. The required qualities may be obtained by adjusting the molar ratios of the components, and it is worth mentioning that the bulk of the produced DESs have hydrophobic properties [3]. Therefore, the novelty in the present work is represented in the use of a new type of eutectic solvent with new molar ratios to provide desirable physical properties of the solvent to enhance CO₂ capture that have not been previously discussed in the research and compared with the results of other researchers’ research who used ionic solvents under similar conditions. This study aims to capture CO₂ from simulation gas (CO₂, N₂) using a deep eutectic solvent (DES). The eutectic point is reached, through an experiment of cell absorption. This work investigates the absorption efficiency of CO₂ from gas with different parameters to find the best operating conditions of absorption, which include: solvent, temperature, temperature, and reaction time, using amine-based solvents alone and comparing them with eutectic solvents and determining the best of them, also comparing DES with ionic liquids to find the best loading of CO₂.

**Choline Chloride**

2-Hydroxy-ethyl-tri-methyl-ammonium cation or HOCH₂CH₂N+(CH₃)₃, commonly known as choline chloride, has a structure, as shown in Fig. 2. Choline chloride is biodegradable, non-toxic, and cheap to manufacture. It has been defined as a pro-vitamin in Europe. It is made on a massive scale as an animal feed addition, reaching mega-ton volumes. A single-step gas-phase reaction involving HCl, ethylene oxide, and tri-methyl-amine is used in the manufacturing process. This technique produces very little extra waste [5]. Except for the composition temperature, heat capacity, and ecotoxicity, many of the features of choline-based DESs are identical to those of ordinary ILs. These solvents’ reduced heat capacity contributes to less sensible heat with increasing temperature, resulting in lower energy use in the CO₂ extraction process. The non-ecotoxicity, biodegradability, and low cost of choline chloride-based DES indicate an excellent use for an alternative eco-friendly CO₂ capture medium [10]. Choline chloride is the primary focus of this work; choline chloride-based DES has shown great potential for CO₂ adsorption with good electrical conductivity, which is suitable for electrochemical conversion because of lower ohmic losses. Amine-based DES has also been considered for the study due to higher CO₂ absorption.
2. EXPERIMENTAL PART

2.1. Materials

Choline chloride (AR, 98%) and monoethanolamine (AR, 99%) were purchased from Aladdin Pharma Co. CO₂ gas (99.99%) and N₂ (99.999%) were purchased from Guizhou Sanhe Gas Co., Ltd., China.

2.2. Equipment

The equipment used in this work is listed in Table 2.

2.3. Solvent Preparation

The DES composition utilized in this experiment was a 1:6 mol ratio of Choline Chloride (ChCl) and Monoethanolamine (MEA). This mole ratio was selected based on its successful synthesis and the ideal balance of ChCl and MEA, according to Li et al. [21,22], who discovered that a mole ratio of 1:6 was optimum among the ChCl to MEA ratios of 1:2 to 1:5. Fig. 3 shows the structure of choline chloride monoethanolamine DES (a) and crystallization in a ChCl:MEA (1:6) mixture (b). To make the DES, the required amounts of ChCl and MEA were individually weighed and mixed to obtain the requisite 1:6 mole ratio. After that, the mixture was transferred to a beaker and set on a magnetic hot plate with a stirrer. The liquid was heated to 60 °C and then agitated at 300 revolutions per minute for three hours. The resulting clear, white, and uniform liquid was bottled and allowed to settle undisturbed for 48 hours. If the DES demonstrated phase stability throughout this period, it was used in further experiments.

2.4. Fourier Transform Infrared Spectroscopy (FTIR)

Figure 4 depicts the Fourier-Transform Infrared Spectroscopy (FTIR) setup. This apparatus is used to detect distinct bonds in the solvent and how and when new bonds form, producing diverse compounds. The equipment emits infrared radiation ranging from 10,000 to 100 cm⁻¹ through the material. Some of the radiations are absorbed, while others pass through. Radiation received by molecules is transformed into rotation and/or vibration energy. The integrated data logger supports traceability and provides complete documentation (HACCP/IFS/ISO) model atmocheck DOUBLE O₂/CO₂/ U.S.A. The resultant signal from the detector is shown as an absorption spectrum. For this specific machine, the wavenumbers in the spectrum are from 4000 to 400 cm⁻¹. The spectrum generated is a series function of absorbed energy. This machine uses a zinc selenide crystal, providing more durability at the cost of minor errors. For higher resolution, germanium crystal could be used. This experimental setup measures 16 iterations per sample and the resolution of 2 cm⁻¹.

Table 2 List of Tools and Devices Used in this Work.

<table>
<thead>
<tr>
<th>No.</th>
<th>Equipment/Facilities</th>
<th>Model</th>
<th>Properties</th>
<th>Purpose of use</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hot plate stirrer</td>
<td>Labtech/Korea</td>
<td>60 – 1 rpm, Max. temperature 380 °C</td>
<td>Analytic and preparation</td>
</tr>
<tr>
<td>2</td>
<td>Analytical balance</td>
<td>OHAUS /U.S.A</td>
<td>Readability 0.0001 g</td>
<td>Preparation</td>
</tr>
<tr>
<td>3</td>
<td>Glass flask</td>
<td>Glassco /India</td>
<td>100ml</td>
<td>Desorption</td>
</tr>
<tr>
<td>4</td>
<td>Glass condenser</td>
<td>Glassco /India</td>
<td>Air (25–250) ml/min</td>
<td>Desorption</td>
</tr>
<tr>
<td>5</td>
<td>Flow meter</td>
<td>Flowtech/U.S.A</td>
<td>CO₂ (25–250) ml/min</td>
<td>Absorption</td>
</tr>
<tr>
<td>6</td>
<td>Thermometer</td>
<td>Germany</td>
<td>Mercury (0 – 200) °C</td>
<td>Desorption</td>
</tr>
<tr>
<td>7</td>
<td>Absorber cell</td>
<td>India</td>
<td>50 ml</td>
<td>Absorption</td>
</tr>
<tr>
<td>8</td>
<td>CO₂ analyzer</td>
<td>Atmocheck DOUBLE O₂/CO₂/ U.S.A</td>
<td>Range (0.00 – 100) %</td>
<td>Analysis</td>
</tr>
<tr>
<td>9</td>
<td>Water bath</td>
<td>England</td>
<td>Cooling/heating range -15°C to 200°C</td>
<td>Analytic and preparation</td>
</tr>
<tr>
<td>10</td>
<td>Pressure gauge</td>
<td>Visto/German</td>
<td>Range (0 – 50) bar</td>
<td>Pressure gauge</td>
</tr>
</tbody>
</table>

(a) DES Structure (b) Crystals in ChCl:MEA

Fig. 3 (a) ChCl:MEA(1:6) DES Structure (b) Crystals in ChCl:MEA(1:6) [11].
1.1. Material and Methods

2.3.1. Experimental Design

2.3.2. Data Analysis

2.6. Design Expert Software

3. Results and Discussion

4.1. Analysis of Variance (ANOVA)

4.2. Optimizing the Model

4.3. Validation

5. Conclusion

Appendix

References

Table 1: Independent Variables and Levels in the Design

Table 2: Measured and Calculated Results

Table 3: Measured Range and Dimensions of Independent [1-CHCL] [6-MEA] Components in the Absorption

Table 4: Measured Range and Dimensions of Independent [1-CHCL] [6-MEA] Components in the Absorption
measurements were performed at different time intervals to ensure the stability of the outside percentage of carbon dioxide to the required temperature after the arrival of the water bath. Then, Carbon dioxide and nitrogen gas were passed to the absorption cell and the solution to cause the absorption process. The carbon dioxide and nitrogen flow rate was maintained to ensure the accuracy of the measurements read by the carbon dioxide analyzer, as a measurement was taken after five minutes throughout the entire experiment period by the carbon dioxide analyzer. In this study, the run time (60 to 120 min) was tracked when a carbon dioxide analyzer showed a significant change in the amount of carbon dioxide. Figs. (6, 7) depict the experiments for the adsorption step utilized in this study, respectively. After the liquid ring was set correctly, the carbon dioxide gas was pumped from the gas cylinder through the preset tube and valve to direct the gas stream directly into the carbon dioxide absorption cell, adjusted to the desired level. It must be noted here that the above experimental procedure was applied in this study for all absorbances for the two solvents, once with monoethanolamine alone and once with the solution containing (DESs+H$_2$O), where their results were compared.

![Fig. 6](image_url)
**Fig. 6** The Schematic Diagram for CO$_2$ Absorption.

![Fig. 7](image_url)
**Fig. 7** Photograph of the Whole Experimental Setup.

**3. THE RESULTS OF CENTRAL COMPOSITE DESIGN MODEL**

Batch testing supported revising the central composite design (CCD) of the key factors influencing parameter computation (CO$_2$ outlet, absorption rate, CO$_2$ loading, and CO$_2$ capacity and solubility). The mathematical equations used to forecast the parameters were found by analyzing the findings of the solvents using design expert software (DE). The Response Surface Method (RSM), a widely used statistical technique for designing experiments across various engineering and research fields, was employed in this study. A three-core compound design (CCD) was used to examine the impacts of independent variables (solvent temperature, concentration, and absorption time). Twenty experimental runs, five repeated at the center spots, were necessary for each approach. The Design-Expert 11 software was used for the trials. The computer software suggests a quadratic model to derive the response regression equation from the experimental data in Table 4. Eqs. (5) - (9) for
the solvent [1-chcl], [6-MEA] are a list of all computational parameters of the response equation that were used to forecast parameters in cryptographic object relationships.

For example, the following Eq.: 

\[
\text{CO}_2 \text{ outlet rate} = +0.0571 - 0.5400A_i + 4.15B_i + 2.88C_i + 0.0625A_{Bi} - 0.0875A_{Ci} + 1.91B_{Ci} + 4.33A_i^2 - 1.92B_i^2 - 1.97C_i^2
\]

(5)

Absorption rate = +0.0537+0.0034A_i - 0.0257B_i - 0.0167C_i -0.0007A_{Bi} + 0.0007A_{Ci} - 0.0107B_{Ci} -0.0251A_i^2+0.0130B_i^2+0.0111C_i^2

(6)

\[
\text{CO}_2 \text{ loading} = +4.87+0.3209A_i - 2.57B_i + 0.1509C_i -0.2099A_{Bi} + 0.2316A_{Ci} - 1.71B_{Ci} - 2.35A_i^2+1.08B_i^2+0.5996C_i^2
\]

(7)

\[
\text{Solubility} = +0.1226 + 0.0126A_i - 0.0155B_i + 0.0022C_i - 0.0299A_{Bi} + 0.0099A_{Ci} - 0.0013B_{Ci} - 0.0127A_i^2 - 0.0537B_i^2 - 0.0014C_i^2
\]

(9)

### Table 4 Experimental Data Points and Response Used in Central Composite Design (CCD).

<table>
<thead>
<tr>
<th>Std.</th>
<th>Run</th>
<th>Factor 1 A: Temp. °C</th>
<th>Factor 2 B: Conc. mol/l</th>
<th>Factor 3 C: Time min</th>
<th>Response 1 CO₂ outlet %</th>
<th>Response 2 Absorption rate mol/kg/min</th>
<th>Response 3 CO₂ loading mol/kg</th>
<th>Response 4 CO₂ capacity g/g solv.</th>
<th>Response 5 Solubility mol CO₂/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>1</td>
<td>35</td>
<td>1.5</td>
<td>60</td>
<td>3.4</td>
<td>0.0655</td>
<td>3.99</td>
<td>175.50</td>
<td>0.1323</td>
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<tr>
<td>8</td>
<td>2</td>
<td>45</td>
<td>3</td>
<td>120</td>
<td>14.7</td>
<td>0.00173</td>
<td>0.208</td>
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<td>17</td>
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<td>18</td>
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<td>9</td>
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</tr>
</tbody>
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### 3.1.1 Effect of Temperature and Concentration on the CO₂ Outlet Concentration

The chemical absorption is attributed to the ability of the choline chloride to form hydrogen bonds with the amines. 

Fig.8 shows that the solubility of CO₂ increased with the molar ratio of amine in the DES [13,14]. For example, at a temperature of 35°C and concentration of 1.5 mol/l, the CO₂ outlet was 7.1 vol.%. Nevertheless, the temperature was 45°C, the concentration was 3 mol/l, and the CO₂ outlet was 14.9 vol.% at the constant time.

### 3.1.2 Effect of Temperature and Time on the CO₂ Outlet Concentration

Figure 9 shows that the CO₂ outlet concentration increased with temperature and time due to higher temperature leading to a higher reaction rate constant and, consequently, higher mass transfer rate and decreased absorption efficiency [18]. For example, at a temperature of 35°C and after 60 minutes, the CO₂ outlet was 3.4 vol.%; however, at a temperature of 45°C and after 90 minutes, the CO₂ outlet was 12.5 vol.% at a constant concentration.
3.1.3. Effect of Concentration and Time on the CO₂ Outlet Concentration

Figure 10 shows the effect of concentration and time on the CO₂ outlet concentration. This observation can be explained by one reason. All DESs studied could be observed to have good stability at a temperature of 35°C, where the regeneration process was conducted. Moreover, the MEA-based DESs exhibited better stability than the phenol-based DESs. Increasing the solvent content additionally elevated viscosity, which in many situations hampers the liquid’s ability [13]. For instance, at 1.5mol/l and following 60 minutes, the CO₂ outflow was 3.4 vol.%. However, at 3mol/l and after 90 minutes at a steady temperature, the CO₂ outlet was 10.1 vol.%.

3.1.4. Effect of Temperature and Concentration on the CO₂ Absorption Rate

Figure 11 shows that the absorption rate decreased when the temperature and concentration of the deep eutectic solvent [1-chcl] [6-MEA] increased. It results from the interaction between CO₂ molecules and DESs, in which the CO₂ molecules occupy the “free space.” A significant quadrupole moment and Van der Waals forces were used inside the DESs structure [13]. For example, at 35 °C and 1.5 mol/l level, the absorbing velocity was 0.06650 mol/kg.min, whereas at 45 °C and 3 mol/l concentration, the absorbance value was 0.000173 mol/kg.min.

3.1.5. The Impact of Temperature and Time on CO₂ Absorption Rate

At a fixed concentration, the absorption rate decreased with increasing duration and temperature, as illustrated in Fig.12, due to the capacity of the exothermic CO₂ absorption thermodynamics system to generate reversible responses [14]. As an illustration, at 25°C and after 90 minutes, the absorption rate was 0.0682 mol/kg.min; however, when the temperature was raised to 35 °C, and after 120 minutes with fixed concentration, the absorbance level was 0.0441 mol/kg.min.

3.1.6. Effect of Time and Concentration on the CO₂ Absorption Rate

As shown in Fig.13, the process of absorption efficiency declined with time and increased with increasing the solvent content at a constant temperature. This decrease might be because raising the amount of solvent made the liquid thicker, making it more difficult to spread and delaying the mass transfer [18]. The absorption rate was 0.0682 mol/kg.min after 90 minutes at a concentration of 1.5mol/l. Nonetheless, after 120 minutes at a constant temperature and a concentration of 3mol/l, the absorption rate was 0.025 mol/kg.min.
Fig. 10 Effect of Concentration and Time on the CO₂ Outlet Concentration, (a) 2D Counter Plot, and (b) 3D Plot.

Fig. 11 Effect of Temperature and Concentration on the CO₂ Absorption Rate, (a) 2D Counter Plot and (b) 3D Plot.

Fig. 12 Effect of Temperature and Time on the CO₂ Absorption Rate, (a) 2D Counter Plot, and (b) 3D Plot.

Fig. 13 Effect of Concentration and Time on the CO₂ Absorption Rate (a) 2D Counter Plot and (b) 3D Plot.
3.1.7. Effect of Temperature and Concentration on the CO₂ Loading

Carbon dioxide loading the solution was the most influential process parameter on the overall mass transfer coefficient compared to the temperature and concentration of the solvent. The loading of CO₂ decreased with increasing temperature and solvent concentration, as shown in Fig. 14, because of the active absorbent (MEA) concentration; the lower its concentration, the higher the CO₂ loading [19]. For instance, at 35 °C with an average concentration of 1.5 mol/l, the amount being loaded of CO₂ was 5.355 mol/kg, whereas, at 45 °C and a density of 3 mol/l, the loading of CO₂ was 4.092 mol/kg.

3.1.8. Effect of Temperature and Time on the CO₂ Loading

Figure 15 shows that the CO₂ loading increased as time and temperature decreased because the chemical reaction involving MEA caused greater CO₂ loading. This phenomenon may be attributed to its existence. For example, at 45 °C and 105 minutes, the CO₂ loading reached 8.243 mol/kg. Meanwhile, at 35 °C and 120 minutes, the CO₂ loading was 6.613 mol/kg while keeping a steady concentration [15].

3.1.9. The Influence of Concentration and Time on CO₂ Loading

Figure 16 shows CO₂ loading decreased as time and solvent concentration rose. This finding might be attributable to a lack of water content at high concentrations of [1-chol] [6-MEA] [16]. For example, at a concentration of 1.5 mol/l for 60 minutes, the CO₂ loading was 3.99 mol/kg. The CO₂ loading dropped to 2.565 mol/kg at a concentration of 3 mol/l after a period of 90 minutes, and a constant temperature.

3.1.10. Effect of Temperature and Concentration on the CO₂ Absorption Capacity

The absorption capacity decreased with increasing the temperature and solvent content, as seen in Fig. 17, demonstrating the presence of parallel physical and chemical absorbance processes [13]. For example, at 35 °C and a concentration of 1.5 mol/l, the absorption capacity was 175.56 mg CO₂/gm solvent. Nevertheless, at 45°C and 3 mol/l levels, the absorption capacity reduced to 170.882 mg CO₂/gm solvent.

3.1.11. Effect of Temperature and Time on the CO₂ Absorption Capacity

The absorption capacity declined with increasing time and temperature due to a drop-in absorption rate, as illustrated in Fig. 18, due to replacing the acidic hydrogen on the C₂ carbon of the [MEA] cation with a methyl group and changing the organization of the anion and CO₂ a little in comparison to the cation. For example, at 25 °C and 60 minutes, the absorption capacity was 132 mg CO₂/gm solvent. However, at 35 °C and 90 minutes, the absorbance rate was 112.68 mg CO₂/gm solvent with a constant level [17].

![Fig. 14 Effect of Temperature and Concentration on the CO₂ Loading, (a) 2D Counter Plot, and (b) 3D Plot.](image1)

![Fig. 15 Effect of Temperature and Time on the CO₂ Loading, (a) 2D Counter Plot, and (b) 3D Plot.](image2)
3.1.12. The Impact of Concentration and Time on the Capacity of CO$_2$ Absorption

As shown in Fig. 19, the capacity for absorption reduced as the solvent content increased due to a reduction in absorption rate [18]. For illustration, at 1.5 mol/l and after 90 minutes, the rate of absorption capability was 99.396 mg CO$_2$/gm solvent. In contrast, at 3 mol/l and after 120 minutes at the same temperature, the absorbing capacity was 9.152 mg CO$_2$/gm liquid.

3.1.13. Effect of Temperature and Concentration on the CO$_2$ Solubility

The solubility decreased with increasing the temperature and solvent concentration, as shown in Fig. 20. The choline chloride’s capacity to create hydrogen bonds with the amines caused the chemical absorption. As the molar ratio of amine in the DES rose, the solubility nature of the quantity of CO$_2$ also increased. This increase makes sense because the possibility of a hydrogen bond network developing with the choline chloride increased with the amine concentration [13]. At 25°C and 1.5 mol/l concentration, a measure of dissolving was 0.0469 mole CO$_2$/mole. However, at 35°C and 3 mol/l level, the steady-state solubility was 0.0409 mole CO$_2$/mole.
3.1.14. The Impact of Time and Temperature on the CO₂ Solubility

Figure 21 shows that solubility increased with time and temperature. The CO₂ solubility increased with the molar ratio of MEA in the DES. This relationship can be explained by increasing the MEA concentrations, resulting in stronger chemical and physical CO₂ absorption [7]. For example, at 25 °C and 90 minutes, the solubility reached 0.0469 mole CO₂/mole. However, after 120 minutes at 35 °C at a steady concentration, the solubility improved to 0.055 mole CO₂/mole.

3.1.15. The Impact of Time and Concentration on the CO₂ Solubility

Solubility declined with increasing time and the solvent content, as shown in Fig. 22. It was found that when the molar ratio of the amine in the DES rose, the solubility of CO₂ [19] also increased. For example, at a concentration of 1.5 mol/l for 60 minutes, the solubility was 0.0469 mole CO₂/mole. Nevertheless, at a concentration of 3 mol/l at a steady temperature for 90 minutes, the solubility dropped to 0.0409 mole CO₂/mole.
Fig. 23 FT-IR Spectra of [1-CHCL] [6-MEA] Before Absorption.

According to the above results, there was no change in the chemical structure of the solution after the absorption process, indicating its high efficiency and thermal and chemical stability.

4. OPTIMIZATION CHOICES

Reaction optimization specifies which parameters best respond. This study used three variables, i.e., concentration, absorption rate, CO$_2$ loading, and solubility, to determine the maximum CO$_2$ outflow. The primary purpose of this research is to determine the optimal operating parameters (temperature, concentration, and absorption duration) for maximal absorption. Obtaining the optimal working conditions is shown in Table 5, in which the temperature, solvent concentration, and absorption time for [1-Chcl] are 29.025 °C, 1.878 mol/l, and 101.058 min, respectively. These values for [6-MEA] are economically beneficial compared to prior investigations; however, the absorption efficiency decreased under these conditions. The first solvent [1-Chcl] [6-MEA] was better than the monoethanolamine solvent under the best conditions, as it achieved a higher (absorption rate, CO$_2$ loading, and solubility). Also, the solubility in [1-Chcl] [6-MEA] was higher than monoethanolamine because mixing DESs with aqueous amine reduced the saturated vapor pressure of the substance by adding DESs-
water of 1-choline chloride-6-monoethanolamine; also water losses decreased using an aqueous solution because the carbonate formed by the interaction of MEA with CO₂ was insoluble in monoethanolamine [18]. The CO₂ by dissolution behaviors of conventional DESs were unique, e.g., increased carbon dioxide solubility and lower volume expansion, which may be due to the free-size mechanism in which CO₂ molecules occupy vacant holes in DESs previously available within the relatively solid ion structure. Although the HBD structure was less impacted, the HBA structure appeared to be one of the most important in determining the solubility of CO₂ [22].

**Table 5 Process Optimization Solution for [1-chl] [6-MEA].**

<table>
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<tr>
<th>NO.</th>
<th>Temp.</th>
<th>Conc.</th>
<th>Time</th>
<th>CO₂ Outlet (%)</th>
<th>Absorption Rate (mol/kg.min)</th>
<th>CO₂ Loading (mol/kg)</th>
<th>Absorption Capacity (mg CO₂/g Solvent)</th>
<th>Solubility (mole CO₂/mole)</th>
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5. **MASS TRANSFER COEFFICIENT**

The mass transfer coefficient was calculated by dividing the reaction rate by the partial pressure of the best solvent [1-CHCL] [6-MEA] under the best conditions at a temperature of 29°C and concentration of solvent 1.8 mol/l at a time 101 min. The results showed that the value of the mass transfer coefficient equaled (0.145) mol/bar.l.min. Moreover, it was found that the deep eutectic solvent has a higher mass transfer coefficient than the monoethanolamine solvent, which equaled (0.152) mol/bar.l.min due to the deep eutectic viscosity, which significantly reduced the CO₂ absorption, is one of the most significant challenges [23]. The overall mass transfer coefficient (Kₐ) can be calculated by the following Eqs. (10) - (12) [24]. The overall mass transfer was calculated according to [15].

\[ R_{CO₂} = KG \cdot P_{CO₂} \]  

(10)

Where:

- KG: Mass transfer coefficient (mol/bar.l².min)
- \( R_{CO₂} \): CO₂ reaction rate (mol/l.min).
- \( P_{CO₂} \): Partial pressure of CO₂ (bar).

\[ P_{CO₂} = \frac{RT}{V} = \frac{3 \times 10^{-7} \times 0.008314 \times 302}{50 \times 10^{-3}} = 0.151 \text{ bar} \]  

(11)

\[ R_{CO₂} = KG \cdot P_{CO₂} \rightarrow KG = \frac{R_{CO₂}}{P_{CO₂}} = 0.023 \]  

(12)

\[ KG = 0.152 \text{ mol/bar.l².min} \]

6. **COMPARISON WITH OTHER STUDIES**

It would have been advantageous to investigate the equation established from the statistical investigations, which estimate CO₂ absorption capacity while considering operating circumstances and water content in the present study. Applying this equation, a projection for the CO₂ absorption capacity of pure ChCl-MEA 1:6 DES at (35°C, 1 bar) was produced, obtaining a value of 0.044 mol CO₂/mol DES. This estimate closely matches the previously published value of 0.043 mol CO₂/mol DES Islam et al. [25]. Sarmad et al. [26] studied the CO₂ absorption capability of ChCl-MEA 1:6 DES at absorption pressures ranging from 10 to 20 bar in their study. The CO₂ absorption capacity of ChCl-MEA 1:6 DES was determined to be 0.0210 mol CO₂/mol DES at (25 °C, 1 bar). This result is equivalent to the 0.203 mol CO₂/mol DES value reported in the present study. The disparity in results might be attributable to a difference in operating temperatures in the present study, which was done at 45 °C, and Sarmad et al.’s [27] study was conducted at 25 °C. According to Sarmad et al. [26], the minor variation in molar ratios between 1:6 in this research and 1:7 in Sarmad et al.’s study does not result in a substantial change in CO₂ absorption capacity. Sarmad et al. [27] achieved a CO₂ absorption capacity value of 0.290 mol CO₂/mol DES in tests at (25 °C and 20 bar), which is equivalent to the estimated value of 0.301 mol CO₂/mol DES derived using the equation used in this study.

7. **CONCLUSIONS**

The present study presents novel data about the solubility of CO₂ in amine-based DESs, notably ChCl-MEA, at a molar ratio of 1:6. The results showed that DESs formulated with amines have much better CO₂ absorption capacity than pure amine solvents and typical DESs. It was found that increasing the amine’s molar ratio in the DES increased CO₂ solubility. ChCl-MEA had the greatest CO₂ absorption capability among the examined compounds, exceeding monoethanolamine. The increase in CO₂ absorption per mol of ChCl-MEA DES was
observed when the DES had high water content, low temperature, and high pressure. This phenomenon in the DES can be attributed to the improved mass transfer of CO$_2$ in the presence of water. It was found that the maximum CO$_2$ absorption capacity reached 0.379 mol CO$_2$/mol DES when the DES was absorbed with water at 29 °C and 1 bar. The rate of CO$_2$ absorption by ChCl-MEA DES was influenced positively by pressure and the amount of water present. However, the interaction between these two factors did not result in a synergistic effect, as a water content of up to 50% aided in the dispersion of the absorbent but did not alter the absorption mechanism. Gas analysis reveals that increasing the pressure allowed a higher intake of CO$_2$. However, when the temperature rose from 29 °C to 45 °C, the concentration of CO$_2$ in the air decreased from 8.14 % to 7.13 %, primarily due to increased CO$_2$ absorption. The solvent concentration negatively impacted the amount of CO$_2$ absorbed, suggesting that CO$_2$ absorption by ChCl-MEA DES was more effective at lower temperatures, resulting in an increasing CO$_2$ absorption capacity and concentration in the output gas. Before DES can be utilized in commercial applications, several challenges must be addressed. These include the high viscosity of DES, the lack of research on amine-based DES regeneration, and toxicity evaluation. Mathematical models, molecular simulations, and process simulations could aid in understanding how DES absorbs CO$_2$; however, it will take time to reduce the cost of the amine capture process. Thermogravimetric analyses have shown that DES-based products are more thermally stable than freestanding MEA, and the degradation temperature of ChCl-MEA 1:6 was around 140 °C. Deep eutectic amino solvents were useful because they fix broken amines and prevent them from being lost through evaporation.

**ABBREVIATION**

<table>
<thead>
<tr>
<th>HBA</th>
<th>Hydrogen Bond Acceptor</th>
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<tr>
<td>HBD</td>
<td>Hydrogen Bond Donor</td>
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<td>AMP</td>
<td>2-aminomethyl-1-propanol</td>
</tr>
<tr>
<td>CCU</td>
<td>Carbon capture and utilization</td>
</tr>
<tr>
<td>ChCl</td>
<td>Choline Chloride</td>
</tr>
<tr>
<td>DEA</td>
<td>diethanolamine</td>
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<tr>
<td>DES</td>
<td>Deep Eutectic Solution</td>
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<tr>
<td>FITR</td>
<td>Fourier-transform infrared spectroscopy</td>
</tr>
<tr>
<td>GHGs</td>
<td>Greenhouse gases</td>
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<td>ILs</td>
<td>Ionic liquid solvent</td>
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<td>MEA</td>
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**REFERENCES**


