RESEARCH PAPER

Solubility of CO₂ in Aqueous Solutions of Diethanolamine (DEA) and Choline Chloride

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Abstract

In this study, the solubility of CO₂ in DEA in the presence and absence of choline chloride was reported at different temperatures of 276.15, 298.15, 313.15, and 333.15 K, and pressure range of 4-15 bar. The solubility of CO₂ was evaluated using the pressure decay method in a batch isochoric stirred absorption cell. Also, the design of experiments performed with Qualitek-4 software using the Taguchi method. Henry's law constants at three different temperatures were calculated from the correlation of solubility data. Results showed that increasing the initial pressure and DEA concentration and also decreasing the temperature, increases the solubility of CO₂. Optimum operating conditions to maximize the amount of CO₂ absorption including the temperature of 276.15 K (minimum level), the initial pressure of 15 bar (maximum level), the concentration of DEA of 40 wt.% (maximum level), and the concentration of choline chloride of 5 wt.% (middle level). Also, Qualitek-4 software predicted the amount of solubility at the optimum conditions which was 7.5% different from the measured value.

Introduction

CO₂ emissions principally caused by energy usage eventuate to variant environmental issues such as global warming [1,2]. Certain technologies such as membranes separation, distillation, and absorption with solvents have been extending to remove CO₂ from gas streams [3]. The most popular methods to separate CO₂ are absorption with chemical solvents such as alkanolamines [4,5]. Diethanolamine (DEA) is one of the alkanolamine that immensely used to separate CO₂ from flue gas [6]. It has high efficacy, low cost, easy reclamation. Latterly, ionic liquids (ILs) were suggested as appropriate solvents for CO₂ since they have overall preferences comparing with other solvents [7]. RTILs are typically a combination of many cations and anions and specified by low volatility, high thermal, and electrochemical stability [7–13]. Their unique attributes make them an ideal category of separation media for several sample preparation techniques [14–17]. However, they have not been widely used because of the high cost and low sustainability of moisture [18,19]. A new class of RTILs has been reported as, deep eutectic solvents (DESs), which are new environmentally friendly chemicals [20]. They are synthesized by blending replaced quaternary ammonium salt with metal halide or hydrogen bond donor (HBD) and contain a greatly lower melting point [21]. Composite of choline chloride with urea was presented as a first DES [22]. Many similar DESs were expanded to other areas such as liquid separations and catalysts in reactions or bio-transformations [23–27].

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Generally, the most analyzed DESs show very low CO_2 lading capability in comparison to amine-based solvents [28]. Hence, researchers are trying to find other options to have green properties of DESs and also the high efficiency of amines [29-31]. In fact, the functioning of DESs in absorbing CO_2 can be dramatically amended by integrating an amine function in the structure of the DESs. However, according to this idea, researches on the alkanolamines [32-34] have primarily concentered on tertiary alkanolamines such as MDEA, and very few researches on the secondary alkanolamines such as DEA can be found. Furthermore, the ILs considered in these papers were commonly [Bmim][BF4] or [Bmim][OAc], which have not good thermal stability and suffer from their high viscosity [35]. The high viscosity causes some drawbacks in processes and may lead to lower reaction rates [36].

Leron et al. [37] reported the solubility of CO_2 in the DES compound of choline chloride and urea with the mole ratio of 1:2 under the wider temperature of 303.15 to 343.15 K. Recently, Leron et al. [23] developed the DESs scope to the mixture of choline chloride and ethylene glycol for CO_2 dissolution with acceptable results. Li et al. [38] represented the absorption of CO_2 in choline chloride-urea mixture over a range of temperatures (313.15 K to 333.15 K) under pressure up to 13 MPa. Francisco et al. [39] studied the CO_2 removal using DES composed of choline chloride and natural lactic acid (1:2 mole ratio).

Costa et al. [40] developed a new concept for the separation of CO_2 from high CO_2 content natural gas by the use of ionic-liquid [Bmim][NTf2]. The suggested process had this novelty that it can operate at high-pressure for CO_2 stripping.

Filippov et al. [41] investigated different categories of water-based choline-contained ionic liquids for CO_2 absorption. In the structures of these solvents, different cations and anions were presented. They stated that the ionic liquid could be re-cycled by evaporating water and stripping CO_2 at low pressure and high temperature. Palomar et al. [42] conducted a comprehensive survey of 50 ionic liquids to evaluate the role of thermodynamics and kinetics on the physical absorption of CO_2 by these widely researched solvents. They prepared results indicated that ionic liquids do not exhibit better absorbent performance in the CO_2 capture unit than conventional organic solvents already used in the industry.

As can be seen, the application of amine/ionic liquid solutions for CO_2 capture was observed to proceed rapidly and efficiently. Although this solvent has many of the acceptable characteristics of ionic liquids for CO_2 absorption, it has not their inherent drawbacks [43]. A review of the literature has indicated that DEA can be used for CO_2 absorption in an ionic liquid that contains a tethered 1° alcohol. Also, DEA was found to be immiscible with ionic liquids that contain solely alkyl substituents [44]. Ionic liquids have this ability to be tuned for any requirement regarding their compatibility and solubility. These solvents can be used for CO_2 absorption at low- and high-pressure range.

In this work and due to the similar function with the task-specific ionic liquids, choline chloride has been chosen. It is a commercially available and inexpensive quaternary ammonium salt with inherent properties such as biodegradable, non-toxic, and non-explosive nature. It can be synthesized from fossil reserves in large-scale quantities through a very high economic process [45]. The purpose of the present work is to measure the total CO_2 loading in aqueous DEA solutions mixed with choline chloride at temperatures ranging from 276.15 K to 333.15 K under pressures ranging from 4 to 15 bar using isochoric saturation method. Due to a large number of parameters and levels, Qualitek-4 software was used to design the experiment by the Taguchi method. Considering 4 levels for each parameter, 16 experiments were selected to analyze the results. Furthermore, Henry's law constant was calculated from the correlation of the solubility data.

Experimental

Materials
DEA was supplied from Bandar Imam Petrochemical Company (BIPC), Mahshahr, Iran with the purity higher than 99.5 %wt. Choline chloride (> 0.985 %wt.) was purchased from Merck Company, and carbon dioxide with the purity of 99.9 %mol was purchased from Balon Gas Co. Iran. All the chemicals were used without further purification and their purities were attained from suppliers.

Experimental Setup
An isochoric saturation method was implemented for measuring the solubility of CO_2 in DEA containing ionic liquid. The experimental apparatus used in this work was the same as one used in other previous researches [46-55]. As illustrated in Fig. 1, the experimental set up was mainly composed of three main parts: (i) CO_2 cylinder, (ii) stainless steel absorption cell, and (iii) temperature and pressure measuring instruments. The other equipment consisted of a middle cell, regulators, vacuum pump, and data acquisition system. The absorption cell and the middle cell were stainless steel vessels with volumes of 320 cm^3 and 500 cm^3, respectively. The equilibrium cell was designed to tolerate the pressure of up to 25 bars. The total gas to be introduced to the absorption system, initially charged in the middle cell. The middle cell is fabricated to stabilize the gas temperature and pressure at predominated value. Moreover, the recorded initial pressure of the middle cell is applied to calculate the total moles of CO_2 introduced to the absorption system.

The temperatures of the middle cell and the absorption cell were carefully controlled using two Pt-100Ω thermo-resistances with a precision of ± 0.2 K. The pressure of the gas was measured using pressure transmitter (model PSCH0025BCIJ from Sensys Co., with the precision of ±0.01 bar). The temperature of the water bath of the middle cell and the absorption cell was kept at a steady temperature. During each experiment, a mixer was used to continuously homogenize the vessel content with 300 rpm speed. The purpose of using a magnetic stirrer was to increase the mass transfer rate and reduce the time needed to achieve equilibrium.

In this work, experimental data on the solubility of CO_2 in aqueous solutions of DEA in the presence of choline chloride was presented at temperatures of 276.15 K, 298.15 K, 313.15 K, and 333.15 K, and DEA concentrations of 10, 20, 30 and 40 %wt. and choline chloride concentration of 3%, 5%, and 7 %wt.

Before each measurement, the absorption cell was cleaned perfectly with water. Then, the vacuum pump was used to evacuate any air inside the experimental rig. For each of the predominated concentrations, a mother solution formerly prepared by weighting the proper amount of each constituent of water, DEA, and Choline chloride and mixing them. Then, 100 ml of the mother solution was introduced to the absorption cell. Before starting each experiment, the absorption cell, the middle cell, and the connecting tubing were evacuated by a vacuum pump (JB Industries DV-200N, USA).

When the setup was under vacuum, the valve connecting the gas cylinder to the equilibrium cell was closed. Then the isolation valve between the absorption cell and middle cell was closed.

The gas was initially charged in the middle cell which was entirely isolated from the absorption cell and enough time was paid to ensure that the pressure and temperature of gas initially charged in the middle cell were stable. Then the isolation valve was opened and the volume of the gas phase increased suddenly and the pressure of gas-phase decreased due to the sudden volume expansion. After the gas and liquid are brought into contact, the absorption process began and proceeded until the liquid was saturated by the gas. The absorption process caused the pressure of gas-phase to drop gradually. The pressure drop of the gas was recorded until no pressure drop was observed which means the equilibrium was established. By

evaluating the difference between final and initial pressure in the absorption cell, the solubility of CO_2 can be measured.

The main characteristic of this experimental procedure is that no analysis of the liquid phase is necessary since the variation of CO_2 pressure during the absorption can be utilized to calculate the amount of CO_2 absorbed. The absorbed moles of solute can be obtained experimentally as follows:

$$n = \frac{P_i.V_i}{R.T.Z_i} - \frac{P_f.V_f}{R.T.Z_f} \tag{1}$$

where n stands for the number of carbon dioxide moles absorbed in the solvent, V_i, P_i, and Z_i are the isolated middle cell volume, pressure, and compressibility factor, respectively and V_f, P_f and Z_f are volume of the gas phase, the pressure of the system, and compressibility factor at the final equilibrium state, respectively. The compressibility factors at the initial and final conditions were calculated using PR-EOS [56]. It was assumed that the swelling, i.e. volume change of liquid according to gas uptake, was negligible and the volume of liquid and gas phase was considered to be constant during the absorption process. This assumption is important in absorbed gas calculations and has been considered by others [47].
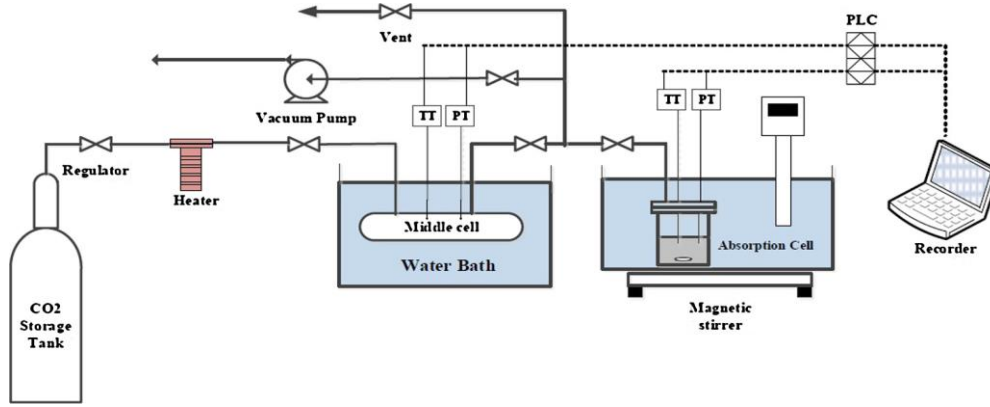

Fig. 1. Schematic diagram of the experimental apparatus

Uncertainty Analysis

Uncertainty analysis is carried out by considering the error of the measured variables in the calculated value of n. The uncertainty of n arises from measuring error of temperature, pressure, and gas-phase volume. The uncertainty of the compressibility factor which is due to the temperature and pressure uncertainty should also be considered using the Peng-Robinson equation of state. The maximum possible error of each measured variable is listed in Table 1.

According to Eq. 1 and the procedure described by Moffat [56], the following relation should be implemented for determining the uncertainty of n:

$$[dn]^2 = \left[\frac{\partial n}{\partial P_i}dP_i\right]^2 + \left[\frac{\partial n}{\partial V_i}dV_i\right]^2 + \left[\frac{\partial n}{\partial Z_i}dZ_i\right]^2 +$$
$$\left[\frac{\partial n}{\partial P_f}dP_f\right]^2 + \left[\frac{\partial n}{\partial V_f}dV_f\right]^2 + \left[\frac{\partial n}{\partial Z_f}dZ_f\right]^2 + \left[\frac{\partial n}{\partial T}dT\right]^2 \tag{2}$$

After the required differentiation, the maximum uncertainty of n was calculated at 3.2%. It can be shown that that measurement of pressure had a 45% contribution in the uncertainty of the equilibrium mole fraction which is the most important effect. Indeed, some experiments were repeated later to check the experiments have sufficient reproducibility. The results showed that the experiments were reproducible with less than 3.9% error which is an acceptable value.

The uncertainty of n_L arises from the error of weighting each constituent in preparing the mother solution. This error may also occur in weighting the 100 ml of the solution to calculate n_L. Eq. 3 represents the relation between n_L and the mass of constituents in mother solution preparation.

$$n_L = \frac{m_L}{m_s}\left(\frac{m_1}{M_1} + \frac{m_2}{M_2} + \frac{m_3}{M_3}\right) \tag{3}$$

Where M stands for the molecular weight of any constituents. The rest of the parameters are defined in Table 1. The required differentiation was performed similarly to Eq. 2 and the maximum uncertainty of n_L was obtained at 2.3 %. For evaluation of the uncertainty of mole fraction, x, the following relation was considered.

$$x = \frac{n}{n + n_L} \tag{4}$$

$$[dx]^2 = \left[\frac{\partial x}{\partial n}dn\right]^2 + \left[\frac{\partial x}{\partial n_L}dn_L\right]^2 \tag{5}$$

Finally, the maximum uncertainty of mole fraction calculated as 4.5% according to Eq. 5.

Table 1. The maximum error of different variables

Variable	Description	Measurement device	Maximum error
T	System temperature	PT-100 thermo-resistance	0.2 °C
P_i	Initial middle cell pressure	Pressure transducer	0.01 bar
P_f	Final system pressure	Pressure transducer	0.01 bar
V_i	Initial gas volume	Graduated cylinder	5 ml
V_f	Final gas volume	Graduated cylinder	5 ml
m_1	Mass of water in preparing mother solution	Electronic digital balance	0.1 g
m_2	Mass of water in preparing mother solution	Electronic digital balance	0.1 g
m_3	Mass of water in preparing mother solution	Electronic digital balance	0.1 g
m_s	Mass of mother solution	Electronic digital balance	0.3 g
m_L	Mass of 100 mL	Electronic digital balance	0.1 g

Optimization Methodology

Taguchi – Design of Experiments

To perform the experiments, Taguchi's orthogonal scheme was used to form the matrix of experiments by using the standard orthogonal arrays. Meanwhile, it will be possible to obtain maximum information from the minimum number of experiments [57]. For this purpose, Qualitek-4 software version 4.75 was applied which is the Windows version software for the design of experiments by the Taguchi method of analysis. In this study, the Taguchi orthogonal array (OA) approach was utilized. All factors that had a substantial effect on the solubility of CO_2 were selected as well as their levels. Temperatures, pressure, concentrations of DEA, and concentration of choline chloride were investigated in four levels. Totally 16 experiments were suggested according to L16 orthogonal array include four factors each one at four levels. The Factors and their levels for the design of experiments are presented in Table 2.

Table 2. Factors and their levels for design of experiments

symbol	factors	Level 1	Level 2	Level 3	Level 4
A	Temperature (K)	276.15	298.15	313.15	333.15
B	Pressure (bar)	4	8	12	15
C	Concentration of Amine (wt. %)	10	20	30	40
D	Concentration of choline chloride (wt. %)	0	3	5	7

Totally, 16 runs were undertaken in this experimental investigation (Table 3). The orthogonal array was selected in order to ignore any interaction between the parameters. Each row of the matrix represents one run. The alphabets A, B, C, and D represent the aforementioned factors. Consequently, the average of the results was used to apply a standard analysis to measure the experimental results. In the Taguchi method, the quality characteristics can be performed in three different shapes including: "higher is better", "nominal is the best", "lower is the best" [58]. Because in this study it was aimed to achieve the maximum amount of absorption of CO_2 gas in DEA in the presence and absence of choline chloride, the quality characteristics with HB are required. Therefore, it is possible to combine the L16 orthogonal array and the values of presented levels in Table 2 to obtain the experimental results (the amount of CO_2 absorption in mol) in Table 3.

Table 3. Design of Experiment using L16 orthogonal array

	Factors levels				
Run no.	A	B	C	D	n (mol)
1	1	1	1	1	0.03164
2	1	2	2	2	0.06716
3	1	3	3	3	0.11421
4	1	4	4	4	0.14313
5	2	1	2	3	0.04744
6	2	2	1	4	0.06434
7	2	3	4	1	0.12335
8	2	4	3	2	0.10811
9	3	1	3	4	0.05601
10	3	2	4	3	0.10630
11	3	3	1	2	0.08809
12	3	4	2	1	0.08560
13	4	1	4	2	0.04990
14	4	2	3	1	0.08012
15	4	3	2	4	0.10307
16	4	4	1	3	0.09873

Standard Analysis (ANOVA)

Analysis of variance (ANOVA) is one of the important characteristics of Taguchi analysis for the optimization of a process. Using ANOVA as a computational technique enables us to estimate the relative contributions of each influencing parameter. ANOVA implements some statistical techniques like the sum of the squares method to compare the average responses of the control factor with the mean experimental response. ANOVA can also predict the percent contribution of each influencing parameter for system optimization. It can be calculated for each factor as follows [59, 60]:

$$\text{Percent}\left(\%\right) = \frac{\text{PS} - \left(\text{DOF.V}_{\text{Er}}\right)}{\text{SS}} \times 100 \tag{6}$$

where DOF is a degree of freedom that can be calculated for each factor by subtracting one from the number of levels. The total sum of squares, SS, is described as [59,60]:

$$SS = \sum_{j=1}^{m} \left(\sum_{i=1}^{n} Y_I^2 \right) - mn(\bar{Y}_T)^2 \tag{7}$$

The pure sum, PS, is calculated as [59,60]:

$$PS = \frac{mn}{L} \sum_{k=1}^{L} (\bar{Y}_k^F - \bar{Y}_T)^2 \tag{8}$$

The variance can be calculated as:

$$Variance = \frac{PS}{DOF} \tag{9}$$

Indeed, the variance of error can also be calculated as:

$$V_{Er} = \frac{SS - \sum PS}{m(n-1)} \tag{10}$$

The pure sum, PS, was individually calculated for each factor by replacing $\bar{Y}_k^F$ and $\bar{Y}_T$ in Eq. 8. Then, the total sum of squares, SS, was defined using Eq. 7. After that, the values of the variance of each factor and the variance of error were calculated using Eqs. 9 and 10, respectively. Eventually, the percentage contribution of all the factors would be obtained using Eq. 6. Table 4 shows the values of the percentage contribution of each factor.

Results and Discussions

Kinetic Analysis

Fig. 2 shows the analysis of pressure variation during CO_2 absorption in the DEA solution containing 7 wt.% choline chloride. This pressure reduction equivalent to the amount of gas absorbed in the solvent. The pressure of the gas phase reduces continuously until the solvent becomes saturated, and equilibrium is instituted between the two phases. In this study, it was assumed that when the gas phase pressure did not change for about 20 min the equilibrium point was obtained. Fig. 2 demonstrates the variation of the absorbed moles of CO_2 in DEA+ choline chloride as a function of time. These data were calculated using Eq. 1.

Fig. 3 compares the pressure decay data during CO_2 absorption in 40% DEA solution + 5% choline chloride at the initial pressure of about 10.2 bar and two temperatures of 276.15 and 313.15 K. As can be seen, the absorption kinetic data showed three distinct zones. These zones were also seen in the study of Azizi et al. [61] for propylene absorption in NMP.

Fig. 3 shows the different trends of the two pressure decay curves during the absorption. Temperature is an important factor that can determine the curvature of these kinetic curves. Therefore, Azizi et al. [61] suggested three parts on a typical absorption kinetic curve:
• Part (I): In which, the absorption is controlled by "solubility". So, more pressure decays would be obtained at the lower temperatures.
• Part (II): In this part, the absorption is controlled by "diffusion". As a result, the rate of pressure decay would be increased at higher temperatures.
• Part (III): This section is again under the influence of "solubility". It is expected that more pressure decay obtained at the lower temperatures.
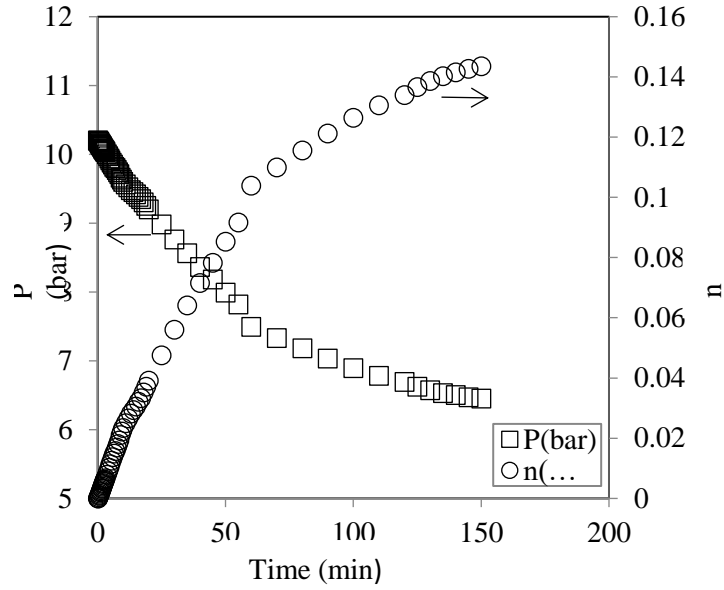
Fig. 2. Pressure decay and number of absorbed moles during CO_2 absorption at 276.15 K and initial middle cell pressure of 15 bar in 40% DEA solution containing 7% choline chloride
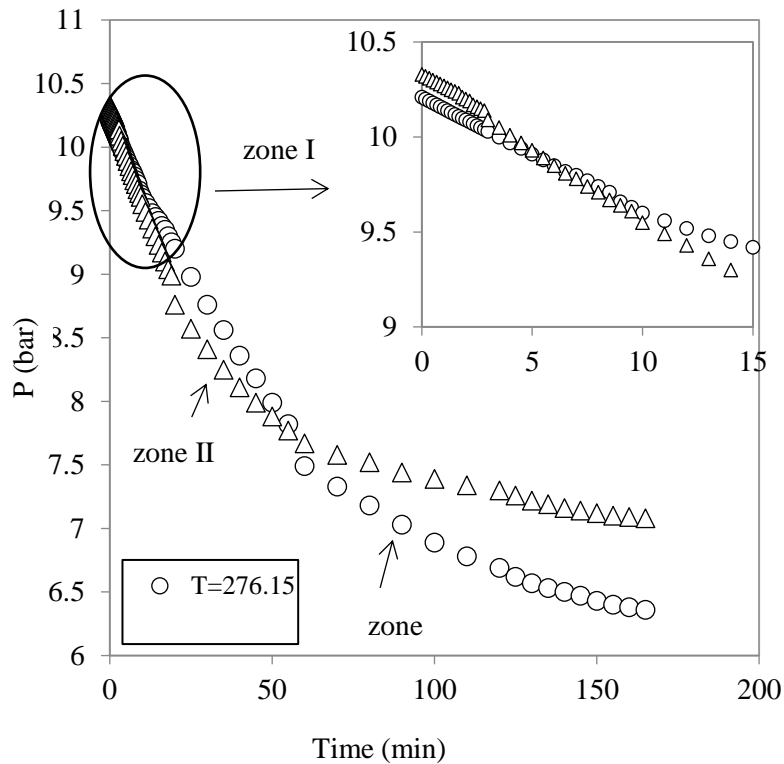

Fig. 3. The experimental data for CO_2 absorption in the solvent containing 40 %wt. DEA solution + 5 %wt. choline chloride at two temperatures

Henry's law constant

In this study, Henry's law was used to correlate the experimental data of gas solubility. Henry's law can be given for binary systems with a non-ideal gas phase as [62]:

$$y_{CO_2} . \varphi_{CO_2} . P_f = k . x_{CO_2} \tag{11}$$

In this study, the solvent (DEA+ ILs) has negligible vapor pressure, so, it can be possible to consider the vapor phase as a pure gas, i.e. $y_{CO_2} = 1$. The fugacity coefficient can be given as:

$$\varphi_{CO_2} = \frac{f_{CO_2}}{P_f} \tag{12}$$

The fugacity coefficient of CO_2 in each pressure was calculated using the Peng-Robinson equation of state. Henry's law constant can be calculated as:

$$k = \frac{\varphi_{CO_2}.P_f}{x_{CO_2}} \tag{13}$$

It should be noted that in this study, the experimental points with the minimum equilibrium pressure was implemented to calculate Henry's law constant. Therefore, the value of the fugacity coefficient is very close to unity. Table 4 gives the calculated Henry's law constants as a function of temperature. It is clear that it increases when the temperature rises. It is equivalent to say that when the solubility experiments perform at a higher temperature, it is expected that lower solubility obtained in comparison with that at lower temperatures. It should be noted that at a given temperature, it cannot be possible to increase the operating pressure unlimitedly since the dew point pressure of the gas would be reached. So, if one likes to operate at higher operating pressures, it is mandatory to work at higher temperatures.

Table 4. Henry's law constants for CO_2 / solvent (containing 40 %wt. DEA solution + 5 %wt. choline chloride) at different temperatures.

Temperature (K)	P_{eq}	φ_{CO2}	H (bar)
276.15	2.34	0.98	164.88
298.15	1.78	0.98	202.5
313.15	1.34	0.99	258.06

Taguchi Results

16 experiments were conducted sequentially based on the recommendation of the design of experiments based on Taguchi orthogonal array which previously shown in Table 3. The influence of each control factor was calculated using the average experimental data. Figs. 4 and 5 show the effects of temperature, pressure, the concentration of DEA, and choline chloride on the amount of absorption of CO_2 gas. Fig. 4 shows that increasing pressure and decreasing temperature increases the amount of CO_2 absorption. It should be noted that both physical and chemical dissolution may occur in this system. Although pressure has a weak effect on liquid-phase reactions, it should be noted that one of the main feeds of this reaction is supplied from the gas phase. As pressures increases, the solubility of a gas in liquid increases. It means that more CO_2 is introduced in the liquid phase and the concentration of feed in the chemical reaction increases. This phenomenon leads to more gas uptake and a positive effect on chemisorption.

Fig. 5 proved that increasing the amine concentration improves the response while the concentration of choline chloride shows the maximum point. One mechanism that may cause this reduction in the amount of CO_2 absorption with increasing the concentration of choline chloride is the so-called salting-out effect. Liu et al. [63] showed that with adding inorganic salts the solubility of different substances decreases in aqueous solutions. Thus, the decrease in the CO_2 solubility can be attributed to the salting-out effect. This phenomenon is due to the fact that when the ions are presented in water, the number of water molecules available for solute reduces, and as a result, it may salt out from the aqueous phase.
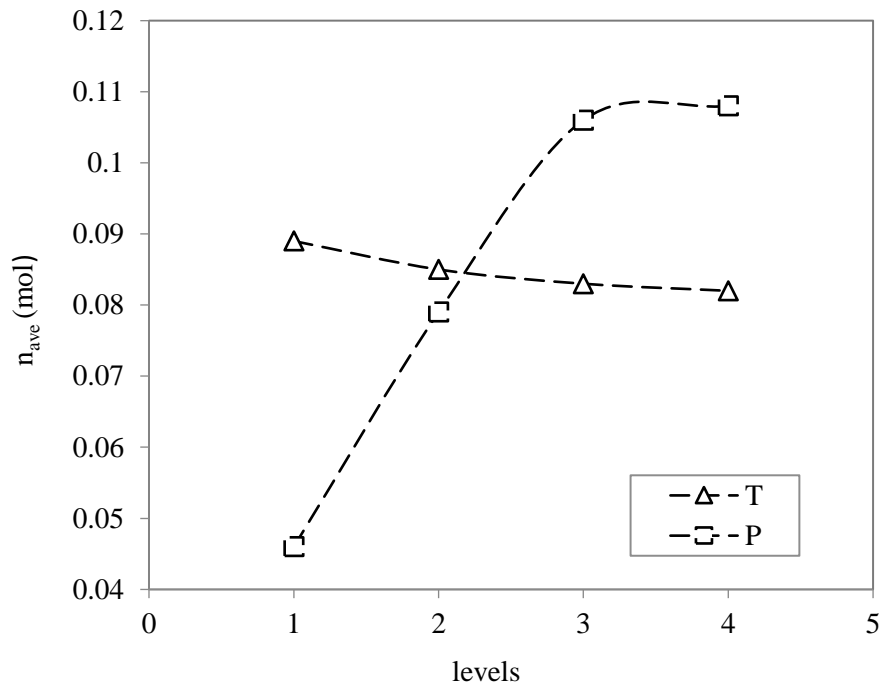
Fig. 4. Effects of pressure and temperature factors on the amount of CO_2 absorption
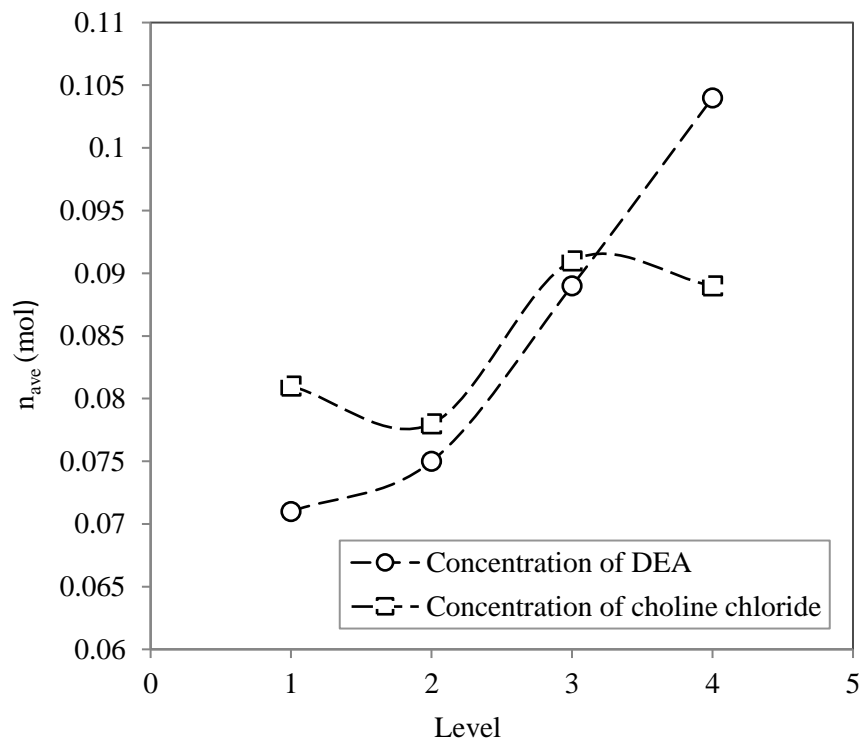

Fig. 5. Effects of Concentration of DEA and choline chloride on the amount of CO_2 absorption

Analysis of Variance (ANOVA) Results

The ANOVA for this work is shown in Table 5. The last column of ANOVA shows the influences of different factors on the results. The last row is about the sources of errors in the results. The error may be originated from uncontrollable parameters, factors which not considered in the experimental runs, and error in experimentation. As can be seen, pressure

with 70.65% has the highest percentage of contribution to the amount of CO_2 absorption and, after that, are the concentration of DEA and the concentration of choline chloride with 17.74% and 1.85%, respectively. It should be noted that since the degree of freedom of error was three, it was possible to perform the test of significance in order to omit the factors that have a negligible effect on the response. At first, the parameters having less confidence level than 95% were pooled from ANOVA analysis. Table 5 shows the ANOVA table after pooling. As can be seen, different interactions between factors were of less importance to be considered. All the interactions had less than 1% contribution before pooling.

One of the most important features of ANOVA analysis is that it can find the optimum conditions for the experiment. The performance at the optimum conditions can be calculated using QT4 software on the basis of the chosen quality characteristics. Table 6 shows the optimum conditions and the maximum possible number of absorbed moles of CO_2 in the solvent. According to the Taguchi method, the best setting for control factors is:

1) The temperature of 276.15 K (the lowest level),
2) The pressure of 15 bar (the highest level),
3) The concentration of DEA of 40 wt. % (the highest level),
and 4) Concentration of choline chloride 5 wt.% (one of the middle levels).

The current grand average for the amount of CO_2 absorption is around 0.085 mol. However, at optimum conditions, the amount of CO_2 absorption is predicted by 0.135 mol.

Table 5. ANOVA for the amount of absorption of CO_2

Factor	DOF	Sum of sqrs	Variance	F Ratio	Pure Sum	Percent
Temperature	3	0	0	0.366	0	0
Pressure	3	0.011	0.003	32.68	0.01	70.56
Concentration of DEA	3	0.002	0	8.958	0.002	17.74
Concentration of choline chloride	3	0.01	0	1.833	0	1.85
Error	3	0.01	0.01	-	-	9.74

Table 6. Optimum conditions and performance of the number of absorbed moles of CO_2

Factor	description	Level	Contribution
Temperature (K)	276.15	1	0.004
Pressure (bar)	15	4	0.022
Concentration of Amine (wt. %)	40	4	0.019
Concentration of choline chloride (wt. %)	5	3	0.005
Total	--	--	0.049

Confirmation Test

As can be seen in the previous section, the optimum condition was found by the statistical analysis. Generally, it is possible to conduct an extra experiment exactly at this condition to check the prediction ability of the model. Table 7 shows the result of this extra test at the optimum condition. As can be seen, a very good agreement exists between the experimental results and model prediction, and deviation is about 7.5%. It proved that using the design of experiment was appropriate for the modeling of the amount of CO_2 absorption in the solvent in only 16 runs instead of 256.

Table 7. Results of confirming the experiment and statistical model at optimum conditions

Operating conditions				Predicted result	Experimental result
Temperature (K)	Pressure (bar)	Concentration of DEA (wt. %)	Concentration of choline chloride (wt. %)		
276.15	15	40	5	0.135	0.146

Conclusions

The solubility of CO_2 in DEA in the presence and absence of choline chloride was examined at different temperatures and pressures. Effects of the following controllable factors on the amount of CO_2 absorption have been studied using Taguchi analysis: pressures (4, 8, 12, and 15 bar), temperature (276.15, 298.15, 313.15 and 333.15 K), DEA concentration (10, 20, 30, and 40 %wt.), choline chloride concentration (zero, 3, 5, and, 7 %wt.).

The measured solubility data showed that when the temperature decreased or pressure and DEA concentration increased, the solubility enhanced. Optimum operating conditions for maximizing the amount of CO_2 absorption including the temperature of 276.15 K, the pressure of 15 bar, DEA concentration of 40 wt.%, and choline chloride concentration of 5 wt.%. The results of the software showed that pressure has the most impact on the amount of solubility of CO_2 among the other parameters.

In the end, an extra experiment was also carried out to check the prediction ability of the model. It was shown that the statistical model could predict the result at the optimum condition with only 7.5% deviation. All this information was obtained from the Taguchi method for the modeling of the amount of CO_2 absorption by conducting only 16 experiments instead of 256. Finally, it is important to say that it is not costly to add even a small amount of choline chloride to DEA to obtain a very small improvement in the absorption rate.

Nomenclature

DEA	Diethanolamine
DES	deep eutectic solvents
DOF	degree of freedom
ILs	ionic liquids
$k_{H, CO2}$	Henry's constant
m	number of experiments
m_1	Mass of water in mother solution preparation
m_2	Mass of DEA in mother solution preparation
m_3	Mass of Cholin Chloride in mother solution preparation
m_s	Total mass of mother solution
m_L	Mass of 100 ml solution
n	number of repetitions under the same experimental conditions
n_{CO2}	the number of absorbed moles of CO_2
P_f	Final equilibrium pressure
P_i	Middle cell initial pressure
PR-EOS	Peng–Robinson equation of state
PS	pure sum
QT4	Qualitek-4
R	gas constant
RTILs	room temperature ionic liquids
SS	total sum of squares
T	Temperature
V_f	final volume of the gas
V_G	gas volume
V_L	liquid volume
V_{Er}	variance of error
V_i	Middle cell volume
x	CO_2 solubility

y_{CO_2}	gas composition on the vapor phase
$\bar{Y}_T$	average value of the results
Y_i	value of the measurement results of a certain run
$\bar{Y}_k^F$	average value of the measured results in kth level
Z	compressibility factor
φ_{CO_2}	gas fugacity coefficient

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