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Solvent dependency of carbon dioxide Henry's constant in aqueous solutions of choline chloride-ethylene glycol based deep eutectic solvent

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Abstract

The Henry's constants of carbon dioxide absorbed in aqueous solutions of ethaline (choline chloride-ethylene glycol) were determined for temperatures ranging from 303.15 to 323.15K based on solubility measurement at CO₂ pressure ranging from 0 to 6 bar (0.6 MPa). These studies revealed that the Henry's constant increased with the increase of temperature. Data indicated the highest capacity of CO₂ absorption is obtained for ethaline and the lowest temperature dependency of absorption capacity is reported for aqueous solution of ethaline based deep eutectic solvent (0.3 mole fraction of water). The dependence of Henry's constant on solvent composition and solvent properties was investigated using preferential solvation model and linear free energy relationship method. Results showed that CO₂ was preferentially solvated by ethaline in aqueous solution. Furthermore it revealed that solute-solvent interactions related to the scale of hydrogen bond donor ability of the solvent were the main



parameter which controls the solubility of CO₂ in the studied system. Presented methodology is useful for selection of best absorbent composition for systems of hot off-gases treatment. Interesting and practical results obtained in this work, indicated that precisely selected composition of the deep eutectic solvent based absorbent provide low sensitivity of the treatment performance in respect to the temperature of the treated gas.

Keywords: Deep eutectic solvent; Carbon dioxide; Henry's constant; absorption; Linear free energy relationship.

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1. Introduction

The concentration of carbon dioxide (CO₂), as one of the most important greenhouse gases, has continuously risen in atmosphere due to human activities. The increasing CO₂ concentration is related to the global warming phenomenon. Although CO₂ emission to atmosphere is known as environmental hazard, CO₂ capture and storage is an important technology due to its noticeable applications in different types of the industries. Some of these applications are based on CO₂ used as a green solvent in supercritical conditions to perform chemical reactions [1,2] and extraction process [3–6]. It is used also as a key reactant in petrochemical industry [7–10]. Other applications relate to its usage in carbonated beverage industry and other food industries.

Carbon capture and storage (CCS) is a process of capturing carbon dioxide emitted as a product of combustion of fossil fuels, transporting it to a storage site where it is placed out of access to the atmosphere [11]. This process is helpful to prevent the release of large quantities of CO₂ into the atmosphere from heavy industry. Although there are several methods for removal CO₂ as post-combustion technologies, the most commonly method for capturing carbon dioxide is the absorption into suitable solvents. The solubility of gases in solvents follows from physical interactions or chemical reaction taking place between CO₂ and components of the absorbent. Among chemical methods, amine scrubbing has emerged as the preferred method for CO₂ sequestration [12,13]. Despite the high efficiency of chemical absorption of CO₂, physical absorption is still on the spotlight of scientists [13–15]. The advantages of this method are facility, reversibility, and being economically comparable with



amine absorption which involves the use of volatile amine solvents, environmental drawbacks and energy consumption for solvent regeneration [13,15].

Recently, many academic reports have explored the potential of some new solvent such as ionic liquids (ILs) and deep eutectic solvents (DESs) as alternative green solvents to volatile amine absorbents as CO₂ capture media [16–21]. The extremely low vapor pressure, high thermal and chemical stability, non-flammability, high solvation capacity, and specially cost-effectivity of DESs resulted in high interest on their application for many analytical as well as industrial applications [22–26]. Recent researches explored the capacity of DESs based on choline chloride for CO₂ absorption [27–30]. DESs are obtained by mixing two (or more) components – one having function of hydrogen bond acceptor (HBA) and second a hydrogen-bond donor (HBD). Such a mixture have a melting point much lower (often much low than room temperature) than the melting point of pure components [31,32].

Since water vapor is co-emitted with carbon dioxide during the combustion process of fossil fuels, the study of CO₂ absorption in aqueous solutions of DESs is important particularly when the selectivity is a key parameter in applied absorption system. In this contribution, we have reported experimental data on Henry's constant for the system CO₂-aqueous ethaline (choline chloride + ethylene glycol) solution and its calorimetric properties in binary systems of ethaline and water in the temperature range of 303–323 K. The solvent-solvent interactions in binary and ternary solvent mixtures affect the solubility of solutes and therefore the capacity of the absorbent for capture of carbon dioxide. Solubility data in the aqueous solutions of ethaline



clearly demonstrated the influences of solute-solvent and solvent-solvent interactions on the solubility of carbon dioxide.

2. Experimental section

2.1. Materials

Carbon dioxide with purity of 99.9% in liquid phase was purchased from Spadana Gas, Iran. Choline chloride ($\geq 98\%$) was purchased from Sigma-Aldrich and dried for 72 h at 323K with a high-vacuum oven. Ethylene glycol ($\geq 99.8\%$) was purchased from Merck and dried by 3Å molecular sieve. The water content of the dried compounds was determined by coulometric Karl Fischer titration (Mitsubishi Moisture meter MCI CA-02) yielding <200 ppm residual water for ethylene glycol and <700 ppm for choline chloride. The summary of the chemicals used, their purities, and supplier are summarized in Table 1.

Ethaline was obtained by mixing choline chloride and ethylene glycol at the mole ratio of 1:2 in an inert atmosphere and subsequent stirring under heating up to 353.15 K until a homogeneous, colorless liquid was formed [32]. The aqueous solutions of ethaline over the entire range of ethaline mole fractions were prepared gravimetrically (approximately 10 ml) before each measurement.

2.2. Apparatus and procedure

In order to determine Henry's constant of CO_2 in solvent, we used the apparatus and procedures similar to that described in the research of Dalmolin *et al* [33]. The experimental



setup, procedure, and method of analysis used were the same as those presented in our previous work [34]. The apparatus is composed of CO₂ cylinder, water bath, CO₂ gas equilibrium cell with magnetic stirrer, gas reservoir, pressure transmitters and a vacuum pump as showed in Figure 1. The equilibrium cell and gas reservoir are immersed in a temperature controlled water bath where its temperature is monitored continuously by a PT-100 thermocouples with a precision of 0.1 K. The volume of equilibrium cell along with its connection was exactly 75 cm³. The role of the gas reservoir is to store the gas until it will reach a constant temperature. A defined amount of carbon dioxide is introduced into the gas reservoir equipped with pressure transmitter. Then, the equilibrium cell is purged with incubated CO₂ in desired temperature for 10 minutes. Finally, a known mass of the solvent or binary solvent mixture is loaded into the equilibrium cell. Gas is immediately injected into the equilibrium cell at a known pressure. The solution is agitated by magnetic stirring to reach equilibrium after approximately 30-60 minutes, corresponding to the temperature and depending on the type of solvent. The vapor pressure of the solvent and the mole fraction of the solvated gas are measured by using the initial and final (equilibrium) pressure readings of the equilibrium cell corresponding to introduced method by Nitta *et al.* [35].

Densities of all the neat solvents and mixtures under different temperatures are used from the literature [36]. The volume of liquid solution used in each measurement was directly obtained from the mass and density of solvent at temperature of preparation. The volume expansion of the liquid in equilibrium cell because of the dissolution of CO₂ was very small and neglected.



All experiments were done at least in triplicate and results are averaged. The relative standard deviation (RSD) of all data points used in this paper was lower than 5%. Data were evaluated using SPSS and Origin software.

3. Results and Discussion

In order to validate and test the reproducibility of the procedure and apparatus the solubility of the CO₂ in water was first measured at room temperatures. These measurements were also performed for the solubility of CO₂ in ethaline at temperatures of 303.15, 313.15, and 323.15 K. Figure 2 shows that the solubility data are in good agreement with data reported in the literature [28,33]. Although there is a few data for solubility of CO₂ in ethaline at low pressure, the experimental solubility data in ethaline follows the expected trend in the literature at low pressures (Figures 2b, 2c, and 2d) [28]. These results confirm the validity of the procedure and equipment used in this work.

3.1. Temperature and solvent dependence of Henry's constants

The experimental values of the Henry's constant of CO₂ in the aqueous solutions of ethaline at different temperatures of 303.15, 313.15, and 323.15 K and different DES compositions were determined based on solubility data and according to the procedure reported previously [34]. Figure 3 shows the variation of Henry's constant as a function of temperature and solvent composition. As expected, the values of the Henry's constant increase when temperature increases. On the other word, the CO₂ absorption capacity decreases in higher temperature.



Figure 4 has been plotted according to Versteeg hypothesis that proposed a non-linear temperature dependence of Henry's constant as shown in Equation (1) [37].

$$\ln H_{\text{CO}_2} = a_H + \frac{b_H}{RT} \quad (1)$$

In which a_H and b_H are the constants of relationship. The values of parameters a_H and b_H along with the standard deviation derived from equation (1) are summarized in Table 2. Clearly, the slope, b_H/R , decreases firstly to its minimum value at $x_w = 0.5$, increases secondly through a maximum at $x_w = 0.8$, and then decreases to its value in pure water. According to this discussion, the noticeable result is that although the absorption capacity of ethaline is higher comparing to its binary mixtures with water and it can be consider as a better absorbent for CO_2 , the aqueous solution of ethaline with 50% mole water content has the minimum temperature dependence compared to other solvent compositions. Low sensitivity (temperature dependency) of the absorption system in relation to temperature is advantageous especially in the case of absorptive system used for treatment of hot gases produced from combustion process.

On the other hand, it is clear from Figure 3 that the Henry's constant increases (or the solubility of CO_2 decreases) as the water content of ethaline increases. It is in accordance with some previous reports those have shown that water acts as an anti-solvent to push out the dissolved CO_2 in the DESs [30,38]. Also, a mild negative deviation from ideal behavior can be observed on the basis of variation of Henry's constant related to the solvent composition. It can be attributed to the effect of solute-solvent and solvent-solvent interactions on the solubility of



CO₂ (see section 3-2). This non-ideal behavior can be interpreted by O'Connell equation as presented in equation (2) [39].

$$\ln H_{\text{CO}_2,\text{mixed}} = x_w \ln H_{\text{CO}_2,\text{w}} + x_{\text{eth}} \ln H_{\text{CO}_2,\text{eth}} - \alpha_{\text{D,E}} x_w x_{\text{eth}} \quad (2)$$

In this equation, x_w and x_{eth} are the mole fractions of water and ethaline, respectively, and $\alpha_{\text{D,E}}$ is a so-called interaction term. The values of the empirical parameter $\alpha_{\text{D,E}}$ were obtained by fitting equation (2) using the experimental results as a non-linear regression. Its obtained values are given in Tables 3 along with the standard deviations. The Lines in Figure 3 have been created from equation (2) and show the ability of the models in reproduction of the experimental data.

3.2. Thermodynamic properties

From the data of Henry's constants, the solution thermodynamic properties such as the Gibbs energy ΔG , enthalpy ΔH and entropy ΔS of the solution for the CO₂ in aqueous solutions of ethaline were calculated as it has been reported elsewhere and summarized in Table 4 [34]. The negative value of ΔH indicates that the dissolution of CO₂ in solvents is exothermic, on the other word, is favourable in terms of enthalpy. The highest values of ΔH are observed at $x_w = 0.8$ that it is related to the high temperature dependency solute-solvent interactions in this composition. As expected, the negative value of ΔS like many gas dissolution processes can be attributed to decreases in the degree of ordering of the liquid-gas mixture.

Solute-solvent physical interactions play a key role in the physical/chemical properties of the absorbent. For instance, the solubility of CO₂ can be impressed with solute-solvent interactions



if solvents behave chemically inert. In the binary mixtures of the solvents, the influence solvent mixture as media might be much more complex than those in pure solvent due to specific interactions between the solvent components. The investigation of the solubility changes of CO₂ in the solvent mixtures can characterize these interactions [34]. It can be accomplished by using both non-linear preferential solvation (PS) and linear free energy relationship (LFER) methods.

Preferential solvation model as a nonlinear equation may provide valuable solute-solvent and solvent-solvent structural information. The PS model is based on a physical exchange of two solvents in microsphere solvation layer of a solute (like CO₂) according to the following equations [40,41]:



where I stands for the solute, S1 and S2 for the pure solvents, and S12 for the solvent formed due to solvent-solvent interaction (yielding a composite structure). I(S1), I(S2) and I(S12) represent the solute solvated by the S1, S2 and S12 species. The Gibbs free energy of the solution (ΔG) in the solvent mixtures as a property which is caused by solvation process is calculated as an average of these properties in pure solvents S1, S2, and S12 (ΔG_1 , ΔG_2 , and ΔG_{12} , respectively) according to the mole fractions of each solvent in the mixture (x_2^0), as follows:

$$\Delta G = \frac{\Delta G_1(1 - x_2^0)^2 + \Delta G_2 f_{2/1}(x_2^0)^2 + \Delta G_{12} f_{12/1}(1 - x_2^0)x_2^0}{(1 - x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1 - x_2^0)x_2^0} \quad (5)$$



where $f_{2/1}$ and $f_{12/1}$ are the thermodynamic equilibrium constants of equations (3) and (4), respectively and they refer to the difference of solvent composition between microsphere solvation of solute and the bulk media.

The Gibbs free energy of the solution listed in Table 4 was fitted to the proposed equation (5) and calculated parameters were given in Table 5. Statistical parameters are in good agreement as shown in Figure 5, which confirms the ability of equation (5) in determination of ΔG . Analysis of the data revealed, that $f_{2/1}$ value is less than a unit. It means that the CO_2 as a solute is preferentially solvated by ethaline in the solution. In addition, the $f_{12/1}$ parameter has a value of more than a unit which reveals the presence of the composite solvent in the microsphere solvation of molecules. In other words, water in the microsphere solvation of CO_2 is not present as a free molecule but it is in strong interaction with ethaline molecules, .

The LFER model can determine the influence of solute-solvent interactions on the solubility of CO_2 . It is based on finding linear multi parameter relationship between the Gibbs free energy of the process and solute-solvent interaction parameters like Kamlet-Taft parameters [34]. The Kamlet-Taft parameters for binary mixtures of ethaline-water are available as a function of solvent composition. The most commonly used parameters known as Kamlet-Taft values include the polarity/polarizability, π^* , hydrogen bond donor ability, α , and hydrogen bond acceptor ability, β , abilities of the solvent [42]. The values listed in Table 4 used in this paper were determined during our previous studies.



The general LFER model was developed on the basis of changes of the standard Gibbs free energy values for CO₂ solution based on data compiled in Table 4. Finally equation (6) was obtained:

$$\Delta G = -48.011(\pm 17.235) + 18.434(\pm 1.987)\alpha + 17.467(\pm 4.468)\beta + 31.946(\pm 13.018)\pi^*$$

$$n = 11, \quad r^2 = 0.970, \quad \sigma = 0.451, \quad F = 37.34 \quad (6)$$

where n , r^2 , σ , and F are the number of data, square of regression coefficient, standard deviation, and statistical Fischer number.

In order to compare the effect of each independent (Kamlet-Taft) parameters on dependent variable (Gibbs free energy of the solution), standardized coefficients should be determined. As defined previously, the standardized coefficient or beta coefficient as a statistical parameter is the estimate of an analysis performed on variables that have been standardized, so that they have variance of 1 [43]. The standardized coefficients of equation (6) have been obtained as 1.261, 0.821, and 0.424 for α , β , and π^* , respectively. These coefficients demonstrate that the hydrogen bond donor ability of solvent is the most effective parameter on the CO₂ solubility in aqueous solution of ethanol. On the other hand, the polarity/polarizability of the media shows minimum effect on the Gibbs free energy of the solution. Also, it is clear that Gibbs free energy increases with the increasing of Kamlet-Taft parameters values. In other words, the dissolution of CO₂ is thermodynamically favourable in aqueous solutions which have low α , β , and π^* .

4. Conclusions



The main goal of this paper was to evaluate thermodynamical and practical aspects of application of DESs based on aqueous solutions of choline chloride-ethylene glycol (ethaline) as absorbent for CO₂ capture. This study revealed, that the Henry's constant of CO₂ in the solvent increases with the increasing mole fraction of water in the absorbent. It means that ethaline can be used as a better media for CO₂ capturing comparing to pure water. On the other hand, the aqueous solution of ethaline with 30% mole water content showed the minimum temperature dependence which proposes it as a good absorptive system used for treatment of hot gases. The thermodynamic properties of the formation of CO₂-containing solution, including the standard enthalpy, entropy, and Gibbs free energy of the solution, confirmed that the process was exothermic, along with decreasing entropy, and it is thermodynamically non-spontaneous. Preferential solvation model revealed that CO₂ molecule is preferentially solvated by ethaline in its binary mixture with water. Linear free energy relationship investigations indicated the direct effects of hydrogen bond donor ability of solvent as a main factor on the solubility of CO₂.

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Table 1. Provenance and mass fraction purity of chemicals used in the study.

| Chemical | Abbreviation | Mass fraction purity by the supplier | Supplier | Purification Method |
|------------------|-----------------|---|-----------------------|--|
| Carbon dioxide | CO ₂ | >0.999 | Spadana Gas Co., Iran | |
| Choline Chloride | ChCl | >0.98 | Sigma-aldrich | Under vacuum for 72h at 323K, final water content<700 ppm |
| Ethylene glycol | EG | >0.998 | Merck | Molecular sieve, final water content<200 ppm |

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Table 2. The values of coefficients, a_H , b_H , and σ (standard deviation) obtained from equation (1).^a

| x_w ^b | a_H | $-b_H / \text{kJ} \cdot \text{mol}^{-1}$ | σ |
|--------------------|-------|--|----------|
| 0 | 8.842 | 13.91 | 0.110 |
| 0.1 | 8.989 | 13.71 | 0.111 |
| 0.2 | 8.255 | 11.23 | 0.399 |
| 0.3 | 7.721 | 9.22 | 0.417 |
| 0.4 | 8.934 | 11.74 | 0.371 |
| 0.5 | 10.97 | 15.53 | 0.421 |
| 0.6 | 10.97 | 16.03 | 0.196 |
| 0.7 | 11.88 | 18.12 | 0.395 |
| 0.8 | 12.91 | 20.42 | 0.132 |
| 0.9 | 12.77 | 19.40 | 0.212 |
| 1 | 12.09 | 17.19 | 0.126 |

^a Standard uncertainties u are $u_r(x_w) = 0.01$ and $u(T) = 0.05$ K.

^b x_w is the mole fraction of water in aqueous solutions of ethaline.



Table 3. The interaction term ($\alpha_{D,E}$) of solvent composition relationship of Henry's constant.

| T / K | $-\alpha_{D,E}$ | $10 \times \sigma$ |
|--------|-----------------|--------------------|
| 303.15 | 0.3926 | 0.97 |
| 313.15 | 0.4301 | 1.01 |
| 323.15 | 0.3117 | 0.60 |

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Table 4. Calculated standard enthalpy of the solution (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) at 0.1 MPa and $T = 303.15 \text{ K}$ ^a along with Kamlet-Taft parameters in each solvent composition.

| x_w^b | $\Delta H/\text{kJ}\cdot\text{mol}^{-1}$ | $\Delta S/\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$ | $\Delta G/\text{kJ}\cdot\text{mol}^{-1}$ | α | β | π^* |
|---------|--|--|--|----------|---------|---------|
| 0 | -13.93 | -93.0 | 14.26 | 0.89 | 0.55 | 1.14 |
| 0.1 | -13.72 | -120.6 | 14.75 | 0.94 | 0.64 | 1.09 |
| 0.2 | -11.24 | -87.9 | 15.41 | 0.94 | 0.64 | 1.10 |
| 0.3 | -9.23 | -83.5 | 16.78 | 0.95 | 0.64 | 1.10 |
| 0.4 | -11.75 | -93.3 | 16.53 | 0.97 | 0.64 | 1.10 |
| 0.5 | -16.55 | -110.3 | 16.89 | 0.97 | 0.64 | 1.10 |
| 0.6 | -16.04 | -110.5 | 17.46 | 1.03 | 0.68 | 1.10 |
| 0.7 | -18.14 | -118.1 | 17.66 | 1.03 | 0.63 | 1.11 |
| 0.8 | -20.44 | -126.9 | 18.03 | 1.06 | 0.58 | 1.14 |
| 0.9 | -19.42 | -125.4 | 18.60 | 1.14 | 0.52 | 1.14 |
| 1 | -17.20 | -119.6 | 19.06 | 1.26 | 0.43 | 1.14 |



^a Standard uncertainties of x_w and T are as defined in Table 2. **Table 5.** PS parameters obtained from equation (5) in binary mixtures of ethaline (1) and water (2). n , r^2 , and σ are the numbers of experimental data, regression coefficient, and standard deviation, respectively.

| T / K | ΔG_1 | ΔG_2 | ΔG_{12} | $f_{2/1}$ | $f_{12/1}$ | n | r^2 | σ |
|----------------|--------------|--------------|-----------------|-----------|------------|-----|-------|----------|
| 303.15 | 14.19 | 19.07 | 18.22 | 0.201 | 1.77 | 11 | 0.997 | 0.102 |

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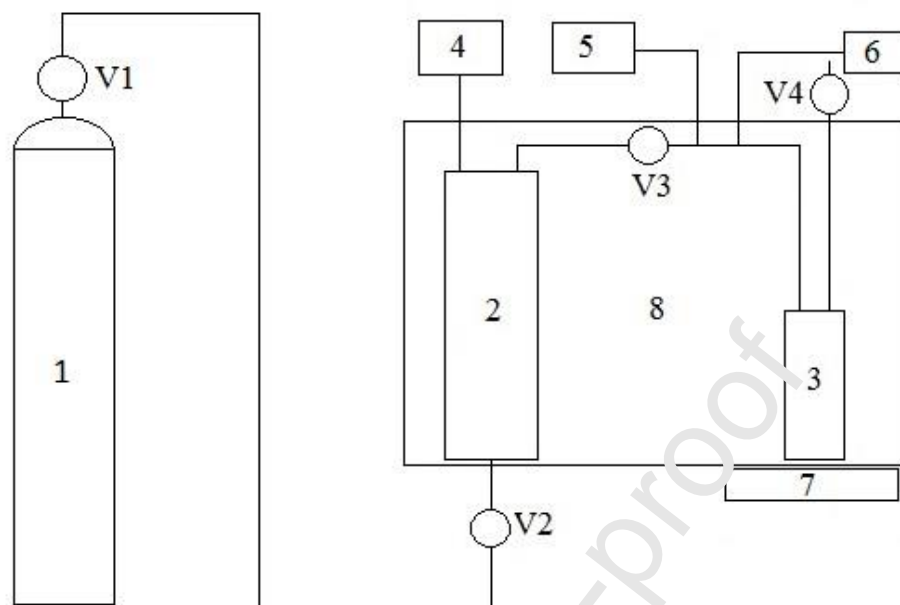


Figure 1. Schematic diagram of the experimental apparatus. (1) gas cylinder; (2) gas reservoir; (3) equilibrium cell; (4) and (5) pressure transducers; (6) vacuum pump; (7) magnetic stirrer; (8) water bath; V1, gas regulator; and V2 - V4, ball valves.

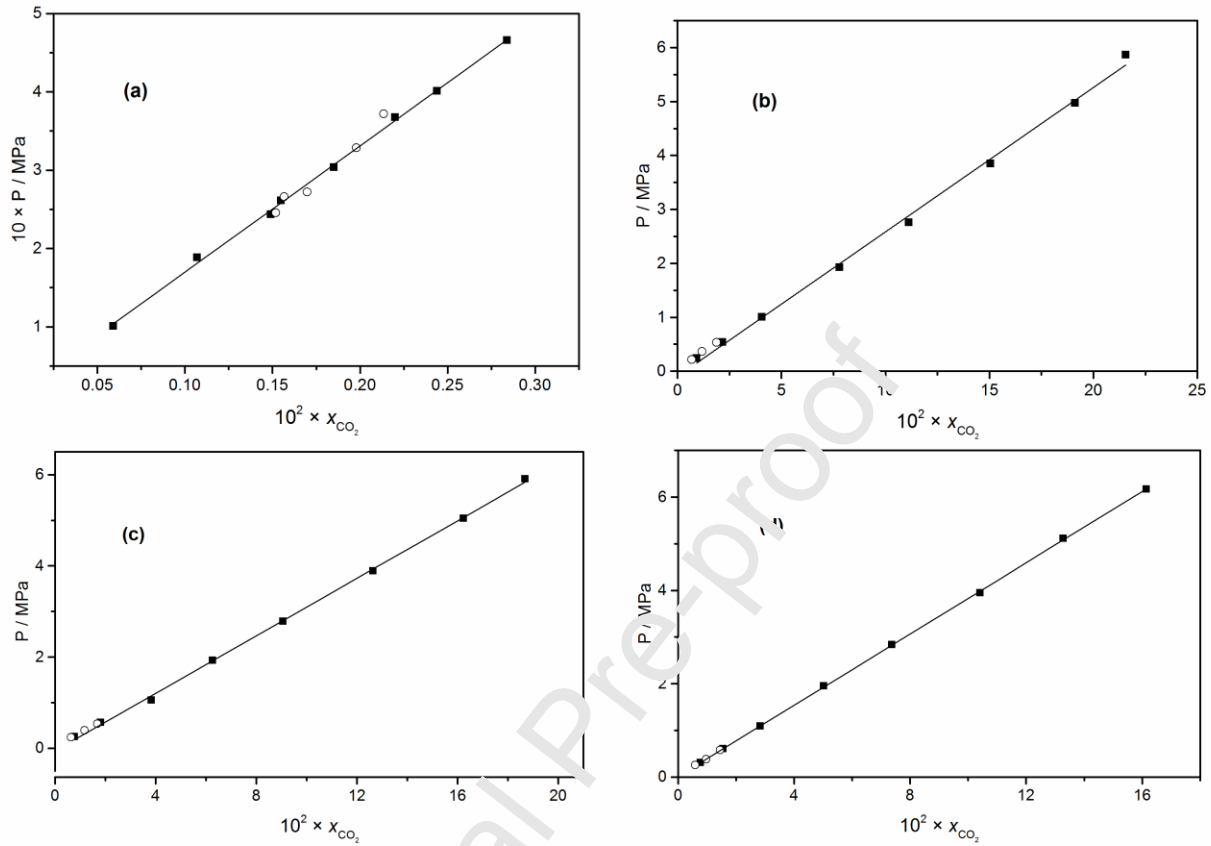


Figure 2. Comparison of experimental data trend of solubility of CO₂ in water at 298.15 K (a), ethaline at 303.15 K (b), 315.15 K (c), and 323.15 K (d) with literature data. Open circles are the experimental data and squares have been obtained from references [28,33].

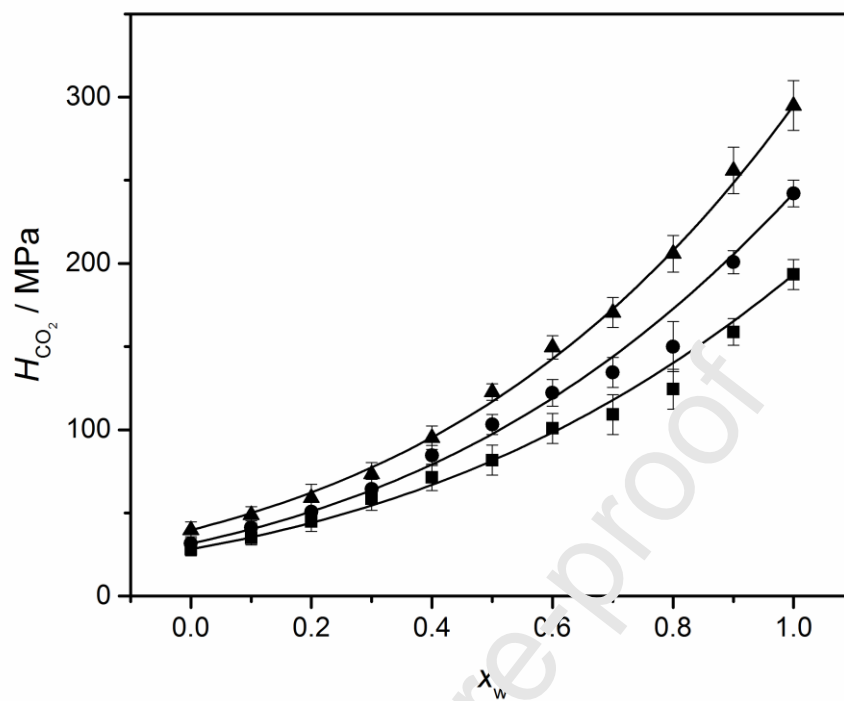


Figure 3. The variation of Henry's constant as a function of water mole fraction in aqueous solutions of ethaline. Points are the obtained values from experimental data and lines show fitted data based on equation (2).

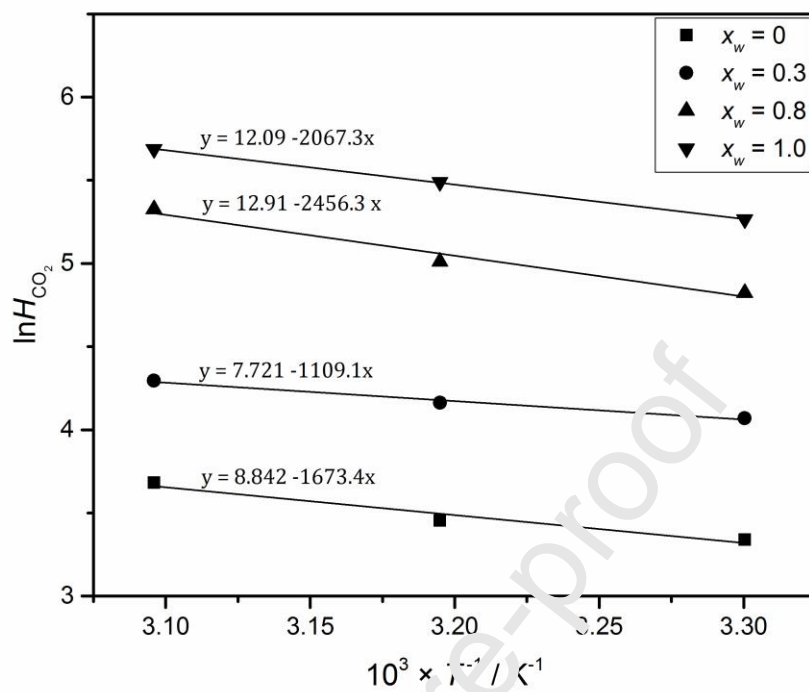


Figure 4. The typical plot of Henry's constant of CO₂ in aqueous ethaline solutions at some solvent compositions as a function of temperature.

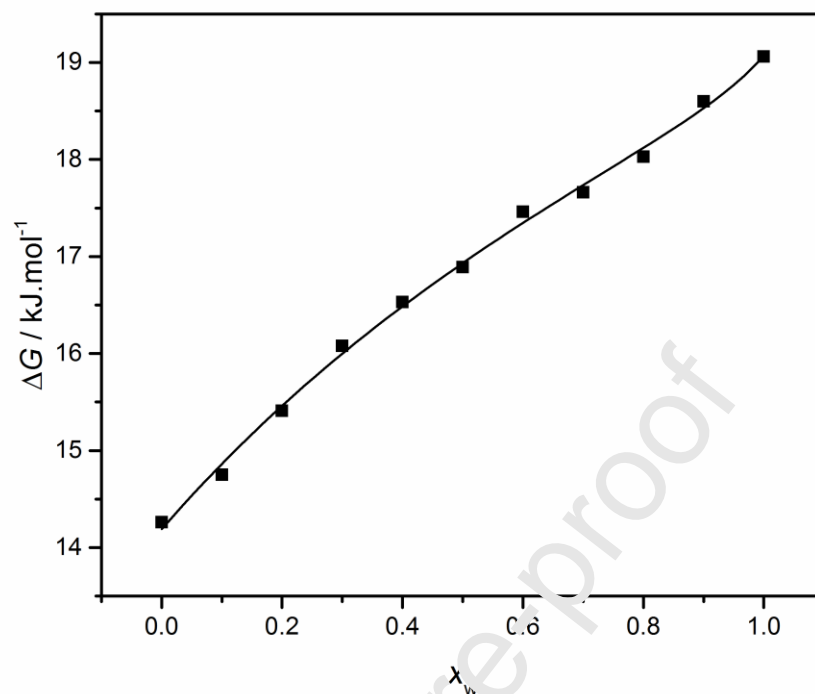
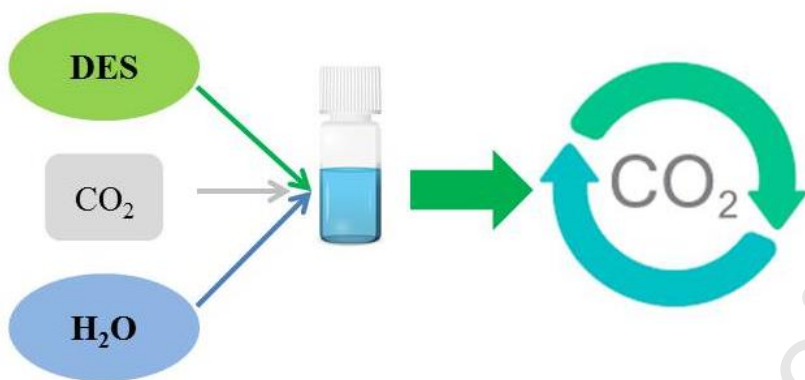


Figure 5. The variations of solution Gibbs free energy in ethaline aqueous solutions as a function of solvent composition. Points show the experimental data and line has been calculated from coefficients of equation (5) given in Table 5.

Graphical Abstract



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Manuscript No.: MOLLIQ_2020_2448 titled: **Solvent dependency of carbon dioxide Henry's constant in aqueous solutions of choline chloride-ethylene glycol based deep eutectic solvent**

CRediT author statement

The individual contributors of authors are:

Ali Reza Harifi-Mood: Supervision, technical work, software, Writing-Original draft preparation.

Fereshteh Mohammadpour: MSc student, Experimental work, Calculations and Data processing.

Grzegorz Boczkaj: Advisor, Final preparation of manuscript, reviewing and editing.

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Manuscript entitled: “Solvent dependency of carbon dioxide Henry’s constant in aqueous solutions of choline chloride-ethylene glycol based deep eutectic solvent”

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- Usefulness of obtained data for modeling of absorption process.
- Absorbent selection protocol for treatment of hot off-gases
- Carbon dioxide Henry's constants were measured in aqueous solutions of ethaline.
- The effect of solute-solvent interactions on solubility was investigated in term of solvatochromic parameters.

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