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Experimental measurement and thermodynamic modelling of the solubility of carbon dioxide in deep eutectic solvent

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Abstract

In the present work, an amine-based deep eutectic solvent (DES) was prepared using ethanolamine hydrochloride (EAHC) as a hydrogen bond acceptor (HBA) and diethylenetriamine (DETA) as a hydrogen bond donor (HBD) with the molar ratio of 1:9. The synthesized DES was further diluted by adding 30 v% water in the prepared DES. The solubility of carbon dioxide was measured in the aqueous DES at various pressures and temperature ranging from 0.4 to 1.6 MPa and 303.15 to 333.15 K, respectively. The solubility tends to increase at higher pressures and showed a decreasing trend at the higher temperatures i.e. 333.15 K. The highest solubility of 3.770 mol/mol was recorded at 303.15 K and pressure of 1.6 MPa. In modelling the measured CO_2 solubility data in aqueous deep eutectic solvent, the system was deemed as a quasi-binary of CO_2 and a mixed solvent. It was further assumed that the gas phase is solely consisted of CO_2. Then, the gas phase was described by the Peng-Robinson equation of state while the unsymmetrical NRTL, 2-suffix Margules, and a modified Margules equation were utilized for the modelling of the liquid phase. Henry's law constants for the solubility of CO_2 in the aqueous deep eutectic solvent were estimated and reported. It was found that the NRTL equation described the aqueous solvent phase better than the 2-suffix Margules equation; however, inferior with respect to the modified Margules equation. The coupling of the Peng-Robinson equation of state with the modified Margules equation led to an average absolute relative deviation of 3.36%.

Keywords Solubility · Carbon dioxide · Deep eutectic solvent · Equation of state · Henry's law · Activity coefficient

List of symbols

A_1, A_2	Parameters for Margules equations (Pa. $m^3 kmol^{-1}$)
b_{12}, b_{21}	Binary interaction parameters of the NRTL equation (Pa.$m^3 kmol^{-1}$)
$C_1 ... C_4$	Parameters for Henry's law constant (different units)
f	Fugacity (MPa)
H	Henry's law constant (MPa)
G_{12}, G_{21}	Pairwise interaction coefficients of the NRTL equation
n	Number of moles (mol)
P	Pressure (MPa)
R	Gas constant (8.314×10^{-3} MPa.m^3.$kmol^{-1}$.K^{-1})
T	Temperature (K)
$\bar{v}$	Partial molar volume (m^3.$kmol^{-1}$)
V	Total volume (m^3)
x	Mole faction
z	Compressibility factor

Greek letters

α	Loading (moles of CO_2 / moles of solvent)
α_m	Mean value of the NRTL constant (0.2)
γ	Activity coefficient
τ_{12}, τ_{21}	Binary interaction parameter between solute and solvent
Ω	Objective function

Subscripts/superscripts

*	Unsymmetrical
∞	Infinite dilution
cal	Calculated
exp	Experimental
g	Gas
l	Liquid
m	Mean
ms	Mixed solvent
sat	Saturated
T	Total
w	Water

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Introduction

The pathway to decarbonize the industrial sector in general and energy sector in particular heavily relies on the efforts of carbon capture and storage (CCS) around the globe. There are various CCS technologies which are employed to meet the industrial needs, commonly known as pre-combustion and post-combustion (Ugwu et al. 2022). In the energy producing sector, amine based chemical absorption technology is widely deployed to capture carbon dioxide (Dong et al. 2022; Ali et al. 2016). However the amine based technology suffers from high regeneration cost, corrosion, loss of solvent, thermal degradation and high toxicity. Therefore the quest to develop suitable solvents, which can overcome the aforementioned shortcomings, still continues to meet the future ever increasing carbon challenges which is expected to go as high as one gigaton (GT) CO_2 per year by 2030 (Pérez-Calvo and Mazzotti 2022; Banacloche et al. 2022; Zhao et al. 2017; Haider et al. 2020).

Over the past two decades intense work on the development of green solvents have been reported which could potentially replace the conventional amines as well as could offer improved properties as mentioned earlier (Li et al. 2019; Wang et al. 2016). The immense versatility of ionic liquids (ILs) made them quite attractive and considerable alternate to capture CO_2. This is due to their very low vapor pressure, good thermal stability and being environmental friendly (Zhao et al. 2017; Wang et al. 2016; Mjalli et al. 2017; Huang et al. 2019). ILs are low melting salts which can be synthesized by organic cation and inorganic/organic anion. This made ILs task specific solvents through careful selection of ILs' constituents to fine tune the undesirable properties (Aparicio et al. 2010; Karadas et al. 2010; Tang et al. 2012). However, there are still some challenges to apply ILs at large scale industrial applications due to the complicated synthesis process, pretreatment, high viscosity, high cost and low CO_2 capacity (Ali et al. 2016; Wang et al. 2016; Gabriele et al. 2019; Romero et al. 2008; Kareem et al. 2010).

In the recent past, new class of solvents got immense attention around the world, known as deep eutectic solvent (DES). DES have been reported as an alternate to the ILs in literature (Ali et al. 2016). DES shows a number of advantages over conventional CO_2 capture solvents which include simple preparation methods, low cost, less volatile, low thermal degradation, biodegradable and less toxic which make these DES quite attractive for various applications, especially for CO_2 capture (Wang et al. 2016; Hsu et al. 2014). The first DES was reported in 2003 which was a mixture of choline chloride and urea which exhibited a much lower melting point compared to the DES components (Abbott et al. 2003). DES is a mixture of organic compounds known as hydrogen bond accepter (HBA) and hydrogen bond donor (HBD). There are a number of DES prepared from various combinations of HBA (choline chloride, tetramethylammonium chloride, tetrabutylammonium chloride oxalic, citric, succinic acid) and HBD (urea, glycerol, amines).

In the past decade, a number of researchers reported the solubility of CO_2 in several DESs prepared from various combinations of HBDs and HBAs. (Li et al. (2008) reported the CO_2 solubility in various ratios of choline chloride:urea mixtures up to a pressure of 16 MPa and at various temperatures. The molar ratio of 1:2 (ChCl:urea) demonstrated the highest CO_2 solubility compared to the other studied ratios. The pressure shows positive effect on CO_2 loading whereas the loading capacity of DESs decreased at higher temperatures (Li et al. 2008). Leron et al. (2013) also studied the CO_2 solubility in ChCl:urea (1:2) based DES mixtures for a wide range of temperature from 303.15 to 343.15 K and pressure up to 6.0 MPa. They also reported that the increase in temperature has negative effect on CO_2 loading whereas high pressure conditions positively influence the CO_2 loading in the reported DES (Leron et al. 2013). The CO_2 solubility was also reported in ChCl-based-DES mixtures of dihydric alcohols at a pressure range up to 0.6 MPa. The DES with 1:4 molar ratio (chcl:2, 3-butanediol) exhibited the highest CO_2 loading capacity (Chen et al. 2014). Another group of researchers reported the CO_2 solubility in ChCl-based-DESs with various HBD such as phenol, diethylene and triethylene glycol. The solubility was investigated at various temperatures ranging from 293.15 to 323.15 K and pressures up to 600.0 kPa. The CO_2 solubility in ChCl:TEG (1:4) was found to be better than all studied DESs (Li et al. 2014). CO_2 solubility was further investigated in levulinic acid (LA) and quaternary ammonium salts up to a pressure of 0.6 MPa and temperatures ranging from 303.15 to 333.15 K (Deng et al. 2016). Many other researchers explored numerous HBDs and HBAs combinations to take part in the efforts to mitigate CO_2 from the environment (Adeyemi et al. 2017; Ji et al. 2016; Liu et al. 2017; Lu et al. 2015; Haider et al. 2018; Ghaedi et al. 2017a; Pishro et al. 2021; Pishro et al. 2020a). The immense amount of work on CO_2 solubility in DESs shows that this can be a breakthrough towards the quest to find suitable green solvent to capture CO_2 from various gaseous streams. Most recently Pishro et al. (2020a, 2021) reported the solubility of CO_2 and physical properties in various DESs at 323.15 K and at a pressure of 0.8 MPa. They reported a total of twenty DESs prepared from various ratios of HBDs; namely, ethylenediamine (EDA), monoethanolamine (MEA), tetraethylenepentamine (TEPA), triethylenetetramine (TETA), diethylenetriamine (DETA) to monoethanolamide hydrochloride

(EAHC) salt as a HBA. The highest solubility of 0.7 mol / mole of DES (1EAHC:9TEPA) followed by 0.66 mol / mol of DES (1EAHC:9DETA) were reported (Pishro et al. 2020b). In another study, DES prepared from EAHC:TEPA (1:9) was further investigated for CO_2 solubility up to a pressure of 1.6 MPa and temperatures ranging from 303.15 K to 333.15 K. The solubility of 1.74 mol CO_2 / mole of solvent was reported at 303.15 K and at a pressure of 1.6 MPa (Pishro et al. 2021). However, despite of all the fundamental works reported earlier, the industrial application is still not viable due to the high viscosity which hinders DESs application to a larger scale. The fine tuning, selection of appropriate constituents (HBD & HBA), operating conditions and addition of water can considerably increase the viability of their application at the industrial scale (Gabriele et al. 2019).

Therefore the objective of this work is to further investigate the CO_2 solubility in the DES prepared from EAHC:DETA (1:9) with water at a wide range of pressure and temperature since non aqueous DES has already showed promising results towards the mitigation of CO_2 (Gabriele et al. 2019). In addition to the solubility measurements, equation of state (EoS) was used to model the measured solubility data. Ali et al. (2014) used the Peng and Robinson (PR) (Peng and Robinson 1976) EoS together with van der Waals mixing rules and a temperature-dependent binary interaction parameter in calculating CO_2 solubility in phosphonium- and ammonium- based DESs. Similarly, (Mirza et al. (2015) applied a modified PR EoS in correlating the solubility of CO_2 in three DESs (reline, ethaline and melinine) for a temperature range from 309 to 329 K and pressures up to 160 kPa, They found an average absolute relative deviation (AARD) of less than 1.6% for a solubility range less than 0.004 mol fraction. Haghbakhsh and Raeissi (2018) and Haghbakhsh et al. (2021) employed Soave–Redlich–Kwong (SRK) (Soave 1972) EoS and Cubic-Plus-Association (CPA) (Kontogeorgis et al. 1996) in correlating the solubility of CO_2 in several DES systems for wide ranges of temperature and pressure. They found CPA better than SRK in the CO_2 solubility modelling with an average absolute deviation (AAD) circa 6%. Sarmad et al. (2020) observed carbamate formation in amine functionalized DESs and succeeded in modelling such systems using a generic Redlich–Kwong (RK) (Redlich and Kwong 1949) EoS with a compositional- dependent binary interaction parameter. Samad and co-workers modelled the solubility of CO_2 up to a mole fraction of 0.36 in the DES systems for a temperature and pressure range less than 298 K and 2 MPA, respectively.

DES systems are associating fluids by interacting through hydrogen bonding. As such the RK, SRK and PR EoS, which designed for normal fluids, cannot describe DES systems adequately. In addition, in these calculations the critical properties of DES systems were estimated effectively using Lydersen-Joback–Reid group contribution method (Lydersen 1955; Joback and Reid 1987). Therefore, the inadequacy of the cubic EoSs together with the plausible accuracy of critical properties is lumped in binary interaction parameter. Haghbakhsh and Raeissi (2018) pointed out that an AARD of at least 7% should be expected in modelling CO_2 solubility in DES systems using the SRK EoS. Additionally, Haghbakhsh and Raeissi (2018) employed the CPA EoS to account for self and cross association between DES molecules. Compared to the SRK EoS, the CPA EoS is considerably more complicated; however, the improvement in calculating CO_2 solubility was found trivial. While the SRK EoS relies on the critical properties of DES systems to estimates the EoS parameters, CPA needs vapor pressure and liquid density calculations in determining the 5 parameters of the EoS. They found an AARD of circa 6%. The inability of CPA in improving the correlation of CO_2 solubility in DES systems could be attributed to the CPA parametrization. As a matter of fact the DES substances do not have appreciable vapor pressures while CPA parameters should be estimated by objective functions minimising the deviations of calculated vapor pressures and liquid densities of the DES substances from experimental values. Consequently, the lack of vapor pressures obliged the investigators to apply objective functions for minimizing the deviations in liquid densities of DES substances which clearly cannot adequately optimize energy-related parameters.

There are evidences that chemical reactions happen during the absorption of carbon dioxide in aqueous amine solutions and so in DES solvents containing amine counterparts. Because the reactions were not known to us, we ignored the reactions explicitly and assumed the chemical effect was lumped into an effective Henry's law constant (Lia et al. 2017; Pentila et al. 2011). We have then decided to apply a $\varphi\gamma$ approach in modelling CO_2 + aqueous DES systems. The vapor phase is described by the PR EoS. The liquid phase is, however, described by the asymmetric NRTL (Renon and Prausnitz 1968), 2-suffiix Margules (Prausnitz et al. 1999) and a modified 2-suffix Margulus equations. The modelling led to a simple correlation with 2 generalized adjustable parameters. The average absolute deviation (*AAD*) in modelling CO_2 solubility in aqueous DES systems was found quite satisfactory.

Methods & materials

All the consumables including such as ethanolamine hydrochloride (EAHC) and diethylenetriamine (DETA) were purchased from Sigma-Aldrich. The gases such as CO_2 and N_2 were also supplied by a local suppler in Oman with the stated purity of 99.99% and 98%, respectively. These chemicals were used without any further purification.

Preparation of the DESs

The DES synthesized in this study to capture CO_2 was prepared by mixing EAHC and DETA with the molar ratio of 1:9. The constituents of the DES were carefully weighed using a digital balance (Shimadzu, model AUW220D) with a measuring uncertainty of ± 0.1 mg. The constituents of DES were mixed at a constant rpm of 400 for at least 3 h and temperatures was fixed to 353.15 K. The clear solution was kept in an air tight sample bottle and observed for 48 h to see if there was any phase change occurred. The corresponding DES aqueous solution was prepared by adding the appropriate amount of water (30 v%) into the DES since higher concentrations cause the weakening of hydrogen bonding between the DES components and consequently could cause the phase change. This new mixture was stirred for at least 2 h until we achieved a clear aqueous solution. Further details can be found elsewhere (Gabriele et al. 2019; Pishro et al. 2021; Soave 1972).

Carbon dioxide solubility measurement

A high pressure gas solubility cell was used to measure the CO_2 loading capacity in the aqueous DES as shown in the Fig. 1. The set-up consists of two cells; pressure vessel (150 ml) which is used to acquire the desired pressure to conduct the experiment and the second cell is an equilibrium cell (50 ml), where the CO_2 solubility was measured based on the pressure drop principal respectively. The temperature of the both cells was regulated by water bath supplied

with two heaters (HAAKE D1, A512.0). Before taking any measurements, both cells were flushed with distilled water and acetone followed by the purging of N_2 gas to remove any remains of chemical traces. The pressure of the system was measured using digital pressure sensor (nVision) with a measuring accuracy of ± 0.001 MPa. Once the desired temperature was achieved, 6 mL of the solvent was injected into the equilibrium cell. After reaching the desired pressure (0.4–1.6 MPa) and temperature, CO_2 was then transferred from pressure vessel to the equilibrium cell and pressure was noted. The pressure of the cell was observed to decrease with time and it gets stabilized in 6 h which was indicated by a uniform peak of pressure. When there was no more drop in pressure observed, equilibrium was assumed to be achieved. (Hosseini Jenab et al. 2005; Ghaedi et al. 2017b; Garg et al. 2016).

The number of moles of CO_2 transferred were calculated by the following equation (Abbott et al. 2003; Aftab et al. 2018):

$$n_{CO_2} = \frac{V_{CO_2}}{RT}\left(\frac{P_1}{z_1} - \frac{P_2}{z_2}\right)$$

(1)

where V_{CO2} denotes the volume of the pressure vessel (CO_2), R is the gas constant and T is the temperature of the system. Pressure P_1 and P_2 represents respectively the CO_2 pressure before and after transferring the amount of gas from pressure vessel to the equilibrium cell. This information was required to calculate number of moles initially transferred to equilibrium cell. Z_1 and Z_2 represent the compressibility factors at

Fig. 1 Schematic diagram for the solubility measurement apparatus
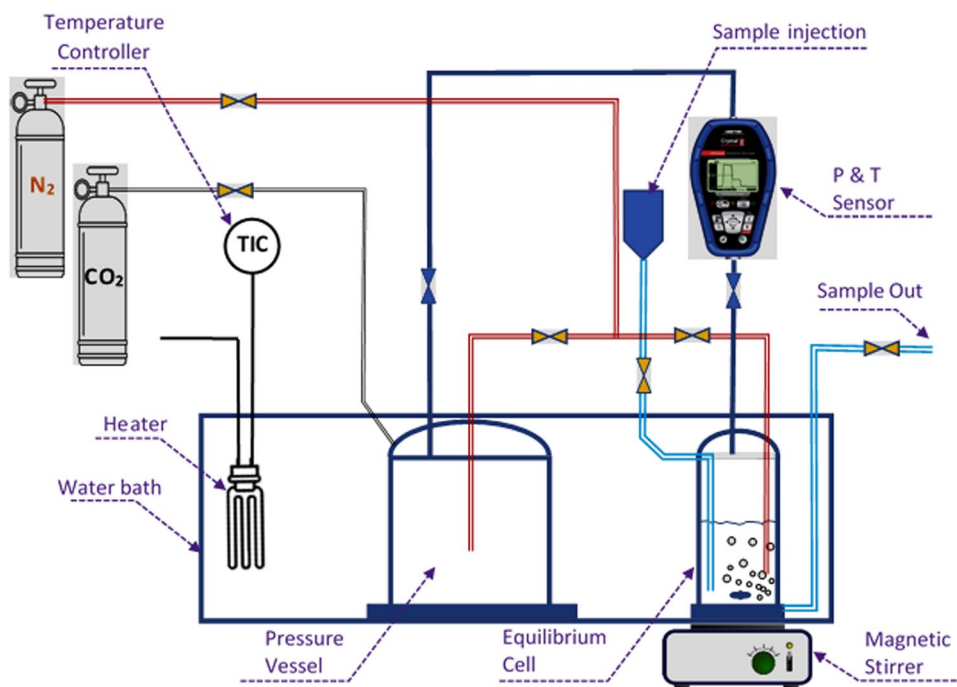
system temperature T and pressure P_1 and P_2, respectively. The equilibrium pressure (P_{CO_2}) was recorded when there was no change in pressure after approximately 7 hours and the moles of CO_2 (in a gas phase) were calculated by the following equation;

$$n_{CO_2}^g = \frac{V_g P_{CO_2}}{z_{CO_2} RT} \tag{2}$$

where P_{CO2} is the equilibrium pressure and V_g represents the gas volume in the equilibrium cell, which is the difference in volume of the equilibrium cell and the volume of solvent introduced in the equilibrium cell. The number of moles of CO_2 absorbed in the aqueous DES and CO_2 solubility (α) was calculated by the following equations;

$$n_{CO2}^l = n_{CO_2} - n_{CO2}^g \tag{3}$$

$$\alpha = \frac{n_{CO_2}^l}{n_{solvent}} \tag{4}$$

The measurements were repeated at least three times and only the average values were reported. The relative uncertainty of the experimentally measured CO_2 solubility was estimated to be $\pm 5 \times 10^{-4}$.

Modeling

In modeling the vapor–liquid equilibrium (VLE) of the system carbon dioxide + water + DES, we assume that the gas phase contains entirely of carbon dioxide. The liquid phase is, however, described by a quasi-binary of carbon dioxide + mixed solvent (water + DES). To account for high pressure, Poynting correction factor is used and to describe the non-ideality of carbon dioxide in the aqueous phase, unsymmetrical activity coefficient is employed. It is worth stressing that similar to models in Refs. Haghbakhsh and Raeissi (2018), Haghbakhsh et al. (2021), we have ignored the effect of chemical absorption explicitly. We assumed the chemical effect is lumped into the Henry's law constant. Hence, the VLE criterion can be expressed by:

$$f_{Pure\ CO_2}^g = x_{CO_2,ms} H_{CO_2,ms} \gamma_{CO_2,ms}^* \exp\left[\frac{\overline{v}_{CO_2}^\infty \left(P - P_{ms}^{sat}\right)}{RT}\right] \tag{5}$$

where f is the fugacity, x is the carbon dioxide mole fraction in the mixed solvent, H is the Henry's law constant, γ^* is the unsymmetrically normalized activity coefficient, $\overline{v}_{CO_2}^\infty$ is the partial molar volume at infinite dilution for carbon dioxide in the mixed solvent, R is the gas constant, T is the temperature and P is the pressure. The subscript ms stands for the

mixed solvent, the superscript g for the vapor phase, and *sat* for the saturated liquid phase. Further, it was assumed that the vapor phase is solely carbon dioxide. This assumption is reasonable knowing that the vapor pressure of DES is almost zero and the vapor pressure of water is quite low at the performed temperatures of the experiments.

Henry's law constant for the solubility of carbon dioxide in aqueous DES

At low pressures the Poynting correction (the exponential term) approaches unity and the solubility of carbon dioxide in the mixed solvent is expected to be small. As such, $\gamma_{CO_2,ms}^* \rightarrow 1$ and Eq. (5) simplifies to:

$$f_{Pure\ CO_2}^g = x_{CO_2,ms} H_{CO_2,ms} \tag{6}$$

where $H_{CO_2,ms}$ is supposed to be a function of temperature for a specific mixed solvent. The parameter $H_{CO_2,ms}$ is called the Henry's law constant at the system temperature for the solubility of carbon dioxide in aqueous DES solvent. If the solvent were entirely water, Eq. (6) would be expressed by:

$$f_{Pure\ CO_2}^g = x_{CO_2,w} H_{CO_2,w} \tag{7}$$

where $H_{CO_2,w}$ is the Henry's law constant at the same temperature as the aqueous DES system for the solubility of carbon dioxide in water.

Comparing Eq. (7) with Eq. (8) yields:

$$\frac{H_{CO_2,ms}}{H_{CO_2,w}} = \frac{x_{CO_2,w}}{x_{CO_2,ms}} \tag{8}$$

Indeed, $H_{CO_2,w}$ is a function of temperature and is available in literature. On the right-hand side of Eq. (8) the ratio of $x_{CO_2,w}/x_{CO_2,ms}$ can be estimated without difficulty by setting $x_{CO_2,ms}$ from the measured values in this work at the given temperatures and the lowest pressures. The solubility of CO_2 in water $x_{CO_2,w}$ can be calculated from $f_{Pure\ CO_2}^v/H_{CO_2,w}$ at the same conditions using the PR EoS.

Table 1 Thermodynamic properties of carbon dioxide (Chapoy et al. 2008)

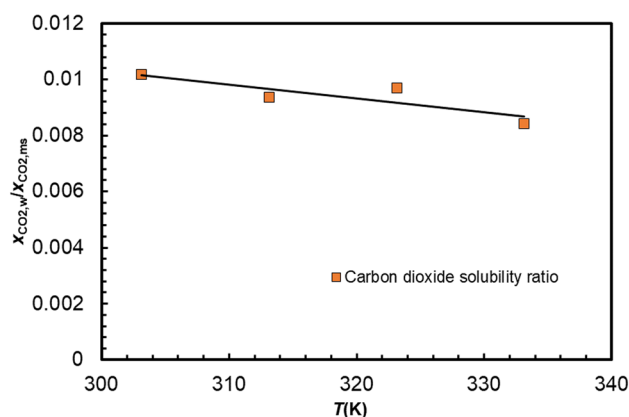|	
T_C (K)	304.19
P_C (MPa)	7.3815
w	0.2276
Henry law parameters	
C1	74.424
C2 (K)	−3796.5
C3	−21.6779
C4 (K-1)	0.00056

Fig. 2 Solubility ratio of carbon dioxide as a function of temperature

In calculating the fugacity of carbon dioxide in the gas phase, the PR EoS is used with the critical properties and acentric factor of carbon dioxide provided in Table 1. In Fig. 2, the calculated $x_{CO_2,w}/x_{CO_2,ms}$ was plotted as a function of temperature. It can clearly be observed from Fig. 2 that the trend seems to be linear with temperature. The linear fit was best represented by $0.025 - 0.0156(T/T_m)$, where $T_m = 318.15$. Combining the linear fit with Eq. (8) yields Henry's law of carbon dioxide in the mixed solvent:

$$H_{CO_2,ms} = H_{CO_2,w}\left[0.025 - 0.0156\left(\frac{T/K}{T_m}\right)\right] \quad (9)$$

Here, the expression for $H_{CO_2,w}$ is given by:

$$\lg_{10}\left(H_{CO_2,w}/Pa\right) = C_1 + \frac{C_2}{(T/K)} + C_3 \lg_{10}(T/K) + C_4(T/K) \quad (10)$$

where C_1 to C_4 are given in Table 1. The Henry's law constants for carbon dioxide in water and aqueous DES solvent
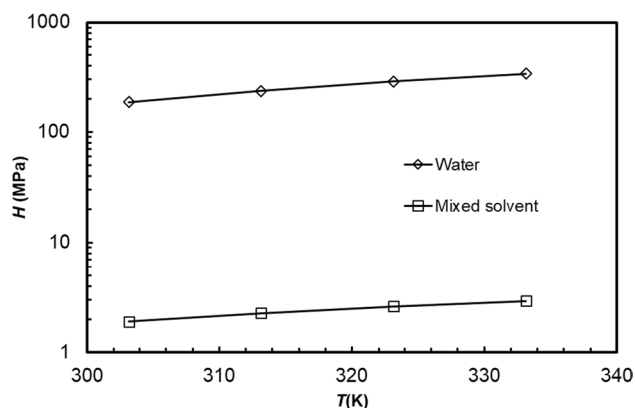

Fig. 3 Henry's law constant of carbon dioxide in water and in the aqueous DES

were calculated by Eqs. (9–10) and presented in Fig. 3. Henry's constants of carbon dioxide in aqueous DES solution were found to be linear with temperature and the values of $H_{CO_2,w}$ to be two orders of magnitude larger than $H_{CO_2,ms}$. In other words, the solubility of carbon dioxide in the mixed solvent is approximately 100 times more than in water at low pressures.

High solubility of carbon dioxide in the aqueous DES system

Because of the high solubility of carbon dioxide in aqueous DES system, the activity coefficient of carbon dioxide in the solvent should not be avoided. The 2-suffix Margules and NRTL equations are then used in this work to describe the liquid phase.

The 2-suffix Margules equation (Prausnitz et al. 1999) is expressed by:

$$RT \ln \gamma_{CO_2,ms} = A_1 x_{ms}^2 \quad (11)$$

where A_1 is a constant. Upon normalization, the unsymmetrical 2-suffix Margules activity coefficient $(\ln \gamma^* = \ln \gamma - \ln \gamma^\infty)$ can be expressed by:

$$RT \ln \gamma_{CO_2,ms}^* = A_1\left(x_{ms}^2 - 1\right) \quad (12)$$

A better activity coefficient correlation; however, can be obtained by a phenomenological extension of Eq. (12) as given below:

$$RT \ln \gamma_{CO_2,ms}^* = A_1\left(x_{ms}^2 - 1\right) + A_2\left(x_{ms}^2 - 1\right)^2 \quad (13)$$

where A_2 is a constant as well. The impact of this modification will be discussed in the following section.

The NRTL activity coefficient model (Renon and Prausnitz 1968) is expressed by:

$$\ln \gamma_{CO_2,ms} = x_{ms}^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \frac{G_{12}\tau_{12}}{(x_2 + x_1 G_{12})^2}\right] \quad (14)$$

and

$$\ln \gamma_{CO_2,ms}^\infty = \tau_{21} + \tau_{12}G_{12} \quad (15)$$

Here, $G_{12} = \exp(-\alpha_m \tau_{12})$ and $G_{21} = \exp(-\alpha_m \tau_{21})$ and α_m is set to 0.2. The parameters τ_{12} and τ_{21} are defined by:

$$\tau_{12} = \frac{b_{12}}{RT} \quad (16)$$

$$\tau_{21} = \frac{b_{21}}{RT} \quad (17)$$

where b_{12} and b_{21} are adjustable parameters. Subtracting Eq. (15) from Eq. (14) yields the logarithm of unsymmetrical NRTL activity coefficient $\ln \gamma^{*}_{CO_2,ms}$.

The effect of pressure

In order to employ the Poynting correction factor (the exponential term), the vapor pressure of aqueous DES is required. Because the vapor pressure of the DES solvent is extremely low, the vapor pressure of the aqueous solvent was estimated to be the vapor pressure of water. As such, $P^{sat}_{ms} \approx P^{sat}_{w}$ was used in Eq. (5).

Results and discussion

The CO_2 loading in aqueous DEA (1:9) with 30 v% water was measured using the pressure drop method as discussed earlier. However, before performing the gas solubility measurements the equipment was calibrated and the results were compared with the known data available in literature. Therefore, CO_2 loading at 313.15 K and pressure ranging from 0.5

Fig. 4 Comparison of CO_2 solubility in 30 wt% aqueous MEA solution with literature

to 2.4 MPa was measured in aqueous solution (30 wt%) of monoethanolamine (MEA) and compared with literature as shown in Fig. 4 (Harris et al. 2008; Shen and Li 1992). The measured values of this work and literature values show a good agreement, which is represented by an AARD of 1.87% from Ref. Shen and Li (1992) and 1.7% from Ref. Harris et al. (2008), respectively.

The measured CO_2 solubility loadings (α) in terms of moles of CO_2 per moles of DES are provided in Table 2 as a function of temperature and pressure. It can clearly be observed that the CO_2 loading increases by increasing the pressure up to 1.6 MPa at any given temperature. This increase in loading could be due to the physical absorption phenomenon at higher pressure (Yan et al. 2022). However, temperature affects the solubility negatively as increasing temperature yields low loading capacities and this could be due to the exothermic nature of the absorption process. The CO_2 solubility decreased from 1.185 mol / mol to 0.714 mol / mol when the temperature was increased to the maximum value of 333.15 K from 303.15 K, which is consistent with the reported values in the literature (Leron et al. 2013; Leron and Li 2013; Haider et al. 2021). On the other hand, the maximum solubility of 3.770 mol / mol was reported at 1.6 MPa and 303.15 K.

In the modelling effort, the CO_2 solubility in the aqueous DES system was predicted using various models and calculated values by different activity coefficient equations are compared in Fig. 5a–d at four various temperatures ranging from 303 to 333 K with the experimental values. The solubility of CO_2 in aqueous DES solutions were first modelled by implementing Henry's law constant only, i.e.

$$x_{CO_2,ms} = f^{v}_{CO_2}/H_{CO_2,ms} \tag{18}$$

The AARD was found to be 22.34%. The high value of error manifests itself in the non-ideality of carbon dioxide in the presence of the aqueous DES solvent. Hence, in order to account for the non-ideality emerging from high solubility of carbon dioxide in the aqueous solution, the unsymmetrical Margules equation (Eq. 12) was applied to facilitate the correlation of experimental data:
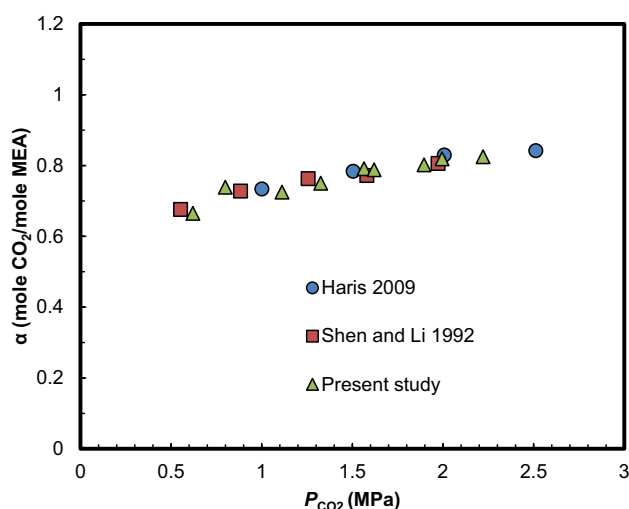
Table 2 Solubility of CO_2 in aqueous DES; EAHC:DETA (1:9) 30 v%

303.15 K		313.15 K		323.15 K		333.15 K	
P/MPa	α mol/mol	P/Mpa	α mol/mol	P/MPa	α mol/mol	P/MPa	α mol/mol
0.4194	1.185	0.4247	1.025	0.4672	0.850	0.4268	0.714
0.8206	2.204	0.8750	2.008	0.8573	1.813	0.8096	1.658
1.2527	2.935	1.2334	2.755	1.2481	2.598	1.2160	2.360
1.6262	3.770	1.6157	3.441	1.6658	3.179	1.6762	3.017

Fig. 5 **a** Experimental and modelling solubility of carbon dioxide in ▶ the aqueous DES at 303 K. **b** Experimental and modelling solubility of carbon dioxide in the aqueous DES at 313 K. **c** Experimental and modelling solubility of carbon dioxide in the aqueous DES at 323 K. **d** Experimental and modelling solubility of carbon dioxide in the aqueous DES at 333 K

$$x_{CO_2,ms} = \frac{f^g_{Pure\ CO_2}}{H_{CO_2,ms} \exp\left\{\frac{A_1}{RT}[(1 - x_{CO_2,ms})^2 - 1]\right\}} \quad (19)$$

when Eq. (19) was used to fit the measured experimental data in this work, A_1 was found to be -1.1429. The objective function was expressed by:

$$\Omega = \sum_j^{np} \left(\frac{x_j^{cal} - x_j^{exp}}{x_j^{exp}}\right)^2 \quad (20)$$

It is worth mentioning that Eq. (19) is implicit in $x_{CO_2,ms}$ and it should be solved iteratively. After, correlating the measured data, the AARD was found to be 9.15%. Comparing the AARDs in calculating the solubility of carbon dioxide in the aqueous DES system reveals that the activity coefficient term should not be neglected. Afterwards, the effect of pressure on the aqueous phase and consequently on the solubility of carbon dioxide was evaluated. Nonetheless, the use of Poynting correction factor was not effective as the quality of fit was not improved. In fact, the AARD was improved slightly from 9.15% to 8.57%. Clearly, the pressure was not high enough to considerably affect the solubility of carbon dioxide in aqueous DES. Then, we employed Eq. (13) to describe the non-ideality of the liquid phase better and fit the experimental data more effectively. The governing equation became;

$$x_{CO_2,ms} = \frac{f^g_{Pure\ CO_2}}{H_{CO_2,ms} \exp\left\{\frac{A_1}{RT}[(1 - x_{CO_2,ms})^2 - 1] + \frac{A_2}{RT}[(1 - x_{CO_2,ms})^2 - 1]^2\right\}} \quad (21)$$

Once the nonlinear regression was performed to fit Eq. (21) with Eq. (20) as objective function, the AARD was augmented to 3.36%. Additionally, when the NRTL equation was used to describe the liquid phase non-ideality, the AARD was found to be 5.79%.

Clearly, the NRTL equation would improve the model in correlating the solubility of CO_2 in aqueous DES systems when it is compared to 2-suffix Margules equation. However, when compared to the modified 2-suffix Margules equation, the NRTL is less satisfactory. Although Fig. 5a–d reveal that the modified Margules and NRTL equations satisfactorily correlate the experimental solubility data, the modified Margules is somewhat better.
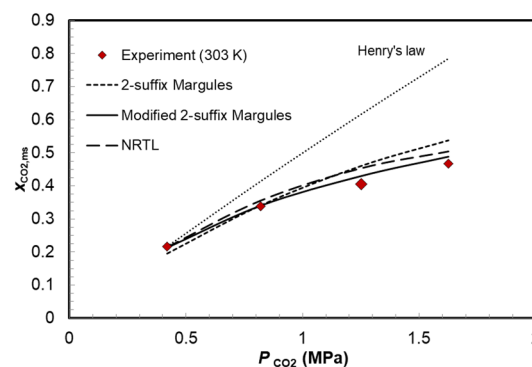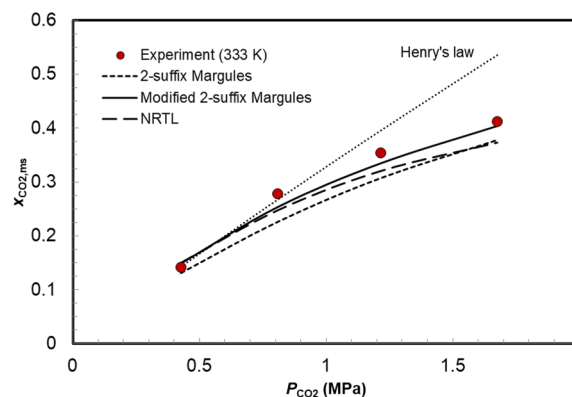

a Experimental and modelling solubility of carbon dioxide in the aqueous DES at 303 K
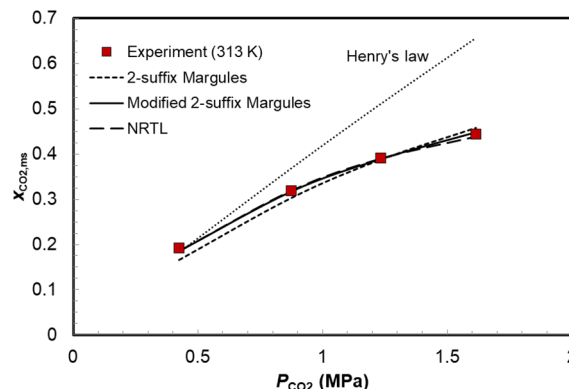
b Experimental and modelling solubility of carbon dioxide in the aqueous DES at 313 K
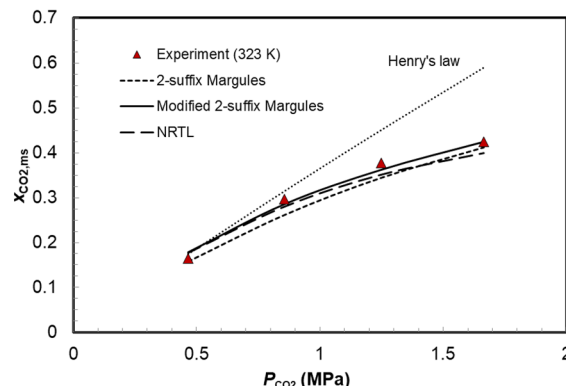
c Experimental and modelling solubility of carbon dioxide in the aqueous DES at 323 K

d Experimental and modelling solubility of carbon dioxide in the aqueous DES at 333 K
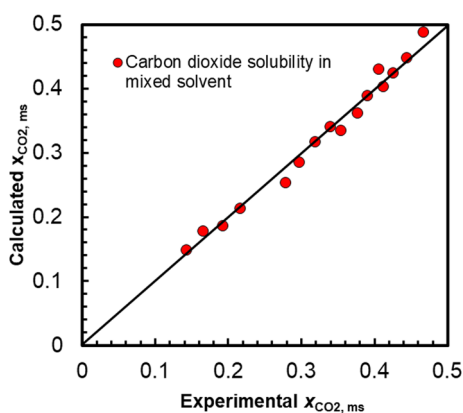
Fig. 6 Experimental and calculated solubility of carbon dioxide in the aqueous DES using 2-suffix Margules equation

The measure and calculated data of CO_2 solubility at all ranges of temperature and pressure using the modified Margules equation is illustrated in Fig. 6. It can be clearly seen that the calculated values distributed evenly around the diagonal line which shows a good agreement between the measured and calculated values.

The behaviors of the activity coefficient models employed in this study with the solubility of CO_2 in the aqueous DES solvent calculated using various models are compared and illustrated in the Fig. 7. It is worth stressing that the aqueous DEA is a mixed associating solvent and representing the CO_2 + mixed solvent system by a quasi-binary solution may not adequately capture the total non-ideality of the system. Nevertheless, the values of AARD clarifies that the model with modified Margules or NRTL equations is quite satisfactory. The parameters of the models and respective AARDs in modeling CO_2 solubility in aqueous DES solutions are provide in Table 3. Figure 7
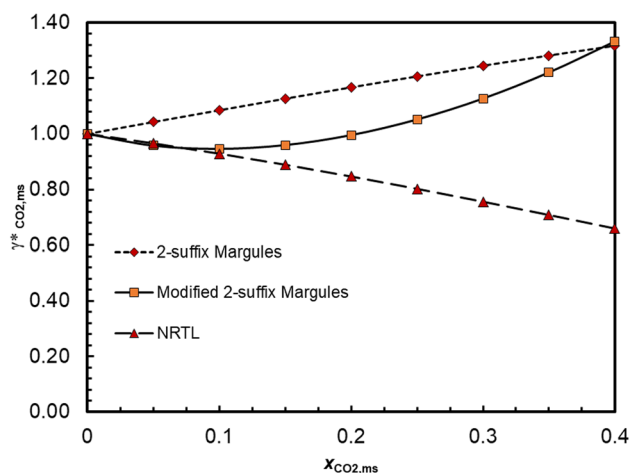
Table 3 Parameters of the models employed to calculate CO_2 solubility in the aqueous DES

Model	Adjustable Parameters	%AARD
Margules equation	$A_1 = -1.1429$ Pa.m^3.kmol^{-1}	9.15
Margules equation + Poynting correction	$A_1 = -0.0241$ Pa.m^3.kmol^{-1} $\overline{v}_{CO_2}^{\infty} = 0.5743$ m^3.kmol^{-1}	8.57
modified Margules equation	$A_1 = 1.6053$ Pa.m^3.kmol^{-1} $A_2 = 4.3706$ Pa.m^3.kmol^{-1}	3.36
NRTL equation + Poynting correction	$b_{12} = 14.7322$ Pa.m^3.kmol^{-1} $b_{21} = -0.7858$ Pa.m^3.kmol^{-1} $\overline{v}_{CO_2}^{\infty} = 0.9100$ m^3.kmol^{-1}	5.79

illustrates that activity coefficients start from 1. The value of 1 for activity coefficients as the solubility of carbon dioxide approaches 0 is expected because activity coefficient models were normalized unsymmetrically (Prausnitz et al. 1999). The two-suffix Margules activity coefficient increases with the solubility of carbon dioxide in DES solvent while NRTL decreases and the modified two-suffix Margules initially decreases and then increases. The differences in models behaviours stem from the parameters values which were found from fittings. Since the models are quite simplified (quasi-binary), the authors believe that the parameters have lost their physical significance. Thus, the models can be considered the best fits to the complex mixtures of carbon dioxide + aqueous DES system.

Conclusions

The solubility of CO_2 in the aqueous EAHC:DETA (1:9) was measured and its thermodynamic characteristics were also modelled. Compared to pure DES, the aqueous DES solution has shown a remarkable increase in its capability to capture carbon dioxide. This may be attributed to the fact that adding water to dilute the DES is an effective method to reduce its viscosity and improve fluidity and mass transfer characteristics of the DES-water mixture. The DES aqueous system has been deemed as a quasi-binary solution and was modelled by a $\varphi\gamma$ approach. A modified Margules equation together with the PR EoS were best in modelling the solubility of CO_2 in the aqueous DES system. Henry's law parameter for the solubility of CO_2 in the aqueous DES has been estimated and reported as a function of temperature. The calculated low values of average absolute relative deviations of the model predictions of CO_2 solubility as compared to experimental values illustrates the reliability of the investigated thermodynamic models at all tested operating conditions. The successful thermodynamic modelling of this new absorbent opens the door for further CO_2 capture process

Fig. 7 Unsymmetrical activity coefficient model behavior at 320 K

scale-up and design calculations which will certainly be helpful in the efforts to mitigate carbon from various industries.

Data availability All the relevant data is already presented in the manuscript.

Declarations

Conflict of interest It is acknowledged that I, on behalf of all authors, state that there is no conflict of interest related to the above mentioned manuscript.

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