Measurement of CO_2 Solubility in Amine Based Deep Eutectic Solvents

Khatereh Ali Pishro, Ghulam Murshid, Farouq Sabri Mjalli, and Jamil Naser

***Abstract*—The climate change assumes the warming of the climate systems due to increase of global average temperature to the observed increase of the greenhouse gas (GHG) concentration in the atmosphere. Carbon dioxide (CO_2) is considered the most important GHG. The processes of CO_2 capture are gaining a great attention on the scientific community as an alternative for decreasing CO_2 emission and reducing its concentration in ambient air. In this study, we report a new deep eutectic solvents (DESs) made of monoethanolamine hydrochloride-diethylenetriamine exhibits a great candidate for CO_2 capture. We developed solubility and physical properties studies at different pressures and temperatures, and regression model was well in agreement with the calculated αCO_2 values with R-square: 0.976. The strong properties of DESs in CO_2 capture make them as a suitable solvent for absorption CO_2 to replace the conventional amine based scrubbing technology and are worth for further exploration.**

***Index Terms*—CO_2 capture, solubility, eutectic solvents, vapor-liquid equilibrium.**

I. Introduction

The global energy demand increased after industrial revolution by burning fossil fuels to generate electricity in power plants and in consequence, the large amount of greenhouse gases (GHG) are released in the atmosphere, which cause a global environmental problem in the form of global warming. Carbon dioxide (CO_2) is the major GHG subsidizing of global warming [1]. The concern of global warming due to GHG led to the United Nations Framework Convention on climate change (UNFGGG) in 1992, The main objective of this meeting was to discuss methods for stabilization of GHG concentrations in the atmosphere by using non-carbon energies, the renewable energies such as biomass, solar and wind energies. The high cost of changing the technological systems which are provided for fossil fuel energy is considered as a major barrier. Thus, the energy continued to be obtained majorly from fossil sources and carbon capture and storage is the most indicated technology to stabilize the CO_2 concentration in the atmospheres [2]. Post combustion CO_2 capture technology have been employed industrially for 50 years old are majorly based on the liquid absorption by industrially primary alkanolamine MEA [3].

Indeed, primary and secondary amines studied with CO_2 loading capacity range 0.5-1 mole of CO_2 per mole of amine, and the reaction of CO_2 with tertiary amines such as N-methyldiethanolamine (MDEA) and Sterically hindered amines occur with higher loading capacity of 1 mol of CO_2 per mole of amine [4].

Furthermore, Deep eutectic solvents (DES) prepared by mixing of two or more solvents to form a eutectic with melting point lower than the individual components [5]. DESs have noticeable advantages such as simple synthesis, lower ingredients cost, and biodegradable nature. Although, many researches carried on study of DESs for CO_2 capture, there are still a little report on CO_2 absorption study by amine based DESs [6], [7].

Several studies on the solubility of CO_2 in different DESs have been reported in many literatures [8]-[12].

Abbot *et al.* [11] reported the formation of a eutectic solvent of choline chloride (ChCl)/ urea at 285 K, which is much less than both starting components (melting points: ChCl = 575 K and urea = 406 K). The melting point cannot be indicated for some DESs, but a glass transition temperature can be found. Therefore, DESs are titled as low-transition-temperature mixtures (LTTMs) [12].

Reline is the short name of the widespread type of a DES made of ChCl/ urea mix. ChCl melts at a temperature of 575.15K and urea's melting temperature is 406.15K. The blend melting temperature is 285.15 K for a molar ratio of 1: 2, respectively. For Reline, the HBA is ischolinium chloride as it is cheap, low toxic level, can be degraded biologically, and biocompatibility and Urea is the HBD [13].

A novel DESs developed by Tirivedi, *et al.* [14]using; monoethanolammonium chloride: ethylenediamine [MEA·Cl][EDA] or [EAHC][EDA] at 1 : 3 mole ratio, at 30°C. The large CO_2 uptake in [MEA·Cl][EDA]-based DESs was assumed to depend on the change in polarity and basicity.

Later on, [15] Shukla, *et al.* studied CO_2 solubility of [MEA·Cl] DESs with more long chain amines of HBDs such as; diethylenetriamine(DETA), tetraethylenepentamine (TEPA) pentaethylenehexamine ([PEHA]), 3-amino-1-propanol ([AP]) and aminomethoxypropanol ([AMP]) and analyzed the outcome in terms of the specific polarity parameters. Among the various combinations of HBAs and HBDs, these four - [MEACl][EDA]-, [MEACl][AP]-, [HMIMCl][EDA]- and [HMIMCl][AP] - showed highest CO_2 uptake, which was further improved upon increasing the mole ratio of HBA: HBD from 1: 1 to 1: 4.

The solubility measurements of CO_2 in DESs are carried out with the use of a VLE setup (Vapor liquid Equilibrium). Utilizing DES for CO_2 absorption is comparatively a novel subject, few work have been carried out experimentally

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[16]-[18], revealed that CO_2 solubility in DESs is influenced by three factors:

- The DES mixture composition, which has a considerable influence on the solubility of CO_2 (constant operating conditions). It was establish that the molar ratio of 1 ChCl: 2 urea displays higher CO_2 solubility in comparison to 1: 1.5 and 1: 2.5.
- Pressure: CO_2 solubility increases with pressure
- Temperature: CO_2 solubility reduce with raising temperature at all pressure values.

Herein, we worked on a measurement method based on determining the pressure drop during the CO_2 absorption process [19], [20]. In this study, we report the solubility of CO_2 in the prepared DESs; 1EAHC:9DETA at different pressure and temperatures. To predict the CO_2 capture at not experimented point of temperature and pressures, a regression analysis method were developed successfully using Matlab® R2017b software. Moreover, the physical properties such as density, viscosity and reflective index of prepared 1EAHC:9DETA were studied. The properties were reported over the range of temperature from 298.15 to 343.15 K at 5 K interval.

II. Experiment

A. Material

The Ethanolamine hydrochloride (EAHC), diethylenetriamine (DETA) of >99% purity, were supplied by Sigma-Aldrich. In order to prevent moisture and any contamination, all material were isolated in a controlled condition. Purified food grade Carbon dioxide (CO_2) gas with purity of 99.999% and nitrogen (N_2) gas with purity of 98% were purchased from Muscat International Oil and Gas, Oman.

B. Sample Preparation and Physical Studies

The method for preparation of DESs has been explained in previous studies [5], [21], [22], DESs are prepared by mixing two components, namely hydrogen bond acceptors (HBAs) such as amine salts and hydrogen bond donors (HBDs) such as amines, to form low melting temperature solutions by means of hydrogen bonding interactions [10]. In this study, the DES were prepared with the EAHC to DETA ratio 1:9, using a magnetic stirrer equipped with a temperature control assembly. The mass of all pure components were measured with a digital balance (Shimadzu, model AUW220D), with an estimated accuracy of ± 0.1 mg. The combination was mixed at 400 rpm for at least 3 hours under atmospheric pressure and temperature between 333.15 K to 343.15 K under a fume hood until a homogeneous liquid without any precipitation is formed.

C. Density, Viscosity and Refractive Index Measurement

The densities were determined using a densitometer Anton paar 4500, the reflective index (RI) checked using Metler TOLEDO and Kinematic viscosity test were performed using viscometers CANNON-Fenske Routin, type U-tube reverse in a thermostatic bath Koehler (KV3000 SERIES) at temperature 298.15K to 343.15 K.

D. Carbon Dioxide Solubility Measurements

Solubility measurement using pressure drop which is used in this study is one of the widely reported technique for CO_2 absorption [23]-[25]. The volume of solvent is kept constant and the pressure drop is monitored. The pressure drop method is simple, precise, and requires less computational effort to determine accurate gas absorption. The Fig. 1 shows a schematic of the solubility cell used in this study.

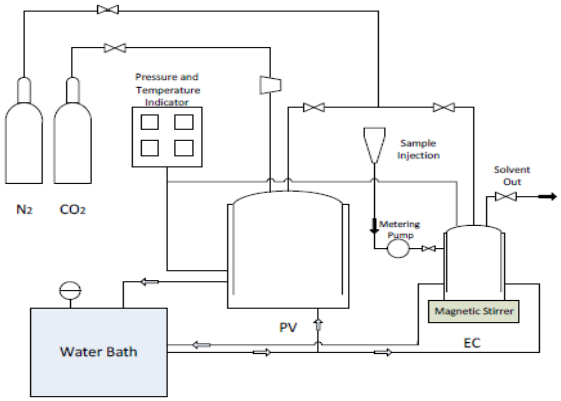
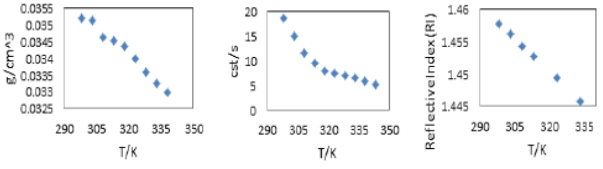


Fig. 1. Schematic of solubility cell used in this study.

III. Results and Discussion

A. Physical Studies

It is essential to identify the behavior of density with respect to temperature in DESs, due to its effect on operation processes [26]. In this study, the densities of the DES; 1EAHC:9 DETA were measured over the temperature range 298.15K to 338.15 K. Fig. 2.a shows the variation of densities with temperature. As a result, the densities decrease by temperature increasing. Viscosity is also an important property that must be addressed; herein, the kinematic viscosities of the selected DES; 1EAHC:9DETA were measured at various temperatures in the range of 298.15K to 343.15 K. It has been reported in Fig. 2. b. that increasing temperature leads to decreasing viscosity due to increasing mobility of free species. It is well known that higher viscosity in liquid is due to a massive hydrogen bond network between each component, resulting in a lower mobility of free species. [10]. The experimental reflective index of the prepared DES; 1EAHC: 9DETA were also measured as a function of temperature and repeated three times and reported in Fig. 2. c. The result shows that the value of reflective index decreases with an increase in temperature.



(a) (b) (c)

Fig. 2. Variation of densities (a), viscosities (b) and Reflective Indexes (c) with temperature.

B. Solubility of CO_2 in DESs

The equipment was first calibrated by investigating the

CO_2 solubility in 30 wt% aqueous monoethanolamine (MEA) solution at 313.15 K in pressure 0.552, 0.883, 1.256 and 1.58 MPa. The solubility of CO_2 in DES reported as (α), (α) is mole CO_2 (mole DES)$^{-1}$. The (α) which we obtained for 30 wt% aqueous at 313.15 K in pressure 0.552, 0.883 1.256 and 1.58 were 0.65, 0.754, 0.730 and 0.795, respectively. The results are in good agreement with the data reported previously [27] along with average standard deviations 3.68%.

After calibration of the equipment, the equipment was used to investigate the loading capacity of prepared DES; 1EAHC:9DETA at 313.15 K in different pressure 0.4194, 0.8206, 1.2527 MPa. The set up and solubility calculation were similar to the one used by Haris *et al.* and Sahil *et al* [25]. Fig. 3 shows the graphical representation of experimental CO_2 solubility data in term of (α) versus CO_2 partial pressure. As it has been seen, CO_2 increases with the increase in CO_2 partial pressure. The solubility of CO_2 were reported 0.41871, 0.65784 and 0.78317 in the pressure 0.4194, 0.8206 and 1.2527; respectively, at the same concentration of prepared DES and temperature 303.15 K. The absorption capability of this novel DESs shows a strong nearby α with which were reported for 30 wt% aqueous monoethanolamine (MEA) absorption at similar pressures [27].

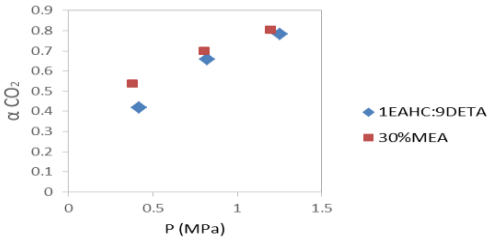


Fig. 3. Solubility of CO_2 in prepared DES; 1EAHC:9DETA at 303.15 K, in comparison with 30% MEA [27] at 303.15 K in similar partial pressure CO_2.

Afterward, the equipment was used to study the solubility of EAHC: DETA (1:9). The experimental CO_2 data were listed in Table I at various temperatures 303.15, 315.15, 323.15 and 333.15 K and pressure 4, 8, 12 and 16 bar. The solubility values are moreover presented in fig 4 in term of CO_2 loading (mole CO_2 per mole of DES) versus CO_2 pressure. As shown in Fig. 4, CO_2 solubility increased with the increase in CO_2 pressure, while it decreased with the rise in system's temperature. The solubility of CO_2 in previous studied DESs and Ion liquids at different pressures and temperatures had reported the similar results The CO_2 solubility increased with the increase in CO_2 pressure, while it decreased with the rise in system's temperature [28], [29].

TABLE I: CO_2 SOLUBILITY DATA IN NON-AQUEOUS DES; 1EAHC:9DETA AT TEMPERATURE 303.15, 313.15, 323.15, 333.15 K.

T=303.15 K		T=313.15 K		T=323.15 K		T=333.15 K	
P_{CO2}/bar	α $_{CO2}$	P_{CO2}/bar	α $_{CO2}$	P_{CO2}/bar	α $_{CO2}$	P_{CO2}/bar	α $_{CO2}$
4.194	0.41871	4.247	0.3962	4.672	0.37735	4.268	0.36567
8.206	0.67556	8.75	0.65263	8.573	0.59773	8.096	0.51821
12.527	0.78317	12.334	0.75096	12.481	0.72888	12.16	0.5888
16.262	1.01736	16.157	0.90608	16.658	0.86956	16.762	0.6664

To correlate data, regression analysis was developed using Matlab® R2017b software for prediction of α. The predictive equation was obtained by the regression model of α in relations of codded factors as following:

$$\alpha_{CO_2} = -11.05 + 0.07173T - 0.1638P_{CO_2} - 0.0001145T^2 + 0.0006983TP_{CO_2} - 0.0009835P_{CO_2}^2$$

where αCO_2 is the CO_2 loading (mole CO_2 per mole of DES), and T and P are temperature and P_{CO_2}, respectively.

The developed regression model was well in agreement with the calculated αCO_2 values with R-square: 0.976, Adjusted R-square: 0.9639, SSE: 0.01395 and RMSE: 0.03735.

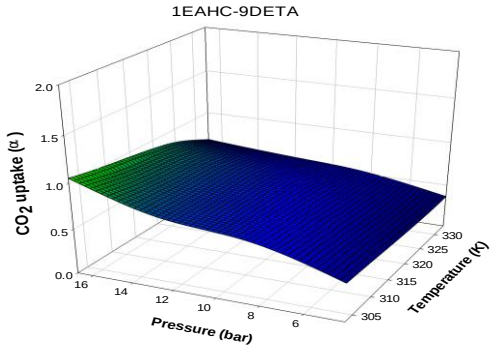


Fig. 4. Plot of αCO2 at different pressures and temperatures.

IV. CONCLUSION

In conclusion, we have studied a novel family of amine based DESs prepared by EAHC and DETA with ratio 1:9, a strong CO_2 absorber with (α) reported near to aqueous monoethanolamine (MEA) solution. The solubility of EAHC: DETA (1:9) has been studied at different temperatures, pressures, and regression analyses were developed successfully. Besides, the physical properties of the prepared DES including; densities, viscosities and Reflective Index have been reported. The present study reveals that amine based DESs can contribute significantly to the family of solvents for CO_2 capture and are a great candidate for further exploration.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

The tasks of individual authors in brief; Dr. Ghulam Murshid supervised the research; Prof. Farouq Sabri Majalli and Dr. Jamil Naser supported analyzing of the data, Khatereh Ali Pishro wrote the paper and handled the research.

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