Spectroscopic analysis of CO2 Solubility in DBU Ionic Liquids: Synthesis, Experimental and COSMO-RS Study

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Abstract

In this study, four DBU based ILs namely [DBU][Ac], [DBU][TFA], [DBU][MSA] and [DBU][TFMSA] (1,8-diazabicyclo[5.4.0]undec-7-ene as cation and acetate, trifluoroacetate, methanesulfonate and trifluoromethanesulfonate as anions) were synthesized for CO2 capture. The neat and dried ILs was characterized by 1H NMR and 13C NMR spectroscopic methods. The systematic analysis of CO2 solubility in ILs was performed at 10 bar, 15 bar and 20 bar pressure and at T=(303.15 and 313.15) K. Among the four ILs, [DBU][Ac] showed highest CO2 sorption efficiency (0.7992 mol/mol IL at 20 bar pressure and at 303.15 K) due to the formation of new compound during the absorption process. From the experimental data (pressure-concentration-temperature), Henry's constant (KH) was predicted to calculate the absorption tendency of ILs. The sign and magnitude of thermodynamic properties such as Henry's constant (KH), Gibbs free energy (ΔG_o), enthalpy (ΔH_o) and entropy (ΔS_o) reveals the CO2 sorption efficiency.

Abstract

Ionic liquids (ILs) present a new alternative for post-combustion CO_2 capture because their properties can be tuned by means of different cation-anion combinations. The absorption of CO_2 can be enhanced by the basic character of the IL. The fluorination of the cation or the anion can also contribute to enhance the gas solubility. In this study, four DBU based ILs namely [DBU][Ac], [DBU][TFA], [DBU][MSA] and [DBU][TFMSA] (1,8-diazabicyclo[5.4.0]undec-7-ene as cation and acetate, trifluoroacetate, methanesulfonate and trifluoromethanesulfonate as anions) were synthesized for CO_2 capture. The neat and dried ILs was characterized by[1]H NMR and ^{13}C NMR spectroscopic methods. The systematic analysis of CO_2 solubility in ILs was performed at 10 bar, 15 bar and 20 bar pressure and at T=(303.15 and 313.15) K. The experimental method used was shown to be accurate, low solvent utility and low gas consuming to evaluate the solubility of CO_2 in ILs. Among the four ILs, [DBU][Ac] showed highest CO_2 sorption efficiency (0.7992 mol/mol IL at 20 bar pressure and at 303.15 K) due to the formation of new compound during the absorption process. From the experimental data (pressure-concentration-temperature), Henry's constant (K_H) was predicted to calculate the absorption tendency of ILs. The obtained results were defined the type of absorption occurred between solute and solvent. The sign and magnitude of thermodynamic properties such as Henry's constant (K_H), Gibbs free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) reveals the CO_2 sorption efficiency. The absorption of CO_2 significantly influenced by the temperature, pressure, viscosity, surface tension, concentration and type of substituents attached to the anion is investigated. The experimental and thermodynamic results are confirmed that the solubility efficiency of CO_2 in studied ILs as following order: [DBU][Ac] > [DBU][TFAc] > [DBU][TFMSA] > [DBU][MSA]. FTIR analysis was performed to determine the CO_2 sorption in ILs, there are two new absorption bands were observed at 1701 cm^{-1} and 1695 cm^{-1} which are attributed to the stretching vibration of COO$^-$(=N-COO-) for acetate based ILs. On the other hand, COSMO-RS study was performed to analyze the solubility tendency of CO_2 in various ILs through

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the geometry optimization, energy levels, and solubility predictions.

Key words : CO_2 solubility; Ionic liquid; COSMO-RS study; FTIR analysis; Thermodynamic function.

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Introduction

The combustion of fossil fuels such as natural gas, coal and petrol are a major source of carbon dioxide which is considered as most substantial greenhouse gases [1]. Among the anthropogenic greenhouse gases, carbon dioxide is one of the most important gas which contributions with over 84% energy related emissions [2]. There are enormous technologies for CO_2 removal such as adsorption, absorption and membrane separation[3,4], each technology takes advantages of high CO_2 capture affinity solvents or functional materials[5].

Traditionally, aqueous amine solutions have been used at industrial level through absorption process. The primary amines possess more CO_2 capture efficiency relatively than secondary and tertiary amines because of their higher basicity. For post combustion CO_2 capture process, 30wt% monoethanolamine (MEA) is the common absorbent owing to its unique applications such as low price, high absorption capacity and high reactivity tendency. Although efficient, this solvent possesses some limitations such as high equipment corrosion, low vapor pressure and large volume of absorber required. Furthermore, amine regeneration also requires high energy consumption as capture of CO_2 with amines comprises a chemical reaction with a large reaction enthalpy[6]. As a result a large amount of heat is required to get rid of captured CO_2 in the regeneration step. Ideally a liquid can be regarded as best CO_2 sorbent which can adsorb CO_2 rapidly and reversibly with desirable physical properties such as low volatility, low viscosity, low heat capacity and high thermal stability[7]. Recently, a new class of absorbing materials, known as ionic liquids (ILs), has been offered as a substitute to the corrosive, volatile, and degradation sensitive amine solvents [8]. In a regeneration step ILs can be used instead of traditional solvents, the required enthalpy to release the CO_2 which is physically absorbed is about 20 kJ·mol^{-1}, which is only a quarter of the energy consumed by amine-base solvents[9].

However, ILs have also been wildly used in various fields such as catalyst and solvents in synthesis[10], separation process, heat transfer media, as electrolytes in dye sensitized solar cells, bio-mass treatment[11,12], as absorbents for gas separation from petrochemicals[13] due to their tunable properties [14]. There is much large number of experimental studies available on solubility of CO_2 in ILs, still some more data to be required. Bates*et al.* [15]studied the functionalized ILs with amino group tethered at the cation whereby the result showed up to 0.5 mol/mol CO_2 sorption due to the formation of carbamate which follows the mechanism 2:1. Anthony *et al.*[16] measured CO_2 solubility in ILs 1-n-butyl-3-methylimidazolium hexafluorophosphate, [Bmim][PF$_6$], and 1-n-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF$_4$] compared their results with conventional technology using MEA. The authors noticed that although physical absorption took place, the Henry's constants were so high that the CO_2 absorption through this way was no competitive with the traditional process based on CO_2 capture with amines. Li *et al* .[17] have reported that [C$_2$mim][Ac] IL was used for the separation of CO_2 and SO_2 gas from fuel gases, the initial absorption capacity of CO_2 in IL decreased by 48% after 5 cycles of regeneration. Pedro *et al* .[18] have described that CO_2 solubility in two acetate based ILs namely [C$_4$mim][Ac] and [C$_4$mim][TFA] at high pressure and temperatures. Fluorine substituted ILs have shown higher absorption capacity at high pressure, whilst [C$_4$mim][Ac] gave better at low pressure. Bihong *et at* .[19] have stated that dual functionalized ILs as amine substituted amino acids was efficiently to be used as CO_2 absorbents. The absorption capacity was 1.23 mol CO_2/mol IL, which was higher than that most of the dual functionalized ILs in aqueous solutions. Shengjuan *et al* .[20] have determined the absorption loading and apparent absorption rate constant for CO_2 in aqueous solutions. The mixture [Cho][Gly] (30% IL) showed highest CO_2 absorption capacity (1.019 mol CO_2/mol IL) than compare to [Cho][Ala] and [Cho][Pro] (0.924 and 1.020 mol CO_2/ mol IL, respectively). Amine, acetate and ether functionalized task specific ILs have also been used to enhance the CO_2 absorption capacity through the chemisorption mechanism [21-23]. Recently, Chen *et al* .[24] have reported a new method for effective synthesis of 3(2*H*)-furanones by reaction of CO_2 with a series of base functionalized ILs including [DBUH][Im]. Liang

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Wei *et al* .[25] have studied a series of ethoxyacetate anion based protic ILs with different amine cations, notably the solubility of CO_2 in 90% of [DMAPHA][EOAC] showed up to 2.44 mol/Kg, which possess more benefit than some molecular or functional ionic liquids.

However, few researchers have focused on CO_2 capture using polyamino ILs. Water content and temperature are important factors that influence CO_2 absorption by ILs. Hui Hu and his coworkers were studied an influencing factors and mechanism of CO_2 absorption by poly-amino-based ionic liquids in presence of water. The CO_2 sorption capacity of ILs can be found as 0.96 mol CO_2/mol IL at 293 K was achieved with pure [TETAH][BF$_4$] and as 2.04 mol CO_2/mol IL at 293 K with [TETAH][BF$_4$] containing 40% water[26]. Whereas, 1-(3-propylamino)-3-butyllimidazolium-tetrafluoroborate ([APBIM][BF4]) absorbed 0.5 mol /mol at 1 atm pressure. The CO_2 sorption of di-amino ionic liquid [AEMim][Tau] showed 0.9 mol /mol at 303 K and the sorption value of 0.1-1.26 mol/mol for other aminate ILs were reported[27].

The scope of the present study is synthesis of four DBU based ILs as absorbers for CO_2 capture at different pressure and temperature conditions. The results were predicted in terms of thermodynamic parameters such as Henry's constant, Gibbs free energy, enthalpy and entropy. FTIR spectrophotometry was performed to understand the interaction (absorption) between anion of the ILs and CO_2 molecule. COSMO-RS model was used to understand the effect of structural variations of the studied ILs on the solubility of CO_2 in the ILs, compare the experimental results of CO_2 sorption with the theoretical models.

1. **Experimental Methods**
2. **Materials:** All starting materials were purchased from Sigma-Aldrich, which were used for the synthesis of ILs without further purifications, *viz.* in mass fraction. 1,8-diazabicyclo[5.4.0]undec-7-en-8-ene (>0.99), acetic acid (>0.99), trifluoroacetic acid (0.99), methanesulfonic acid (>0.99), trifluoromethanesulfonic acid (>0.98) and methanol (>0.99, Merck).
3. **Synthesis of ionic liquids:** In this study, four ILs *i.e* [DBU][Ac], [DBU][TFA], [DBU][MSA] and [DBU][TFMSA] were synthesized and characterized by spectroscopic techniques. Method of synthesis and spectrums were reported in earlier publication[28]. Prior to experimental work, water content of the ILs was measured by Karl Fischer Titrator, Mettlor Toledo DL39 model. The measured water content of all neat ILs was < 0.1%. The magnitude of spectrums of ^{1}H NMR and ^{13}C NMR of synthesized ILs are as follows:
4. **Characterization of Ionic liquids:**
5. NMR Spectroscopy (500 MHz, MeOH-d$_4$, δ ppm):

[DBU][Ac] : ^{1}H NMR: 1.72 (m, 6H), 1.93 (s, 3H), 2.04 (m, 2H), 2.71 (t, 2H), 3.37 (t, 2H), 3.57 (t, 2H) and 3.63 (t, 2H).

^{13}C NMR: 19.0, 23.5, 26.1, 28.6, 32.3, 37.9, 54.0, 115.7, 118.1, 161.3 and 166.1.

[DBU][TFAc] : ^{1}H NMR: 1.72 (m, 6H), 2.04 (m, 2H), 2.71 (t, 2H), 3.37 (t, 2H), 3.57 (t, 2H) and 3.63 (t, 2H).

^{13}C NMR: 19.0, 23.5, 26.1, 28.6, 32.3, 37.9, 53.9, 115.7, 118.1, 161.6 and 166.1.

[DBU][MSA] : ^{1}H NMR: 1.73 (m, 6H), 2.04 (m, 2H), 2.71 (s, 5H), 3.38 (t, 2H), 3.58 (t, 2H) and 3.64 (t, 2H).

^{13}C NMR: 19.0, 23.5, 26.1, 28.6, 32.3, 37.9, 38.2, 48.5, 54.0 and 166.1.

[DBA][TFMSA] : ^{1}H NMR: 1.73 (m, 6H), 2.04 (m, 2H), 2.70 (t, 2H), 3.37 (t, 2H), 3.57 (t, 2H) and 3.63 (t, 2H).

^{13}C NMR: 19.0, 22.4, 23.6, 26.1, 28.6, 32.4, 37.9, 48.5, 54.0 and 166.1.

FT-IR Spectroscopy:

FT-IR spectrophotometer was used to determine the IL-CO_2interactions. The model of an instrument is Nicolet iS10 (Thermo Scientific) and the spectral range is 7800-350 cm^{-1}. The spectral resolution would be

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better than 0.4 nm. It has two beam splitters (standard and optional) KBr/Ge mid infrared optimized and XT-KBr/Ge for extended range and mid-infrared range, respectively.

CO$_2$ sorption measurements:

An instrument used for the CO_2 absorption measurements was shown in Fig. 1. The cell is cylindrical shape made up by stainless steel with 13 cm^3 internal volume and has screw tight facility at one end. The temperature and pressure was measured with high precision thermometer and pressure transducer, the accuracy of temperature and pressure is ±0.1 K and ±0.01 bar, respectively. The system was calibrated with standard organic compound like MEA (mono ethanolamine). The system was ensured not to have leakage, as it leads to imprecision during the measurements. The more details of an instrument such as brand, model and country of origin has been reported in literature[9,29,30]. As shown in Fig. 1, valve A and valve B which are extending from high pressure CO_2 cylinder, which was used to adjust the desired pressure. Once the required pressure is achieved, the cell system (from valve B to valve C) was degassed by vacuum pump for 10 min, and then about 3.0-3.5 g of IL was placed in a sample cell. Once the system reaches to desire temperature and pressure, valve C was closed and then CO_2 gas was slowly released into the sample cell with the help of valve B. The pressure drop was recorded for every minute until the cell pressure remains stable (reached to equilibrium state). Each experiment was processed for about 7-8 hrs at constant temperature. The cell system was immersed in a circulated water bath to get desired and uniform temperature. The captured CO_2gas in mol/mol IL was calculated as following equation,

$$n = \frac{P_{ini} \cdot V_{tot}}{Z_{ini} \cdot T_{ini} \cdot R} - \frac{P_{eq}(V_{tot} - V_{samp})}{Z_{eq} \cdot T_{eq} \cdot R} (1)$$

Where, $n = CO_2$ captured mol/ mol IL,P_{ini} = initial pressure without sample,V_{tot}= total volume of the system,Z_{ini}=compressibility factor (P_{ini} × T_{ini}),T_{ini}=initial temperature, T_{eq}=equilibrium temperature, P_{eq}=equilibrium pressure with sample,Z_{eq}= compressibility factor (P_{eq} × T_{eq}),

V_{samp} = volume of the IL and R= 0.0821 atm.L/mol.K.

Peng-Robinson equation was used to calculate the compressibility factor. It accurately characterizes the relation among the temperature, pressure and phase compositions in binary and multi component systems. It could also predict the vapor pressure and volumetric behavior of single component system, phase behavior and volumetric behavior of binary, ternary and multiple component systems. All the experiments of CO_2 capture were performed three times and the estimated average standard deviation was less than 0.05%.

Thermodynamic Properties: Henry's equation was used to predict the CO_2solubility in the studied ILs. The gas solubility increased as pressure increases and decreased with increases of temperature. The fugacity of gas dissolution in given liquid with its concentration is determined as below:$K_H(T,P) = \left[\frac{P_{CO_2}}{X} \right] (2)$ Where, K$_H$, Henry's constant which is inversely proportional to the mole fraction (x) of the gas in liquid.

Henry's constant can be found by fitting a second-order polynomial equation which can calculate the limiting slope as the solubility approaches to zero given as below:

$$K_H = Ax^2 + Bx + C \ (3)$$

$$K_H(T,P) = \left[\frac{P_{CO_2}}{x} \right] = B (4)$$

The standard Gibbs energy (ΔG^o) of the mixtures were calculated from Henry's constant at infinity dilutions as given follows:

$$\Delta\Gamma^o = -RT \ ln \left[\frac{P^o}{K_H} \right] (5)$$

Where, standard pressure, P^o=1.01325 bar and R=8.314 J·mol^{-1}·K^{-1}.

For small temperature ranges, the standard enthalpy of solution is considered as constant, the equation can be written in the terms of Henry's constant as follows:

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$\ln K_H = ln K_o + \frac{\Delta H^o}{PT}$ (6)

For wide range of temperatures, the standard enthalpy of solution is temperature dependent. So, ΔH^o can be obtained from the equation as given below:

ΔH^o

englishR$= \left[\frac{\partial ln K_H}{\partial / T} \right]$ (7)

Henry's law constant at infinity dilution is not a constant at different temperature; the temperature dependent equation can be written as given below:

$\ln K_H = A + \frac{B}{T} + \frac{C}{T^2}$ (8)

$\Delta H^o = R \left[B + \frac{2C}{T} \right]$ (9)

The standard entropy of mixtures may be calculated from the Eq.10 as given below:

$\Delta \Sigma^o = \left[\frac{\Delta H^o - \Delta \Gamma^o}{} \right.$

englishT(10)

COSMO-Rs Study:

COSMO-RS (Conductor like Screening Model for Real Solvents) predictive method was introduced to understand the interaction between the ILs and gas (IL-CO_2) molecule. Which provides an alternative approach to predict the thermodynamic properties of fluids in various systems, including ILs such as solubility, activity coefficient and phase equilibria [31]. The statistical thermodynamics approach based results of unimolecular quantum chemical calculations were used[32]. Herein, the basic structures of the ILs and CO_2 molecules are drawn by using Avogadro's open source tool, the generated structures were imported into geometry optimization at COSMOthermX17. The version COSMOthermX_C21_0111 was used to complete all the calculations. The parametrization scheme BP_TZVP_C30_1301 (COSMOlogic GmbH & Co KG.Leverkusen, Germany)[28,33] model was used for the calculation of energy gaps, sigma profile and solubility of CO_2 in the ILs. These calculations were performed on the gas phase model without considering the solvent effect.

The activity coefficient of component i, is related to chemical potential, μ_i[34] was calculated as follows:

$\gamma_i = exp(\frac{u_i - u_o^i}{RT})$ (11)

Where u_i^o is the chemical potential of pure compound i, R is an ideal gas constant and T is absolute temperature. In all calculations, ILs is always treated as an equimolar mixture of cation and anion thus, the scale by a factor of 0.5. The best predictions were obtained with the lowest energy conformations or with global minimum for both cation and anion. Thus, in this work the lowest energy conformations of all the species involved were used in the COSMO-RS calculations[32,35].

Further step has taken to explore the interaction between ions and CO_2 molecule, equimolar concentration was considered for both IL and CO_2 to predict the data by using the COSMOthermX prob. The activity coefficient (γ), solubility ($\log_{10}p$), van der Waal's force (vdW) and excess enthalpy (H^E) of CO_2 with ILs were calculated at 303.15K. The excess enthalpy of CO_2-IL mixtures can be predicted summation of hydrogen bonding, electrostatic interactions and van der Waal's force as given below:

$H^E = H^E (H - bonding) + H^E (\text{misfit}) + H^E (\text{vdW})$(12)

Results and Discussion

The solubility of CO_2 in synthesized DBU based ILs was measured at 303.15 K and 313.15 K at 10 bar, 15 bar and 20 bar pressure. The pressure drop with respect to time and temperature for all ILs was graphically represented in Figs. S1-S4. The solubility capacity of CO_2 in the ILs was calculated by using Eq.1 and

depicted in Table 1. The graphical representation of CO_2solubility in the studied ILs with pressure and temperature was represented in Fig. 2.

Effect of pressure on CO_2 sorption:

As expected, the CO_2 sorption ability in the ILs increases with increasing pressure for all ILs. At low pressure higher sorption was noticed due to the chemical sorption process and then further increase at high pressure due to physical absorption process. The CO_2 sorption by DBU based ILs at high pressure merge the characteristic of chemical sorption as well as physical sorption[36].

As depicted in Fig. 2 CO_2 solubility in [DBU][Ac] showed highest value than compared to other ILs at all pressures. From Table 1, sorption values of acetate based IL is 0.4108, 0.5861and 0.7992 (mol/mol) at 10 bar, 15 bar and 20 bar, respectively at 303.15 K. The observed change in gas solubility is 30% and 56% (compare to sorption at 10 bar) higher for every 5 bar and 10 bar pressure variations, respectively. For fluorinated acetate based IL, [DBU][TFAc] showed a lower absorption tendency than acetate based IL which was 35.5% lower at 20 bar and 303.15K. In general, many researchers reported that fluorination of either cation or anion can enhance the CO_2 capture because, increases the interaction ability between CO_2 molecule and ions[37,38]. In other hand, decreases the CO_2 capture tendency with decreases the surface tension of ILs (γ= 35.94 and 31.98 mN.m^{-1} for acetate and fluorinated acetate ILs, respectively) due to more promising to the formation of cavities in mixture [39]. The sorption of CO_2 in [DBU][TFAc] at 303.15 K was increased 54% and 71% at 15 bar and 20 bar pressure, respectively.

Similarly, as depicted in Table 1 and Fig.2, CO_2solubility in [DBU][MSA] and [DBU][TFMSA] increased with increasing the pressure. Herein, the fluorine atom of anion played a key role on solubility of CO_2 in IL at all pressures. The IL, [DBU][TFMSA] showed higher CO_2 solubility efficiency than [DBU][MSA] at all composition ranges. The fluorinated [MSA] showed 0.4937 mol/mol absorption value which was 18.5% higher than that of [MSA] ionic liquid at 20 bar pressure. Whereas, CO_2 sorption in [DBU][TFMSA] was 0.1225 mol/mol at 10 bar which was 52% and 75% lower than that sorption at 15 bar and 20 bar, respectively. In the same way, the sorption value for [DBU][MSA] was 0.0936 mol/mol at 10 bar which was 53.2% and 76.8% lower than that sorption at 15 bar and 20 bar, respectively. The reason could be described in terms of thermodynamics, increases an interaction between the gas molecules and ions and/or decreases the surface tension of ILs. The surface tension of [DBU][MSA] and [DBU][TFMSA] was 41.35 mN.m^{-1} and 29.80 mN.m^{-1} respectively, at 303.15 K[28]. Lower surface tension of ILs is more favorable to make the holes (cavities) between the ions and caused to more absorption tendency. The order of the CO_2 sorption in terms of pressure for studied ILs as follows:

[DBU][Ac] > [DBU][TFAc] > [DBU][TFMSA] > [DBU][MSA]

Effect of temperature on CO_2 sorption:

The CO_2 solubility in all studied ILs decreases with increasing temperature from 303.15K to 313.15K. The observed sorption values for [DBU][Ac] was 0.7992 and 0.7010 mol/mol at 20 bar, 303.15 K and 313.15 K, respectively. The observed changes in CO_2 solubility was 14.1% for 10 K temperature variance. Similarly, 7.7%, 10.4% and 11.7% solubility variance were observed with temperature at 20 bar for [DBU][TFAc], [DBU][TFMSA] and [DBU][MSA] ILs, respectively. This can be explained as at room temperature, the CO_2 sorption is saturated with a plateau exists as function of temperature (between 25 to 35°C) with little effect on temperature. Beyond 308.15 K, the CO_2 sorption capacity decreases, indicating that the absorption equilibrium is shifting towards the desorbed state, as expected since desorption is endothermic[40]. From the above data, the order of the CO_2 sorption in all ILs (the % of variance has been considered) in terms of temperature as follows:

[DBU][Ac] > [DBU][MSA] > [DBU][TFMSA] > [DBU][TFAc]

Comparison of CO_2 sorption with other ILs:

In order to compare the solubility efficiency of studied ILs, the standard absorber MEA (mono ethyl amine)

showed 0.48 mol/mol which is slightly lower than the value reported in literature (0.55 mol/mol)[41] in THF solution. The IL, [DBU][Ac] showed higher sorption than [DBU][TFAc] at all experimental conditions. Similar behavior was reported by Carvalho *et al.* [18] that the solubility of CO_2 in 1-butyl-3-methylimidazolium acetate, [Bmim][Ac] and 1-butyl-3-methylimidazolium trifluoroacetate, [Bmim][TFAc] at different pressure and temperatures. They have noticed an interesting behavior between two ILs that [Bmim][Ac] showed higher sorption (0.587 mol/mol) than [Bmim][TFAc] (0.238 mol/mol) due to the formation of new compound during the sorption process (chemisorption). Gimeno *et al* .[42] studied on CO_2 solubility in imidazolium cation with various anions, imidazolium acetate [Bmim][Ac] showed highest sorption behavior than other fluorinated and non-fluorinated ILs owing to the chemical reaction taken place during the absorption process. The observed x (CO_2) sorption for [Bmim][Ac] at 303.15 K was 0.38, 0.36 and 0.32 at 2 Mpa, 1Mpa and 0.5 Mpa, respectively. Another reasons, CO_2 solubility in fluorinated ILs decreases with increases of viscosity by increasing the number of fluorine groups. This statement may be supporting to present work that the observed viscosity for [DBU][Ac] and [DBU][TFAc] were 84.7 and 493.8 mPa.s, respectively at 303.15 K.

Yokozeki *et al.* [43] have measured the CO_2 solubility in the series of ILs, Emim[Ac], Emim[TFA], Bmim[Ac] and Bmim[TFA] at 298.15 K and 20 bar (2 Mpa) pressure. The CO_2 solubility in acetate based ILs showed higher than that of fluorinated acetates, the sorption values found to be 0.43, 0.28, 0.43 and 0.28 mol/mol, respectively. Sabahat *et al.*[9] presented the CO_2 sorption efficiency of C_4mim[Ac] and C_4mim[TFA] at different pressure and temperatures, the observed values for C_4mim[Ac] x CO_2=0.25 (T=333K, P=1.27Mpa) and 0.59 (T= 323 K, P=75.5 Mpa) whereas sorption data for C4mim[TFA] x CO_2=0.23 (T=293 K, P=1Mpa) and 0.68 (T= 293 K, P=43.6 Mpa). Zhou *et al* .[44] have reported that multi fluoro fuctionalized ILs showed high CO_2 capture tendency then non-fluorinated ILs, the sorption in C_4mim[$CF_3CF_2CF_2CF_2SO_3$] found to be 0.54 mol/mol at 293 K and 0.37 Mpa. Furthermore, a series of amino acid based poly ionic liquids have been used[29] as absorber for CO_2 capture. Among the eight poly ILs, Poly[VBTMA][Arg] showed highest sorption capacity (1.14 mol/mol) and Poly[VBTMA][Ala] showed lowest sorption capacity (0.56 mol/mol), the tendency of CO_2 capture increased as pressure increased and decreased as temperature increased. Zhu *et al* .[45] have synthesized DBU imidazolium and multi substituted imidazolium anion based protic ionic liquids for CO_2 capture, among the series of ILs, [DBU][Im] showed more sorption than multi substituted imidazolium based ILs. The CO_2 sorption value for [DBU][Im] was found to be 0.9 mol/mol at 313.15 K, the reason may be due to the formation of new compound (DBU Im-CO_2^-) between imidazole and CO_2 molecule through the chemisorption process. The CO_2 solubility of five ILs have been measured[9] at 298.15 K with a pressure range of 1 to 4 MPa, it was observed that CO_2 molar uptake increased continuously with increasing pressure with the order of [bnmim][AMPS] <[bpyn][AMPS] < [bmim][AMPS] < [bmpyr][AMPS] <[emim][AMPS]. Among the three imidazolium-based ILs studied, a marginal increase in CO_2 solubility was observed for [emim][AMPS], that was, 0.40 mole at 1 MPa, as compared to that for [bmim][AMPS] and [bnmim][AMPS] which have shown 0.22 and 0.15 mole at 298.15 K, respectively. Karadas *et al* .[46] measured CO_2 sorption of [emim][Tf_2N], [bmim][Tf_2N], and [bmim][PF_6] at 318 K and 338 K for pressures up to 20 MPa. The CO_2 sorption for [emim][Tf_2N] was larger than that for [bmim][Tf_2N] at 318 and 338 K. It was found that at 318 K and 0.995 MPa, x (CO_2) for [emim][Tf_2N], [bmim][Tf_2N], and [bmim][PF_6] was found to be 0.16, 0.14, and 0.08, respectively. The ILs, [emim][Tf_2N] and [bmim][Tf_2N] are moderately viscous (34.1 and 51 mPa·s, for [emim][Tf_2N] and [bmim]-[Tf_2N], respectively at 298.15 K and 0.1 MPa), while the viscosity for [bmim][PF_6] was larger (270.9 mPa·s at 298.15 K and 0.1 MPa44).

From the results of above presented, DBU based ILs particularly, [DBU][AC] captured more CO_2 gas except the amine based polymerized ILs and bicyclic imidazolium ILs,[DBU][Im]. The reason for this variance due to the presence of malty-substituted anions, surface area of poly ILs and amine substituents may influence the CO_2 sorption.

Henry's constant and relevant thermodynamic properties:

The gas solubility can be expressed in terms of Henry's constant (K_H), it was calculated to determine the type of interaction, whether physical or chemical sorption. It gives a relation between the mole fractions of substance in liquid phase to its partial pressure in the gaseous phase. Henry's law states that at constant

temperature, the dissolution of gas in given liquid, the volume of the liquid is directly proportional to the partial pressure of gas in equilibrium with that liquid[47]. As pressure of gas increases, isotherms of CO_2 equilibrium in ILs showed a non-linear trend as described in Fig. 3.

Henry's constant data (K_H) at infinity dilution was listed in Table 2. The decreasing order of K_H values indicate that an increase in degree of gas solubility in ILs. In general, a small constant values at less than 3 MPa pressure and at low temperature significantly chemical absorption (formation of new compound between the gas and ILs)[48]. In order to calculate the Henry's constant, a graphical representation of CO_2 concentration verses pressure with respect to temperature was depicted in Fig. 3. Among the four ILs, [DBU][Ac] was the most promising solvent for CO_2 sorption because, which showed lowest constant values. Henry's constant values increase with increase of temperature for [DBU][Ac] was 14.71 and 19.74 for 303.15K and 313.15K respectively. While, [DBU][MSA] exhibited highest constant values (98.12 and 113.35 at 303.15K and 313.15 K, respectively) than [DBU][MSA] (123.15 and 131.29 at 303.15K and 313.15 K, respectively) because of lower CO_2 absorption capacity. Similarly, the constant values for [DBU][TFAc] was 81.17 and 101.71 at 303.15K and 313.15 K, respectively. Whereas, [DBU][TFMSA] showed as 98.12 and 113.35 at 303.15K and 313.15 K, respectively. From Fig.3, the order of the Henry's constant for studied ILs at all composition ranges as follows:

[DBU][Ac] > [DBU][TFAc] > [DBU][TFMSA] > [DBU][MSA]

The solubility behavior of CO_2 in ILs was clearly understood in terms of thermodynamic functions such as standard Gibbs energy (ΔG^o), standard enthalpy (ΔH^o) and standard entropy (ΔS^o). As it can be seen from Table 2 that the positive values of ΔG^o corresponds to the dissolution of CO_2 in ILs is a non-spontaneous process at all temperature ranges. The values increase with temperature indicating that the solution (CO_2+ILs) consumes more energy. The acetate based ILs exhibited more ΔG^o values than sulfonate based ILs, which were noticed for four ILs at 303.15 K as 6.74, 11.04, 11.53 and 12.10 kJ·mol^{-1}, respectively. The negative magnitude of ΔH^o indicates that CO_2 can associate with ILs at defined temperatures. For higher solubility of gas-liquid mixtures, the enthalpy of condensation dominates and results in an overall partial molar change in enthalpy *i.e* negative and large negative values significance of stronger CO_2-IL interaction [49]. Which indicates that CO_2 molecule has highest interaction with [DBU][Ac], (ΔH^o = -76.57 kJ·mol^{-1} at 303.15 K) than compare to other ILs. The observed ΔH^o values for [DBU][TFAc], [DBU][TFMSA] and [DBU][MSA] at 303.15 K were -58.73, -37.57 and -16.66 kJ·mol^{-1}, respectively. The effect of temperature on standard enthalpy is very low and negative enthalpy values indicate an exothermal solvation process. The negative values were observed for entropy which can be explained by the structural effects caused by the specific interactions between the solute and charged centers of the IL[50]. The data predicted from thermodynamic properties, the efficiency of CO_2 solubility can be estimated for four studied ILs as follows:

[DBU][Ac] > [DBU][TFAc] > [DBU][TFMSA] > [DBU][MSA]

FT-IR Spectral analysis:

FTIR spectroscopic technique was studied to distinguish the type of absorption existed. The chemical reaction occurred through the formation of bond between aromatic ring and CO_2 molecule as result of proton shifting towards Lewis base. From Fig. 4, there are two new absorption bands were observed at 1701 cm^{-1} and 1695 cm^{-1} which were attributing to the stretching vibration of COO$^-$ (=N-COO$^-$) for acetate based ILs[42,45,51]. The spectrum of [DBU][MSA] and [DBU][TFMSA] do not showed such absorption bands corresponds to the stretching vibration of COO$^-$. IR spectra showed a peak at 2340 cm^{-1}, which corresponding to the vibration frequency of the CO_2 molecule. This could be explained by the fact that a flow of CO_2 was fed through the reaction cell during the IR spectra measurements and that it was not the result of a possible CO_2 desorption[42].

From this results, sulphonate ILs involved in physical absorption (physical absorption takes place between every gas and solid or liquid molecules because, van der Waal's force can exist among the molecules of every two substances) and acetate based ILs involved in chemical absorption. Similar behavior was reported by researchers, imidazolium trifluoro sulphonate (triflate) ILs followed the physical absorption and acetate

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based ILs involved in chemical absorption phenomena[42,52].

From the results of Henry's constant, standard Gibbs energy, standard enthalpy, standard entropy and FTIR studys, chemisorption was observed in acetate based ILs including [DBU][Ac] and [DBU][TFAc] and physisorption was observed in sulfonate based ILs such as [DBU][MSA] and [DBU][TFMSA]. In terms of Lewis acid and base concept, acetate based ILs act as strong Lewis base and leaving group (H$^+$) capture tendency of acetate ILs is more than sulfonate based ILs. This phenomenon could be explained by the help of HOMO and LUMO theory. Similar behavior was reported by Yokozeki*et al* .[43] that both physical and chemical absorption can be observed when RTILs as absorber.

COSMO-RS Study:

The geometry of the individual ion structures was optimized at high-level quantum chemical calculations. For this calculations independent counter-ion method (cation+anion model) was applied. The optimized structures of CO_2 with four anions and cation are shown in Fig.S5. From Fig.S6, the σ-profile of cation, four anions and CO_2 molecules can be observed. The broad peak was observed about -0.02 e/Å^2 corresponds to the hydrogen bond donor effect (-N-H of bicyclic ring) and the area lies in between -0.01to 0.01 e/Å^2 significance of non-polar region due to the alkyl groups. The region of σ> 0.01 corresponds to the hydrogen bond accepter tendency of four anions. The strength of either hydrogen bond accepting or donating tendency depends on charge density of ions [53]. As can be seen from Fig.6 that acetate ion exhibits more hydrogen bond accepting tendency (σ>0.02) than other three ions (σ<0.02). Hence, non-polarity plays a significant role in the interaction of ILs with CO_2 (σ [?]0.005, DBU ring)[34]. Thus, the affinity of CO_2 is increasing toward more non polar ILs (bicyclic ring). Therefore, ILs with high polarity displays less interaction towards CO_2[54].

On other hand, CO_2-ILs interaction ability could be investigated in terms of HOMO- LUMO theory (highest occupied molecular orbital and lowest unoccupied molecular orbital). For this calculations Kohn-Sham density functional theory, which is form Koopmann's theory at DFT level was used [55]. The difference of HOMO- LUMO can give the amount of energy required to add or remove electron in molecule, high energy gap indicates that more stable and resistance to charge distribution while, low energy gap indicates that high polarizability that leads to small amount of energy required to get excited state. From Fig. 5, the possible interaction views of ions with CO_2 molecule. The energy gap of cation with CO_2 showed lowest value (ΔE=0.1013 eV) than compare to other ions due to the delocalization of Π-electros and moving towards CO_2 molecule to form a new -N-COO$^-$ group. The leaving proton can easily transferred to Lewis base, the proton accepting ability decreases for sulfonate ILs owing to the weak Lewis basicity. The energy gap values for [Ac], [TFAc], [TFMSA] and [MSA] with CO_2 molecule were ΔE= 0.1396 eV, ΔE= 0.1481 eV, ΔE=0.1511 eV and ΔE=0.1585 eV, respectively.

Furthermore, the activity coefficient (γ$_i$) of CO_2 in ILs were calculated and presented in Table 3. As it can be seen, the trend of the γ$_i$ increased in the order of [DBU][Ac] < [DBU][TFAc] < [DBU][TFMSA] < [DBU][MSA]. The lower activity coefficient values significance of strong interaction between IL and CO_2 molecule. Among the four ILs, [DBU][Ac] exhibited lowest γ$_i$ (0.210) and [DBU][MSA] showed highest γ$_i$ (0.274) may be due to their viscosity, size and shape differences[56]. The excess enthalpy (H^E) of dissolution of CO_2 in the ILs were calculated, the H^E values were negative for all ILs with CO_2 molecule, at low concentration of CO_2 which showed exothermic solvation process[57]. The order of the ILs based on the H^E was [DBU][Ac] > [DBU][TFAc] > [DBU][TFMSA] > [DBU][MSA]. From this prediction, [DBU][Ac] strongly interacted with CO_2 molecule than compare to other studied ILs. The solubility of CO_2in the ILs was predicted by COSMO-Rs, the values of $\log_{10} P$ were observed in the order as [DBU][MSA] > [DBU][TFAc] >[DBU][TFMSA] > [DBU][Ac]. However, from above order, there are some differences between the trend obtained from experimental results and COSMO-RS based prediction. This may be due to the solubility of CO_2depends on other factors such as viscosity of ILs in addition to interaction between CO_2 and ILs molecules which can be addressed by COSMO-RS model[56]. Finally, the another thermodynamic parameter van der Waal's force was calculated, the obtained values were negative for all systems. The order of the values for studied ILs was [DBU][Ac] > [DBU][TFAc] > [DBU][TFMSA] > [DBU][MSA], among the four

ILs, [DBU][Ac]-CO_2 showed highest value (-12.041 J.mol^{-1}) than compare to other systems (-11.371, -10.994 and -11.166 J.mol^{-1}) may be due to viscosity and size of the IL. Among these contributions, the van der Waals force between gas and IL molecules is predominant[58].

Conclusions:

In this study, Four DBU based ILs was synthesized and characterized by spectroscopic techniques. The solubility of CO_2 was measured at 303.15 K and 313.15 K temperature and at 10 bar, 15 bar and 20 bar pressure. As expected, the solubility of CO_2 in studied IL increased with pressure increases while decreased with increasing temperature. Among the four ILs, [DBU][Ac] showed highest CO_2 solubility efficiency (0.7992 and 0.7010 mol/mol at 20 bar pressure and at 303.15 K and 313.15 K, respectively) than compared to other ILs due to formation of new chemical compound through the chemisorption. To determine the CO_2 sorption efficiency in studied ILs, Henry's constant at infinity dilution was predicted from experimental data. Henry's constant for [DBU][Ac] was determined to be 14.71 which was 63.7%, 85.1% and 88.1% lesser than that of [DBU][TFAc], [DBU][TFMSA] and [DBU][MSA], respectively. The constant values is low, the sorption efficiency of ILs is high. The solubility behavior of CO_2-ILs is clearly understood by computing the thermodynamic functions such as ΔG^o, ΔH^o and ΔS^o from experimental data. The thermodynamic properties also reveals that acetate based IL,[DBU][Ac] exhibited highest CO_2 sorption efficiency the other studied ILs at all experimental conditions. Furthermore, FTIR spectrum reveals that there are two new absorption bands were observed at 1701 cm^{-1} and 1695 cm^{-1} which were attributing to the stretching vibration of COO$^-$ (=N-COO$^-$) for acetate based ILs. The data of experimental analysis, Henry's constant, thermodynamic properties and FTIR spectrum are supporting that both chemical and physical absorption occurred between CO_2 and ILs. Moreover, COSMO-RS was performed to understand the CO_2-ILs interactions by study the energy levels and thermodynamic properties. The predicted COSMO-RS data was good agreement with experimental values.

This study provides a viable route to enhance the CO_2 sorption by tuning the physicochemical properties using structural variations in counter ions of ILs. Considering the advantages of high absorption capacity, low cost, easy regeneration including fast absorption rate, we believe the [DBU] based ILs can be recommended as alternatives to some volatile organic amines to be applied in CO_2 capture.

Acknowledgements:

List of abbreviations:

[DBU]: 1,8-diazabicyclo[5.4.0]undec-7-ene

[Ac]: Acetate

[TFA]: Trifluoroacetate

[MSA]: Methanesulfonate

[TFMSA]: Trifluoromethanesulfonate

[C$_2$mim][Ac]: 1-ethyl-3-methylimidazolium acetate

[TETAH][BF$_4$]: Triethylenetetrammoniun borontetrafluoride

C4mim[CF$_3$CF$_2$CF$_2$CF$_2$SO$_3$]: 1-butyl-3-methylimidazolium Nonafluorobutylsufonate

[VBTMA][Arg]: Poly[vinylbenzyltrimethylammonium][Arginate]

[VBTMA][Ala]: Poly[vinylbenzyltrimethylammonium] [alanine]

[emim]:1-ethyl-3-methylimidazolium

[bmim]:1-butyl-3-methylimidazolium,

[bnmim]: 1-benzyl-3-methylimidazolium

[bmpyr]: pyrrolidinium (1-butyl-1methylpyrrolidinium

[bpyn]: pyridinium (N-butylpyridinium

[AMPS]: 2-acryloamido-2-methylpropanesulfonate

PF_6: Hexafluorophosphate

Tf_2N: bis(trifluoromethyl sulfonyl)imide

[BF_4]: tetrafluoroborate

[DMAPHA]: 3-(dimethylamino)-1-propylamine

[EOAC]: ethoxy acetate

[APBIM]: 1-(3-propylamino)-3-butyllimidazolium

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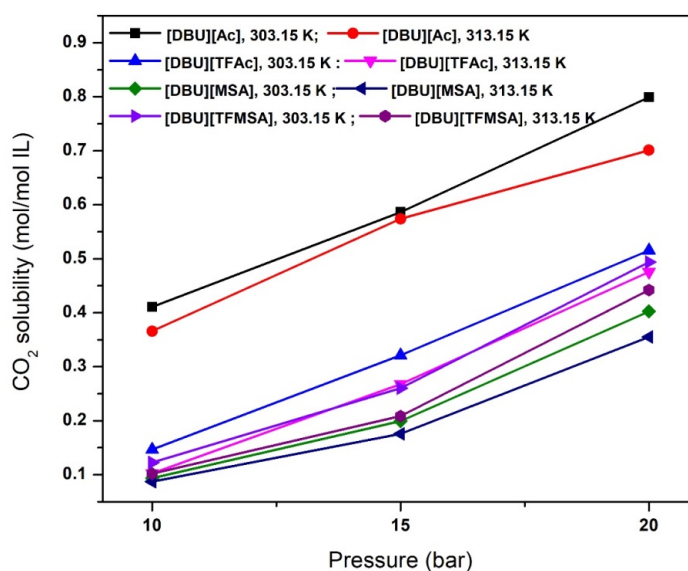**Fig.1** : Block diagram of CO_2 gas solubility system

Fig.2: CO_2 solubility (mol CO_2/mol IL) in studied ILs at 303.15 K and 313.15 K.
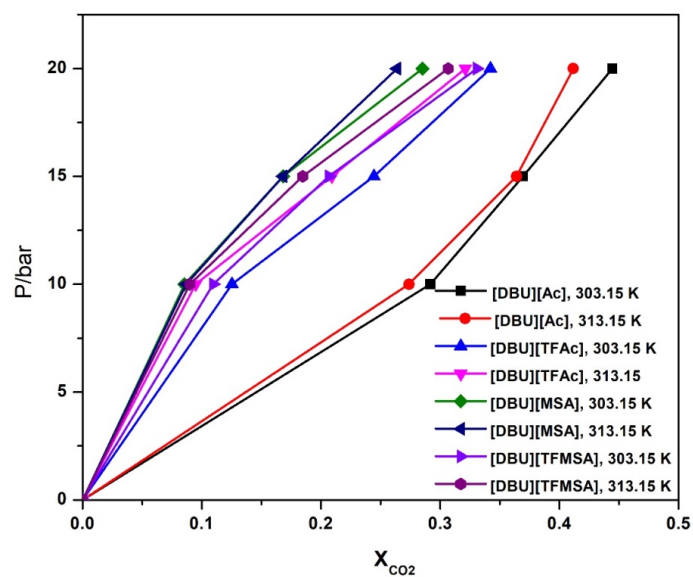
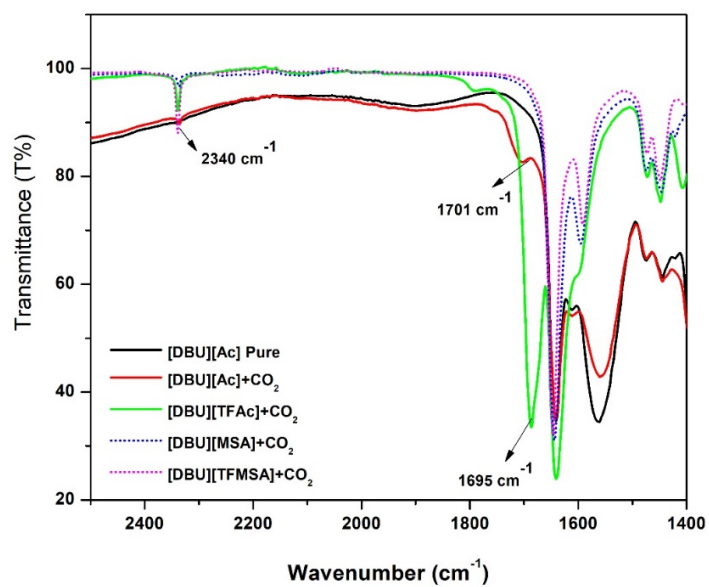**Fig.3** : Henry's constan representation for studied IL at 303.15 K and 313.15 K.

Fig.4: FTIR spectrum of studied ILs after CO_2 capture.

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Fig.5: HOMO-LUMO energy levels of anions and cation with CO_2.

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