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Research Article

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Posted Date: September 20th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-857017/v1

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Version of Record: A version of this preprint was published at Environmental Science and Pollution Research on January 8th, 2022. See the published version at https://doi.org/10.1007/s11356-021-17154-6.
Effect of Physical Properties of Synthesized Protic Ionic Liquid on Carbon dioxide Absorption Rate

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Abstract
Concentration of carbon dioxide gas has accelerated from the last two decades which cause drastic changes in the climatic conditions. In industries, carbon capture plants use volatile organic solvent which causes many environmental threats. So, a low-cost green absorbent has been formulated with nontoxicity and high selectivity properties for absorbing carbon dioxide gas. This paper contains the synthesis process along with the structure confirmation using ¹H NMR, ¹³C NMR, FT-IR, and mass spectroscopy. Density, viscosity, and diffusivity are measured at different ranges with standard instruments. The kinetic studies were also conducted in a standard predefined-interface stirred-cell reactor. The kinetic parameters were calculated at different parameters like agitation speeds, absorption temperature, initial concentrations of ionic liquid, and partial pressure of carbon dioxide. The reaction regime of carbon dioxide absorption is found to be in fast reaction kinetics with pseudo first order. The reaction rate and the activation energy of CO₂ absorption are experimentally determined in the range of 299 K to 333K with different initial concentrations of ionic liquid (0.1-1.1 kmol/m³). The second order rate constant and activation energy of carbon dioxide absorption in the synthesized ionic liquid is found to be (6385.93 to 12632.01 m³ mol⁻¹ s⁻¹) and 16.61 kJ mol⁻¹ respectively. This solvent has shown great potential to absorb CO₂ at large scale.

Keywords: Protic Ionic Liquids (PILs); Gas-Liquid Interface; NMR; FTIR; Carbon-dioxide Absorption; Stirred-Cell Reactor; Kinetic Studies.
Abbreviations

A  Arrhenius Pre-exponential factor, m³/mol s
a  volumetric Gas-Liquid Interfacial Area, m⁻¹
B  base (water)
C_A  the concentration of species A in the liquid phase in the foam film, k mol/m³
C_B  the concentration of reactant B in the liquid phase in the storage section at time t, k mol/m³
C_B0  the initial concentration of reactant B in the liquid stream entering the storage section, k mol/m³
C_TETAL  initial Concentration of [TETA] [Lactate], k mol/m³
CO2  Carbon-dioxide gas
C_{2i}  CO₂ concentration at G-L interface, mol/m³
D_A  the diffusion coefficient of reactant A in the liquid phase, m²/s
D_{CO₂}  diffusion coefficient of carbon dioxide in the [TETA] [Lactate] solution, m²/s
D_{H₂O}  diffusivity of CO₂ in water, m²/s
D_s  the diameter of impeller blades in the liquid-phase, m
D_{Stirred−cell}  the inner diameter of stirred tank reactor, m
E_a  Activation energy, kJ/mol
E_A  enhancement Factor
E_i  instantaneous enhancement factor
G-L  Gas-Liquid Interface
H_{CO₂}  Henry’s constant for carbon-dioxide on [TETA] [Lactate] solution
Ha  Hatta Number
ILs  ionic Liquids
k_{i,a}  volumetric mass transfer coefficient, m/s
k_{-1}  the backward first-order reaction rate constant, s⁻¹
k_2  the forward second-order reaction rate constant for the formation of the zwitterion, m³/mol. s⁻¹
k_{ap}  overall pseudo-first order reaction rate constant, s⁻¹
k_B  Rate constant for the deprotonation of the zwitterion by a base, m³/mol. s
n  number of moles, k mol
1. Introduction

Carbon dioxide (CO\(_2\)) levels rose by 2.6 ppm in 2019, faster than the average rate for the last ten years, which was 2.37 ppm. This has drawn a concerned mark globally. The major sectors responsible for CO\(_2\) emission are manufacturing industries and fossil-fuel based industries (Li et al., 2019). So, there is a high demand of improving the existing mitigation methods for minimising the CO\(_2\) level in the atmosphere. Currently, in absorption technology, CO\(_2\) gas is scrubbing using alkanolamines. Among alkanolamines, monoethanolamine (MEA), diethanolamine (DEA), and methyl diethanolamine (MDEA) along with some promoters are widely used. Research is ongoing to find new and eco-friendly solvent having high selectivity and absorption capacity for carbon dioxide that react faster and require less energy to regenerate in comparison to the existing solvents (Liu et al., 2018). The rate of CO\(_2\) absorption and regeneration rate of CO\(_2\)–rich solvent depends upon their chemical composition and thermo physical properties. The biggest limitation with the protic ionic liquids are their continuous increase in viscosity on absorbing carbon dioxide due to the formation of carbamate. So, this article covers the development of ionic liquid from amine, their structure elucidation using \(^1\)H NMR, \(^{13}\)C NMR, FTIR, and mass Spectroscopy. The effect of density and viscosity on the rate of CO\(_2\) absorption also investigated experimentally. In earlier publications, limited reaction kinetics of CO\(_2\) in protic ionic liquids are available. They concluded that these ionic liquids reacted rapidly with CO\(_2\) and were capable of absorbing a high quantity of CO\(_2\) stoichiometrically. This article also contains the detailed kinetic studies of CO\(_2\) absorption in stirred cell reactors. The stirred-cell reactor is a stirred vessel with an undisturbed (flat) gas-liquid interface and both the phases are stirred separately. Due to which the \(k_L (\text{liquid} – \text{side mass transfer coefficient})\) value decreases in comparison to the other reactors like bubble column, jet reactor, etc. For fluids like water and gases like CO\(_2\), O\(_2\) the \(k_L\) values are lying in the range of 2-15×10\(^{-3}\) cm/sec (Gates 1985). For kinetic studies in gas-liquid reactions, stirred cell contactor is probably the most versatile reactor to employ at the lab scale. Many gas absorption studies have been taken in the stirred cells operated at the speed of 20-150 rpm without significant vortex formation. Sauchel and group studied the absorption of ammonia in aqueous acid solution for the manufacture of nitrogenous fertilizers (Sauchel 1960). In 1964, Sharma reported CO\(_2\)-absorption in carbonate buffers with or without a catalyst (Sharma 1964). The absorption studies of oxygen in aqueous sodium sulfite (Linek 1966). Gupta and Sharma, 1967, worked on CO\(_2\)-absorption in barium sulphide (Gupta and Sharma 1967). Miller, 1969, examined the absorption of C\(_2\)H\(_4\) in ethylene dibromide (Miller 1969). Chaudhari and Doraiswamy, 1974, used mechanically agitated contactor for absorption of phosphine in aqueous solutions of formaldehyde and HCl (Chaudhari and Doraiswamy 1974). Sridharan and Sharma (1976) studied the carbon-dioxide absorption rate in amines and...
alkanolamines dissolved in organic solvents such as isopropanol, n-butanol, cyclohexanol, aqueous diethylene glycol, toluene, and o-xylene in the stirred contactor. Oyevaar and Westerterp, 1989, investigated solubility of phosphine in aqueous solutions of sodium hypochlorite and sulfuric acid (Oyevaar and Westerterp 1989). Lahiri et al., 1981, did experimental studies on the dissolution of NO in aqueous solutions of alkaline sodium dithionite (Lahiri, Yadav, and Sharma 1981). Kucka et al., 2003, studied the absorption of CO$_2$ in MEA solution in a stirred cell (Kucka et al. 2003). Jean-Mare et al., 2009, investigated the CO$_2$-absorption in the mixture of N-methyl diethanolamine and triethylenetetramine (Jean-Mare, Amann, and Bouallou 2009). Zhou et al., 2012, analyzed the CO$_2$-absorption kinetics in tetramethylammonium glycinate [N$_{1111}$] [Gly] and 2-amino-2-methyl-1-propanol solution (Stevanovic et al. 2013). Ying and Eimer, 2013, performed a kinetic study of CO$_2$-absorption in aqueous MEA solution at different temperatures and concentrations of MEA (Ying and Eimer 2013). Iliuta et al., 2014, worked out CO$_2$-absorption in diethanolamine/ionic liquid emulsions (Ying and Eimer 2013). All these studies were performed in a stirred tank reactor. Some of the activation energies of CO$_2$ absorption with the stirred cell reactor at ambient condition are tabulated in Table 1.

**Table 1:** Activation energy of the systems studied for CO$_2$ absorption

| CO$_2$ Capturing system | Activation energy (kJ mol$^{-1}$) | References |
|-------------------------|----------------------------------|------------|
| Hexamethylenediamine (HMDA) and sodium glycinate (SG) | 10.76 | (Mondal and Samanta, 2020) |
| BZA–H$_2$O–CO$_2$ | 25.6 | (Mukherjee, Bandyopadhyay and Samanta, 2018) |
| MDEA and [C$_2$OHmim][Gly] | 11.24 | (Sun et al., 2017) |
| [N$_{1111}$] [Gly] and 2-amino-2-methyl-1-propanol | 13.4 | (Zhou, Jing and Zhou, 2012) |
| AMP and [Hmim][Gly] | 8.08 | (Zhou et al., 2016) |
| MEA and [Bmim][NO$_3$] | 11.25 | (Zhang et al., 2014) |
| MDEA and [Bmim][BF$_4$] | 9.06 | (Ahmady, Hashim and Aroua, 2012) |
| MEA and [Bmim][BF$_4$] | 10.04 | (Lu et al., 2013) |
| [P$_{66614}$][pro] and tetraglyme | 43 | (Gurkan et al., 2013) |
| [P$_{66614}$][2-CNpyr] and tetraglyme | 18 | (Gurkan et al., 2013) |
| [TETA] [Lactate]+H$_2$O | 16.61 | This work |
1.1 Proposed Reaction Mechanisms

The chemical absorption reactions of carbon-dioxide with primary and secondary amines are identified well in literature initially by Caplow (1968) followed by Danckwerts (1979) (Sun et al., 2017). This mechanism involves two steps:

(I) First Step: formation of the CO$_2$-amine complex (Caplow, 1968). It includes two steps.

(i) Formation of zwitterion intermediate complex:

\[
CO_2 + R_1R_2NH \rightarrow R_1R_2N^+HCOO^- \quad \ldots (1)
\]

(ii) De-protonation of the zwitterion (Danckwerts, 1979):

\[
R_1R_2N^+HCOO^- + B \rightarrow R_1R_2NCOO^- + BH \quad \ldots (2)
\]

(II) Second Step: Ter-molecular mechanism (Crooks & Donnellan and Alper, 1989) (Thummuru and Mallik, 2017).

Theoretically, one mole of carbon-dioxide gas reacts with two moles of amines, i.e. 0.5 moles of CO$_2$ react per mole of amine, whereas in case of a tertiary amine absorb CO$_2$ in 1:1 mole ratio (Lee et al., 2007). In this research, the synthesized ionic liquid is composed of four amine groups, having two primary amines and two are secondary amines. As per the basicity rule, the secondary amines are more basic and have higher affinity towards CO$_2$ than the primary amines, so the reaction takes place initially at secondary amine.

2. Experimental Work

2.1. Chemicals and Methodology

All chemicals and gases specified in Table 2, were used as purchased, no further purification was carried.

**Table 2**: CAS Reg. No Suppliers, Mass Fraction purity Molecular weight and Molecular formula of the chemicals used

| Chemical | CAS Reg. No. | Suppliers | Mass fraction and Purity | Molecular Weight and Molecular formula |
|----------|--------------|-----------|--------------------------|----------------------------------------|
Purity of gases was checked by ULTIMA-2100 series gas chromatograph of Nettle make. All solutions were prepared using de-ionised water in volumetric glassware.

2.2. Synthesis of Ionic Liquid

Equi-molar quantities of triethylenetetramine and lactic acid were taken in a three-necked round bottom flask equipped with a reflux condenser, a pressure funnel, and a mechanical stirrer. Initially, triethylenetetramine was taken in the round bottom flask and then lactic acid added drop by drop using a pressure funnel with constant stirring at 120 rpm using the mechanical stirrer. As the neutralization reaction produces a lot of heat, which is equal to -9 kcal/mol, the round bottom flask was kept in an ice-water mixture. To avoid any contamination with air, the reaction mixture was placed under the N2 atmosphere. It was then stirred for several hours at room temperature. The completion of the reaction was monitored by TLC. The product was a pale yellow viscous liquid. Product was then washed with dichloromethane 2-3 times to remove impurities. Residual water is removed by vacuum heating at 80°C for 12 hours. The ionic liquid was finally stored-in an airtight flask. The water content of the ionic liquid was analysed using the TGA analysis and found to be 0.01% (w/w).

2.3. Saturation studies of Carbon dioxide absorption

In all absorption experiments, pure carbon-dioxide gas is used. The gas was pre-dried using infrared lamps and passed through a packed bed of 3 Å molecular sieves. The flow rate was 0.002 m³ min⁻¹. Experiments were conducted in a round bottom glass reactor with an effective volume of 500 cm³. The equilibrium study of carbon dioxide absorption was conducted in a 0.7 M solution of the ionic liquid at a temperature of 298.15 K and 1 atm for 70 hours. The reactor was loaded with approximately 300 cm³ of the 0.7 M ionic-liquid solution. The reactor was then sparged with nitrogen to remove all the air impurities present above the interface of the solution before
each experiment. The vapour pressure of the ionic-liquid and solvent in the gas phase of the reactor was assumed to be constant, and equal to the total equilibrium pressure before the introduction of solute gas carbon dioxide to the reactor. Carbon dioxide was introduced into the reactor via mass flow controller (MFC) and a carbon dioxide rota-meter. Absorption reached a thermodynamic equilibrium after a sufficient time period, corresponding to the solubility limit of the gas in the ionic liquid at that temperature. Sample about 1ml of the reaction mixture were taken out at regular intervals of 5 minutes and weighed. The samples were then titrated with 2M HCl solution to analyse the carbon dioxide loading at a regular interval. The experimental setup is depicted in Figure 1.

\[
\text{Moles of CO}_2 \text{ absorbed (}\alpha\text{)} = \frac{(760 \text{ mmHg} - \text{vapour pressure of water at ambient condition in mmHg})(\text{Volume of displaced fluid} - \text{Volume of 2M HCl})}{(\text{wt.of CO}_2 \text{ rich sample } \times R \times T \times 1000)}
\]

2.4. Determination of physical properties of ionic liquids

The physical properties of the pure ionic liquid have a significant impact on gas-liquid reactions (Chen et al., 2020). The viscosity, density, diffusivity, and Henry constant of the synthesized ionic liquid plays an important role in the diffusion process due to which the absorption rate of the carbon dioxide is affected (Littel, Versteeg, and Van Swaaij, 1992). These properties are determined using the standard instruments experimentally and theoretically both.
2.4.1. Viscosity

The dynamic viscosity of the pure ionic liquid was measured at different temperatures from 273 to 388 K using a Rheometer (Make: Anton Paar, Model: MCR302 SN81193479). Watanabe et al. (Tsuzuki et al., 2009) reported that the three main factors for the high viscosity of ionic liquids are due to its size, shape, and interaction between the anion and the cation. The interaction forces between anion and cation are coulombic forces, van der Waals forces, and hydrogen-bonding. Out of these forces, the coulombic forces are responsible and in carbon di-oxide absorbed ionic liquid hydrogen-bonding mainly cause viscosity. The viscosity of ionic liquid limited the diffusivity of the gas molecule in the ionic liquid.

2.4.2. Density

The density of synthesized ionic liquid was measured from 293 to 363 K using a densitometer (Make: DE45, Model: Mettler Toledo). The density of ionic liquid depends on the length of the alkyl chain. With each increase in –CH₂ group, the density of ionic liquid decreases which increases the free volume or sites available for CO₂ interaction.

2.4.3. Diffusivity \(D_{\text{CO}_2}\)

The rate of diffusion plays a significant role in the rate of absorption of a gas in liquid. So, the diffusivity of CO₂ has been determined using the Stokes-Einstein equation at various temperatures in the reactive solution.

I. Diffusivity of CO₂ in water is given by

\[D_{\text{CO}_2}^\mu = 2.35 \times 10^{-6} \exp\left(-\frac{2119}{T}\right) \text{ m}^2\text{s}^{-1}\]  \(\ldots(5)\)

II. Diffusivity of CO₂ in aqueous amine was considered the same for amine-based ionic liquids. (Versteeg and Van Swaaij, 1988)

\[D_{\text{CO}_2}^{\text{aque.amine}} = D_{\text{CO}_2}^\mu \left(\frac{\mu_{\text{H}_2\text{O}}}{\mu_{\text{aque.amine}}}\right)^{0.8} \text{ m}^2\text{s}^{-1}\]  \(\ldots(6)\)

2.4.4. Henry’s law constant \(H_{\text{CO}_2}\)

The solubility of a gas depends on the pressure exerted by a gas on the liquid surface. The pressure is different at different temperatures. So, it is also an important parameter in CO₂ absorption.

The values of Henry’s law constant for the CO₂-H₂O system at different temperatures were obtained from Sander, R. (2015) (Sander, 2015)

\[H_{\text{CO}_2} = 3.03 \times 10^3 \exp\left[-2400 \left(\frac{1}{T} - \frac{1}{298.15}\right)\right] \text{ mol m}^3\text{ Pa}^{-1}\]  \(\ldots(7)\)
2.5. Kinetic Studies

2.5.1. Stirred-cell reactor

In gas-liquid absorption systems, semi-batch and counter-current contacting schemes predominate for better efficiency and absorption (Levenspiel, 1999). A double jacketed stirred-cell reactor was used for the determination of the kinetics of CO$_2$-absorption in ionic liquid solutions. A schematic representation of the stirred-cell reactor, dimensions of the reactor and its internals are shown in fig. 1 and table 3.

Table 3. Dimensions of the Stirred-cell Contactor and its elements

| Element                                      | Dimension/Measurement   |
|----------------------------------------------|-------------------------|
| Volume of the reactor                        | $1.33 \times 10^{-3}$ m$^3$ |
| Total length                                 | 0.2 m                   |
| Inner diameter                               | 0.105 m                 |
| Diameter of gas-side impeller blades         | 0.056 m                 |
| Diameter of liquid-side impeller blades      | 0.05 m                  |
| Number of baffles                            | 4                       |
| Liquid-phase volume                          | $0.5 \times 10^{-3}$ m$^3$ |
| Cross-sectional / gas-liquid interface area  | $8.65 \times 10^{-3}$ m$^2$ |

Figure 2. Schematic representation of Stirred-cell Contactor (adapted from Doraiswamy and Sharma (1984) (1. Gas-outlet port, 2. Gas-inlet port, 3. Gas-side impeller, 4. Liquid-side impeller, 5. Liquid sample port, 6. Shaft).
Both phases were stirred separately using the different impellers to minimize the mass transfer resistance. A pair of 6-bladed-disk-turbine impellers and 4-bladed-disk-turbine impellers of stainless steel were used in gas phase and liquid phase simultaneously. These impellers were mounted on a standard shaft. Digital temperature sensors (PT100) and pressure gauge were provided to monitor the temperature and pressure in real time for measuring CO$_2$-absorption. The temperature inside the reactor was maintained constant to within ± 0.1 °C using a double jacket in which water is circulated continuously. A vacuum pump is also equipped with the gas-outlet port to remove the gases and volatile impurities from the reactor at the beginning and end of the absorption experiments.

2.5.2. Methodology

All experiments were conducted in the above-mentioned reactor in a semi-batch mode with the 0.5 M aqueous solution of synthesised ionic liquid. The ionic liquid solution is charged in/as a batch, and pure CO$_2$ gas is passed continuously through it from the bottom in a semi-batch mode of process. The CO$_2$-absorption experiment begins with the sparging of N$_2$ gas into the reactor at 2 LPM for 15 minutes to eliminate all residues of CO$_2$ or all the gaseous impurities present. Leakages of gas and liquid from the experimental setup were also tested prior to the conduction of experiments using soap solution. A calibrated rota-meter was used to measure the CO$_2$ flow rate, accompanied by a digital mass-flow controller (MFC). Initially, 500 mL of an aqueous solution of ionic liquid was charged into the reactor and then pure CO$_2$ gas was introduced in it through the gas inlet-port. During the experiment, both phases were stirred constantly and individually. At the beginning and end of the experiment, temperature and pH of the liquid-phase were recorded using the pre-calibrated fitted instruments. After a specific period, 1mL of the reacted solution was sampled and tested by the Chittick apparatus (Crossno, Kalbus and Kalbus, 1996) for calculating CO$_2$ gas loading. In-flow of the CO$_2$ reactor and the agitation were stopped at the time the sample was drawn. The absorption runs were repeated for different times until the ionic liquid solution got saturated with CO$_2$ gas. The absorption experiments are also conducted using the same method and by varying the different parameters. Arrhenius plot is also made by conducting the absorption studies at different temperatures and activation energy of CO$_2$ absorption were calculated.

2.5.3. Equations and reactions involved
Figure 3. Schematic representations of (a) Stirred-cell contactor with flat interface, and (b) Partial-pressure and concentration profiles of CO$_2$ in the gas phase and liquid phase, respectively during the diffusion and chemical reaction of CO$_2$ in ionic liquid (fast reaction regime).

The gas-absorption system, i.e. a stirred-cell contactor chosen is shown schematically in fig. 3, illustrates the concentration profiles of carbon dioxide in gas-phase bulk, in gas film, and in the film and in the bulk liquid.

Let us assumed that CO$_2$ gas absorption in ionic liquid solution is an irreversible second order reaction and can be represented as:

General equation for second-order reaction,

\[ A_g + nB_l \rightleftharpoons P_l \quad \ldots (8) \]

Here, A represents the CO$_2$ gas, B represents ionic liquid, and P is the liquid product formed after the chemical absorption reaction between A and B. For our system, the above equation can be modified as,

\[ CO_2(g) + zTETAL(l) \rightarrow P(carbamate)(l) \quad \ldots (9) \]

Consider the following cases of absorption as,

Case 1: When the carbon dioxide reacts entirely in the gas-liquid interface film with film thickness ($\delta$), the enhancement factor is calculated from the following expression (Dudukovic, 1986)

\[ E_A = \frac{J_{CO_2}a}{k_L c_{CO_2}^a} = \frac{1}{k_L a} \cdot \frac{k_H}{V_{aq. TETAL}} \cdot \frac{V_{CO_2}}{P_{CO_2}RT} \left( \frac{dP_{CO_2}}{dt} \right) \quad \ldots (10) \]

\[ Ha = \sqrt{2 \cdot \frac{m}{k_L} \cdot \frac{k_{CO_2} k_{TETAL} (c_{CO_2}^n c_{TETAL}^{m-1})}{c_{TETAL}}} \gg 1 \quad \ldots (11) \]

Case 2: When there is no change in the concentration of ionic liquid in the liquid film, the following condition will be satisfied
The enhancement factor, $E$, is a function of the Hatta number (Ha) and the instantaneous enhancement factor ($E_i$) defined as

$$E_i = \frac{D_{CO_2} + C_{TETAL}^{\partial C_{CO_2} / \partial x}}{2C_{CO_2}^{\partial C_{CO_2} / \partial x}} ... (13)$$

Case 3: For the fast pseudo-first order reaction regime, the following conditions should be satisfied,

Ha > 2, $E_i / H_a > 5$, $H_a \approx E$, and $H_a$ and $k_{ov}$ are related by

$$H_a = \frac{D_{CO_2} k_{ov}}{k_L} , \text{ or } ... (15)$$

The second-order forward reaction-rate constant, $k_2$, can therefore be calculated from

$$k_2 = \frac{(k_{CO_2})^2}{(CO_2)^2 D_{CO_2} C_{TETAL}} ... (17)$$

The governing differential equation for the diffusion and chemical reaction of carbon dioxide in the film can thus be written as

$$D_{CO_2} \frac{d^2 C_{CO_2}}{dx^2} = k_{mn} C_{CO_2}^{m} C_{TETAL}^{n} ... (18)$$

$$= k_m C_{CO_2}^{m} ... (19)$$

Where

$$k_m = k_{mn} C_{TETAL}^{n}$$

and the concentration of the ionic liquid in the solution remains constant throughout the film.

Then, the specific rate of CO$_2$ absorption can be calculated as,

$$R_{CO_2} = C_{CO_2}^{*} \sqrt{2 m+1 D_{CO_2} k_{mn} (C_{CO_2}^{*})^{m-1} C_{TETAL}^{n}} ... (20)$$

The rate of transfer of CO$_2$ from gas to liquid phase can be expressed by the rate expression for liquid film by

$$R_{CO_2}(t) = k_L a (C_{CO_2}^{*} - C_{CO_2}^{bulk}) ... (21)$$

The second-order reaction rate constant, $k_2$, may then be obtained using equation (20).
3. Results and discussion

3.1. Characterization of synthesized ionic liquid

The photograph of synthesized ionic liquid shown in fig.4 is a pale-yellow oily appearance liquid. The structure of ionic liquid was confirmed using various instrumental techniques, viz. FT-IR, $^1$H NMR, $^{13}$C NMR, and Mass spectroscopy. The structure of prepared ionic liquid is shown in table 4.

Table 4. Proposed structure of ionic liquid with IUPAC nomenclature

| Ionic Liquid | Common Name | IUPAC Nomenclature |
|--------------|-------------|--------------------|
| TETAL        | triethylene tetra ammonium Lactate | $\{2-[2\text{-}(\text{aminoethyl})\text{amino}\text{ethyl}]\text{N}(\text{2-azaniumylmethyl})\ \text{amine 2-hydroxypropanoate}}$ |

The prepared ionic liquid is the result of transformation of triethylenetetramine (TETA) to triethylenetetrammonium (TETA⁺) cation and Lactate anion from Lactic acid.

3.1.1. FT-IR data

The IR spectrum of ionic liquid (TETAL) was done using the PerkinElmer infrared spectrophotometer and results are explained using fig.5 and table 5. A Perkin Elmer Spectrum 400 FTIR/FT-NIR Spectrometer was used to analyse both the LDPE and PS dissolving product samples (Perkin Elmer, New Delhi). For analysis, a small layer of sample is put between two KBr pallets. Before testing, KBR powder was finely powdered with a mortar and pestle and dried in a vacuum oven at 60 °C before being formed into pellets with a thickness of 0.8 mm. The
wavelength range of 4000–650 cm\(^{-1}\) was used to obtain infrared spectra. Before comparison with standard spectrum, all spectra were baseline corrected and normalised using the spectrum in-built feature.

Table 5. FT-IR of ionic liquid with its molecular vibrations at different wavelength

| Type of molecular vibrations       | Wave number (cm\(^{-1}\)) |
|------------------------------------|---------------------------|
| N-H stretching,(-NH\(_2\))         | 3390.49 and 3291.22       |
| N-H stretching,(-NH)               | 3354.69                   |
| N-H bending                        | 1597.02                   |
| C-N stretching (aliphatic amines)  | 1141.06-1116.18           |
| N-H wagging                        | 973.67-732.96             |
| NH\(_3^+\) bending                 | 1451.57                   |
| N-CH\(_2\)                         | 2789.61 - 2809.79         |
| -CH\(_2\) (Aliphatic methylene chain) | 2842.76 - 2933.06       |

From FTIR studies, it is revealed that the given synthesised molecule contains both primary and secondary amine basic sites. The presence of basic sites make it suitable for absorbing acidic gases. The molecule is showing multiple strong bands in the range of 2789.61-2809.79 and 2842.76 – 2933.06 for aliphatic amines (–N-CH\(_2\)) and aliphatic alkyl chain.
3.1.2. NMR

Two types of NMR were done: proton NMR (¹H-NMR) and carbon-13 (¹³C-NMR) to check the position and environment of different hydrogen atoms and carbon atoms in the molecular structure of ionic liquid. The characterization was done using a Bruker 300 MHz spectrometer having N₂ as carrier gas. A sample was prepared in deuterated DMSO-d₆. To eliminate the noise disturbance between the DMSO-d₆ and the ionic liquid, a separate capillary tube was used for loading DMSO-d₆ with the ionic liquid in the NMR tube.

¹H-NMR

The residual proton in DMSO-d₆ appeared at 2.50 ppm set as the ¹H NMR external reference. The positions and environment of different hydrogen atoms or protons present in ionic liquid is shown in Figure 6.

![Figure 6. ¹H NMR of synthesized Ionic liquid](image)

**Table 6. ¹H-NMR of synthesized ionic liquid**

| Chemical Shift (ppm) | Proton Environment                      |
|----------------------|-----------------------------------------|
| 1.119                | (small)- 3H, CH₃, DMSO-d₆               |
| 2.347, 2.724, 2.593  | CH₂N                                    |
| 4.4                  | (broad and small)- NH, NH₂              |

The proton NMR of synthesised ionic liquid shows the characteristic chemical shifts which helps in confirming the structure of ionic liquid. The chemical shift at 2.34-2.72 ppm represents the protons associated with carbon and nitrogen in the structure. The broad and small peaks visible at 4.4 ppm denotes the protons associated with primary and secondary amines.
13 C-NMR

13C NMR spectra of ionic liquid was also obtained using Bruker 300 MHz spectrometer having N₂ as carrier gas to finalize the position of different carbon atoms present in the ionic liquid. The different chemical shifts for various types of carbon present in DMSO-d₆ and ionic liquid are discussed below in table 7.

Figure 7. 13C NMR of Synthesized ionic liquid

Fig.7 contains the 13C Chemical Shifts of the ionic liquid cation relative to trimethylsilane (TMS). The 13C Chemical Shifts at 40, 45, and 50 ppm shows the presence of carbon atoms in the environment of primary and secondary amines respectively. The characteristic peak at 179.38 is the confirmed peak of the carboxyl group present in the lactate ion. The carbon associated with the -OH group in lactate ion is shown at 67.38 ppm.

Table 7. 13C NMR of synthesized ionic liquid

| Chemical Shift (ppm) | Type of C-atom   |
|----------------------|------------------|
| 39.5                 | DMSO-d₆, reference peak |
| 40                   | - CH₂N           |
| 45                   | -CNH₂            |
3.1.3. Mass Analysis

The mass analysis of ionic liquid is done using a mass spectrometer with cation and anion moieties, quadrupole, and model: MICROTOF II. The base peak appears at 279.20 m/z and the molecular ion peak appears at 206.1245 m/z. The molecular mass of ionic liquid was approximately 256.20 g mole\(^{-1}\) depicted from the mass spectrum shown in fig. 8.

Figure 8. Mass Spectrum of synthesized ionic liquid

3.2. Saturation studies of Carbon dioxide absorption

The experimental studies of CO\(_2\) absorption reveals that 0.7 M aqueous solution of ionic liquid can absorb up to 1.57 mole of carbon dioxide per mole of ionic liquid at ambient conditions as shown in fig. 9. There is a continuous increase in the CO\(_2\) concentration in ionic liquid with time. After 70 hours of continuous bubbling, the solution
became very viscous which stops the further diffusion of CO$_2$ molecules in it and it showed levelling off in the concentration of CO$_2$.

![Figure 9: carbon dioxide absorption in 0.7M aqueous solution of TETAL](image)

As per the literature, in the beginning of absorption the carbamate formation predominated but the end carbamate is converted into bicarbonates which are water soluble. By wet chemistry test, it was confirmed as the end product is ammonium bicarbonate. A lower energy is required to break the bicarbonate bond in comparison to the carbamate as calculated from Gaussian 03. Thus, carbon dioxide rich ionic liquid requires less energy for regeneration.

\[
\text{NH}_4\text{HCO}_3 \xleftrightarrow{} \text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}, \quad \Delta H = 15.8 \text{ kcal/mol}
\]

\[
\text{RNHCOOH} \xleftrightarrow{} \text{RNH}_2 + \text{CO}_2, \quad \Delta H = 38.6 \text{ kcal/mol}
\]

The kinetic studies of CO$_2$ absorption reaction in the synthesized ionic liquid triethylenetetrammonium lactate (TETAL) were conducted at different temperatures 299, 308, 313, 323, and 333 K and initial concentrations of TETAL ranged from 0.1 to 1.1 kmol m$^{-3}$. The effect of various factors and experimental conditions are discussed in detail in this section.
3.3. Effect of different parameters on rate of CO$_2$ absorption

3.3.1. Viscosity

Viscosity of solvent in gas liquid absorption reactions plays a very important role in chemical kinetics. Most of the ionic liquids are highly viscous due to which the pumping cost increases (Mota-Martinez et al., 2018). The viscosity of the ionic liquid affects the diffusivity of gas molecules. Therefore, the viscosity of the synthesized ionic liquid was measured as a function. The change in viscosity is very fast with increase in temperature as shown in fig. 10.

![Figure 10. Variation in Viscosity of [TETA] [Lactate] with temperature](image)

This indicates that at 308 K its viscosity is similar to water solvent. On this basis the diffusivity constant can be taken as the same for the same concentration and temperature. All the other hydrodynamic properties which play an important role in CO$_2$ absorption are calculated and tabulated below in table 8.

**Table 8:** Calculated Viscosity, Henry’s constant and diffusivity data of [TETA] [Lactate] at different temperatures and different concentrations

| C$_{\text{TETAL}}$ (kmol m$^{-3}$) | T (K) | $\mu$$_{\text{aq.TETAL}}$ ($\times 10^{-3}$ Pa s) | $H_{\text{CO}_2}$ ($\times 10^{-4}$ mol m$^{-3}$ Pa$^{-1}$) | $D_{\text{CO}_2}$ ($\times 10^{-9}$ m$^2$ s$^{-1}$) |
|---|---|---|---|---|
| 0.1 | 299 | 1.091 | 2.14 | 1.64 |
|    |    |    |
|----|----|----|
| 308 | 1.052 | 1.92 | 1.78 |
| 313 | 1.001 | 1.75 | 1.92 |
| 323 | 0.948 | 1.57 | 2.14 |
| 333 | 0.892 | 1.43 | 2.48 |
| 299 | 1.097 | 2.1  | 1.63 |
| 308 | 1.064 | 1.9  | 1.77 |
| 313 | 1.021 | 1.71 | 1.91 |
| 323 | 1.001 | 1.54 | 2.11 |
| 333 | 0.923 | 1.41 | 2.53 |
| 0.5 | 299 | 1.104 | 2.06 | 1.62 |
|     | 308 | 1.084 | 1.86 | 1.74 |
|     | 313 | 1.071 | 1.67 | 1.84 |
|     | 323 | 1.050 | 1.51 | 2.06 |
|     | 333 | 0.929 | 1.39 | 2.50 |
|     | 299 | 1.156 | 2.02 | 1.61 |
|     | 308 | 1.100 | 1.82 | 1.73 |
| 0.7 | 313 | 1.080 | 1.63 | 1.86 |
|     | 323 | 1.056 | 1.48 | 2.05 |
|     | 333 | 1.020 | 1.37 | 2.47 |
|     | 299 | 1.117 | 1.98 | 1.61 |
|     | 308 | 1.092 | 1.78 | 1.73 |
| 0.9 | 313 | 1.048 | 1.59 | 1.85 |
|     | 323 | 0.942 | 1.45 | 2.15 |
|     | 333 | 0.899 | 1.35 | 2.40 |
|     | 299 | 1.124 | 1.94 | 1.60 |
|     | 308 | 1.102 | 1.75 | 1.72 |
| 1.1 | 313 | 1.052 | 1.55 | 1.84 |
|     | 323 | 0.995 | 1.42 | 2.06 |
|     | 333 | 0.902 | 1.31 | 2.39 |
3.3.2. Density

The density of synthesized pure ionic liquid was measured using densitometer (Model: DE45 Mettler Toledo) with a precision of ± 0.005 kg/m³ in the range of 283 to 363. The volume of the sample taken was 15 mL. The decrease in density is showing linear profile with respect to the increase in temperature as depicted in fig. 11. The density and viscosity of the liquid phase have the greatest impact on the packing height design as well as the absorption unit’s capital cost.

![Graph showing the behavior of Density of [TETA] [Lactate] with temperature](image)

Figure 11. The behavior of Density of [TETA] [Lactate] with temperature

3.3.3. Influence of Stirring Speed

In a gas-liquid absorption reaction, the rate of gas absorption also depends on the reactor dimensions, the geometry and number of impellers, and the stirring speed. The absorption rate is directly affected by the diffusional domain for which a large interfacial area was required. In a stirred reactor, the stirring improved the diffusion of the gas into the liquid film (Contreras Moreno et al., 2017). The influence of the stirring speed on the liquid side mass-transfer coefficient was investigated. The agitation speeds were kept relatively low to avoid disturbing the planar interface. The liquid-side mass-transfer coefficient can be represented as (Littel, Versteeg and Van Swaaij, 1992)

\[
k_L = f(\rho, \mu, D_{CO_2}, D_s, N_L, D_{Stirred\, cell}) \quad \text{...}(22)
\]

\[
\frac{dC_{CO_2}}{dt} = \frac{k_La}{V_L} (C^*_{CO_2} - C_{CO_2}^{bulk}) \quad \text{...}(23)
\]

In equation (22), \(k_L \) (liquid side mass transfer coefficient) is a function of \(\rho\), density of absorbing solution, \(\mu\), viscosity of absorbing solution, \(D_{CO_2}\), diffusivity of CO₂ in the absorbing solution, \(D_s\), the diameter of impeller blades in the liquid-phase, \(N_L\), Stirring rate in liquid phase, \(D_{Stirred\, cell}\), the inner diameter of a stirred tank reactor.
It was noticed that the measured $k_La$ increased on increasing the stirring speed up to a certain extent and then it remained constant. This is due to the decrease in the liquid film thickness $\delta$ responsible for the resistance to the mass transfer of carbon dioxide gas molecules. From the experimental measurements shown in the Fig. 12, it is observed that the rate of CO$_2$ absorption appear practically constant between 60-80 rpm. In this range, values of volumetric mass transfer coefficient is same ($k_La$) (fig. 13), therefore the reaction is in the kinetic regime at this stirring speed.

Figure 12. Effect of stirring speed on CO$_2$-absorption rate in 0.1 kmol/m$^3$ ionic liquid solution at 299K and 101.325 kPa
3.3.4. Effect of Initial Concentration of Ionic Liquid and Partial Pressure of CO2 gas

In this study, the pure carbon-dioxide gas was bubbled in different initial concentrations of ionic liquid at 308 K and 101,325 kPa at a flow rate of $2.83 \times 10^{-5}$ m$^3$ s$^{-1}$. The rate of CO$_2$ absorption was also determined with respect to the different partial pressure of CO$_2$ gas by pressure dropping method. As per the studies, on increasing the concentration of ionic liquid, the carbon - dioxide uptake increases up to a certain limit and then becomes constant. During CO$_2$ absorption, the solution temperature also increased by ± 5°C due to an exothermic process but try to maintain it using a double jacket filled with circulated water. From the experimental data, the rate constant at different concentrations of ionic liquid is calculated using the equation is tabulated in table 9. It is also observed that with CO$_2$ uptake, the viscosity of the absorbing solution also increases, which in turn decreases the diffusivity of further CO$_2$ gas and thus the rate becomes constant after some time. The experimental data is plotted in fig. 14.
Figure 14. Effect of initial concentration of [TETA] [Lactate] and partial pressure of carbon dioxide on the rate of absorption (T = 308 K, P = 101.325 kPa, stirring rate in liquid phase, N_L = 80 rpm, stirring rate in gas-phase, N_G = 120 rpm.

Table 9: Calculated value of rate constant of pseudo first order reaction at T = 308 K and P = 101.325 kPa

| C_{TETAL} (kmol m^{-3}) | k_2 (Experimental) (\times 10^3 m^3 mol^{-1} s^{-1}) |
|------------------------|--------------------------------------------------|
| 0.1                    | 1.27                                              |
| 0.3                    | 1.47                                              |
| 0.5                    | 1.67                                              |
| 0.7                    | 1.88                                              |
| 0.9                    | 2.08                                              |
The reaction rate for the studied chemical absorption reaction is found to be first order with respect to both initial concentration of [TETA] [Lactate] and partial pressure of CO$_2$ which is in the good agreement of the available literature (Yuan and Rochelle, 2018) (Blauwhoff, Versteeg and Van Swaaij, 1984).

### 3.3.5. Effect of Temperature on Absorption

The effect of temperature has also been tested on the rate of CO$_2$ absorption. As per the theory, the rate of reaction doubles at every 10 °C increment in temperature. Initially, with an increase in the temperature, the rate of absorption of CO$_2$ gas increases as shown in Fig. 15. At different temperature, the second-order reaction rate constant, $k_2$, can be calculated using the Arrhenius expression (Jamal, Meisen and Jim Lim, 2006)

$$k_2 = A \cdot e^{-\frac{E_a}{RT}} \quad \text{(24)}$$

Here, $A$ is the Arrhenius constant or pre-exponential constant (m$^3$ mol$^{-1}$ s$^{-1}$), $E_a$ represents the activation energy (kJ mol$^{-1}$), and $R$ represents the universal gas constant (0.008315 kJ mol$^{-1}$ K$^{-1}$)

![Graph showing the effect of temperature on absorption rate](image-url)
Figure 15. (a) The rate of CO$_2$-absorption at different temperature in 0.1 kmol m$^{-3}$ of [TETA] [Lactate] solution

(b) Arrhenius plot for CO$_2$-absorption reaction in [TETA] [Lactate] solution

The plot of $\ln k_2$ versus 1000/T, leads from the Arrhenius expression for the kinetic constant

$$\ln ln k_2 = \ln ln A - \frac{E_a}{RT} \quad \ldots(25)$$

From the graph,

$$\ln ln k_2 = 15.443 - 1.9976 \left(\frac{1000}{T}\right) \quad \ldots(26)$$

$$k_2 = 5.09 \times 10^6 \exp\left(-\frac{1997.6}{T}\right) \quad \ldots(27)$$

The second order reaction rate constants follow Arrhenius behavior with the activation energy of 16.61 kJ mol$^{-1}$ measured for [TETA][Lactate] which is in good agreement with similar ILs (Gurkan et al., 2013). Table 10, shows the calculated values of second order rate constant for CO$_2$ absorption at various temperatures.

**Table 10.** Calculated values of second-order rate constant from Arrhenius plot

| Temperature (K) | $k_2$ (m$^3$ mol$^{-1}$ s$^{-1}$) |
|-----------------|----------------------------------|
| 299             | 6385.93                          |
| 308             | 7762.61                          |
The overall reaction rate expression for CO\(_2\)-absorption is therefore deduced as:

\[
R_{CO_2} = 9.48 \times 10^3 m^3 mol^{-1}s^{-1} \cdot C_{TOTAL}^{1.026} \cdot C_{CO_2}^{1.146} \quad \cdots (28)
\]

As, 1.026 \approx 1 and 1.146 \approx 1,

\[
R_{CO_2} = 9.48 \times 10^3 m^3 mol^{-1}s^{-1} \cdot C_{TOTAL} \cdot C_{CO_2} \quad \cdots (29)
\]

4. Observations and Conclusion

This technique of transformation proved to be better for CO\(_2\) absorption at high temperature. In this work we have reported the absorption capacity of synthesized ionic liquid and the effect of physicochemical properties on CO\(_2\) absorption rate. The synthesized protic ionic liquid is easy to synthesize and also a low-cost ionic liquid. The carbon dioxide absorption capacity in aqueous solution of ionic liquid reached up to 1.57 mole of carbon dioxide absorbed /mole of ionic liquid. This represents the very good absorption capacity to cost ratio in comparison with the benchmarked solvent, MEA (0.55 mol of CO\(_2\)/mol of amine). The kinetic regime of carbon-dioxide absorption corresponds to a fast pseudo-first-order reaction for the controlled conditions employed in this research. The second order reaction rate constants follow Arrhenius behavior with the activation energy of 16.61 kJ mol\(^{-1}\) measured for [TETA] [Lactate]. The ILs studied in this work exhibit reactivity comparable to or higher than commonly used ammonium based IL. In aqueous [TETA] [Lactate] solution, the pseudo first-order rate constant at different temperatures for the CO\(_2\)-absorption reaction was found to be 9.48\times10^3 m^3 mol^{-1} s^{-1}. The physical properties like viscosity, diffusivity, and density of ionic liquid played a significant role in the rate of reaction kinetics. At last, the authors conclude the statement that transformation of amines into ionic liquid could be the benchmark solvent for carbon dioxide absorption in future.

Ethics approval and consent to participate

N/A

Consent for Publication

N/A
Availability of data and materials

All data generated or analysed during this study are included in this published article.

Declaration of Competing Interest

The authors declared that there is no conflict of interest.

Funding

Amita Chaudhary reports financial support, equipment, drugs, or supplies from CSIR-UGC Delhi as a Junior Research Fellowship and Senior research Fellowship. She get the administrative support, writing assistance from Chemical Engineering Department, Indian Institute of Technology Delhi.

Authors contributions

Amita Chaudhary: Experiments, Conceptualization, Writing - original draft, Data collection and compilation, manuscript processing.

Ashok N Bhaskarwar: Revising original draft of manuscript and technical guidance.

Acknowledgments

The authors are grateful to CSIR-UGC, Delhi, for providing financial support to one of us for conducting this research work. We would also like to acknowledge the Indian Institute of Technology, Delhi, India, for facilitating us with the research facilities for the completion of this research work.

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