CO₂ capture in alkanolamine/room-temperature ionic liquid emulsions: A viable approach with carbamate crystallization and curbed corrosion behavior

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A B S T R A C T
By making use of alkanolamine/room-temperature ionic liquid emulsions, it has been found practicable to capture carbon dioxide up to stoichiometric maximum (0.5 mole of CO₂ per mole of diethanolamine) through crystallization of CO₂-captured product (DEA-carbamate) by avoiding equilibrium limitations. This enabled easy separation of a reasonably smaller (solid carbamate) volume promising cost effective regeneration. The scanning electron microscopy (SEM) and electrochemical corrosion studies further revealed that inclusion of ionic liquid helped suppress corrosion to an extent as low as 0.31 milli-inch per year.

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1. Introduction

In the energy driven by greenhouse gas (predominantly CO₂) constraints, there are mounting concerns over global warming phenomenon being intensified brusquely by anthropogenic activities. Fossil-fuel based power plants are the largest among stationary sources accounting for approximately 78.6% of carbon dioxide emissions. It is perceived that by the year 2100 there may be a rise of 1.9 °C in the global temperature (Stewart and Hessami, 2005; IPCC, 2005). This has turned carbon dioxide capture and sequestration into an extensively investigated topic nowadays. Carbon dioxide capture processes based on aqueous alkanolamines are the most widely used on industrial scale. Nonetheless, these technologies pose a number of drawbacks, including: equilibrium limitations (Barzaghi et al., 2010; Bishnoi and Rochelle, 2000), high regeneration energy penalty (Idem et al., 2006), degradation/evaporation of amines (Bello and Idem, 2005; Strazisar et al., 2003; Davis and Rochelle, 2009), low gas loadings (Mani et al., 2006; Kohl and Nielsen, 1997), and corrosion of equipment (Kladkaew et al., 2009). In order to lessen the severity of solvent degradation as well as corrosion phenomenon gas loading is kept low (Barzaghi et al., 2010). In addition, certain additives like corrosion inhibitors, antifoaming agents are also used to alleviate the process snags (Veawab et al., 2001; Zhou et al., 2010; Chen et al., 2011). This practice not only increases cost but also supplements to toxicity. To deal with such concerns, proprietary physical solvent processes like rectisol and selexol are being employed (Kohl and Nielsen, 1997). Even so, these require high partial pressures of feed gas as well as refrigeration of the gas/solvent.

In order to bring versatility and robustness to the CO₂ capture systems, a great deal of work is being done in exploitation of ionic liquids in carbon dioxide capture. Because of their unique characteristics, i.e., wide liquidus range, thermal stability, negligible vapour pressure, tunable physicochemical nature and quite reasonable CO₂ solubility, ionic liquids are considered as green alternates (Hasib-ur-Rahman et al., 2010). However, to fully explore capabilities of these promising fluids more knowledge is needed to come up with cost-efficient practicable CO₂ capture methods realistically implementable in industry.
Looking into the current information available about utilization of ionic liquids in CO₂ capture, these alone, like common physical solvents, do not appear competitive enough when compared to gas capture efficiency of aqueous alkanolamine systems. In order to make a new process more cost effective, it must possess higher ability of attenuating the drawbacks faced in current state-of-the-art technologies. Coupling advantages of commodity alkanolamines with those of room-temperature ionic liquids (RTILs) might provide a better route regarding global efficacy and stability (Camper et al., 2008).

In the present study, CO₂ capture behavior of emulsions comprising immiscible alkanolamine dispersed in hydrophobic RTIL continuous phase [diethanolamine (DEA)/1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide emulsions] was examined. We opted to use immiscible phases to ascertain:

- Easy separation of the solid product.
- Diminished exposure of CO₂ capture sites to concomitant water vapours in flue gas, through induction of hydrophobic barrier (RTIL continuous phase) between feed gas and amine droplets (dispersed phase).

A systematic series of experiments have made it possible to investigate the fate of gas-captured product (carbamate) as well as the corrosive action of the fluid on carbon steel. The gas absorption profiles were obtained by thermogravimetric analysis and the precipitated carbamate was analyzed using single crystal X-ray technique. Fourier transform infrared spectroscopy (FTIR) as well as ¹³C NMR methods were employed to further complement the characterization. Linear polarization and Tafel plots were used to probe corrosion behavior. This study may elaborate valuable facts about one of more several cost-effective options to be practicable for industrial scale CO₂ capture.

2. Experimental

2.1. Materials and techniques

1-Alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids (99% purity) were provided by IoLiTec Inc. while diethanolamine (DEA) and Triton® X-100 were purchased from EMD Chemicals. All chemicals were used as received without further purification. Carbon dioxide, nitrogen, oxygen and argon (>99% purity) were obtained from Praxair Canada Inc.

Emulsification was carried out using Omni homogenizer (Omni International) fitted with rotor-stator generator. In case of surfactant stabilized emulsion, [hmm][TF₂N] and Triton® X-100 were mixed first in 2:3 ratio (w/w). And then, after addition of DEA, stirring was continued for 3–4 min at a speed of 6000 rpm.

CO₂ absorption plots were obtained by thermogravimetric analyzer (Perkin-Elmer Diamond TG/DTA) isothermally under 100% carbon dioxide atmosphere. The product characterization was done by single crystal X-ray diffraction and ¹³C NMR means. The FT-IR spectra were recorded with a Nicolet Magna 850 spectrometer (Thermo Scientific, Madison, WI) employing attenuated total reflectance (ATR) technique. Ultrafoil™ 1200e pyrometer was used to determine density of crystalline solid while AR-G2 rheometer (TA Instruments) with parallel plate geometry was used for viscosity analysis. Water content measurements were done by Karl Fischer titrator (784 KFP Titirino, Metrohm AG).

2.2. Crystal structure determination

Crystallographic data measurements were made at 200 K on a Bruker APEX II area detector diffractometer equipped with Mo-Kα monochromated radiation (λ = 0.71073 Å). APEX2 and SAINT programs were used for retrieving cell parameters and data collection (APEX2 Version 2.0-2, 2005; SAINT Version 7.07a, 2003). Data were corrected for Lorentz and polarization effects. Face-indexed and multiscan absorption corrections were performed using XPREP and SADABS programs, respectively (XPREP Version 2005/2, 2005; SADABS Version 2004/1, 2004). The structure was solved and refined by full-matrix least-squares against F² using SHELXS-97 and SHELXL-97 programs (Sheldrick, 1997). Refinement of all non-hydrogen atoms was done with anisotropic thermal parameters. The hydrogen atoms were placed at geometrically idealized positions using a riding model (SHELXL Version 6.12, 2001). Neutral atom scattering factors were taken from International Tables for Crystallography (1992, vol. C). This crystal structure gives a satisfactory checkCIF report.

2.3. Electrochemical corrosion tests

Bio-Logic VSP potentiostat was used to evaluate corrosion occurrence utilizing a rotating disc electrode assembly. The electrochemical tests were conducted by bubbling either pure CO₂ or mixture of CO₂ + O₂ (1:1 ratio by volume) after passing through deionised water in order to saturate with water vapours. Carbon steel 1020 was used as working electrode to study the corrosive behavior of aqueous DEA as well as that of DEA/RTIL emulsion. The setup was comprised of three electrode assembly, i.e., platinum counter electrode, silver/silver chloride (Ag/AgCl/ sat. KCl) reference electrode, and carbon steel working electrode. A disc shaped working electrode having surface area of 0.196 cm² was mounted in Teflon cap. The experiments were carried out in 100 cm³ volume corrosion cell using an oil bath for temperature control and a condenser to minimize evaporation of the experimental fluid. For each run, working electrode surface was successively polished with 600 grit SiC paper and alumina (5 μm particle size) suspension, respectively, followed by sequential degreasing with acetone and rinsing with deionized water. Each time, during an electrochemical test, bubbling of respective gas/gaseous mixture was initiated at a flow rate of 70 cm³/min under atmospheric pressure, 1 h prior to the commencement of polarization run. After the accomplishment of required conditions a computer controlled potentiostat was used to carry out linear polarization resistance (LPR) measurements starting from a cathodic potential of −250 mV to an anodic potential of +250 mV (versus open circuit potential) with a scan rate of 0.166 mV s⁻¹. In all the experiments, 500 rpm of rotation speed was maintained for the working electrode. During this practice, the influence of O₂ as well as that of temperature on corrosion rate was assessed for aqueous solutions of DEA. And then the most severe conditions tested in case of aqueous DEA were used to evaluate the corrosion behavior of carbon steel in DEA/RTIL emulsions.

3. Results and discussion

3.1. Fate of CO₂-captured product (carbamate)

To know the behavior of product (carbamate), CO₂ was bubbled through 30% (w/w) DEA/RTIL emulsions for 2 h at 25 °C and atmospheric pressure amid continued rotor-stator stirring (2000 rpm). The gas capture resulted in precipitation of carbamate in each of three categories involving [EMIM][TF₂N], [BMIM][TF₂N] or [HMIM][TF₂N] ionic liquids (Table 1). Although, in case of DEA/[EMIM][TF₂N] and DEA/[HMIM][TF₂N] schemes, the solid phase rose to the surface rather promptly thus making it quite easy to be separable, promising considerably lesser volume to
regenerate, as established in Fig. 1a–c). This trend depicts that RTIL hydrophobicity as well as density difference (between solid and liquid phases) are responsible for carbamate crystals to easily move out of the liquid as a supernatant solid. Yet, hydrophobic nature of the ionic liquid appeared to be dominating factor in segregation of solid product from the fluid phase, which was quite evident from the carbamate orientation in [HMIM][Tf₂N] based system, in spite of markedly higher viscosity of RTIL (compared to that of [EMIM][Tf₂N]) and minor density difference between the solid/liquid phases. Nevertheless, in surfactant (Triton® X-100) stabilized emulsion, the carbamate product remained dispersed transforming emulsion into suspension (Fig. 1d).

3.2. CO₂ absorption

Isothermal absorption of CO₂ in surfactant (Triton® X-100) stabilized DEA/RTIL emulsion was carried out using thermogravimetric analyzer. The results demonstrated the prospect of maximum gas loading capacity (0.5 mole of CO₂ per mole of DEA) of this novel scheme, without undergoing any momentous effect of equilibrium restraint. Regarding the gas capture rate, thermogravimetric analysis does not show much variation in CO₂ uptake array in case of three emulsion types. The slight disparity seemed to arise from difference in viscosities of the three ionic liquids (Table 1; Fig. 2).

However, as shown in Fig. 3, increase in diethanolamine (DEA) ratio from 15% to 30% (w/w) resulted in relatively slower kinetics of the process. This behavior was expected due to decreased diffusivity (Moganty and Baltus, 2010), owing to greater proportion of more viscous DEA.

The CO₂ capture by diethanolamine (DEA) possibly involves a fairly rational mechanism (1) comprising direct interaction of amine with CO₂ forming zwitterion followed by abstraction of proton, thus consuming a second amine molecule to act as a counter

\begin{table}[h]
\centering
\begin{tabular}{|l|l|l|}
\hline
\textbf{Abbreviation} & \textbf{Name} & \textbf{\(\rho (g/cm^3)\)} & \textbf{\(\eta (cP)\)} \\
\hline
[emim][Tf₂N] & 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide & 1.52 & 34.1 \\
[bmim][Tf₂N] & 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide & 1.44 & 49.6 \\
[emim][Tf₂N] & 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide & 1.37 & 73.5 \\
\text{C₆H₅N₂O₃} & DEA carbamate (CO₂ captured product) & 1.36 & - \\
DEA & Diethanolamine & 1.09 & 469 \\
\hline
\end{tabular}
\caption{Density \((\rho)\) and viscosity \((\eta)\) values measured at 25 °C.}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1.png}
\caption{DEA/RTIL system: (a–c) [without surfactant] after CO₂ capture; (d) [with surfactant] before and after CO₂ capture.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig2.png}
\caption{CO₂ capture capacity profiles of DEA/RTIL system (surfactant stabilized emulsion; 30%, w/w) at atmospheric pressure and 25 °C.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig3.png}
\caption{CO₂ absorption isotherms for DEA/[HMIM][Tf₂N] surfactant stabilized emulsion obtained at 25 °C.}
\end{figure}
tion to induce stability to carbamate (Caplow, 1968; Danckwerts, 1979; Kumar et al., 2003).

\[
\text{CO}_2 + \text{RR'NH} \rightleftharpoons \text{RR'NH}^+\text{CO}_2^- \\
\text{RR'NH}^+\text{CO}_2^- + \text{RR'NH} \rightleftharpoons \text{RR'NCO}_2^- + \text{RR'NH}_2^+ 
\]

(1)

The crystallization of the carbamate product enabled the process to reach completion avoiding any equilibrium limitations specifically faced in aqueous amine systems. Furthermore, separation of carbamate solid would provide an imperative opportunity in reducing regeneration costs.

3.3. Characterization of crystalline product

Superior hydrophobicity (Freire et al., 2007), relatively higher CO2 solubility by virtue of longer alkyl side-chain (Anderson et al., 2007; Almantariotis et al., 2010), as well as reasonably good separation of solid carbamate from liquid phase, eased the selection of [HMIM][TF2N] as continuous phase in the process for further evaluation specifically in DEA-carbamate characterization and corrosion studies.

As there is no involvement of water in the gas capturing fluid, single crystal analysis established that there was no question of bicarbonate or carbonate species (found in aqueous amine systems). CO2 absorption occurred only through carbamate formation resulting in 50 mole% mass increase (w.r.t. DEA) as confirmed by the thermogravimetric analysis. The crystallographic information is summarized in Table 2.

![Fig. 4. Basic structural unit in DEA-carbamate (C5H2N2O2) crystal.](image)

The basic structural unit is composed of protonated-DEA cation and DEA-carbamate anion, as shown in Fig. 4. The single crystal X-ray structure analysis has shown that the packing mode is monoclinic with \(Pn\) space group. The average lengths of both \(O(1)-C(1)\) and \(O(2)-C(1)\) bonds (1.2695 Å and 1.2764 Å, respectively; Table S1 in supplementary content) in carbamate anion are quite identical depicting the occurrence of delocalization. Attachment of CO2− moiety (captured CO2) caused to decrease the N(1)−C(2) and N(1)−C(4) bond lengths (1.4596 Å and 1.4633 Å) compared to the respective bonds in counter cation (protonated

<table>
<thead>
<tr>
<th>Table 2: Crystallographic data.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DEA carbamate</strong></td>
</tr>
<tr>
<td>Empirical formula</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_2\text{N}_2\text{O}_6)</td>
</tr>
<tr>
<td>Molecular formula</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_2\text{NO}_4\cdot\text{C}_4\text{H}_2\text{NO}_2)</td>
</tr>
<tr>
<td>Formula weight (M)</td>
</tr>
<tr>
<td>254.29</td>
</tr>
<tr>
<td>Space group</td>
</tr>
<tr>
<td>Monoclinic</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>200(2)K</td>
</tr>
<tr>
<td>Crystal dimensions</td>
</tr>
<tr>
<td>0.47 × 0.11 × 0.09 mm³</td>
</tr>
<tr>
<td>Crystal system</td>
</tr>
<tr>
<td>Monoclinic</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
</tr>
<tr>
<td>(a = 10.684(7)\AA, \alpha = 90^\circ)</td>
</tr>
<tr>
<td>(b = 4.6017(3)\AA, b^\prime = 99.8990(10))</td>
</tr>
<tr>
<td>(c = 12.8334(8)\AA, \gamma = 90^\circ)</td>
</tr>
<tr>
<td>Unit cell volume</td>
</tr>
<tr>
<td>(621.56(7)\AA^3)</td>
</tr>
<tr>
<td>No. of formula units in unit cell (Z)</td>
</tr>
<tr>
<td>(F(000))</td>
</tr>
<tr>
<td>276</td>
</tr>
<tr>
<td>(\theta) range for data collection</td>
</tr>
<tr>
<td>2.30–27.00</td>
</tr>
<tr>
<td>Completeness to (\theta = 27.0^\circ)</td>
</tr>
<tr>
<td>99.8%</td>
</tr>
<tr>
<td>Refections collected</td>
</tr>
<tr>
<td>6808</td>
</tr>
<tr>
<td>Independent reflections</td>
</tr>
<tr>
<td>1356 [(R(\text{int})=0.0183)]</td>
</tr>
<tr>
<td>Observed reflections</td>
</tr>
<tr>
<td>1329 [(I &gt; 2\sigma(I))]</td>
</tr>
<tr>
<td>(R) indices (all data)</td>
</tr>
<tr>
<td>0.0249</td>
</tr>
<tr>
<td>Final (R) indices [(I &gt; 2\sigma(I))]</td>
</tr>
<tr>
<td>0.0244</td>
</tr>
<tr>
<td>Density (calculated)</td>
</tr>
<tr>
<td>1.359 g/cm³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
</tr>
<tr>
<td>0.113 mm⁻¹</td>
</tr>
<tr>
<td>(hkl) range</td>
</tr>
<tr>
<td>(-13 \leq h \leq 13, -5 \leq k \leq 5, -16 \leq l \leq 16)</td>
</tr>
<tr>
<td>Refinement method</td>
</tr>
<tr>
<td>Full-matrix least-squares on (F^2)</td>
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<tr>
<td>Data/restraints/parameters</td>
</tr>
<tr>
<td>1356/2/158</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
</tr>
<tr>
<td>1.266</td>
</tr>
</tbody>
</table>

![Fig. 5. Hydrogen bonding pattern in the compound (DEA-carbamate). H atoms not participating in hydrogen bonding are omitted for clarity.](image)
amine), also evident in $^{13}$C NMR spectra owing to dissimilar environments.

Ionic interactions as well as intensive hydrogen bonding in the crystalline carbamate make impossible for the ionic liquid (1-alkyl-3-methylimidazolium hydrogen bis(trifluoromethylsulfonyl) imide) to dissolve it. The bond distances as well as bond angles, elaborating on the hydrogen bonding configuration, are listed in Table 3. Fig. 5 shows the hydrogen bonding pattern involving two hydrogen bonds for each oxygen of CO$_2^-$ moiety in carbamate anion (see also Fig. S1 in supplementary content). One oxygen is an acceptor of hydrogen bonding from OH of two cations while the other acquires hydrogen bonds from NH$_2$ of two different cations, one of these cations being the same involved in hydrogen bonding with first oxygen of the CO$_2^-$ moiety. A terminal OH of the anion is hydrogen bonded to the equivalent site of neighboring anion while the second terminal oxygen of NH$_2$ moiety forms two hydrogen bonds; with terminal OH of another anion as well as with terminal OH of a cation. Likewise, cation bears five hydrogen bonds. Out of these, two are created between cationic NH$_2$ and CO$_2^-$ moieties of two different anions whereas additional two are formed by one of terminal oxygens (of OH group) with respective CO$_2^-$ and OH moieties of two neighboring anions. The remaining terminal OH forms only one hydrogen bond with CO$_2^-$ moiety of a nearby anion.

The $^{13}$C NMR spectrum (taken in DMSO-d6) of crystalline carbamate displays four peaks in the range of 50.84–61.35 ppm. Out of these, two comparatively more intense peaks (one at 50.843 ppm and another at 58.588 ppm) arise from CH$_3$–CH$_2$ carbons of protonated amine (DEAH$^+$) while two low intensity signals at 51.331 and 61.347 ppm originate from ethylene carbons of carbamate derivative. A low intensity resonance at 162.57 ppm confirms the emergence of carbamate carbon resulting from CO$_2$ capture, as shown in Fig. 6 (see also Figs. S2–S5 in supplementary content). FT-IR technique further validates the existence of carbamate moiety appearing as carbonyl stretching frequency at 1654.68 cm$^{-1}$ in Fig. 7 (see also Figs. S6–S8, supplementary content).

![Fig. 6. $^{13}$C NMR spectrum of crystalline carbamate (retaining traces of [hmim][Tf$_2$N]) taken in DMSO-d6 solvent.](image)

![Fig. 7. FTIR analysis of crystalline product (DEA-carbamate).](image)

<table>
<thead>
<tr>
<th>$\text{D-H - A}$</th>
<th>$d(\text{D-H})$</th>
<th>$d(\text{H - A})$</th>
<th>$d(\text{D - A})$</th>
<th>$\angle(\text{D-H - A})$</th>
<th>Symmetry operators$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(3)-H(3) · O(4)</td>
<td>0.84</td>
<td>1.96</td>
<td>2.7947(19)</td>
<td>176.3</td>
<td>$x - 1/2, -y + 1, z - 1/2$</td>
</tr>
<tr>
<td>O(4)-H(4) · O(5)</td>
<td>0.84</td>
<td>1.92</td>
<td>2.7362(17)</td>
<td>163.2</td>
<td>$x, y - 1, z$</td>
</tr>
<tr>
<td>O(5)-H(5) · O(1)</td>
<td>0.84</td>
<td>1.84</td>
<td>2.6650(15)</td>
<td>168.5</td>
<td>$x + 1/2, -y + 2, z + 1/2$</td>
</tr>
<tr>
<td>O(6)-H(6) · O(1)</td>
<td>0.84</td>
<td>1.88</td>
<td>2.7136(16)</td>
<td>173.6</td>
<td>$x + 1/2, -y + 2, z + 1/2$</td>
</tr>
<tr>
<td>N(2)-H(2A) · O(2)</td>
<td>0.92</td>
<td>1.94</td>
<td>2.8133(16)</td>
<td>158.3</td>
<td>$x, y + 1, z$</td>
</tr>
<tr>
<td>N(2)-H(2B) · O(2)</td>
<td>0.92</td>
<td>1.90</td>
<td>2.7946(16)</td>
<td>163.4</td>
<td>$x, y + 1, z$</td>
</tr>
</tbody>
</table>

$D$: donor atom; $A$: acceptor atom.

$^a$ Symmetry operators used to generate equivalent acceptor atoms.

![Fig. 8. Tafel plots for carbon steel electrode in aqueous DEA under different environments: (a) CO$_2$ bubbling at 25°C, (b) CO$_2$ + O$_2$ bubbling at 25°C, (c) CO$_2$ bubbling at 60°C, (d) CO$_2$ + O$_2$ bubbling at 60°C.](image)

![Fig. 9. Corrosion rate of carbon steel 1020 in: (a) RTIL pure, CO$_2$ + O$_2$ + H$_2$O$_{(\text{aq})}$ bubbling at 60°C, (b) DEA/RTIL emulsion, CO$_2$ + O$_2$ + H$_2$O$_{(\text{aq})}$ bubbling at 60°C, (c) DEA$_{\text{aq}}$, CO$_2$ + O$_2$ bubbling at 60°C.](image)
Table 4
Corrosion rates of carbon steel 1020.a

<table>
<thead>
<tr>
<th>Medium</th>
<th>Environment</th>
<th>Temperature</th>
<th>Corrosion potential (mV)</th>
<th>Corrosion current (µA)</th>
<th>Corrosion rate (mpy)</th>
<th>Water content (%, w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEAaq, 15%</td>
<td>CO₂</td>
<td>25 °C</td>
<td>–729</td>
<td>40.95</td>
<td>95.60</td>
<td>–</td>
</tr>
<tr>
<td>DEAaq, 15%</td>
<td>CO₂ + O₂</td>
<td>25 °C</td>
<td>–604</td>
<td>80.37</td>
<td>187.62</td>
<td>–</td>
</tr>
<tr>
<td>DEAaq, 15%</td>
<td>CO₂</td>
<td>60 °C</td>
<td>–766</td>
<td>124.15</td>
<td>289.82</td>
<td>–</td>
</tr>
<tr>
<td>DEAaq, 15%</td>
<td>CO₂ + O₂</td>
<td>60 °C</td>
<td>–688</td>
<td>137.87</td>
<td>321.84</td>
<td>–</td>
</tr>
<tr>
<td>RTIL (pure)</td>
<td>CO₂ + O₂ + H₂O (exp.)</td>
<td>60 °C</td>
<td>116</td>
<td>0.05</td>
<td>0.11</td>
<td>0.02</td>
</tr>
<tr>
<td>DEAq/IL emulsion</td>
<td>CO₂ + O₂ + H₂O (exp.)</td>
<td>60 °C</td>
<td>–157</td>
<td>0.14</td>
<td>0.31</td>
<td>0.12</td>
</tr>
</tbody>
</table>

a Density: 7.86 g cm⁻³; composition (weight %): 0.20% carbon, 0.50% manganese, 0.04% phosphorus, 0.05% sulfur, balanced by iron.
b Just prior to the start of gas bubbling.

3.4. Corrosion studies

Tafel analysis was accomplished using the extrapolation mode to determine corrosion current (i_corr) which in turn enabled to calculate the corrosion rate, CR:

\[
CR = \frac{(1.29 \times 10^6) \cdot i_{corr} \cdot W}{\rho \cdot A}
\]

where CR is in milli-inches per year (mpy), i_corr is the corrosion current in Amperes, W is equivalent mass of metal specimen in gram per equivalent, \( \rho \) is the density of metal in g cm⁻³ and \( A \) is the area (in contact with experimental fluid) of the rotating disc working electrode in cm².

Fig. 8 presents the Tafel plots generated by performing anodic polarization runs for aqueous amine solutions under different environments. At lower pH (~8) resulting from CO₂ absorption, high temperatures as well as presence of oxygen adjoined to detrimental approach towards corrosion of steel. By increasing the temperature from 25 °C to 60 °C (through 35 °C only), the corrosion rate augmented by more than three-fold. Elevated temperature facilitated fast distribution of corrosion products whereas inclusion of oxygen increased the concentration of oxidizing species, escalating the chances of iron oxidation and thus accelerating the corrosion process.

Potentiodynamic experiments exhibited towering corrosion rate in case of aqueous diethanolamine (15%, w/w) rendering the addition of corrosion inhibitors a mandatory activity that not only adds to the cost but also makes the solvent more toxic (Veawab et al., 2001). The major anodic and cathodic electrochemical reactions occurring in aqueous amine systems during corrosion phenomenon are written below (Soosaiprakasam and Veawab, 2008).

(a) Anodic reaction

\[
Fe \rightarrow Fe^{2+} + 2e^- (oxidation of iron)
\]

(b) Cathodic reactions

\[
2H₂O + 2e^- \rightarrow 2OH^- + H₂↑
\]

\[
2HCO₃⁻ + 2e^- \rightarrow 2CO₃^{2-} + H₂↑
\]

\[
O₂ + 2H₂O + 4e^- \rightarrow 4OH^- 
\]

(c) Corrosion products

\[
Fe^{2+} + 2OH^- \rightarrow Fe(OH)₂
\]

\[
Fe^{2+} + CO₃^{2-} \rightarrow FeCO₃
\]

By replacing aqueous part with hydrophobic room-temperature ionic liquid, [hmim][Tf₂N], it has been possible to reduce corrosion virtually to negligible (Table 4; Fig. 9). Exclusion of water truncated
the probable oxidizers mainly responsible for cathodic reactions (Eqs. (3)–(5)) in aqueous media. This behavior suggests that the RTIL [hmim][Tf2N] was stable under the investigated conditions and did not take part in any of the corrosion-related electrochemical reactions. Thus RTIL not only enabled carbamate product to crystallize out but also made it possible to evade the addition of costly and toxic corrosion inhibitors.

SEM (scanning electron microscope) micrographs of the working electrodes’ surface before and after electrochemical corrosion tests under CO2–O2–H2O(vap.) atmosphere at 60 °C further confirmed the absence of corrosion in case of DEA/RTIL emulsion. Though in aqueous DEA, deterioration of steel is quite evident in Fig. 10.

4. Conclusions

In order to accomplish a more efficient scheme for CO2 capture, we have been able to devise a process by combining advantages of both immiscible alkanolamine (superior CO2 capture efficiency) and hydrophobic room-temperature ionic liquid (excellent thermal stability and practically no volatility). Schimming emulsions with RTIL as continuous phase bearing dispersed alkanolamine droplets may offer a potential opportunity with less CO2 capture cost and enhanced process stability. This has been quite evident from our experimental results for CO2 capture and corrosion rate measurements. Enabling carbamate (CO2–captured product) to crystallize out of the continuous phase, it has been possible to run the process at higher rates reaching maximum gas loading capacity, thus avoiding equilibrium limitations – a major obstacle in case of aqueous alkanolamines. The insolubility of the product also offers the advantage of regenerating a smaller volume with less energy consumption. Negligible corrosion phenomenon further helps establish the benefit of alkanolamine/RTIL emulsions. Though stabilization (through surfactant addition) of emulsion was required for time-consuming thermogravimetric/electrochemical experimentation, carbamate separation and consequently amine regeneration appeared to be far easier and hence cost-effective without the use of Triton X-100. In addition, hydrophobic barrier of RTIL continuous phase might help eliminate the dehydrating step during subsequent regeneration of amine and stripping of pure CO2 from thermal heating of the recovered solid carbamate cake.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijggc.2011.10.014.

References


