CO₂ Capture Process and Corrosion of Carbon Steel in [Bmim][Lys]-K₂CO₃ Aqueous Solutions

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The corrosion of carbon steel in carbonated 1-butyl-3-methylimidazolium lysinate ([Bmim][Lys])potassium carbonate (K_2CO_3) aqueous solution was investigated by using a CHI602E electrochemical analyser. The time-dependent absorption capacity, polarization behaviour and corrosion rate of carbon steel in carbon dioxide (CO₂)-loaded K_2CO_3 aqueous solution and [Bmim][Lys]- K_2CO_3 aqueous solution were measured. The effects of temperature, the mass fraction of [Bmim][Lys]/ K_2CO_3 and CO₂ loading on the corrosion rate were demonstrated. The pH values of CO₂-loaded K_2CO_3 -[Bmim][Lys] aqueous solutions were measured, and the variations in H⁺ concentration and the effect of H⁺ concentration on the corrosion rate were analysed. Our experiments showed that when activated by [Bmim][Lys], K_2CO_3 aqueous solution demonstrated a higher CO₂ absorption capacity, higher CO₂ absorption rate and lower corrosion rate for carbon steel. Compared with the commercially applied diethanolamine (DEA, 3%) - K_2CO_3 (25%) aqueous solution, the [Bmim][Lys] (7.5%)-activated K_2CO_3 (25%) aqueous solution can not only achieve a higher CO₂ absorption capacity, lower the corrosion of carbon steel and achieve a similar CO₂ absorption rate but also decrease the energy cost due to its advantages of higher concentration and lower water content; thus, the investigated solution has very good application potential in the CO₂ capture process.

Keywords: K₂CO₃, [Bmim][Lys], CO₂, absorption, corrosion.

1. INTRODUCTION

In recent decades, the reduction of carbon dioxide (CO₂) emissions has attracted increasing attention around the world [1,2], and many technologies [3-7] have been proposed for separating CO₂ from various gas streams. Among the currently available technologies, chemical absorption is considered one of the most effective approaches due to its satisfactory CO₂ removal efficiency and absorbent regeneration efficiency [8].

As a typical representative of chemical absorption, potassium carbonate (K_2CO_3)-based absorption technology has been commercially used for many years [9,10] because it has the advantages of low cost, low toxicity, low heat of absorption, low solution loss, no formation of heat-stable salts and no thermal and oxidative degradation [10]. However, the K_2CO_3 -based absorption process also has drawbacks such as a slow absorption rate, leading to poor CO₂ mass transfer [11-15]. Since the postcombustion CO₂ absorption process must operate under flue gas conditions, such as a relatively low temperature and atmospheric pressure, enhancing the absorption rate is necessary. In addition to the poor CO₂ mass transfer, the serious corrosion of carbon steel is another drawback in the K_2CO_3 -based absorption process and may severely damage the equipment, such as absorbers, pipelines and valves, and result in a reduction in the process efficiency and increase in maintenance costs.

To minimize the corrosion of carbon steel, many researchers have focused on the control of K_2CO_3 concentration, operating temperature and CO_2 loading; however, a decrease in K_2CO_3 concentration and CO_2 loading may lower the absorption capacity and increase the energy cost. The development of a new absorbent that can simultaneously achieve a higher CO_2 absorption capacity and higher CO_2 absorption rate yet lower the corrosion rate of carbon steel is of great significance for improving K_2CO_3 -based absorption technology.

Previous studies have shown that many activators such as amines [16-21] and amino acids [22-26] can significantly enhance the CO₂ absorption in K₂CO₃ aqueous solutions. In addition to amines and amino acids, ionic liquids (ILs) are considered to be potential activators for facilitating the rate of absorption. As new promising solvents for CO₂ capture, ILs have numerous advantages, such as nonvolatility, a low melting point, ease of recycling, high thermal stability and adjustable physicochemical structures [27-29]. In recent decades, ILs have attracted increasing attention in the CO_2 capture process. Hu [30] investigated the CO₂ absorption performance of five synthesized amino ILs, and the results showed that ILs with more amino groups have a higher CO₂ absorption capacity. Wappel [31] measured the viscosities and CO₂ absorption kinetics of a series of ILs and blends of ILs and compared the results with reference data for 30 wt% K₂CO₃ aqueous solution. The results showed that the viscosities of all diluted ILs and selected IL blends were larger than those of the K₂CO₃ aqueous solutions and that the CO₂ absorption kinetics of the ILs and IL blends were much faster than those of the K₂CO₃ aqueous solutions. Moreover, metals and alloys have a very low corrosion tendency in aggressive solution when ILs containing imidazole and its derivatives are added because the lone electron pairs in nitrogen atoms are likely to promote the adsorption of compounds on metallic surfaces [32-34]. Recently, Zhang [35,36] and Ashassi-Sorkhabi [37] evaluated the corrosion of mild steel in acidic solution containing alkylimidazolium ILs. Their results showed that the mild steel exhibited very low corrosion performance. Zheng [38] investigated the corrosion behaviour of mild steel in sulfuric acid solution containing two imidazolium-based ILs (1-octyl-3-methylimidazolium bromide ([OMIM]Br) and 1-allyl-3octylimidazolium bromide ([AOIM]Br)). Their results showed that the mild steel exhibited a lower corrosion performance in sulfuric acid containing [AOIM]Br than in sulfuric acid containing [OMIM]Br. Therefore, ILs containing imidazolium should cause little corrosion to mild steel equipment when absorbing CO₂. In addition, ILs with anionic amino acids are considered good CO₂ absorbents because they can achieve equimolar CO₂ absorption and take advantage of their negligible vapor pressure and remarkable thermal stability [39-41]. Among ILs, amino-acid ionic liquids (AAILs) are very attractive

because they have large CO₂ solubility and can facilitate CO₂ absorption in aqueous solutions of amines [42-47]; in particular, 1-butyl-3-methylimidazolium lysinate ([Bmim][Lys]) has very strong affinity to CO₂ because there are two primary amine functional groups present in basic and polar side chains on its molecular structure [48,49]. Fu [42] showed that when activated by very small amount of [Bmim][Lys], MDEA-[Bmim][Lys] aqueous solution can absorb CO₂ with a high rate and high capacity.

According to the aforementioned advantages, it is reasonable to expect that both the CO₂ absorption performance and corrosion of carbon steel can be considerably improved in K₂CO₃-[Bmim][Lys] aqueous solution. However, studies concerning the CO₂ absorption capacity and corrosion behaviour of carbon steel in CO₂-[Bmim][Lys]-K₂CO₃ aqueous solution have rarely been reported to date. The main purpose of this work is to simultaneously achieve a higher CO₂ absorption capacity, higher CO₂ absorption rate and lower corrosion to carbon steel by using [Bmim][Lys]-activated K₂CO₃ aqueous solutions. To this end, (1) the time-dependent CO₂ absorption capacity and absorption rate were measured; (2) the polarization behaviour and corrosion rates of carbon steel in CO₂-K₂CO₃ aqueous solutions and CO₂-[Bmim][Lys]-K₂CO₃ aqueous solutions were measured; (3) the pH values of CO₂-loaded K₂CO₃-[Bmim][Lys] aqueous solutions were measured, and the variation in H⁺ concentration and the effect of H⁺ concentration on corrosion rate were analysed; and (4) the effects of solution concentration, temperature and CO₂ loading on corrosion rate were demonstrated.

2. EXPERIMENTAL

2.1 Solutions and materials

The samples used in the absorption experiments are presented in Table 1. They were used without further purification. An analytical balance (Jingtian FA1604A) with an accuracy of 0.1 mg was used to weigh all required chemicals. The water contents (in mass percent) of K₂CO₃ and [Bmim][Lys] were respectively 0.22% and 0.21% (determined by using the Karl Fischer method, as stated by the supplier), and this content were accounted for upon solution preparation. K₂CO₃ and K₂CO₃-[Bmim][Lys] aqueous solutions were prepared by adding deionized water (electrical resistivity >15 MΩ·cm at 298 K) obtained from a Heal Force ROE (reverse osmosis electrodeionization)-100 apparatus to weighed quantities of K₂CO₃ and [Bmim][Lys]. Taking the purities and water contents into account, the uncertainties of the mass fraction of K₂CO₃ and [Bmim][Lys] were estimated to be $u(w) = \pm 0.005$.

The specimens for corrosion tests were made of carbon steel (AISI 1020) in this work. The chemical composition (in mass percent, %) was 0.20 C, 0.25 Si, 0.50 Mn, 0.03 P, 0.03 S and Fe (balance). The specimens (10 mm×10 mm×3 mm) were ground, polished and then sealed with resin with an exposed area of 10 mm×10 mm. The specimens were connected with copper wires to make the working electrodes for the electrochemical tests.

| Chemical name | CAS | Purity (mole fraction, as stated by the supplier) | Water content (mass percent, as stated by the supplier) | Source |
|--------------------------------|--------------|--|---|----------------------------------|
| K ₂ CO ₃ | 584-08-7 | $x \ge 0.99$ | 0.22% | Fuchen Chemical Reagent |
| [Bmim][Lys] | 1084610-48-9 | $x \ge 0.99$ | 0.21% | Chengjie Chemical Reagent |
| carbon dioxide | 124-38-9 | $x \ge 0.9999$ | | Hanjiangxue Gas |
| water | 7732-18-5 | Electrical resistivity > 15 M Ω cm at T = 298 K | | Heal force ROE- 100 apparatus |

 Table 1. Sample description.

2.2 Apparatus and procedure

The experimental system for absorption is shown in Fig. 1, with all the various parts of the apparatus and the measuring devices included. During absorption, CO₂ from a high-pressure tank (concentration $C_0 \ge 0.9999$) passed through the mass flow controller to maintain a constant flow rate of v_{CO2} =200 ml/min, then flowed into the absorption bottle and was absorbed by the solution. The residual and unabsorbed gas first flowed into the desiccator, then into the CO₂ analyser and finally into the mass flow metre (MFM). The CO₂ concentration (C_i) was measured by the CO₂ analyser, and the flow rate (v_i) was measured by the MFM. C_i , v_i and the corresponding time t_i were simultaneously recorded by the computer (interval time $\Delta t = 1$ s). The absorption was terminated when there was almost no change in v_i for 100 s. The mass of absorbed CO₂ was calculated from $273.15 \times 44/22.4 \times [0.9999 v_{CO2}t/T_0 - \Sigma v_i C_i \Delta t/T_1]$, in which t is the total absorption time, and T_0 and T_1 are the temperatures of CO₂ flowing out of the mass flow controller (MFC) and desiccator, respectively. After the mass of absorbed CO₂ was obtained, the CO₂ loading (α) was calculated from $\alpha = n_{CO2}/(n_{K_2CO3} + n_{[Bmim][Lys]})$, in which n_{CO2} is the moles of loaded CO₂, and $n_{K_2CO_3}$ and $n_{[Bmim][Lys]}$ are the moles of K₂CO₃ and [Bmim][Lys], respectively, in the unloaded aqueous solution. Carbonated aqueous solutions with different CO₂ loadings were prepared according to the methods mentioned in the work of Weiland [50], Amundsen [51] and Fu [42,44,52]; once the carbonated solution had been prepared using the equipment shown in Fig. 1, varying proportions of unloaded and loaded solutions were mixed together to produce a set of samples.

The experimental system for corrosion testing was composed of one electrochemical workstation (CHI602E, manufactured by Shanghai Chenhua instrument Co., Ltd.), one thermostat water bath, one corrosion cell and one data recorder. Within 1 hour prior to the electrochemical tests, the specimens were mechanically polished with 600, 1000 and 1500-grit silicon carbide metallurgical papers, degreased with methanol, dried with hot air and stored in a dry cabinet. Electrochemical tests were then carried out in a 500 ml corrosion cell immersed in a thermostatic bath. The temperature ranged from 303.2 K to 323.2 K. A three-electrode electrochemical cell was used (working, reference and counter electrode). The carbon steel was used as the working electrode. A Pt electrode was employed as the counter electrode, and a Hg/HgCl₂ electrode was employed as the reference electrode. Once the open circuit potential

(OCP) of the cell was stable (OCP<1 mV/min), the polarization curves were measured by the CHI602E with a computer recording the data (potential range: -200 mV to +200 mV vs. OCP, scan rate: 0.0002 V/s).



Figure 1. Schematic diagram of absorption.

3. RESULTS AND DISCUSSION

3.1 CO₂ absorption performance

The absorption performances of CO₂ in [Bmim][Lys]-activated K₂CO₃ and diethanolamine (DEA)-activated K₂CO₃ aqueous solution were measured at 313.2 K. The mass fraction of K₂CO₃ (w_{K2CO3}) was 0.25. The mass fractions of [Bmim][Lys] ($w_{[Bmim][Lys]}$) and DEA (w_{DEA}) were 0.075 and 0.03, respectively. Moreover, the absorption performance and capacity of CO₂ in K₂CO₃ aqueous solution at 313.2 K and w_{K2CO3} =0.75 were taken directly from our previous work [53]. The time-dependent CO₂ absorption capacities are shown in Fig. 2. One finds from the plot that without [Bmim][Lys], CO₂ was absorbed slowly in K₂CO₃ aqueous solution. When a small amount of [Bmim][Lys] was added to the K₂CO₃ aqueous solution, the absorption time corresponding to saturation decreased significantly, and the amount of absorbed CO₂ increased substantially. In particular, the mass of absorbed CO₂ changed from 6.46 g CO₂/100 g aqueous solution to 7.53 g CO₂/100 g aqueous solution, which indicates that [Bmim][Lys] can not only be used as an accelerator but also absorb a certain amount of CO₂. Compared with [Bmim][Lys] (7.5%), DEA (3%) also accelerated the absorption of CO₂, but the mass of absorbed CO₂ was only 6.78 g CO₂/100 g aqueous solution.



Figure 2. Time-dependent CO₂ absorption amount in K₂CO₃, K₂CO₃-[Bmim][Lys] and K₂CO₃-DEA aqueous solutions. T=313.2 K. \bullet $w_{K2CO3}=0.25$; \triangle $w_{K2CO3}/w_{[Bmim][Lys]}=0.25/0.075$; \blacksquare $w_{K2CO3}/w_{DEA}=0.25/0.03$. Symbols: experiments from this work. Lines: trend lines.

To quantitatively demonstrate the enhancement derived from [Bmim][Lys] and DEA, we followed Chowdhury [54] and calculated the absorption rate (*V*, g CO₂/100 g aqueous solution/min) by the formula 0.5*m/t_{0.5} (m is the mass of absorbed CO₂, and t_{0.5} is the absorption time at which 50% of the absorption capacity is achieved). The absorption rates (g CO₂/100 g aqueous solution/min) of CO₂ in aqueous solutions of K₂CO₃, K₂CO₃-[Bmim][Lys] and K₂CO₃-DEA were respectively 0.12, 0.34 and 0.37, indicating that DEA and [Bmim][Lys] led to very similar enhancements of the CO₂ absorption rate. Taking into account the much higher absorption capacity and similar absorption rate, [Bmim][Lys]-K₂CO₃ aqueous solution has a better application potential in the CO₂ capture process than DEA-K₂CO₃ aqueous solution.

3.2 Corrosion behaviour

The corrosion behaviour of carbon steel in carbonated aqueous solutions of K_2CO_3 and K_2CO_3 -[Bmim][Lys] were measured. The mass fractions of K_2CO_3 and [Bmim][Lys] ranged from 0.15 to 0.25 and 0.025-0.075, respectively. The temperatures ranged from 303.2 K to 323.2 K.

Fig. 3 shows the effect of temperature on the potentiodynamic polarization curves of carbon steel in CO_2 -saturated K_2CO_3 -[Bmim][Lys] aqueous solutions. Generally, the cathodic and anodic current densities respectively refer to the metal dissolution rate and oxidant reduction rate [55]. An increase in liquid temperature tends to increase both the cathodic and anodic current densities, which may result in

an increase in both the metal dissolution rate and oxidant reduction rate, and the corrosion process can consequently be accelerated [56].



Figure 3. Effect of temperature on the potentiodynamic polarization curves of carbon steel in CO₂saturated aqueous solutions of K₂CO₃-[Bmim][Lys]. $w_{[Bmim][Lys]}=0.075$. $\Box T=303.2$ K; \bullet T=313.2 K; $\triangle T=323.2$ K. (a): $w_{K2CO3}=0.15$. (b): $w_{K2CO3}=0.25$. Symbols: experiments from this work. Lines: trend lines. Fig. 4 shows the effect of solution concentration on the potentiodynamic polarization curves of carbon steel in CO₂-saturated aqueous solutions of K₂CO₃-[Bmim][Lys] and K₂CO₃.



Figure 4. Potentiodynamic polarization curves of carbon steel in CO₂-saturated aqueous solutions of K₂CO₃-[Bmim][Lys] and K₂CO₃. *T*=323.2 K. (a): $\Box w_{K2CO3}/w_{[Bmim][Lys]}=0.15/0.025$; $\blacksquare w_{K2CO3}=0.175$. (b): $\bigcirc w_{K2CO3}/w_{[Bmim][Lys]}=0.20/0.025$; $\blacktriangle w_{K2CO3}/w_{[Bmim][Lys]}=0.20/0.05$; $\Box w_{K2CO3}/w_{[Bmim][Lys]}=0.20/0.075$. Symbols: experiments from this work. Lines: trend lines.



Figure 5. Effect of CO₂ loading on the potentiodynamic polarization curves of carbon steel in carbonated K₂CO₃-[Bmim][Lys] aqueous solutions. $w_{[Bmim][Lys]}=0.075$, T=313.2 K. $\blacksquare \alpha=0.1$; $\bigcirc \alpha=0.2$; $\blacktriangle \alpha=0.3$; $\diamondsuit \alpha=0.4$. (a): $w_{K2CO3}=0.15$. (b): $w_{K2CO3}=0.20$. Symbols: experiments from this work. Lines: trend lines.

One may find from Fig. 4 (a) that under the same solution concentration, the current density of carbon steel in CO_2 -saturated K_2CO_3 aqueous solution was much larger than that in CO_2 -saturated

K₂CO₃-[Bmim][Lys] aqueous solution, indicating the corrosion of carbon steel in CO₂-saturated K₂CO₃ aqueous solution would be more intense than that in CO₂-saturated K₂CO₃-[Bmim][Lys] aqueous solution [57-59]. Moreover, in Fig. 4 (b), with an increase in solution concentration, both the cathodic and anodic current densities increased; e.g., in the case of E/V=-0.80, the anodic current density corresponding to $w_{[Bmim][Lys]}/w_{K2CO3}=0.025/0.20$ and $w_{[Bmim][Lys]}/w_{K2CO3}=0.075/0.20$ at 323.2 K is respectively 3.16 × 10⁻⁴ and 3.98 × 10⁻⁴ (A/cm²).

Fig. 5 shows the effect of CO_2 loading on the potentiodynamic polarization curves of carbon steel in carbonated K₂CO₃-[Bmim][Lys] aqueous solutions. One finds from the polarization curves that a change in CO₂ loading has a great influence on the current density of the cathode but a small effect on the anodic current density, indicating that the increase in CO₂ loading mainly increases the rate of oxidant reduction and thus leads to a more corrosive environment [55].

Table 2 shows the corrosion parameters obtained from the polarization curves shown in Fig. 3-5, including the corrosion potential (E_{corr}), the corrosion current density (i_{corr}) and the anodic and cathodic Tafel slopes (β_a and β_c , respectively).

| | Experimen | ital categ | ories | | Co | rrosion paramete | ers |
|--------|--------------|------------|-----------|--------------------------|--|-----------------------|-----------------------|
| WK2CO3 | W[Bmim][Lys] | T/K | α | E _{corr} (V) | <i>i</i> _{corr} (A/cm ²) | β_a (mV/decade) | β_c (mV/decade) |
| 0.150 | 0.075 | 303.2 | saturated | -0.801 | 2.291E-05 | 93 | 84 |
| 0.150 | 0.075 | 313.2 | saturated | -0.828 | 3.513E-05 | 168 | 86 |
| 0.150 | 0.075 | 323.2 | saturated | -0.844 | 5.346E-05 | 152 | 94 |
| 0.250 | 0.075 | 303.2 | saturated | -0.820 | 3.076E-05 | 159 | 87 |
| 0.250 | 0.075 | 313.2 | saturated | -0.826 | 4.778E-05 | 161 | 129 |
| 0.250 | 0.075 | 323.2 | saturated | -0.844 | 7.222E-05 | 155 | 73 |
| 0.150 | 0.025 | 323.2 | saturated | -0.843 | 4.386E-05 | 105 | 57 |
| 0.175 | 0.000 | 323.2 | saturated | -0.867 | 5.957E-05 | 112 | 55 |
| 0.200 | 0.025 | 323.2 | saturated | -0.849 | 5.455E-05 | 108 | 63 |
| 0.200 | 0.050 | 323.2 | saturated | -0.852 | 5.804E-05 | 155 | 107 |
| 0.200 | 0.075 | 323.2 | saturated | -0.853 | 6.218E-05 | 92 | 67 |
| 0.150 | 0.075 | 313.2 | 0.1 | -0.963 | 1.309E-06 | 82 | 62 |
| 0.150 | 0.075 | 313.2 | 0.2 | -0.929 | 5.455E-06 | 88 | 89 |
| 0.150 | 0.075 | 313.2 | 0.3 | -0.910 | 1.069E-05 | 82 | 51 |
| 0.150 | 0.075 | 313.2 | 0.4 | -0.895 | 1.353E-05 | 112 | 94 |
| 0.200 | 0.075 | 313.2 | 0.1 | -0.949 | 3.055E-06 | 62 | 57 |
| 0.200 | 0.075 | 313.2 | 0.2 | -0.929 | 9.164E-06 | 87 | 90 |
| 0.200 | 0.075 | 313.2 | 0.3 | -0.913 | 1.549E-05 | 108 | 79 |
| 0.200 | 0.075 | 313.2 | 0.4 | -0.889 | 1.833E-05 | 91 | 99 |

Table 2. Corrosion parameters obtained from the polarization curves shown in Fig. 3-5.

In general, the reaction of [Bmim][Lys] with CO_2 is believed to be similar to that of alkanolamines and can be briefly described as follows [55,60,61]:

$$CO_2 + 2RNH_2 \leftrightarrow RNHCOO^- + RNH_3^+$$
 (1)

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$$
(2)

$$RNHCOO^{-} + H_2O + H^+ \leftrightarrow RNH_3^+ + HCO_3^-$$
(3)

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \tag{4}$$

The overall reaction of CO₂ in K₂CO₃ aqueous solutions can be written as [62]:

$$\mathrm{CO}_2 + \mathrm{H}_2\mathrm{O} + \mathrm{CO}_3^{2-} \leftrightarrow 2\mathrm{H}\mathrm{CO}_3^{-} \tag{5}$$

The dissolved CO₂ in aqueous solutions of both [Bmim][Lys]-K₂CO₃ and K₂CO₃ was transformed into carbon species such as HCO_3^- and CO_3^2 , and HCO_3^- is considered as a primary corroding agent. The corrosion reaction between HCO_3^- and iron can be described as [55]:

$$Fe + HCO_3^- \rightarrow FeCO_3 + H^+ + 2e^-$$
(6)

One finds from Eqs. (1)-(6) that the HCO_3^- concentration and pH are directly related to the CO₂ loading, $w_{[Bmim][Lys]}$ and w_{K2CO3} . To quantitatively show the relationship among solution concentration, CO₂ loading and hydrogen ion concentration (H⁺), the pH of carbonated K₂CO₃-[Bmim][Lys] aqueous solution was measured at 303.2 K, as shown in Fig. 6. One may find from Fig. 6 (a) that with increasing $w_{[Bmim][Lys]}$ and w_{K2CO3} , the pH decreases rapidly. Moreover, the higher is the CO₂ loading is, the lower the pH, as also shown in the inset plot of Fig. 6 (b).



Figure 6. (a) Effect of [Bmim][Lys] mass fraction on the pH of CO₂-K₂CO₃-[Bmim][Lys] aqueous solutions. CO₂-saturated, $\bigoplus w_{K2CO3}=0.15$; $\square w_{K2CO3}=0.20$; $\bigstar w_{K2CO3}=0.25$. (b) Effects of CO₂ loading on the pH of CO₂-K₂CO₃-[Bmim][Lys] aqueous solutions. $\bigoplus w_{K2CO3}/w_{[Bmim][Lys]}=0.25/0.075$. (a) and (b): *T*=303.2 K. Symbols: experiments from this work. Lines: trend lines.

It seems that the corrosion of carbon steel is dependent on many operating conditions, including the [Bmim][Lys] concentration, K_2CO_3 concentration, temperature and CO_2 loading (HCO₃⁻). To quantitatively estimate the effects of these conditions, we calculated the corrosion rate (R) by using the following formula [63,64]:

$$R \left[\text{mm/y} \right] = 3.27 \times 10^{-3} \times \frac{A}{n\rho} i_{\text{corr}}$$
⁽⁷⁾

0.200

0.225

0.250

where A is the metal atomic weight, and *n* and ρ are respectively the number of transferred electrons and metal density. By combining the measured corrosion current densities and Eq. (7), the corrosion rates of carbon steel in carbonated K₂CO₃ aqueous solutions and carbonated K₂CO₃-[Bmim][Lys] aqueous solutions were determined and are presented in Tables 3-5.

| | | <i>R/</i> (mpy) | |
|--------|---------|-----------------|---------|
| WK2CO3 | 303.2 K | 313.2 K | 323.2 K |
| 0.150 | 10.9 | 16.6 | 25.1 |
| 0.175 | 11.6 | 17.6 | 27.3 |

12.6

13.5

14.8

19.4

21.2

22.6

29.7

32.4

34.7

Table 3. Corrosion rates (*R*) of carbon steel in CO₂-saturated K₂CO₃ aqueous solutions under different mass fractions of K₂CO₃ (w_{K2CO3}) and temperatures. Pressure (*p*) =101 kPa.^{*a*}

^{*a*} Standard uncertainties *u* are u(T)=0.1 K; $u(w_{K2CO3})=\pm 0.005$; u(p)=2 kPa; u(R)=0.1 mpy.

Table 4. Corrosion rates (*R*) of carbon steel in CO₂-saturated K₂CO₃-[Bmim][Lys] aqueous solutions under different mass fractions of K₂CO₃ (w_{K2CO3}) and [Bmim][Lys] ($w_{[Bmim][Lys]}$) and temperatures. Pressure (*p*) =101 kPa.^{*a*}

| | 141 | <i>R</i> /(mpy) | | | |
|--------|--------------|-----------------|---------|---------|--|
| WK2CO3 | W[Bmim][Lys] | 303.2 K | 313.2 K | 323.2 K | |
| | 0.025 | 8.7 | 13.4 | 20.1 | |
| 0.150 | 0.050 | 9.5 | 14.6 | 22.4 | |
| | 0.075 | 10.5 | 16.1 | 24.5 | |
| | 0.025 | 10.8 | 16.5 | 25 | |
| 0.200 | 0.050 | 11.4 | 17.6 | 26.6 | |
| | 0.075 | 12.2 | 18.8 | 28.5 | |
| | 0.025 | 12.7 | 19.4 | 29.3 | |
| 0.250 | 0.050 | 13.4 | 20.4 | 30.8 | |
| | 0.075 | 14.1 | 21.9 | 33.1 | |

^{*a*} Standard uncertainties *u* are u(T)=0.1 K; $u(w_{K2CO3})=\pm 0.005$; $u(w_{[Bmim][Lys]})=\pm 0.005$; u(p)=2 kPa; u(R)=0.1 mpy.

Fig. 7 shows the effects of $w_{[Bmim][Lys]}$ (plot (a)) and w_{K2CO3} (plot (b)) on the corrosion rates of carbon steel in CO₂-saturated K₂CO₃ and CO₂-saturated K₂CO₃-[Bmim][Lys] aqueous solutions. One may find that the corrosion rate increases monotonously with increasing $w_{[Bmim][Lys]}$ and w_{K2CO3} at a given temperature. The amount of HCO₃⁻ and RNH₃⁺ tends to increase with increases in both $w_{[Bmim][Lys]}$ and w_{K2CO3} , as described in Eqs. (1) - (5), thus leading to an increased corrosion rate [56,65]. One may also find that when activated by [Bmim][Lys], the carbonated [Bmim][Lys]-K₂CO₃ aqueous solution has a lower corrosion rate at given w_{K2CO3} , as shown in Table 3 and Table 4. The above phenomenon may be explained by the competitive influence between the lone electron pairs in nitrogen atoms in the structure of [Bmim][Lys] molecules and the HCO₃⁻/RNH₃⁺ concentration in the carbonated aqueous solution. On

one hand, [Bmim][Lys] contains imidazole, and the lone electron pairs in nitrogen atoms tend to facilitate the adsorption of compounds on metallic surfaces, which may weaken the corrosion tendency [32-34,66,67].

Table 5. Corrosion rates (*R*) of carbon steel in K₂CO₃-[Bmim][Lys] aqueous solutions under different mass fractions of K₂CO₃ (w_{K2CO3}) and [Bmim][Lys] ($w_{[Bmim][Lys]}$) and CO₂ loadings. T=313.2 K. Pressure (*p*) =101 kPa.^{*a*}

| WK2CO3 | W[Bmim][Lys] | <i>R/</i> (mpy) | | | |
|--------|--------------|-----------------|-------|-------|-------|
| | | α=0.1 | α=0.2 | α=0.3 | α=0.4 |
| 0.150 | 0.025 | 2.3 | 4.7 | 7.0 | 8.3 |
| | 0.050 | 1.4 | 3.6 | 5.8 | 7.4 |
| | 0.075 | 0.6 | 2.5 | 4.9 | 6.2 |
| 0.200 | 0.025 | 3.3 | 6.4 | 9.7 | 11.0 |
| | 0.050 | 1.9 | 5.2 | 8.4 | 9.8 |
| | 0.075 | 1.4 | 4.2 | 7.1 | 8.4 |
| 0.250 | 0.025 | 4.3 | 8.7 | 13.7 | 15.6 |
| | 0.050 | 3.1 | 7.3 | 12.1 | 14.2 |
| | 0.075 | 1.9 | 6.6 | 10.5 | 12.5 |

^{*a*} Standard uncertainties *u* are u(T)=0.1 K; $u(w_{K2CO3})=\pm 0.005$; $u(w_{[Bmim][Lys]})=\pm 0.005$; u(p)=2 kPa; u(R)=0.1 mpy.



Figure 7. (a) Effect of mass fraction of [Bmim][Lys] on the corrosion rate of carbon steel in CO₂-saturated K₂CO₃-[Bmim][Lys] aqueous solutions. w_{K2CO3}=0.25. (b) Effect of mass fraction of K₂CO₃ on the corrosion rate of carbon steel in CO₂-saturated K₂CO₃ aqueous solutions. w_{[Bmim][Lys]}=0.0. (a) and (b): ●T=303.2 K; □T=313.2 K; ▲T=323.2 K. Symbols: experiments from this work. Lines: trend lines.

On the other hand, increasing the concentration of [Bmim][Lys] in the carbonated K₂CO₃-[Bmim][Lys] aqueous solution may also lead to an increase in the concentration of HCO₃⁻/RNH₃⁺, thus increasing the corrosion rate, as shown in Table 4. Taking into account such competitive influences, $w_{[Bmim][Lys]}$ is no greater than 0.075 in this work, i.e., the corrosion rate obviously decreased only when a small amount of [Bmim][Lys] was added into K₂CO₃ aqueous solution.

Fig. 8 shows the effects of CO₂ loading on the corrosion rate of carbon steel in carbonated K_2CO_3 -[Bmim][Lys] aqueous solutions and indicates that the corrosion rate increases with increasing CO₂ loading. In general, increasing the CO₂ loading results in higher amounts of HCO₃⁻ and RNH₃⁺, which in turn dissociate and eventually produce more hydrogen ion (H⁺) [55,56,68]. The increase in the H⁺ amount due to increased CO₂ loading is confirmed by the pH reduction reported in Fig. 6 (b). The increase in the amounts of H⁺ and HCO₃⁻ causes the corrosion process to proceed faster, thus resulting in a higher corrosion rate. Frolova [65] studied the effect of HCO₃⁻ concentration on corrosion rate of low- and high-strength steel in 1 N sodium carbonate solution. Their results showed that the corrosion rate decreased with increasing HCO₃⁻. Moreover, at a given CO₂ loading and w_{K2CO3} , the corrosion rate decreased with increasing $w_{[Bmim][Lys]}$ due to the competitive influence between the lone electron pairs in nitrogen atoms in the structure of [Bmim][Lys] molecules and the HCO₃⁻ concentration in the carbonated aqueous solution, as addressed previously.



Figure 8. Effect of CO₂ loading on the corrosion rate of carbon steel in carbonated K₂CO₃-[Bmim][Lys] solution. T=313.2 K. $\bigoplus w_{[Bmim][Lys]} = 0.025$; $\square w_{[Bmim][Lys]} = 0.05$; $\bigstar w_{[Bmim][Lys]} = 0.075$. (a): $w_{K2CO3} = 0.15$. (b): $w_{K2CO3} = 0.25$. Symbols: experiments from this work. Lines: trend lines.

In addition to the corrosion rate of carbon steel in carbonated K_2CO_3 aqueous solution and carbonated K_2CO_3 -[Bmim][Lys] aqueous solution, the corrosion rate of carbon steel in CO₂-saturated K_2CO_3 (25%)-DEA (3%) aqueous solution was also measured at 313.3 K in this work. The obtained

result was 22.1 mpy, which is higher than the corrosion rate of carbon steel in CO₂-saturated K_2CO_3 (25%)-[Bmim][Lys] (7.5%) (21.9 mpy), indicating that [Bmim][Lys] has a lower corrosion tendency toward carbon steel than DEA and thus has better application potential in the CO₂ capture process.

4. CONCLUSIONS

In this work, the CO_2 capture process and corrosion of carbon steel in [Bmim][Lys]-K₂CO₃ aqueous solutions were investigated. The effects of temperature, solution concentration and CO_2 loading on the corrosion rate were demonstrated. Our results show that the following:

(1) At a given w_{K2CO3} and $w_{[Bmim][Lys]}$, the corrosion rate of carbon steel in CO₂-saturated K₂CO₃-[Bmim][Lys] aqueous solution increases with increasing temperature. At a given w_{K2CO3} , $w_{[Bmim][Lys]}$ and temperature, the corrosion rate obviously increases with increasing CO₂ loading;

(2) Increases in both w_{K2CO3} and $w_{[Bmim][Lys]}$ tend to decrease the pH of CO₂-saturated K₂CO₃-[Bmim][Lys] aqueous solution, thus increasing the H⁺ concentration and the corrosion rate of carbon steel;

(3) There may exist a competitive influence between the lone electron pairs in nitrogen atoms and the HCO_3^- concentration; the corrosion rate of carbon steel obviously decreased only when a small amount of [Bmim][Lys] was added to K₂CO₃ aqueous solution;

(4) The [Bmim][Lys]-activated K_2CO_3 aqueous solution had a higher CO_2 absorption capacity, higher CO_2 absorption rate and lower corrosion rate of carbon steel than K_2CO_3 aqueous solution at a given K_2CO_3 mass fraction;

(5) Compared with the commercially applied DEA (3%)- K_2CO_3 (25%) aqueous solution, the [Bmim][Lys] (7.5%)-activated K_2CO_3 (25%) aqueous solution produced a similar CO₂ absorption rate; however, the latter solution has the advantages of a higher CO₂ absorption capacity, lower corrosion of carbon steel, higher concentration and lower water content, and thus has better application potential in the CO₂ capture process.

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References

- 1. A. Višković, V. Franki, V. Valentić, Energy, 70 (2014) 325.
- 2. H.R. Stuart, Science, 325 (2009) 1647.
- 3. P.C. Tseng, W.S. Ho, D.W. Savage, AlChE J., 34 (1988) 922.
- 4. Y. Maham, A.E. Mather, C. Mathonat, J. Chem. Thermodyn., 32 (2000) 229.
- 5. C. Zheng, D. Liu, Q. Yang, C. Zhong, J. Mi, Ind. Eng. Chem. Res., 48 (2009) 10479.
- S.P. Yan, M.X. Fang, W.F. Zhang, S.Y. Wang, Z.K. Xu, Z.Y. Luo, K.F. Cen, *Fuel Process. Technol.*, 88 (2007) 501.
- 7. X.S. Li, H.J. Wu, Y.G. Li, Z.P. Feng, L.G. Tang, S.S. Fan, J. Chem. Thermodyn., 39 (2007) 417.

- 8. F. Barzagli, F. Mani, M. Peruzzini, Energy Environ. Sci., 3 (2010) 772.
- 9. G. Bińczak, W. Moniuk, Z. Mordecka, C. Możeński, Chem. Process Eng., 37 (2016) 83.
- K.A. Mumford, K.H. Smith, C.J. Anderson, S. Shen, W. Tao, Y.A. Suryaputradinata, A. Qader, B. Hooper, R.A. Innocenzi, S.E. Kentish, G.W. Stevens, *Energy Fuels*, 26 (2012) 138.
- 11. V. Augugliaro, L. Rizzuti, Chem. Eng. Sci., 42 (1987) 2339.
- 12. G. Hu, N.J. Nicholas, K.H. Smith, K.A. Mumford, S.E. Kentish, G.W. Stevens, *Int. J. Greenhouse Gas Control*, 53 (2016) 28.
- 13. S. Zhang, Y. Lu, Chem. Eng. J., 279 (2015) 335.
- 14. H. Thee, K.H. Smith, G.D. Silva, S.E. Kentish, G.W. Stevens, Chem. Eng. J., 181-182 (2012) 694.
- 15. S. Shen, Y. Yang, S. Ren, Fluid Phase Equilib., 367 (2014) 38.
- S. Masoumi, P. Keshavarz, S. Ayatollahi, M. Mehdipour, Z. Rastgoo, *Energy Fuels*, 27 (2013) 5423.
- J.T. Cullinane, B.A. Oyenekan, J. Lu, G.T. Rochelle, Aqueous piperazine/potassium carbonate for enhanced CO₂ capture, in: *Greenhouse Gas Control Technologies* 7, Elsevier Science Ltd, (2005) Oxford, United Kingdom.
- 18. J.M. Plaza, E. Chen, G.T. Rochelle, AIChE J., 56 (2010) 905.
- 19. H. Thee, Y.A. Suryaputradinata, K.A. Mumford, K.H. Smith, G.d. Silva, S.E. Kentish, G.W. Stevens, *Chem. Eng. J.*, 210 (2012) 271.
- 20. T.N.G. Borhani, V. Akbari, M. Afkhamipour, M.K.A. Hamid, Z.A. Manan, *Chem. Eng. Sci.*, 122 (2015) 291.
- 21. T.N.G. Borhani, V. Akbari, M.K.A. Hamid, Z.A. Manan, J. Ind. Eng. Chem., 22 (2015) 306.
- 22. M.S. Shaikh, M.S. Azmi, M.A. Bustam, G. Murshid, Appl. Mech. Mater., 625 (2014) 19.
- 23. H. Thee, N.J. Nicholas, K.H. Smith, G. da Silva, S.E. Kentish, G.W. Stevens, *Int. J. Greenhouse Gas Control*, 20 (2014) 212.
- 24. G. Hu, K.H. Smith, Y. Wu, S.E. Kentish, G.W. Stevens, *Energy Fuels*, 31 (2017) 4280.
- 25. Y. Li, L.a. Wang, Z. Zhang, X. Hu, Y. Cheng, C. Zhong, Energy Fuels, 32 (2018) 3637.
- 26. S. Paul, K. Thomsen, Int. J. Greenhouse Gas Control, 8 (2012) 169.
- 27. D. Wappel, G. Gronald, R. Kalb, J. Draxler, Int. J. Greenhouse Gas Control, 4 (2010) 486.
- 28. L.M. Galan Sanchez, G.W. Meindersma, A.B. de Haan, Chem. Eng. J., 166 (2011) 1104.
- 29. Y.S. Zhao, X.P. Zhang, Y.P. Zhen, H.F. Dong, G.Y. Zhao, S.J. Zeng, X. Tian, S.J.Zhang, *Int. J. Greenhouse Gas Control*, 5 (2011) 367.
- 30. H. Hu, F. Li, Q. Xia, X.D. Li, L. Liao, M.H. Fan, Int. J. Greenhouse Gas Control, 31 (2014) 33.
- 31. D. Wappel, G. Gronald, R. Kalb, J. Draxler, Int. J. Greenhouse Gas Control, 4 (2010) 486.
- 32. R. Gašparac, C.R. Martin, E. Stupnišek Lisac, J. Electrochem. Soc., 147 (2000) 548.
- 33. K.M. Manamela, L.C. Murulana, M.M. Kabanda, E.E. Ebenso, *Int. J. Electrochem. Sci.*, 9 (2014) 3029.
- 34. M.A. Quraishi, M.Z.A. Rafiquee, S. Khan, N. Saxena, J. Appl. Electrochem. 37 (2007) 1153.
- 35. Q.B. Zhang, Y.X. Hua, Electrochim. Acta, 54 (2009) 1881.
- 36. Q.B. Zhang, Y.X. Hua, Mater. Chem. Phys., 119 (2010) 57.
- 37. H. Ashassi-Sorkhabi, M. Es'Haghi, Mater. Chem. Phys., 114 (2009) 267.
- 38. X. Zheng, S. Zhang, W. Li, M. Gong, L. Yin, Corros. Sci., 95 (2015) 168.
- P. Sharma, S.D. Park, I.H. Baek, K.T. Park, Y. Yoon, II, S.K. Jeong, *Fuel Process. Technol.*, 100 (2012) 55.
- 40. B. Lv, G. Jing, Y. Qian, Z. Zhou, Chem. Eng. J., 289 (2016) 212.
- 41. B.E. Gurkan, J.C. Fuente, De La, E.M. Mindrup, L.E. Ficke, B.F. Goodrich, E.A. Price, W.F. Schneider, J.F. Brennecke, J. Am. Chem. Soc., 132 (2010) 2116.
- 42. D. Fu, P. Zhang, L. Wang, *Energy*, 113 (2016) 1.
- 43. P. Zhang, X.F. Tian, D. Fu, *Energy*, 161 (2018) 1122.
- 44. D. Fu, P. Zhang, C. Mi, *Energy*, 101 (2016) 288.
- 45. Z.M. Zhou, G.H. Jing, L.J Zhou, Chem. Eng. J., 204–206 (2012) 235.

- 46. Y. Gao, F. Zhang, K. Huang, J.W. Ma, Y.T. Wu, Z.B. Zhang, *Int. J. Greenhouse Gas Control*, 19 (2013) 379.
- 47. H. Yu, Y.T. Wu, Y.Y. Jiang, Z. Zhou, Z.B. Zhang, New J. Chem., 33 (2009) 2385.
- 48. Y. Cao, T. Mu, Ind. Eng. Chem. Res., 53 (2014) 8651.
- 49. S. Mazinani, R. Ramazani, A. Samsami, A. Jahanmiri, B. Van der Bruggen, S. Darvishmanesh, *Fluid Phase Equilib.*, 396 (2015) 28.
- 50. R.H. Weiland, J.C. Dingman, D.B. Cronin, G.J. Browning, J. Chem. Eng. Data, 43 (1998) 378.
- 51. T.G. Amundsen, L.E. Oi, D.A. Eimer, J. Chem. Eng. Data, 54 (2009) 3096.
- 52. D. Fu, H. Hao, F. Liu, J. Mol. Liq., 188 (2013) 37.
- 53. D. Fu, J. Xie, J. Chem. Thermodyn., 102 (2016) 310.
- 54. F.A. Chowdhury, H. Yamada, T. Higashii, K. Goto, M. Onoda, *Ind. Eng. Chem. Res.*, 52 (2013) 8323.
- 55. A. Veawab, P. Tontiwachwuthikul, A. Chakma, Ind. Eng. Chem. Res., 38 (1999) 3917.
- 56. M.F. Hamada, T.M. Zewail, H.A. Farag, Corros. Eng., Sci. Technol., 49 (2014) 209.
- 57. S. Zhang, R. Shi, Y. Chen, M. Wang, J. Alloys Compd., 731 (2018) 1230.
- 58. S. Zhang, R. Shi, Y. Tan, J. Alloys Compd., 711 (2017) 155.
- 59. Y.Z. Jing, S.L. Wang, Y.Y. Chen, M.G. Bao, L. Liu, Int. J. Electrochem. Sci., 13 (2018) 7629.
- 60. Y.S. Sistla, A. Khanna, Chem. Eng. J., 273 (2015) 268.
- 61. P.S. Kumar, J.A. Hogendoorn, G.F. Versteeg, P.H.M. Feron, AIChE J., 49 (2003) 203.
- 62. D. Wappel, S. Joswig, A.A. Khan, K.H. Smith, S.E. Kentish, D.C. Shallcross, G.W. Stevens, *Int. J. Greenhouse Gas Control*, 5 (2011) 1454.
- 63. C. Yu, H.W. Wang, X.H. Gao, Int. J. Electrochem. Sci., 13 (2018) 6059.
- 64. M.N. Ilman, Kusmono, Case Studies in Eng. Failure Anal., 2 (2014) 1.
- 65. L.V. Frolova, M.N. Fokin, V.E. Zorina, Prot. Met., 33 (1997) 249.
- 66. L.M. Rodríguez-Valdez, W. Villamisar, M. Casales, J.G. González-Rodriguez, A. Martínez-Villafañe, L. Martinez, D. Glossman-Mitnik, *Corros. Sci.*, 48 (2006) 4053.
- 67. X. Zhou, H. Yang, F. Wang, *Electrochim. Acta*, 56 (2011) 4268.
- 68. G.H. Sedahem, J. Appl. Electrochem., 15 (1985) 777.

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