

Carbon Steel Corrosion Behaviors in Carbonated Aqueous Mixtures of Monoethanolamine and 1-n-butyl-3-methylimidazolium Tetrafluoroborate

B. Si Ali*, B. H. Ali, R. Yusoff, M. K. Aroua

Department of Chemical Engineering; University of Malaya; 50603 Kuala Lumpur; Malaysia

*E-mail: brahim@um.edu.my

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Recently, aqueous mixtures of alkanolamines and ionic liquids had emerged as potential solvents for CO₂ capture. Solubility data of CO₂ in aqueous mixtures of monoethanolamine (MEA) and 1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim] [BF₄]) are already available in the literature. However, data on the corrosiveness of these new solvents with regards to carbon steel are still scarce. In this work, carbon steel corrosion behavior in carbonated aqueous mixtures of MEA and [bmim] [BF₄] was investigated using potentiodynamic polarization and weight loss methods at fixed CO₂ loading of 0.55 mol/ mol. The corrosion rates were measured for [bmim] [BF₄] concentration ranging from 0.1 to 1.0 M and at temperatures of 40 and 80 °C. Carbon steel corrosion rates obtained from the two methods are in agreement; and showed that the presence of [bmim] [BF₄] in the carbonated solution has reduced the solution corrosivity to carbon steel for carbonated 4.0 M MEA/[bmim] [BF₄] system, but increased that of carbonated 2.0 M MEA/[bmim][BF₄] system. Scanning electron microscopy (SEM) images demonstrated that immersed specimens were severely corroded in carbonated 2.0 M MEA/[bmim] [BF₄] system. While for carbonated 4.0 M MEA/[bmim] [BF₄] system, a protective surface layer was formed as [bmim] [BF₄] concentration and temperature increased, respectively.

Keywords: CO₂ absorption, Corrosivity, Corrosion rate; Potentio-dynamic polarization; MEA/ [bmim] [BF₄]

1. INTRODUCTION

Chemical absorption of acidic gases such as CO₂ and H₂S has been widely used in the industry for the treatment, purification of gaseous feedstocks. The acid gas absorption methods use aqueous solutions of alkanolamines or their mixtures as solvents; the most common alkanolamines used are monoethanolamine (MEA), diethanolamine (DEA) and N methyldiethanolamine (MDEA). The

alkanolamine technology is well established, yet it still suffers from problems associated mainly with the alkanolamine volatility, degradation, and corrosivity. Extensive research works focusing on developing new types of solvents as alternatives to alkanolamines are still ongoing. Room-temperature ionic liquids (RTILs) have been proposed for the capture of acidic gases such as CO₂; ionic liquids (ILs) are potential solvents for CO₂ removal because of their unique properties, such as negligible vapour pressure, non-flammable, high thermal stability, and high solvation capacity [1]. A few researchers carried out the solubility and absorption of CO₂ in mixtures of alkanolamines and ILs. Chinn et al. [2] presented the data for CO₂ absorption into aqueous ionic liquid [bmim] [acetate] with and without MEA and MDEA. Camper et al. [3] studied the solubility of CO₂ in ILs-MEA solutions, at atmospheric pressure and temperature of 40 °C and 50 mol percentage MEA; they found that ILs-MEA is effective for the capture of CO₂. Sairi et al. [4] investigated the solubility of CO₂ in aqueous N-methyldiethanolamine and guanidinium trifluoromethanesulfonate [gua] [OTf] at elevated pressures; they provided a correlation between CO₂ solubility, partial pressure, and temperature. Afshin and coworkers [5] studied the solubility of CO₂ in mixture of [bmim] [BF₄] and MDEA at low pressure and different temperatures; they concluded that the presence of a small amount of [bmim] [BF₄] in MDEA has no effect on the CO₂ loading, but at high [bmim] [BF₄] concentration, CO₂ uptake decreased. The CO₂ absorption mechanism in alkanolamine is well understood, the huge number of published data reflects it. When ionic liquids do not possess an amine functional group, CO₂ absorption mechanism is a physical process. The reaction products of CO₂ absorption into alkanolamine are associated with the corrosion mechanism of carbon steel in carbonated solutions. Veldman et al. [6] reported that carbon dioxide reacts with alkanolamine by the following overall reactions:



where; R designates hydrogen or an organic group such as CH₃ or CH₂CH₂OH: Carbamate formation (reaction (1)) occurs only with primary and secondary amines, whereas bicarbonate formation (reaction (2)) is the only reaction that takes place in tertiary amine systems, but occurs also in primary and secondary amine solutions. A third possibility is that with pKa value of 10.33, carbonate formation is negligible in amine solutions. He also reported that the relationship between carbamate and bicarbonate concentration is a key parameter influencing corrosion; the bicarbonate reacts very easily with iron to form iron carbonate (FeCO₃) providing a passive barrier against additional corrosion. For tertiary amines such as MDEA loaded with CO₂, a very passive uniform layer of FeCO₃ will form and corrosion will be minimal even at high CO₂ loading. Alternatively, with primary and secondary amines or even mixtures of primary or secondary amines with tertiary amines, the passive FeCO₃ layer will not be uniform. The selectivity toward the CO₂ carbamate in these cases results in different and non-uniform morphology of the scale [6]. Parkins and Foroulis [7] reported that; a special consideration for primary amines is CO₂ induced stress corrosion cracking, which was observed in many MEA systems. The interaction between ionic liquid molecules and aqueous carbonated organic media is still not well understood; there are few reports in the open literature

regarding these issues [8-16]. Furthermore, reports on the corrosivity of ionic liquids, against engineering alloys are scarce, and no attempt on the investigation of the corrosivity of carbonated alkanolamine-ionic liquid mixtures. Uerdingen [17] stated that the corrosivity for a given metal is determined by the chemical structure of the ILs cation and the nature of the anion. The selection of construction materials for equipments involving ionic liquids-based chemical processes is of tremendous importance and requires investigation with respect to chemical, electrochemical corrosion mechanisms and its relation to the chemical structure and concentration of ionic liquids. Thus the objective of this paper is to investigate the carbon steel corrosion behaviour in carbonated MEA/[bmim] [BF₄] solution, the carbonated MEA concentrations were at 2.0 and 4.0 M, CO₂ loading was fixed at 0.55 mol/mol and temperatures of 40 and 80 °C. Concentration of [bmim] [BF₄] in MEA/[bmim] [BF₄] blends were varied from 0.1 to 1.0 M. To the best of our knowledge, this work is the first of its kind.

2. EXPERIMENTAL

2.1. Preparation of specimen and chemicals

Carbon steel specimen, with a surface area (0.28 cm²) and chemical composition (wt %) of C: 0.20%, Mn: 0.45%, P: 0.04%, S: 0.05%, Cr: 0.01% and Fe balance, was prepared to fit the specimen holder. Before each experiment, the specimen surface area was polished with silicon carbide paper (600 and 2000 grit), was rinsed with distilled water, was degreased with acetone, and finally was dried with hot air. The same procedures were used for the weight loss methods. Monoethanolamine (MEA) with a purity of 99.5% and ionic liquid, 1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim] [BF₄]) with a purity of 98.0% were obtained from Fisher Scientific and Merck, respectively. The standard solutions, 1.0 M Sodium Hydroxide (NaOH) and 1.0 M Hydrochloric Acid (HCl) were also purchased from Merck. All these chemicals were used as received. Aqueous solutions of 2.0 M MEA, 4.0 M MEA, 2.0 M MEA/ [bmim] [BF₄] and 4.0 M MEA/ [bmim] [BF₄] were prepared for [bmim] [BF₄] concentration ranging from 0.1 M to 1.0 M. Prior to CO₂ saturation, the solution was deoxygenated, by purging N₂ (99.95%) into the solution for 30 min.

The test solutions were saturated by sparging mixtures of CO₂/N₂ or pure CO₂ in order to obtain the desired CO₂ loading; the experiments were carried out at atmospheric pressure and at temperatures of 40 and 80 °C, respectively. The gases (CO₂ and N₂) flow rates were regulated using Brooks gas mass flow meters; model 5850E and 5850C for N₂ and CO₂ respectively. Gas streams were connected to a water saturator which was immersed in the water bath. The gas flow rates were controlled by four channels Brooks mass flow controller model 0154E. Reaction of carbon dioxide with the aqueous solution caused a decrease in alkalinity and the variation solution pH was recorded continuously.

When a constant pH reached, (in which the solution was saturated with CO₂), the solution concentration and the CO₂ loading were determined. In this work, the solutions loading were maintained constant at 0.55 ± 0.05 mol of CO₂/mol of solution. To verify the desired CO₂ loading, an

aliquot of three samples (5 cm³) were taken, mixed with an excess amount of 1.0 M of BaCl₂ and 1.0 M NaOH (50 cm³). These aliquots were heated with agitation for three hours at 70 °C and atmospheric pressure, then were filtered to remove the fine white particles consisting of barium carbonate (BaCO₃), then were washed with distilled water to remove all traces of (NaOH). The dissolved (BaCO₃) was then titrated with standard solution of 1.0 M HCl using a PC controlled Metrohm 716 DMS auto-titrator. The volume of HCl used to neutralize the basic species, was automatically determined from the ends point of the first derivative of the titration curve. The CO₂ loading α, then determined according to equation 3, [18]:

$$\alpha = \frac{V_{HCl} \times M_{HCl}}{V_{sample} \times 2 \times M} \tag{3}$$

Where; α is CO₂ loading in mol of CO₂/mol of solution, is the volume of HCl required to neutralize the BaCO₃ in cm³, is the volume of sample taken for analysis in cm³, M is the molarities of the solution or HCl in mol/l.

2.2. Experiment setup

Figure 1 illustrates the electrochemical setup used in this work; it consists of a 100-cm³ corrosion cell, Gamry Potentiostat/Galvanostat (REF 600 model) equipped with a speed controller (model FCTV101) and a data-acquisition system.

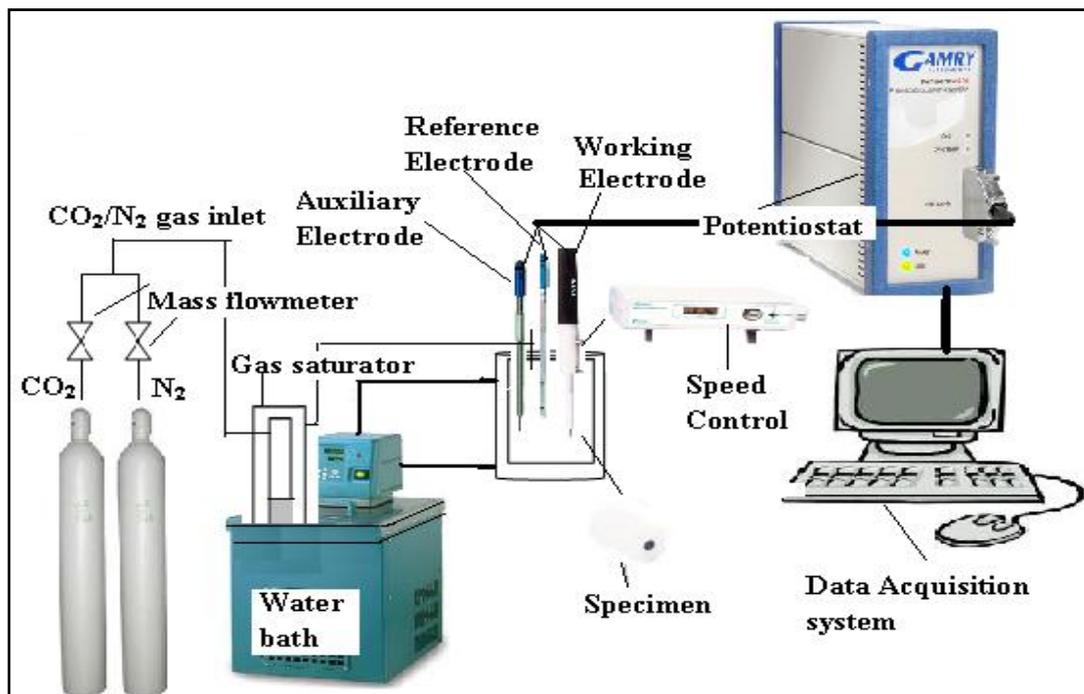


Figure 1. Experimental set up for electrochemical corrosion experiment

Three electrodes system was used, platinum wire as the counter electrode (auxiliary electrode), saturated calomel electrode (SCE) as the reference electrode and the specimen as the working electrode; which was subjected to a constant speed of 600 rpm via the speed control unit.

The corrosion cell was connected to a water bath in order to control the solutions temperature (accuracy ± 0.1 °C). The CO₂ gas was kept flowing but not sparging in the solution, to control the CO₂ loading in the solution. The cell was also equipped with a condenser to prevent water evaporation. A computer controlled Potentiostat/ Galvanostat Gamry (model REF 600) equipped with Echem Analyst 5.6 Software, was used to monitor the experiments and to obtain corrosion measurements.

2.3. Experiment Procedures

The electrochemical corrosion tests were carried out according to ASTM G5-94 [19]. To ensure that the data obtained are reliable, the anodic polarization curve of stainless steel-430 specimen in 0.5 M sulfuric acid (H₂SO₄) at 30 °C was determined. The anodic polarization curve produced was in agreement with that reported by ASTM. Prior to polarization experiment, the working electrode was equilibrated for 30 min at open circuit potential (OCP). Potentiodynamic polarization curves were obtained at 0.9 mV/sec scan rates, covering a potential range of around the free corrosion potential. The corrosion rate was determined using Tafel extrapolation method. Tafel extrapolation method estimates the corrosion current density I_{corr} ($\mu\text{A}/\text{cm}^2$), converted to corrosion rate using equation (4).

$$\text{CR} = \frac{0.00327 \times I_{\text{corr}} \times W}{n \times D} \quad (4)$$

Where CR is the corrosion rate in, W is the atomic weight of specimen (55.85 gm/mol), n is the number of electrons transferred and D is the density of the specimen ($7.88 \text{ gm}/\text{cm}^3$). Before and after each experiment, the conductivity and solution pH were determined using Fisher scientific conductivity-meter and pH probe Metrohm 719S, respectively.

The weight loss measurements were performed according to ASTM G-31-72 [20] in four corrosion cells; each cell has a volume of 100 cm^3 . Prior to transferring the carbonated solution into the cells, carbon steel specimens with rectangular in shape were fabricated ($11\text{mm} \times 20\text{mm} \times 5\text{mm}$); The dimensions were measured with a vernier calipers and were weighted with an analytical balance (Sartorius model, RP221S), The specimen was positioned at the bottom of the cells. The carbonated solution was then immediately transferred into the cell that was connected to a water bath system to control the temperature. The experiments were carried at constant CO₂ loading of 0.55 mol/mol and two temperatures 40, and 80 °C, respectively. The CO₂ loading was held constant by keeping CO₂ flowing into the cells but not sparging into the solution. The incoming CO₂ gas was saturated with water and conditioned at the desired temperature. The CO₂ gas flow rate was, passed through a water saturator and was maintained at the desired temperature in the water bath. After 168 hours, the samples were collected from the cells, and then were kept in vacuum desiccators. Surface morphology characteristics were analyzed at high vacuum with Scanning Electron Microscope (SEM). After SEM

analysis, specimens were cleaned in accordance with ASTM G1-90 [21], the corroded specimens were immersed in a mixture of 1000 cm³ hydrochloric acid (HCl), 20 gm antimony trioxide (Sb₂O₃) and 50 gm of stannous trioxide (SnCl₂). The numbers of cleaning cycles were recorded and the weight loss was taken until a constant weight was obtained, to assure that all the corrosion products were removed. Weight loss determination for the mean corrosion rate in (mm yr⁻¹) was obtained using equation (5).

$$\text{Corrosion rate (mm yr}^{-1}\text{)} = \frac{8.76 \times 10^4 \times \bar{W}}{D \times A \times t} \quad (5)$$

Where; \bar{W} is the mean weight loss (gm), D is the density (g/cm³), A is the exposed area (cm²), t is the exposure time in hour. Conductivity and pH reading were taken at the end of each experiment.

3. RESULTS AND DISCUSSION

3.1. Polarization study

The effects of ionic liquid addition on the polarization behaviour in 2.0 M MEA systems were found to be different from those in 4.0 M MEA-. As such, the results of both systems will be analyzed separately.

3.1.1. Carbonated (2.0 M MEA+ [bmim] [BF₄]) systems

The polarization curves of carbon steel in carbonated solution of (2.0 M MEA+ [bmim] [BF₄]) are displayed in Figure 2 and 3 at temperatures of 40 and 80 °C respectively.

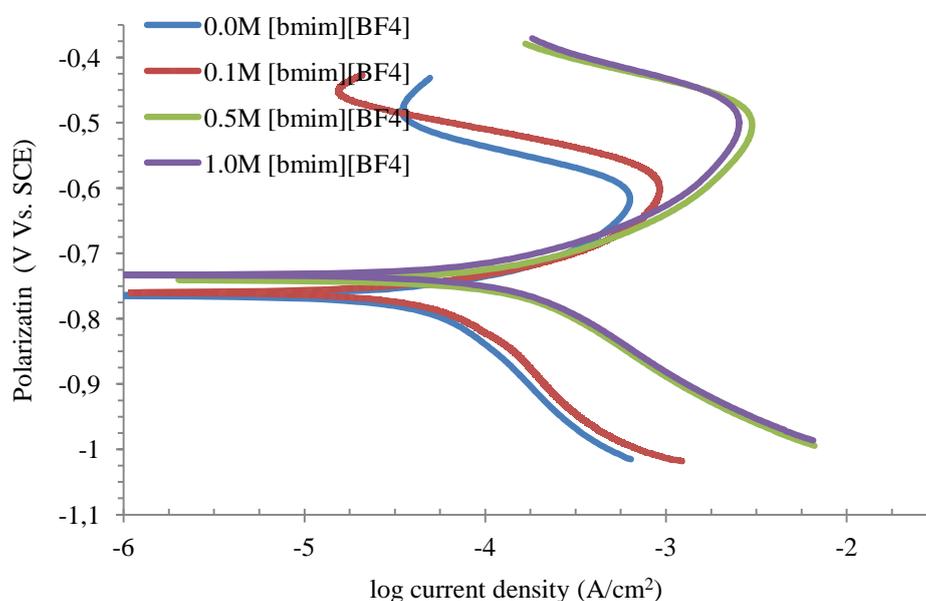


Figure 2. Effect of [bmim] [BF₄] concentration on the polarization behaviour of carbon steel in carbonated MEA/ [bmim] [BF₄] at temperature of 40 °C

As can be seen from Figure 2, there is a shift in the corrosion potential toward the positive direction and also the variation in the current density for both anodic and cathodic portions of the polarization curve, with increasing [bmim] [BF₄] concentration in the mixture MEA/[bmim] [BF₄]. This implies that a change in the corrosion mechanism is taking place. At [bmim] [BF₄] concentration of 0.1 M and at the passivation potential of -0.6 (V vs. SCE) to -0.45 (V vs. SCE), the polarization curve exhibits a decrease in anodic current and a slight decrease in the cathodic current. This behaviour suggests that a change in the surface of the specimen either by deposition of corrosion products or formation of a porous thin film. As the concentration of [bmim] [BF₄] increased to 1.0 M, both anodic and cathodic currents increased. The anodic current, then decreased at the potential of -0.5 (V vs. SCE) and the corrosion potential shifted in the positive direction. These results indicate that the presence of [bmim] [BF₄] in carbonated MEA solution has affected carbon steel corrosion mechanism.

Figure 3 illustrates the effect of [bmim] [BF₄] concentration on the polarization behaviour of carbon steel in carbonated MEA/ [bmim] [BF₄] at temperature of 80 °C. For carbonated 2.0 M MEA without [bmim] [BF₄], the anodic branch of the polarization curve shows a decrease in the anodic current at around -0.5 (V vs. SCE) and the corrosion potential is around -0.87 (V vs. SCE). At [bmim] [BF₄] concentration of 0.1 M, the polarization curve of carbon steel in the carbonated MEA solution, shows an increase in the anodic and cathodic currents densities. The anodic current density reach its peak at the passivation potential at around -0.65 (V vs. SCE), and the corrosion potential at this concentration of [bmim] [BF₄] remained the same as that of carbonated MEA without [bmim] [BF₄]. However, at [bmim] [BF₄] concentration of 0.5 M, the corrosion potential shifts towards the negative direction with no variation in anodic and cathodic currents densities. This behavior implies that there is no change in the corrosion mechanism and the corrosion rate increased was due to the negative shift of the corrosion potential.

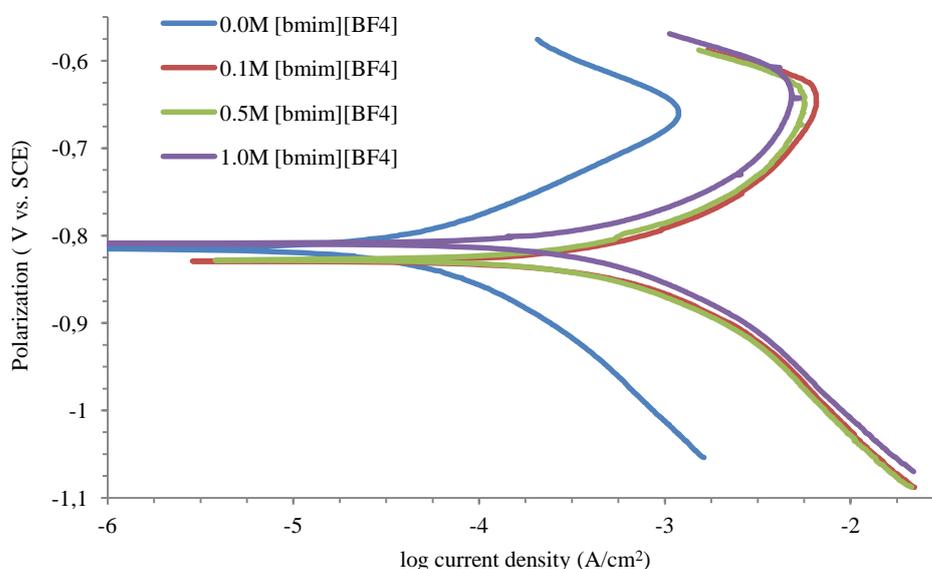


Figure 3. Effect of [bmim] [BF₄] concentration on the polarization behaviour of carbon steel in carbonated MEA/ [bmim] [BF₄] at temperature of 80 °C

At 1.0 M [bmim] [BF₄], the corrosion potential shift towards the positive direction with a small decrease in the anodic current density and a slight increase in cathodic current density. The effect of [bmim] [BF₄] concentration on the carbon steel polarization behavior is demonstrated by the shift of the corrosion potential, initially in the negative direction and then in the positive direction. These explain the change in the surface condition of the specimen, owing to corrosion products deposition or porous thin film formation, which take place at lower [bmim] [BF₄] concentration. However, at [bmim] [BF₄] concentration of 1.0 M the corrosion process is retarded, implying that the surface becomes homogenous and compact.

3.1.2. Carbonated (4.0 M MEA+ [bmim] [BF₄]) systems

In Figure 4, the polarization curves at 40 °C of carbon steel in carbonated 4 M MEA solution with and without [bmim] [BF₄] are shown. The four polarization curves exhibit similar behavior, suggesting that the corrosion mechanism is the same for all [bmim] [BF₄] concentrations. The corrosion potential of carbon steel in carbonated MEA without [bmim] [BF₄] is about -0.80 (V vs. SCE), while in the presence of [bmim] [BF₄] the corrosion potential has shifted towards the positive direction as a result of the decrease in anodic and cathodic current densities. The anodic branch of the polarization curve show a passivation potential ranging from -0.55 to -0.45 (V vs. SCE) for [bmim] [BF₄] concentration range of 0.1 to 1.0 M, respectively.

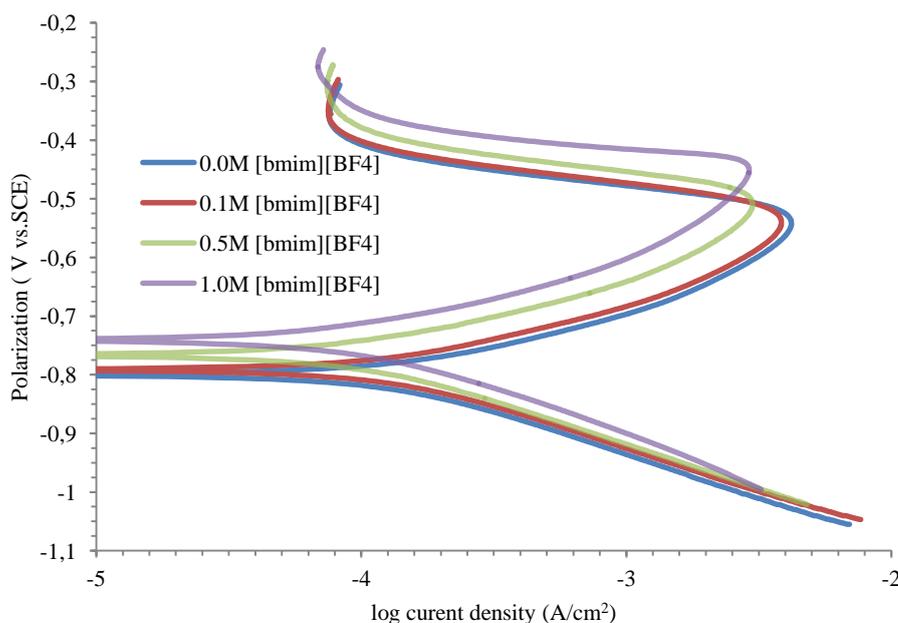


Figure 4. Effect of [bmim] [BF₄] concentrations on polarization behaviour of carbon steel in carbonated (4.0 M MEA+ [bmim] [BF₄]) at 40 °C

The anodic current decreases from its critical current of $3.98 \text{ (mA/cm}^2\text{)}$ to a passive current of $0.077 \text{ (mA/cm}^2\text{)}$ for carbonated MEA without [bmim] $[\text{BF}_4]$. As for carbonated MEA/ [bmim] $[\text{BF}_4]$ system, the anodic current decreases from its critical current of $2.88 \text{ (mA/cm}^2\text{)}$ to a passive current of $0.0676 \text{ (mA/cm}^2\text{)}$. However, the cathodic current remains constant for both systems. This behavior explains the change in the surface of the specimen, which is perhaps due to the passivation or to a different structure and morphology of a new film formation, resulting in carbon steel corrosion rate to be reduced. This result agrees strongly with what was reported in our previous work [22] in relation to corrosion rate of carbon steel in carbonated mixture of MEA and ionic liquid. Figure 5 shows the polarization curves of carbon steel in carbonated mixture of MEA/ [bmim] $[\text{BF}_4]$ at $80 \text{ }^\circ\text{C}$. Polarization curves of carbon steel in carbonated MEA without [bmim] $[\text{BF}_4]$ show a slight decrease in the anodic current, and its corrosion potential is around $-0.86 \text{ (V vs. SCE)}$. The polarization curve shows that the presence of 0.1 M [bmim] $[\text{BF}_4]$ in carbonated MEA solution has shifted the corrosion potential towards the negative direction; the anodic current density increase and there is a slight decrease in cathodic current density. This might be caused by the destruction of the passivation layer or pore formation within the film, resulting in the increased in carbon steel corrosion rate. However, at 0.5 M [bmim] $[\text{BF}_4]$, the cathodic current remained constant while the anodic current decreases, a passivation potential at around $-0.65 \text{ (V vs. SCE)}$ is observed. The mechanism of the corrosion process is the same as that of carbonated 4.0M MEA without [bmim] $[\text{BF}_4]$, the corrosion potential shifts towards the positive direction which reveals a reduction in the corrosion rate of carbon steel. Similar behavior was observed in the presence of 1.0 M [bmim] $[\text{BF}_4]$ in the carbonated 4.0 M MEA solution.

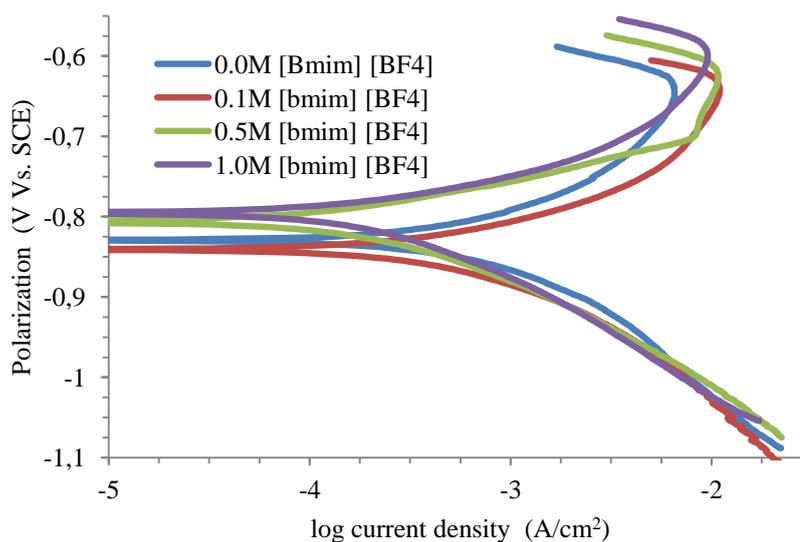


Figure 5. Effect of [bmim] $[\text{BF}_4]$ concentrations on polarization behaviour of carbon steel in carbonated (4.0 M MEA+ [bmim] $[\text{BF}_4]$) at $80 \text{ }^\circ\text{C}$

The polarization parameters such as corrosion current density (I_{corr}), anodic slope (β_a), and cathodic slope (β_c) were extracted from the anodic and cathodic branches of the polarization curve using McCafferty method [23]. Khaled et al. [24] applied the same method for Tafel non-dependence. The Tafel line of cathodic branch is first extended toward the noble direction of corrosion potential, to

give the net current for cathodic reaction, and then the anodic current density (I_a) is determined from equation (6):

$$I_a \text{ (Net experimental)} = I_a - |I_c| \tag{6}$$

Where; I_a and $|I_c|$ refer to the anodic and the cathodic currents, respectively. Thus, the net anodic current density is the sum of the experimentally observed anodic current density and the extrapolated cathodic current density. The details of the method are shown in Figure 6, the extracted value of $I_{corr} = 150 \mu\text{A}/\text{cm}^2$ which is converted to corrosion rate in mm yr^{-1} using Equation (4). The extracted value converted to corrosion rate in mm year^{-1} .

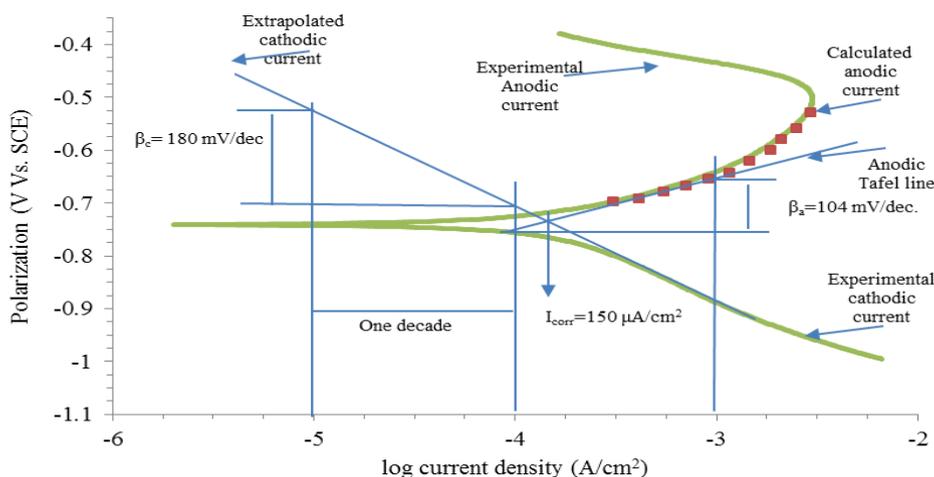


Figure 6. Tafel extrapolation method for corrosion current measurement in carbonated solution of 2.0 M MEA + 0.5 M [bmim] [BF₄] at 40 °C

Table 1 and 2 present the summary of the electrochemical parameters extracted from the polarization curves, together with the measured pH and conductivity of the carbonated solution. The presence of [bmim] [BF₄] in the carbonated 2.0 M MEA solution has increased the conductivity of the solution, consequently, the corrosion rate of carbon steel increased.

Table 1. Summary of the electrochemical parameters extracted from the polarization curve of carbon steel in carbonated solution of 2.0 M MEA/ [bmim] [BF₄].

T (°C)	[MEA] (M)	[bmim] [BF ₄] (M)	pH	σ (mS/m)	β_a (mV/dec)	β_c (mV/dec)	E_{corr} (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	CR (mm yr^{-1})
40	2.0	0.0	8.5	39.0	100	305	-763	63.0	0.73
	2.0	0.1	8.4	44.1	95	300	-760	79.3	0.92
	2.0	0.5	7.8	55.2	104	180	-741	150.0	1.75
	2.0	1.0	7.8	53.6	103	180	-733	138.0	1.60
80	2.0	0.0	7.9	44.0	105	105	-810	138.0	1.16
	2.0	0.1	7.8	45.4	105	120	-829	295.6	5.80

2.0	0.5	7.6	54.4	120	120	-828	281.8	5.00
2.0	1.0	7.6	52.1	115	110	-809	251.0	4.20

Table 2. Summary of the electrochemical parameters extracted from the polarization curve of carbon steel in carbonated solution of 4.0 M MEA/ [bmim] [BF₄].

T (°C)	[MEA] (M)	([bmim] [BF ₄]) (M)	pH	σ (mS/m)	β _a (mV/dec)	β _c (mV/dec)	E _{corr} (mV)	I _{corr} (μA/cm ²)	CR (mm yr ⁻¹)
40	4.0	0.0	8.00	48.7	122	155	-800	151.3	1.755
	4.0	0.1	8.05	48.5	120	155	-791	141.2	1.638
	4.0	0.5	8.10	46.6	120	155	-767	125.0	1.243
	4.0	1.0	8.15	43.4	120	153	-741	95.68	1.110
80	4.0	0.0	7.60	47.1	85	70	-862	258.6	3.00
	4.0	0.1	7.70	49.1	75	100	-841	281.8	3.26
	4.0	0.5	7.75	44.6	50	108	-806	168.2	1.95
	4.0	1.0	7.80	43.9	60	100	-802	148.0	1.71

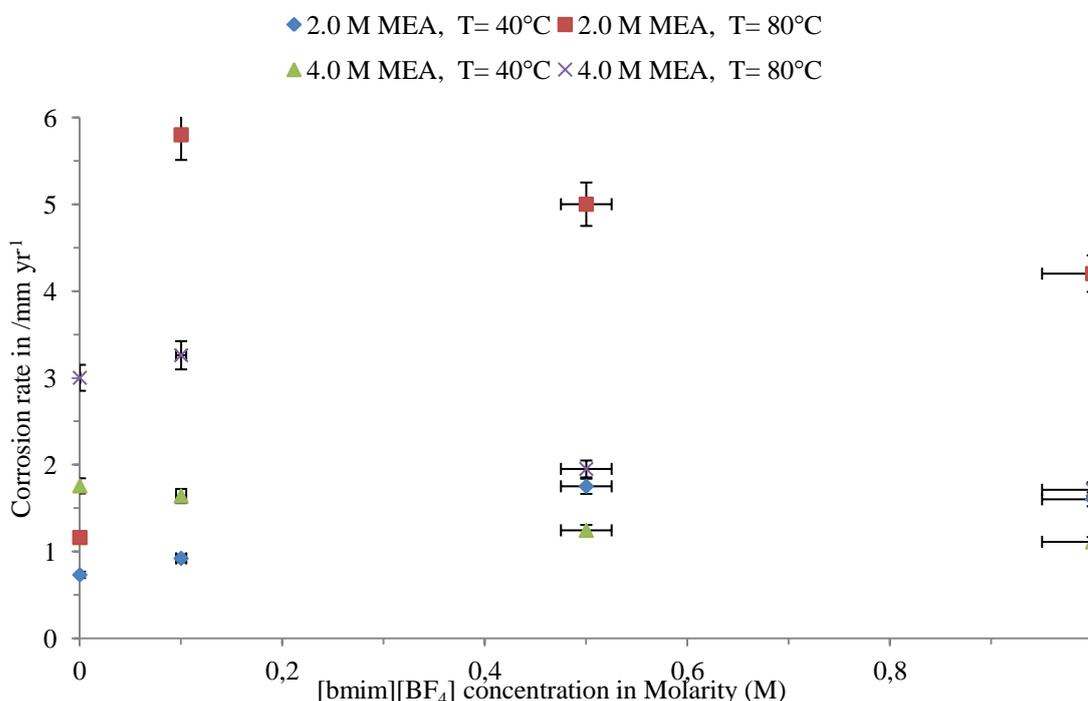


Figure 7. Effect of [bmim][BF₄] concentration on the carbon steel corrosion rate evaluated using polarization method

The presence of low concentration of [bmim] [BF₄] in carbonated MEA solution increases the carbon steel corrosion rate, and then decreases with increasing [bmim] [BF₄] concentration. However, the corrosivity of carbonated 2.0 M MEA without [bmim] [BF₄] to carbon steel, is lower than that of carbonated 2.0 M MEA with [bmim] [BF₄] at the two investigated temperatures. For 4.0 M MEA/ [bmim] [BF₄] systems, the corrosion rate decreased almost linearly with increasing [bmim] [BF₄] concentration at the investigated temperatures. This decrease in corrosion rate is probably attributed to

the lack of water activity in the system and the effect of temperature on the corrosion product formed on the specimen surface. Figure 7 illustrates the effect of [bmim] [BF₄] concentration on corrosion rate for the polarization method.

3.2. Weight Loss Studies

Weight loss method, was carried out to validate the obtained results from polarization, Table 3 and 4 summarize the results. It is clear that the corrosion rate of carbon steel in carbonated solution of 2.0 M MEA/[bmim] [BF₄] system increases as [bmim] [BF₄] concentration increases, at the investigated temperatures of 40 and 80 °C and immersion time of 168 hours. However, at temperature of 80 °C the corrosion rate decreases in the presence of [bmim] [BF₄], which was first observed at 40 °C and at [bmim] [BF₄] concentration of 1.0 M; a slight decrease in corrosion rate as compared to that at [bmim] [BF₄] concentration of 0.5 M was then observed. The effect of [bmim] [BF₄] concentration on the carbon steel corrosion rate for carbonated solution of 2.0 M MEA/ [bmim] [BF₄] at 40 °C, is less than that at 80 °C; as expected high temperature favors high corrosion rate and the adherence of the corrosion products layer onto the specimen surface, which lead to a deceleration of corrosion rates. Carbonated 4.0 M MEA/ [bmim] [BF₄] system, the deceleration in corrosion rate was observed at both temperatures and is more pronounced at 40 °C. The results obtained from weight loss method, are in accordance with those obtained using polarization. Corrosion rate of carbon steel evaluated with two different methods, showed the same pattern; furthermore, the effect of [bmim] [BF₄] concentration on the rate of corrosion at both methods showed the same pattern as well. Figure 8 illustrates the effect of [bmim] [BF₄] concentration on corrosion rate, a parity plot is given in Figure 9 shows the agreement of corrosion rate evaluated using the two methods.

Table 3. Carbon steel corrosion rates using weight loss method when carbon steel was immersed in carbonated solution 2.0 M MEA/ [bmim] [BF₄] systems.

T (°C)	[MEA] (M)	([bmim] [BF ₄]) (M)	pH	σ (mS/m)	CR (mm yr ⁻¹)
40	2.0	0.0	8.4	39.0	0.45
	2.0	0.1	8.4	40.5	0.75
	2.0	0.5	7.8	55.2	1.60
	2.0	1.0	7.6	53.6	1.55
80	2.0	0.0	8.05	42.4	1.4
	2.0	0.1	8.00	42.7	3.5
	2.0	0.5	7.80	52.2	3.4
	2.0	1.0	7.90	47.7	3.0

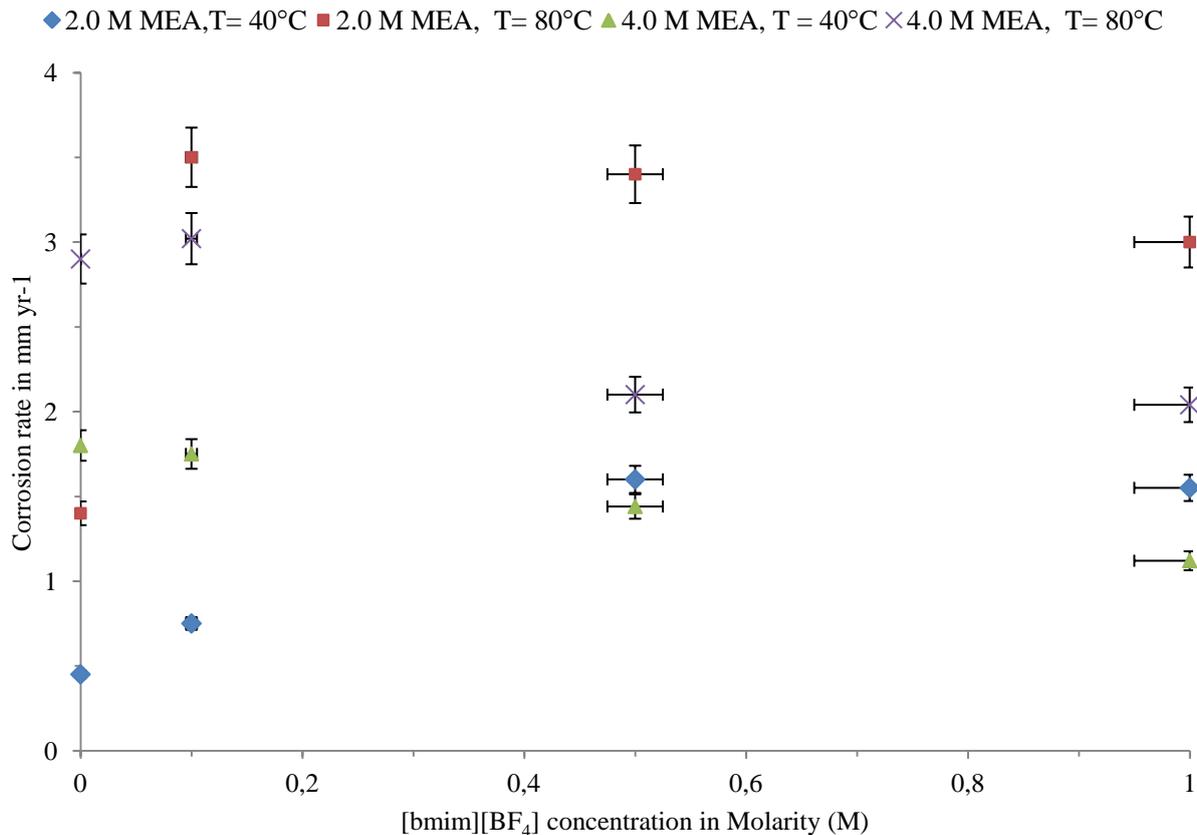


Figure 8. Effect of [bmim] [BF₄] concentration on the carbon steel corrosion rate in carbonated solutions of 2.0 M/[bmim][BF₄] and 4.0 M MEA/[bmim][BF₄], evaluated using weight loss method.

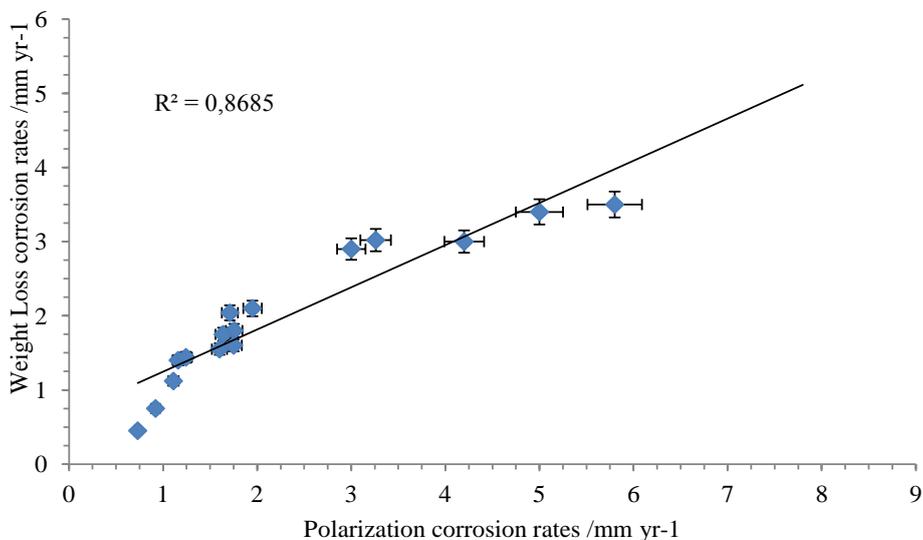


Figure 9. Comparison between corrosion rates obtained between weight loss and polarization method.

Table 4. Carbon steel corrosion rates using weight loss method when Carbon steel immersed in carbonated solution 4.0 MEA/ [bmim] [BF₄] systems at temperatures of 40 and 80 °C, respectively

T (°C)	[MEA] (M)	([bmim] [BF ₄]) (M)	pH	σ (mS/m)	CR (mm yr ⁻¹)
40	4.0	0.0	8.00	48.7	1.80
	4.0	0.1	8.05	48.5	1.75
	4.0	0.5	8.10	46.6	1.44
	4.0	1.0	8.15	43.4	1.12
80	4.0	0.0	7.70	48.6	2.90
	4.0	0.1	7.60	49.2	3.02
	4.0	0.5	7.80	44.6	2.10
	4.0	1.0	7.90	42.0	2.04

3.3. SEM Results

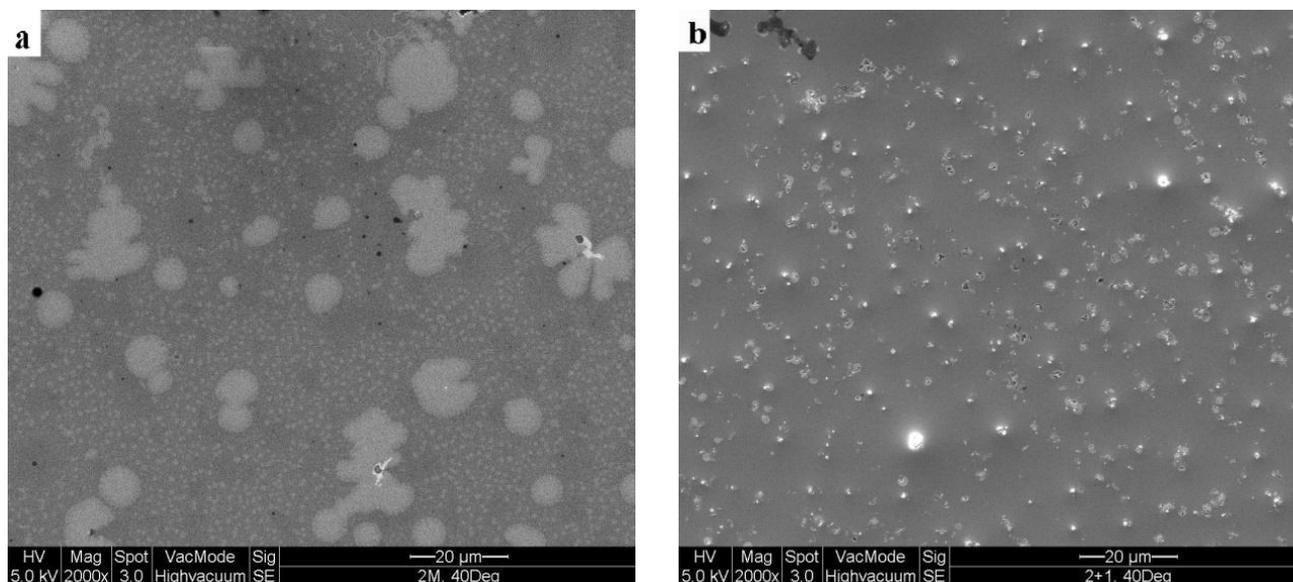


Figure 10. Carbon steel specimen’s SEM image after immersion in carbonated solutions of (a) 2.0 M MEA and (b) (2.0 M MEA + 1.0 M [bmim][BF₄]) at 40 °C

Figure 10 illustrates the SEM image of carbon steel sample after immersion into carbonated 2.0 M MEA and (2.0 M MEA+1.0 M [bmim] [BF₄]) at 40 °C. The specimen’s SEM image for MEA without [bmim] [BF₄] (refer to Figure 10a) shows scattered corrosion products, some pitting spots can be seen on the specimen surface; indicating that the corrosion attack is not uniform. However; for carbonated MEA/ [bmim] [BF₄] system at 1.0 M [bmim] [BF₄] concentration (refer to Figure 10b) shows that the specimen surface appears to be homogeneously covered, blisters scattered at all over the surface. The findings from polarization curves, weight loss method, and SEM are in accordance and

support the idea that the presence of [bmim] [BF₄] in carbonated 2.0 M MEA solution at 40 °C has increased the corrosion rate of the carbon steel specimen for the period investigated. Figure 11 presents the carbon steel specimen's SEM image after immersion in carbonated (2.0 M MEA + 0.1 M [bmim] [BF₄]), (2.0 M MEA+ 0.5 M [bmim] [BF₄]) and (2.0 M MEA + 1.0 M [bmim] [BF₄]) solutions respectively at 80 °C.

Figure 11a shows the SEM image for carbon steel specimen after immersion in carbonated 2.0 M MEA without [bmim] [BF₄]; some preferential attacks can be observed and the corrosion products deposit were spread over the specimen surface.

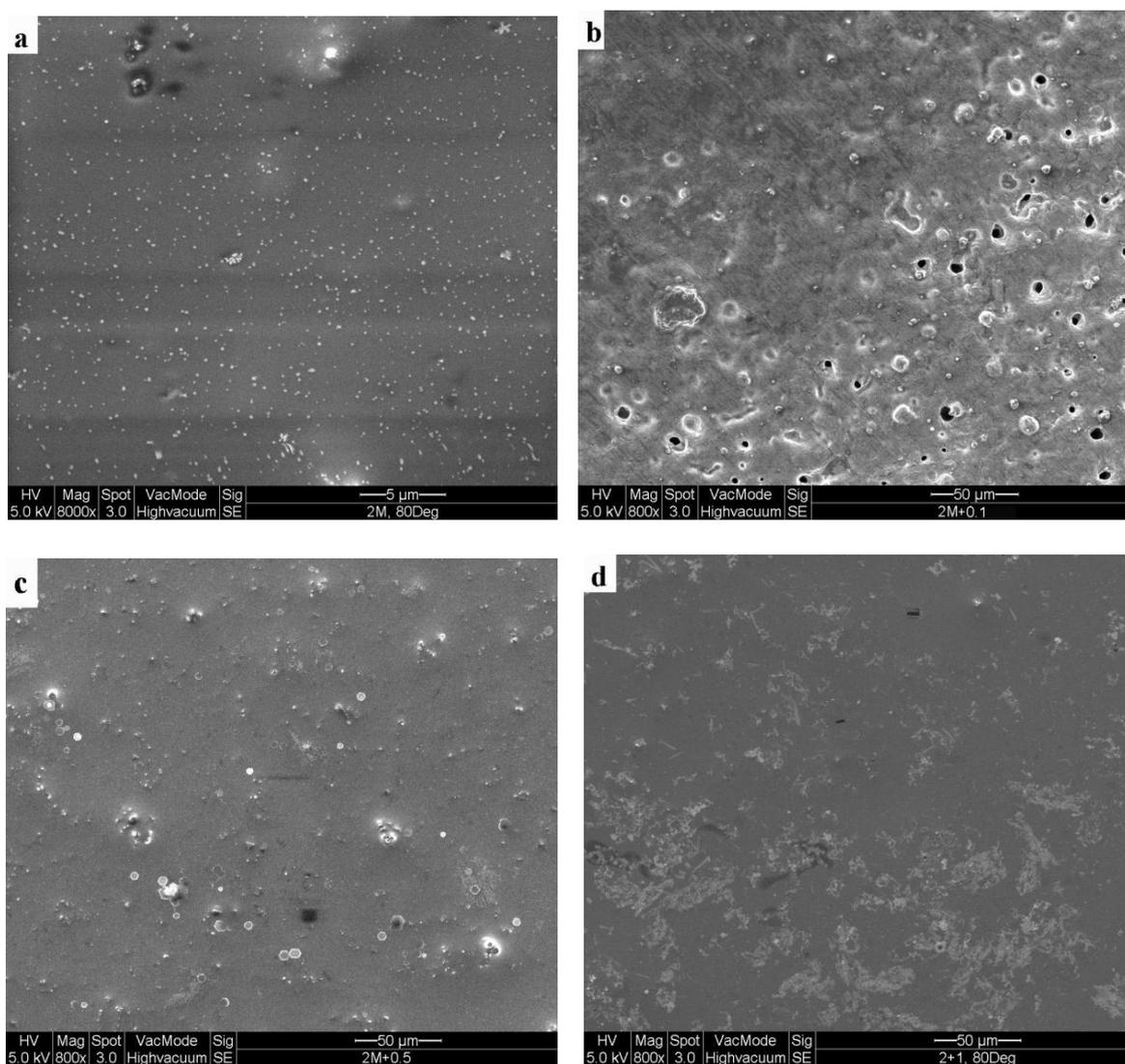


Figure 11. Carbon steel specimen's SEM image after immersion in carbonated solutions of (a) 2.0 M MEA, (b) (2.0 M MEA+ 0.1 M [bmim] [BF₄]), (c) (2.0 M MEA+ 0.5 M [bmim] [BF₄]), (d) (2.0 M MEA+1.0 M [bmim] [BF₄]) at 80 °C

SEM image of carbon steel specimen, immersed in carbonated 2.0 M MEA containing 0.1 M [bmim] [BF₄], (refer to Figure 11b), exhibits scattered pitting or crevice corrosion spots, with different islands of corrosion products. The specimen surface also appears severely attacked as compared to that

immersed in carbonated 2.0 M MEA without [bmim] [BF₄]. However; further increasing of [bmim] [BF₄] concentration, the specimen surface becomes smooth and homogeneous in shape (Figure 11c and Figure 11d); the surface appears to be covered with a corrosion layer. The SEM analysis supports the findings of carbon steel corrosion behaviour in carbonated MEA/ [bmim] [BF₄] system at 80 °C, using polarization analysis and weight loss method. The decrease in corrosion rate demonstrated by the formation of a corrosion layer on the specimen surface, the duration of the layer and its physical properties would be further investigated. Figure 12 illustrates the specimen's SEM image after immersion in carbonated solutions of 4.0 M MEA and (4.0 M MEA+ 1.0 M [bmim] [BF₄]) at 40 °C. Figure 12a shows the structure and morphology of the specimen surface after immersion in carbonated MEA solution without [bmim] [BF₄]; the surface appears inhomogeneous, porous, loose, and dispersed islands of corrosion products. This is an indication of the high rate of the corrosion process, which also supports the corrosion rate results obtained from the other two methods. The specimen's SEM image presents a very rough surface, non uniform corrosion products as compared to that of the specimen's SEM image immersed in carbonated 4.0 M MEA + 1.0 M [bmim] [BF₄], the latter are dense and homogenous (refer to Figure 12b). In the presence of [bmim] [BF₄], the corrosion attacks seem to be non-uniform, rather on preferential sites; this explains the lower corrosion rate obtained using polarization and weight loss methods.

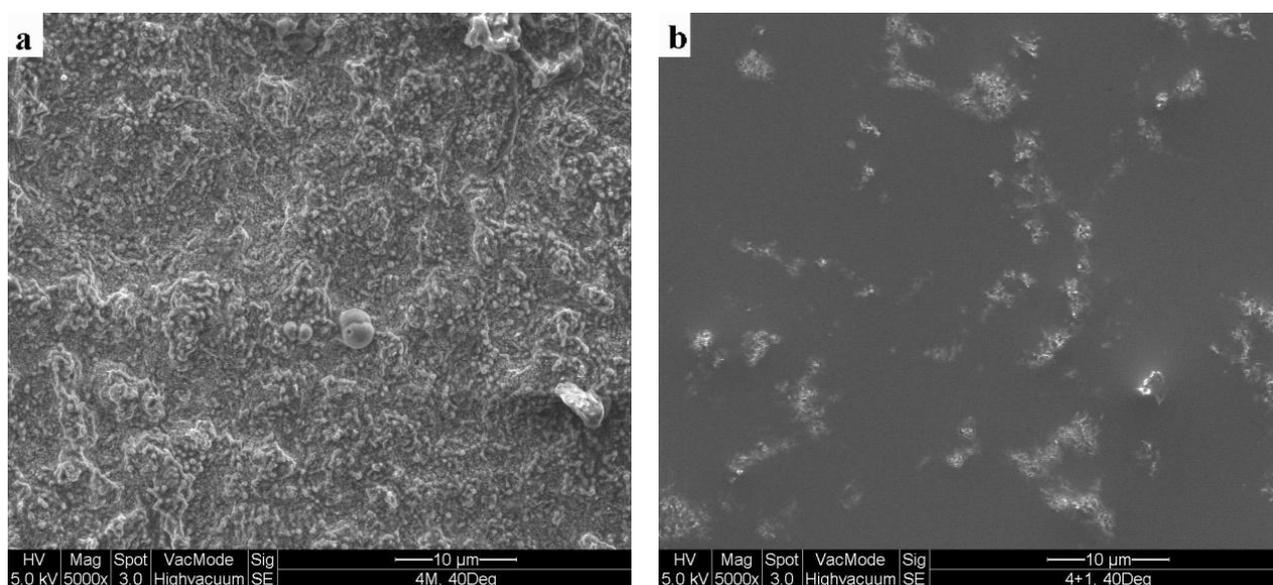


Figure 12. Carbon steel specimen's SEM image after immersion in carbonated solutions of (a) (4.0 M MEA), (b) (4.0 M MEA+1.0 M [bmim] [BF₄]) at 40° C

Figure 13 illustrates the specimen's SEM image after immersion in carbonated solutions of (a) 4.0 M MEA, (b) (4.0 M MEA + 0.1 M [bmim] [BF₄]), (c) (4.0 M MEA + 0.5 M [bmim] [BF₄]), and (d) (4.0 M MEA+1.0 M [bmim] [BF₄]) at 80 °C . The specimen surface after immersion in carbonated MEA without [bmim] [BF₄] are covered with two types of corrosion products; the appearance of cracks can be seen all over the specimen surface which indicates the non-homogeneity of the

morphology of the scale formed. The corrosion layer seems to be more compact than that of the specimen immersed in (4.0 M MEA + 0.1 M [bmim] [BF₄]) which is loose and porous. The SEM analysis of the specimen surface after immersion in (4.0 M MEA + 0.5 M [bmim] [BF₄]) shows less corrosion products as compared to that of specimen immersed in carbonated (4.0 M MEA+ 0.1 M [bmim] [BF₄]) solution, the specimen surface revealed corrosion attacks on some preferential sites. However, for specimen immersed in carbonated (4.0 M MEA + 1.0 M [bmim] [BF₄]) system, the sites reduced to a scattered small spots and the surface layer seems to become compact and dense.

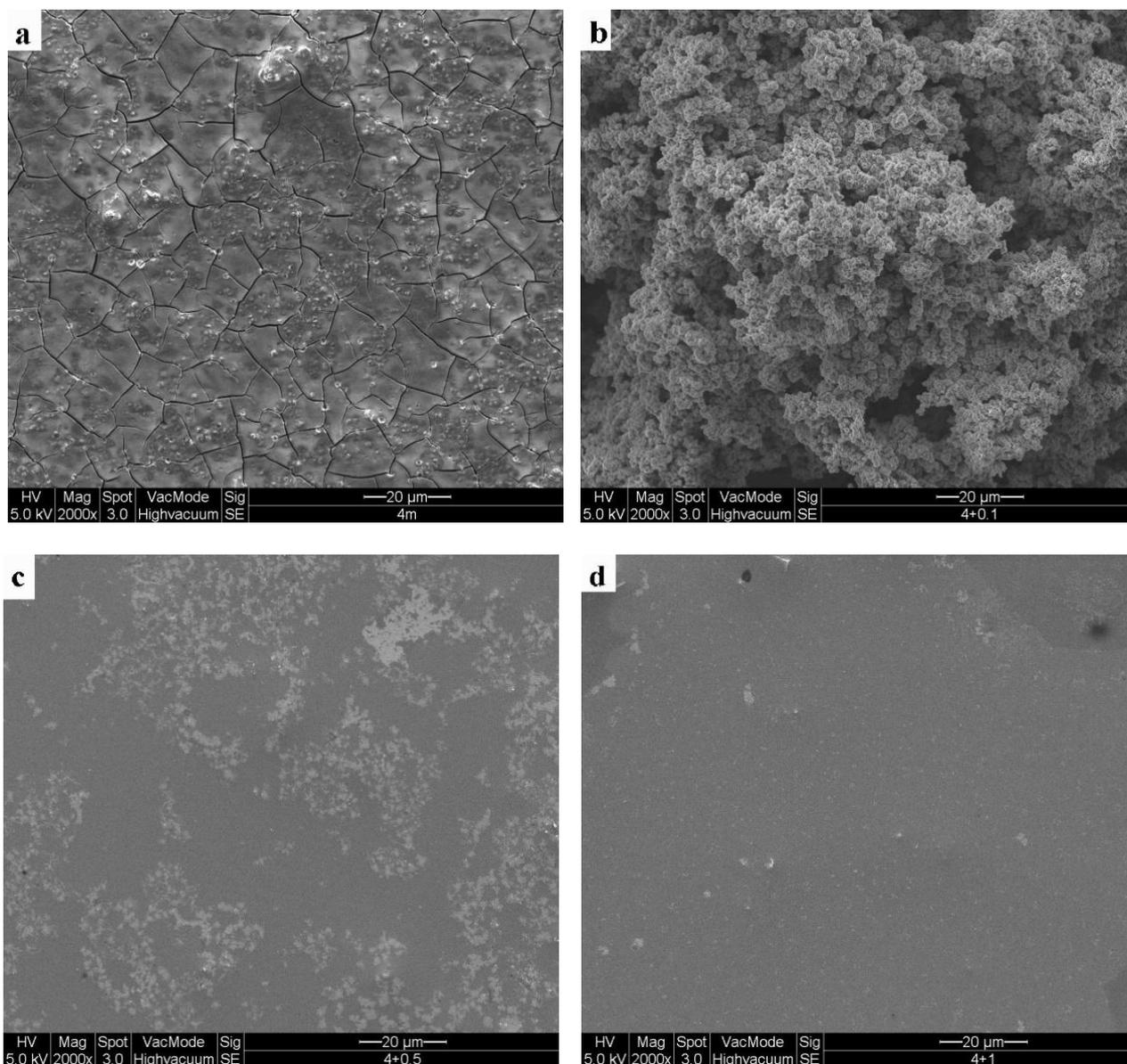


Figure 13. Carbon steel specimen's SEM image after immersion in carbonated solutions of (a) 4.0 M MEA, (b) (4.0 M MEA+0.1 M [bmim] [BF₄]), (c) (4.0 M MEA + 0.5 M [bmim] [BF₄]), and (d) (4.0 M MEA+1.0 M [bmim] [BF₄]) respectively at 80°C

The specimens immersed in carbonated (4.0 M MEA + 1.0 M [bmim] [BF₄]) system have shown a dramatic reduction in corrosion rate, based on investigation finding using polarization and weight loss method, and was confirmed by the specimen's SEM image.

4. CONCLUSIONS

The corrosivity of aqueous carbonated mixtures of MEA/ [bmim] [BF₄] to carbon steel was investigated at CO₂ loading of 0.55 mol/mol and at temperatures of 40 and 80 °C. It was found that the addition of [bmim] [BF₄] has increased the corrosion rate of carbon steel in carbonated aqueous solutions of 2.0 M MEA/ [bmim] [BF₄] systems at both temperatures. However, for carbonated 4.0 M MEA/ [bmim] [BF₄] systems, the corrosion rate of carbon steel has decreased with increasing [bmim] [BF₄] concentration. Corrosion rates obtained from polarization and weight loss methods are in accordance. The polarization method suggested that, there are different corrosion mechanisms taking place onto the specimen surface and images from SEM analysis confirmed these different mechanisms. Carbonated aqueous solution of MEA are well known for their corrosivity to carbon steel compared to other alkanolamine, it is believed that high corrosivity to carbon steel is due to the inhomogeneous FeCO₃ layer formed as corrosion product. The corrosivity of carbonated MEA/ [bmim] [BF₄] system to carbon steel was found to be more than the corrosivity of carbonated 2.0 M MEA at the investigated conditions. This increase in corrosivity is might be due to [bmim] [BF₄] characteristics. Ionic liquid [bmim] [BF₄] does not react with CO₂ but it is physically absorbed. Whether or not [bmim] [BF₄] interact with the carbonated aqueous alkanolamine solutions, the conclusions on the mechanism of the corrosion process in the investigated environments; could not be drawn; until this information is available; however, efforts are being made to investigate interactions between species and interface, which certainly would help to understand the corrosion mechanism.

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Financial support from University of Malaya through the High Impact Research Grant number VC/HIR/001 and PPP grant PS111/2009B are gratefully acknowledged

Nomenclature:

R ₂ NH	Diethanolamine
R ₃ N	N-methyldiethanolamine
R ₂ NH ₂ ⁺	Protonated Diethanolamine
R ₂ NCOO ⁻	Carbamate
HCO ₃ ⁻	Bicarbonate
[MEA]	Concentration of MEA in mol/l
[bmim] [BF ₄]	Concentration of MEA in mol/l

pH	Solution acidity or alkalinity
σ	Solution conductivity in Siemens/cm
β_a	Anodic slop in mV/decade
β_c	Cathodic slop in mV/decade
$E_{\text{corr.}}$	Corrosion potential in mV
$I_{\text{corr.}}$	Corrosion current density in mA/cm ²
CR	Corrosion rate in mm year ⁻¹

References

1. N. S. Allan, T. D. Bonifacio, L. Meng-Hui, *J. Chem. Therm.* 41 (2009) 525-529.
2. D. Chinn, Q. Vu. De, S. D. Michael, L. C. Boudreau, US Patent May 5 (2009) 7,527,775,B2.
3. D. Camper, J. E. Bara, L. Gin Douglas, R.D. Noble, *Ind. Eng. Chem. Res.* 47 (2008) 8496–8498.
4. N. A. Sairi, R. Yusoff, Y. Alias, M.K.Aroua, *Fluid Phase Equilib.* 300 (2011) 89–94.
5. A. Ahmady, M. A. Hashim, M. K. Aroua, *J. Chem. Eng. Data* 55 (2010) 5733–5738.
6. R. R. Veldman, *Corrosion* (Houston, TX, U. S.) 2000 (2000) Paper No. 00496.
7. R. N. Parkins, Z. A. Foroulis, *Corrosion* (Houston, TX, U. S.) 87 (1987) Paper No. 188.
8. L. A. S Ries, F. A. do Amaral, K. Matos, E. M. A. Martini, M. O. de Souza, R. F. de Souza, *Polyhedron* 27 (2008) 3287–3293.
9. L. Cammarata, S. G. Kazarian, P. A. Salter, and T. Welton, *Phys. Chem.* 3 (2001) 5192-5200.
10. J.A. Widegren, A. Laesecke, J. W. Magee, *Chem. Commun.* 12 (2005) 1610–1612.
11. M. Kanakubo, T. Umecky, T. Aizawa, Y. Kurata, *Chem. Lett.* 34 (2005) 324–325.
12. S.G. Kazarian, R.J. Briscoe, T. Welton, *Chem. Commun.* (2000) 2047–2048.
13. L.A. Blanchard, D. Hancu, E.J. Beckman, J.F. Brennecke, *Nature* 399 (1999) 28-29.
14. L. A. Blanchard, Z. Gu, J. F. Brennecke, *J. Phys. Chem. B* 105 (2001) 2437–2444.
15. W. Li, Z. Zhang, B. Han, H. Suqin, Y. Xie, G. Yang, *J. Phys. Chem. B* 111 (2007) 6452–6456.
16. J. Bowers, C.P. Butts, P.J. Martin, M.C. Vergara-Gutierrez, *Langmuir* 20 (2004) 2191–2198.
17. M. Uerdingen, C. Treber, M. Balsler, G. Schmitt, C. Werner, *Green Chem.* 7 (2005) 321–325.
18. A. Benamor, M.K. Aroua, *Fluid Phase Equilib.*, 231 (2005) 150–162.
19. ASTM Standard G5-94, Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements, ASTM, Philadelphia, PA, 1999 (Re-approved 1999).
20. ASTM G 31-72 Standard Practice for Laboratory Immersion Corrosion Testing of Metals (re-approved 1995), vol. 03.02, 1990
21. ASTM Standard Designation G1-90, Standard Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens, ASTM, Philadelphia, PA, 1999 (Reapproved 1999).
22. B. H. Ali, B. Si Ali, R. Yusoff, M. K. Aroua, *Int. J. Electrochem. Sci.*, 6 (2011) 181 -198
23. E. McCafferty, *Corrosion Sci.* 47 (2005) 3202–3215.
24. K.F. Khaled, A. A. Mohammed, *Corrosion Sci.* 51 (2009) 1964–1975.