

# Corrosion of Carbon Steel in Aqueous Solutions of Ionic Liquids and Alkanolamine Containing Carbon Dioxide

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**Abstract** - The new data for corrosion of carbon steel are reported in aqueous mixed solution containing (0.1-1.0 M) 1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF<sub>4</sub>]), (0.1-1.0 M) 1-Butyl-3-methylimidazolium dicyanamide ([bmim][DCA]) and 4M monoethanolamine (MEA) at 60 °C and CO<sub>2</sub> loading 0.55 mol/mol using electrochemical techniques; which were impedance spectroscopy and polarization curves. The experimental results show that the corrosion of carbon steel decreased with increasing concentrations of both ([bmim][DCA]) and ([bmim][BF<sub>4</sub>]) from 0.1-1.0 M. Also the surface analysis scanning electron microscopy (SEM) was carried out to characterize the corrosion products layers on the metal surface. Ionic liquids with dicyandiamide anion provided a better protection than tetrafluoroborate. These results suggest that the nature of the anion of ILs have influence on the corrosion of carbon steel.

**Index Terms** - Ionic Liquids, MEA, Electrochemical Techniques, Carbon Steel and CO<sub>2</sub> Corrosion

## I. INTRODUCTION

Room temperature ionic liquids (RTILs) are molten salts below 100 °C and are composed of a mixture of organic cations and organic/inorganic anions. Examples of these cations are ammonium, imidazolium, pyridinium, pyrrolidinium, piperidinium, phosphonium, and sulfonium and for anions are bromide, chloride and cyanide [1]. A combination of the cations and anions lead to a large number of ILs that provide a great deal of flexibility in choosing a pair, the most appropriate for the application of a specific chemical. ILs exhibits a range of properties, including in some specific cases, flammability, and low vapor pressure, as high thermal stability and large electrochemical window. These properties have made ILs as potential solvents to replace conventional organic solvents of aqueous solution of alkanolamine [2].

Generally, the use of alkanolamine has a few disadvantages including corrosion of amines system limits the concentration of amine in the solution which causes an additional cost, and amines are volatile and lost into the gas stream. In the recent years, ILs have been used successfully in several applications including: solvent and catalyst in reactions, gas separations, liquid separation, solvent for cleaning operation, electrolytes, in fuel cells, lubrication, corrosion inhibitors. ILs based on imidazolium have been approved to show corrosion resistance behavior on mild steel, copper and aluminum in acidic media [3-5]. Camper et al. [6] studied the solubility of CO<sub>2</sub> in IL-MEA solutions at atmospheric pressure, temperature of 40 °C and 50 mol% MEA and found that IL-MEA are effective for the capture of CO<sub>2</sub>. The same approach is discussed by Feng et al. [7], who utilized four different kinds of amino acids ILs with aqueous solutions of MDEA.

The conclusion was that these ILs enhance the absorption rate of CO<sub>2</sub>, reinforcing the capacity for capture in the solvent and showing a method for improvement of commercial solvents.

Corrosion of carbon steel in pure ionic liquids depends strongly on the type of the anion and cation. Marc and co-workers [8] studied the corrosion of several metals in several ionic liquids with different chemical structure under flow conditions at 90 °C. They showed that the corrosion of carbon steel in IL media depends strongly on the chemical structure of the cationic moiety and the nature of anion in the IL molecule. Likhanova and co-workers [9] studied the effect of two types of ionic liquids with imidazolium and pyridinium cations as corrosion inhibitors on mild steel in acid media. They showed that the inhibition effect of ionic liquid based on imidazolium higher than the pyridinium. However, reports on the corrosivity of ionic liquids mixed with alkanolamine against engineering alloys have not been found in the technical literature.

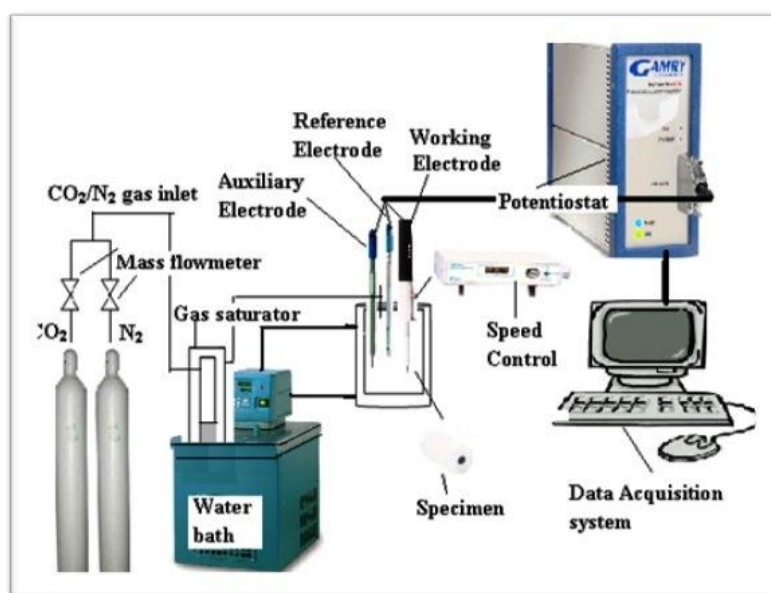
In this work, the corrosive ability of two ionic liquids has been investigated: 1-butyl-3-methylimidazoliumtetrafluoroborate ([bmim][BF<sub>4</sub>]) and 1-butyl-3-methylimidazolium dicyandiamide ([bmim][DCA]) in carbonated solution of monoethanolamine at 60 °C and CO<sub>2</sub> loading 0.55 mol/mol.

## II. EXPERIMENTAL WORK

Fig.1 shows the electrochemical experiment setup was used in this work. It is consist of a double jacketed cell reactor with a capacity of 100 ml, a Gamry potentiostat model (REF600), a water bath, a gas supply set connected to flow meters, a condenser, a rotator with a speed controller, and a data acquisition system. The cell reactor consists of three electrodes system, a platinum wire as counter electrode, carbon steel specimen as working electrode as well as a calomel-saturated electrode (CSE) as reference

electrode. Carbon steel specimen of chemical composition is shown in Table 1, was prepared to fit the specimen holder (working electrode) with a surface area  $0.28 \text{ cm}^2$ . The carbon steel was selected in this work due to it is the most commonly used for the construction of amine plant.

Before each experiment, the carbon steel specimen is polished with a varied grit silicon carbide paper in range of 600-2000, and then rinsed in distilled, water degreased in acetone and dried with hot air. The solvents used in this work to absorb  $\text{CO}_2$  were monoethanolamine (MEA with a purity of 99.5%) and ionic liquids based imidazolium with different anions ([bmim]  $[\text{BF}_4]$ ) and [bmim] [DCA] with a purity of 98.0%), and 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.



**Fig. 1** Experimental set up for electrochemical corrosion experiment

**Table 1** Chemical Composition of Test Specimens.

Carbon steel	Element	Weight percentage
	C	0.20
	Mn	0.45
	P	0.04
	S	0.05
	Cr	0.01
	Fe	balance

For a typical run, a 100 ml of an aqueous carbonated solution of MEA with and without ([bmim]  $[\text{BF}_4]$ ) and [bmim] [DCA] were prepared. The test solutions were prepared by purging a mixture of  $\text{CO}_2/\text{N}_2$  or pure  $\text{CO}_2$  to obtain the desired  $\text{CO}_2$  loading. In this work, the test solution was loaded to 0.55 (mol  $\text{CO}_2$ /mol solution) with an accuracy of  $\pm 0.05$ . Prior to tests, the solution was de-aerated by purging  $\text{N}_2$  (99.995%) for 0.5 hour. The tested parameters include concentration of ionic liquid, concentration of alkanolamine solution,  $\text{CO}_2$  loading in solution and solution temperature ( $^\circ\text{C}$ ). Tested conditions of these parameters are summarized in Table 2.

**Table 2** Tested parameters and conditions for MEA-ILs- $\text{H}_2\text{O}$ - $\text{CO}_2$  systems

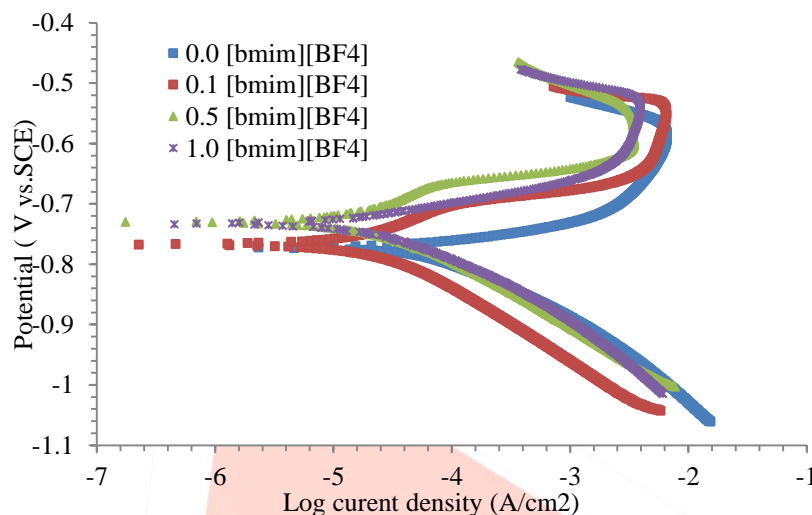
Parameters	Conditions
Concentration of MEA (M)	4.0
Concentration of ionic liquids (M)	0.1, 0.5 and 1.0
$\text{CO}_2$ loading in solution (mol $\text{CO}_2$ /molamine)	0.55
Solution temperature ( $^\circ\text{C}$ )	60

Variation of pH solution was continuously recorded, when a constant pH was reached (solution is saturated with  $\text{CO}_2$ ) the  $\text{CO}_2$  loading is then determined [10]. Prior the corrosion experiment, a steady state of the electrode corrosion was reached as indicated by a stable open circuit potential (OCP). EIS measurements were started using AC signals, of input sine wave voltage 5 mV and the frequency ranging from 100 Hz to 0.01 kHz. All impedance data were fitted with appropriate equivalent circuits using the Gamry Echem analyst software version "5.6". A Potentiodynamic polarization curves also were carried out with a scan rate of 0.9 mV/sec and potential range of 500 mV around the OCP.

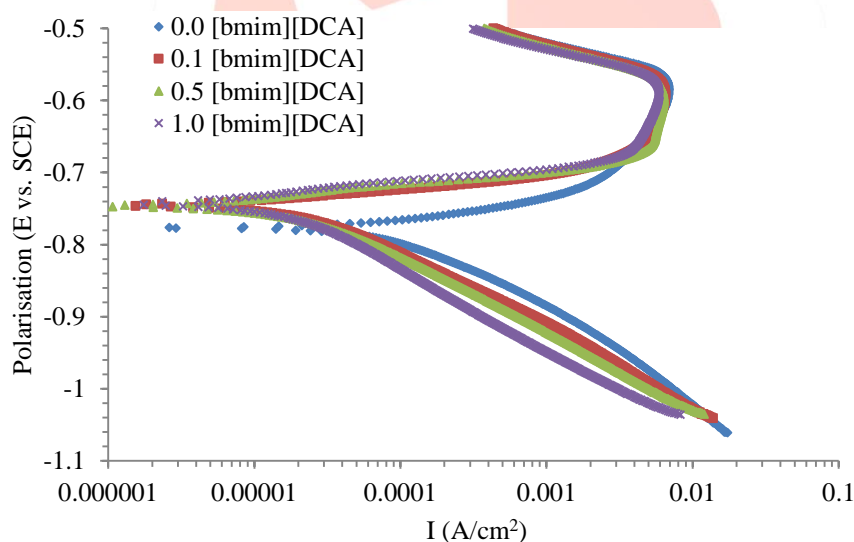
### III. RESULTS AND DISCUSSION

#### Polarization Study

The polarization curves of carbon steel immersed in carbonated solution of 4.0 M MEA, 4.0 M MEA+ [bmim][BF<sub>4</sub>] and 4.0 M MEA+ [bmim][DCA] are shown in Figs. 2 and 3 at CO<sub>2</sub> loading of 0.55 mol/mol and 60 °C. In the presence of both ionic liquids ([bmim][BF<sub>4</sub>] and [bmim][DCA]) the corrosion rate of carbon steel displaced towards lower values when concentration of ([bmim][BF<sub>4</sub>] and [bmim][DCA]) is increased. It is apparent, the addition of ([bmim][BF<sub>4</sub>] and [bmim][DCA]) shifted the corrosion potential towards noble values and caused a decrease in corrosion rate due to the formation of corrosion products; consequently, the dissolution of iron to the solution decreased. However, the addition of ([bmim][BF<sub>4</sub>] and [bmim][DCA]) to 4.0 M MEA decreases both the anodic and cathodic branches of the Tafel plots. This suggests that the ionic liquids retarded both cathodic and anodic (iron dissolution) reactions.



**Fig. 2** Effect of [bmim][BF<sub>4</sub>] Concentrations on Polarization Curve in 4.0 M MEA solution at 60 °C.



**Fig. 3** Effect of [bmim][DCA] Concentrations on Polarization Curve in 4.0 M MEA Solution at 60 °C.

Table 3 presents the summary of the electrochemical parameters extracted from the polarization curves of carbon steel using extrapolation of the Tafel lines in carbonated MEA/ [bmim][BF<sub>4</sub>] and MEA/ [bmim][DCA] mixtures, at 60 °C. It can be seen from Table 3 that the addition of both [bmim][BF<sub>4</sub>] and [bmim][DCA] to 4.0 MMEA has decreased the corrosion current densities of the solution. Consequently, the corrosion rate of carbon steel decreased. The corrosion rate was estimated from Tafel extrapolation method using equation 1.

$$CR = \frac{0.00327 \times i_{\text{corr}} \times w}{n \times D} \quad (1)$$

where, CR is the corrosion rate in (mmyr<sup>-1</sup>), w is the atomic weight of specimen in (55.85 gm/mol), n is the number of electrons transferred in the corrosion reaction “n= 2” and D is the density of the specimen 7.88 gm/cm<sup>3</sup>.

It can be deduced from the above results that the [bmim][DCA] is considered more evidence than [bmim][BF<sub>4</sub>] in carbonated solution of 4.0 M MEA at 60 °C. In addition, it can be seen that both slopes anodic and cathodic in Tafel plots has been affected by both ionic liquids.

**Table 3** Summary of the parameters extracted from the polarization curve of 4.0 M MEA, 4.0 M MEA/ [bmim][BF<sub>4</sub>] and 4.0 M MEA/ [bmim][DCA] at CO<sub>2</sub> loading of 0.55 mol/mol and 60 °C.

	Concentration (M)	B <sub>a</sub> mV/dec	B <sub>c</sub> mV/dec	E <sub>corr</sub> mV	I <sub>corr</sub> $\mu$ A/cm <sup>2</sup>	CR mm yr <sup>-1</sup>
[bmim][BF <sub>4</sub> ] +4.0 M MEA	0.0	44.2	122.5	-776	106	1.226
	0.1	49	121	-768	25.1	0.292
	0.5	43	105.0	-732	22.3	0.26
	1.0	42	100.0	-732	20.4	0.23
[bmim][DCA] +4.0 M MEA	0.0	44.2	122.0	-776	106	1.226
	0.1	25.0	91.31	-745	19.5	0.226
	0.5	67.5	101.7	-746	15.5	0.187
	1.0	44.9	96.40	-746	4.51	0.180

### IMPEDANCE STUDY

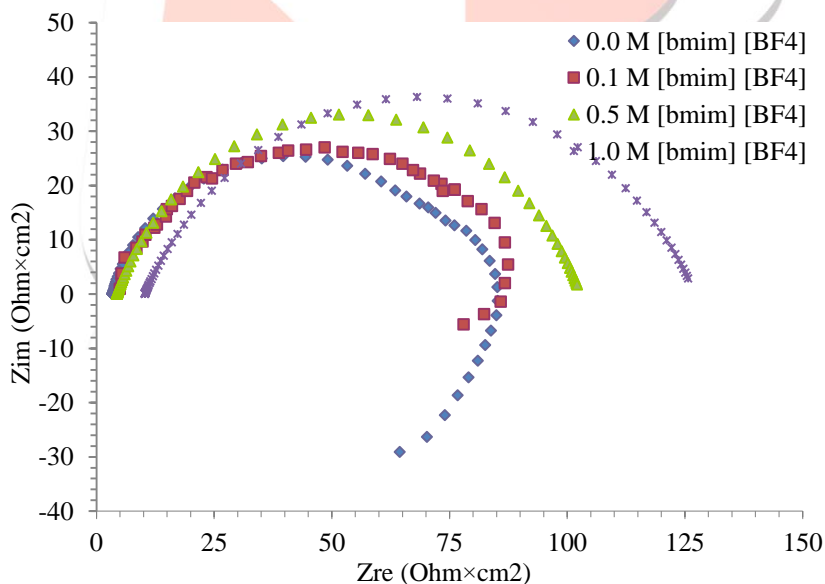
The Nyquist plots and its equivalent Bode plots were produced using EIS method, for MEA/ [bmim][BF<sub>4</sub>] carbonated solutions at 60 °C and CO<sub>2</sub> loading of 0.55 mol/mol. Fig. 4 illustrates typical Nyquist plots of carbon steel in 4.0 M MEA and 4.0 M MEA/[bmim][BF<sub>4</sub>]. The behavior of carbon steel exposed to carbonate 4.0 M MEA, exhibited a depressed capacitive loop at high frequency and an inductive loop at low frequency. The appearance of an inductive loop could be attributed to an adsorption of intermediate products on the carbon steel surface [11].

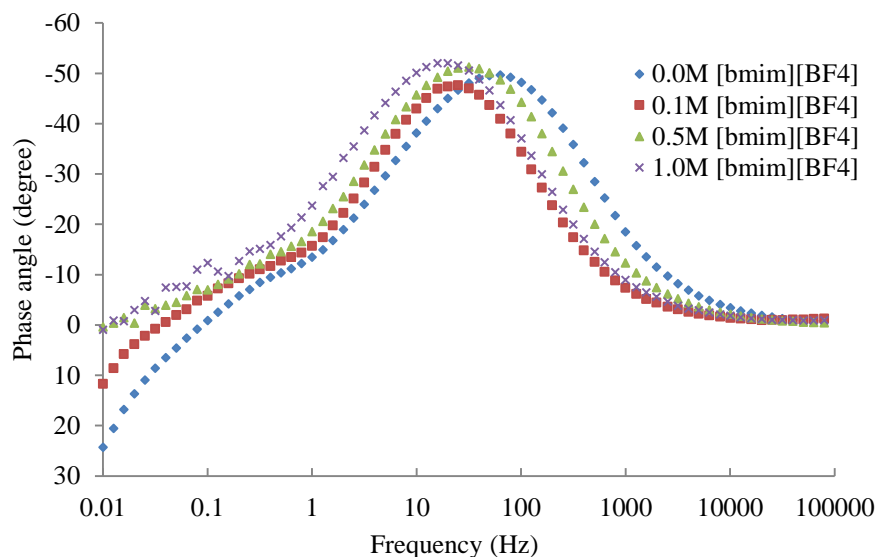
However at carbonated of 4.0 M MEA-0.1 M [bmim][BF<sub>4</sub>] showed two separate capacitive loop without an inductive loop, indicating that the corrosion mechanism changed on the carbon steel surface at concentration of 0.1 M [bmim][BF<sub>4</sub>].

This suggests that the surface layer of corrosion products getting pores. However, at carbonated 4.0 M MEA-0.5 M [bmim][BF<sub>4</sub>] and 4.0 M MEA- 1.0 M [bmim][BF<sub>4</sub>] the Nyquist plots showed a depressed semicircle without a small semicircle at low frequency, this can be attributed to block the pores layer with the corrosion products and the corrosion rate decreased.

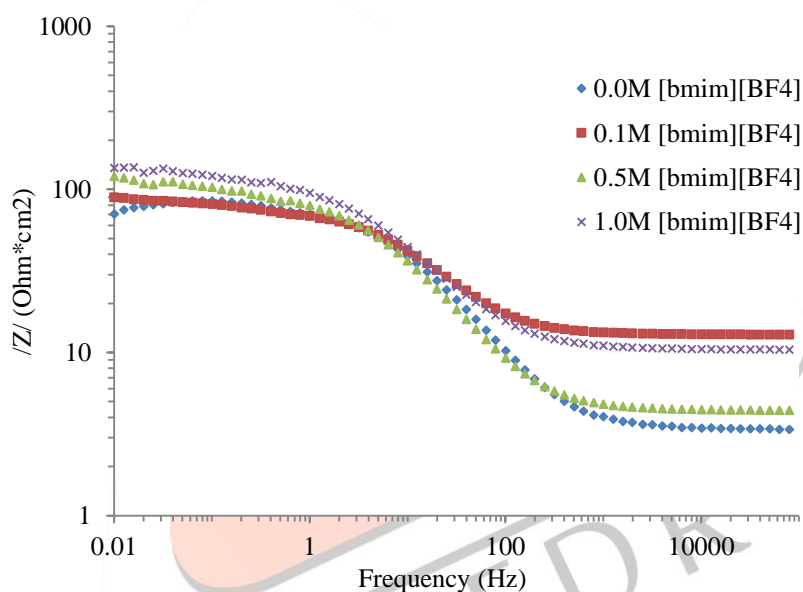
Fig. 5 shows Bode phase angle plots for carbon steel immersed in same condition of the solution mentioned above. It is apparent that the Bode plots for carbonated 4.0 M MEA and 4.0 M MEA-0.1M [bmim][BF<sub>4</sub>] depicted with two time constants, while for carbonated 4.0 M MEA-0.5 M [bmim][BF<sub>4</sub>] and 4.0 M MEA-1.0 M [bmim][BF<sub>4</sub>] only shows one time constant. The appearance of one time constant means that only one electrochemical reaction occurs on the carbon steel surface. The Bode phase angle plots (Fig. 5) show in a general manner that an increase in [bmim][BF<sub>4</sub>] concentration results in an increase in the phase angle.

The Bode impedance plots as shown in Fig. 6 also show that the impedance value in the presence of [bmim][BF<sub>4</sub>] is higher than that of the carbonated 4M MEA solution. This implies that the corrosion rate is decelerated in the presence of [bmim][BF<sub>4</sub>].

**Fig. 4** Nyquist plots of carbon steel in 4M MEA with different concentrations of [bmim][BF<sub>4</sub>] at temperature 60 °C.



**Fig. 5** Phase angle plots of carbon steel in 4M MEA with different concentrations of [bmim][BF<sub>4</sub>] at at temperature 60 °C.

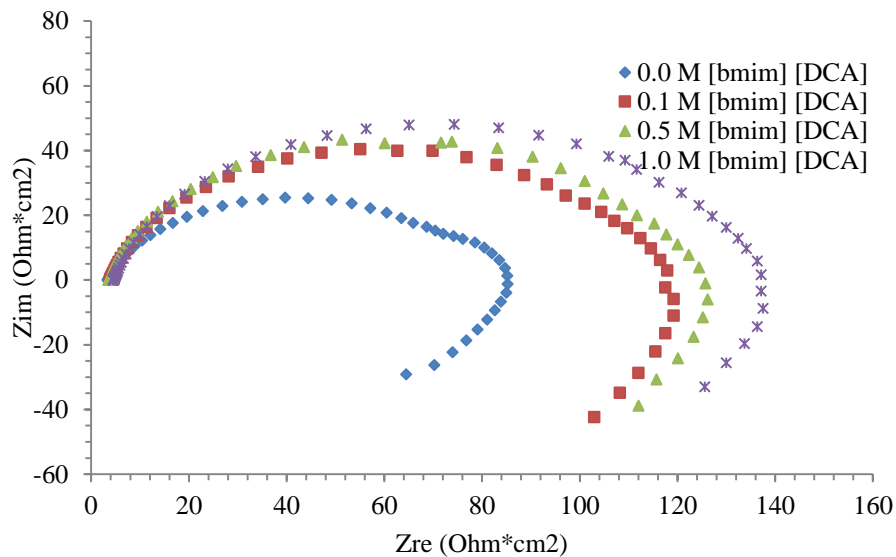


**Fig. 6** Bode impedance plots of carbon steel in 4M MEA with different concentrations of [bmim][BF<sub>4</sub>] at at temperature 60 °C.

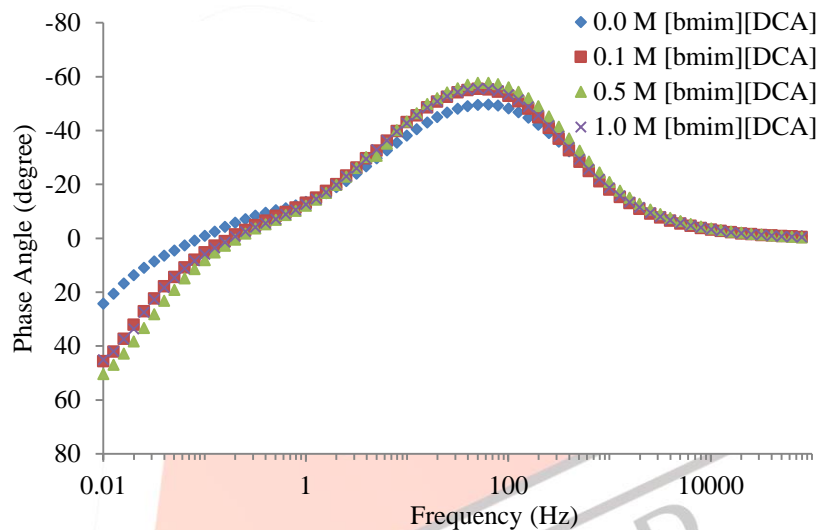
Fig. 7 shows the effect of [bmim][DCA] on the Nyquist plots of carbon steel immersed in carbonated of 4.0 M MEA at 60 °C. All Nyquist plots exhibited with a depressed capacitive loop at high frequency indicating a double layer capacitance as well as an inductive loop at low frequency. It can be observed that the diameter of Nyquist plots increases with increasing the concentrations of [bmim][DCA] from 0.1 to 1.0 M. This suggests that the resistance to charge transfer increased with [bmim][DCA] due to formation of a resistance layer between the surface of carbon steel and bulk solution, consequently the corrosion rate decreased. In general, the addition of [bmim][DCA] did not change the shape of Nyquist from that of 4.0 M MEA alone. This implies that the same corrosion mechanism for the carbon steel in the tests solution. In other words, the increase in semicircle of Nyquist plots has been identified by reducing the anodic and cathodic current densities in polarization curve Fig. 2.

It is observed from Fig. 8 that all Bode phase angle plots have two time constants; the first time constant emerges at high frequency and the other one at low frequency. The apparition of the first time constant indicates that changes to the double layer capacitance and charge transfer resistance; the latter is evidenced by the increase in phase angle magnitude which may be attributed to the adsorption of an intermediate of corrosion products on the carbon steel surface.

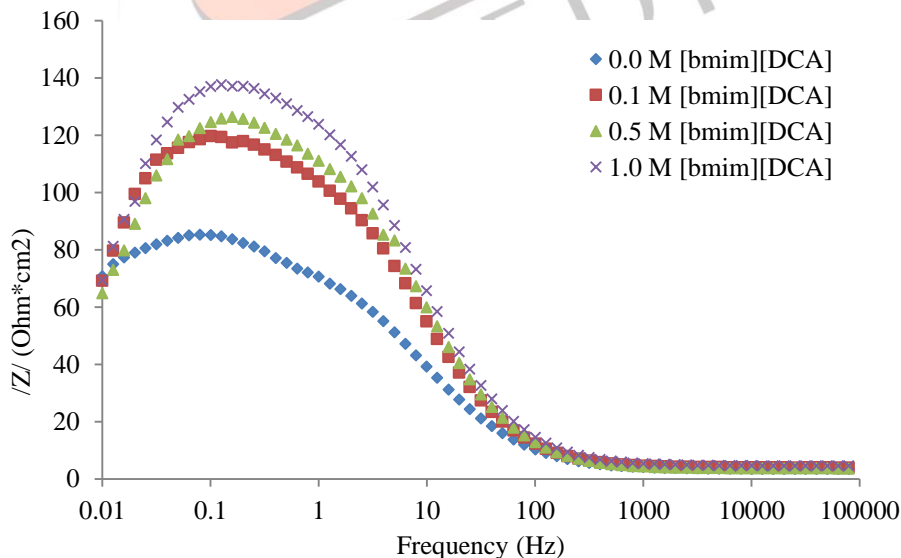
The Bode impedance plots (Fig. 9) illustrates that the impedance value in the presence of [bmim][DCA] is higher than that of the carbonated 4M MEA alone. This signifies that the corrosion rate is decelerated in the presence of [bmim][DCA].



**Fig. 7** Nyquist plots of carbon steel in 4.0 M MEA with different concentrations of [bmim][DCA] at 60 °C



**Fig. 8** Bode plots of carbon steel in 4M MEA with different concentration of [bmim][DCA] at 60 °C.



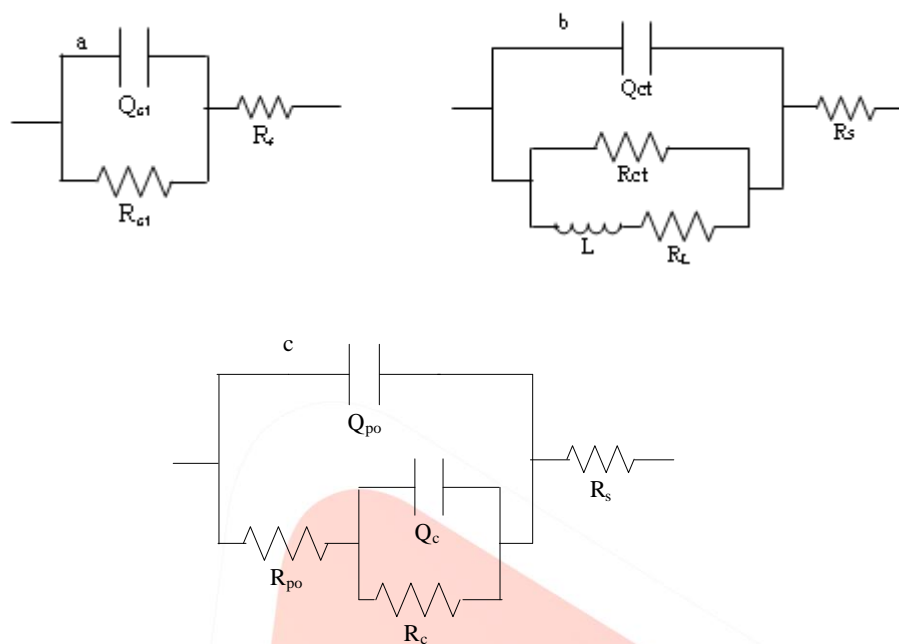
**Fig. 9** Bode impedance plots of carbon steel in 4M MEA with different concentrations of [bmim][DCA] at 60 °C.

Fig. 10 presents the equivalent circuits which were adopted to model the system under investigation. The parameters of interest could be obtained from the equivalent circuits such as electrolyte resistance ( $R_s$ ), charge transfer resistance ( $R_{ct}$ ), and pore resistance ( $R_{po}$ ). ( $Q_{dl}$ ) and ( $Q_{po}$ ) represent constant phase elements which replace the double layer capacitance ( $C_{dl}$ ) and pore capacitance ( $C_{po}$ ) respectively. The CPE impedance is calculated using the following equation [12].



$$Z_{CPE} = Q^{-1} (j\omega)^{-a} \quad (2)$$

where,  $Q$  is proportional to the capacitance of the corroding system [13], and  $a$  is a factor which takes value between 0 and 1. EIS experimental data plotted as Nyquist plots were fitted the equivalent circuit represented in Fig. 10. The best fit parameters of the model for carbon steel in carbonated 2.0 M MEA alone and carbonated mixtures of MEA – [bmim] [BF<sub>4</sub>] at 60 °C are summarized in Table 4.



**Fig.10** Equivalent circuits used to fit the EIS data.

Table 4 shows that the charge transfer resistance increases with increasing the concentrations of [bmim][BF<sub>4</sub>], except at [bmim][BF<sub>4</sub>] concentration of 0.1 M the charge transfer decreased. This indicates that the corrosion products getting pores and the corrosion rate increased. In contrast, the capacitance values ( $Q_{dl}$ ) tend to increase with adding 0.1 M of [bmim][BF<sub>4</sub>] and then decreased when the carbon steel immersed at carbonated solution of 4.0 M MEA+ 0.5 M [bmim][BF<sub>4</sub>] and 4.0 M MEA+1.0 M [bmim][BF<sub>4</sub>]. This can be attributed to a decrease in the dielectric constant and/ or an increase in the double electric layer thickness due to [bmim][BF<sub>4</sub>] adsorption or stepped on the metal/electrolyte interface (Okafor et al., 2009). Table 5 shows the parameters were extracted from Nyquist plots for carbon steel immersed in carbonated of 4.0 M MEA with and without [bmim][DCA] at 60 °C. In the presence of [bmim][DCA], the charge transfer resistance increases with increasing the concentrations of [bmim][DCA], this due to formation of a resistive layer on the surface. In contrast, the capacitance values ( $Q_{dl}$ ) tend to decrease with the introduction of [bmim][DCA]. This can be attributed to a decrease in the dielectric constant and/or an increase in the double electric layer thickness due to [bmim][DCA] adsorption or stepped on the metal/electrolyte interface [14].

**Table 4** Summary of the parameters extracted from the Nyquist plot of 4.0 M MEA and 4.0 M MEA/ [bmim][BF<sub>4</sub>] at CO<sub>2</sub> loading of 0.55 mol/mol and 60 °C.

Parameters	4.0 M MEA+ [bmim][ BF <sub>4</sub> ]			
	0.0	0.1	0.5	1.0
$R_s(\text{Ohm}\times\text{cm}^2)$	3.287	3.801	3.403	3.944
$Q_{dl}(\text{F.s}^{(a-1)})$	$0.945\times10^{-3}$	$0.573\times10^{-3}$	$0.524\times10^{-3}$	$0.587\times10^{-3}$
$R_{ct}(\text{Ohm}\times\text{cm}^2)$	80.55	113.2	122.5	141.3

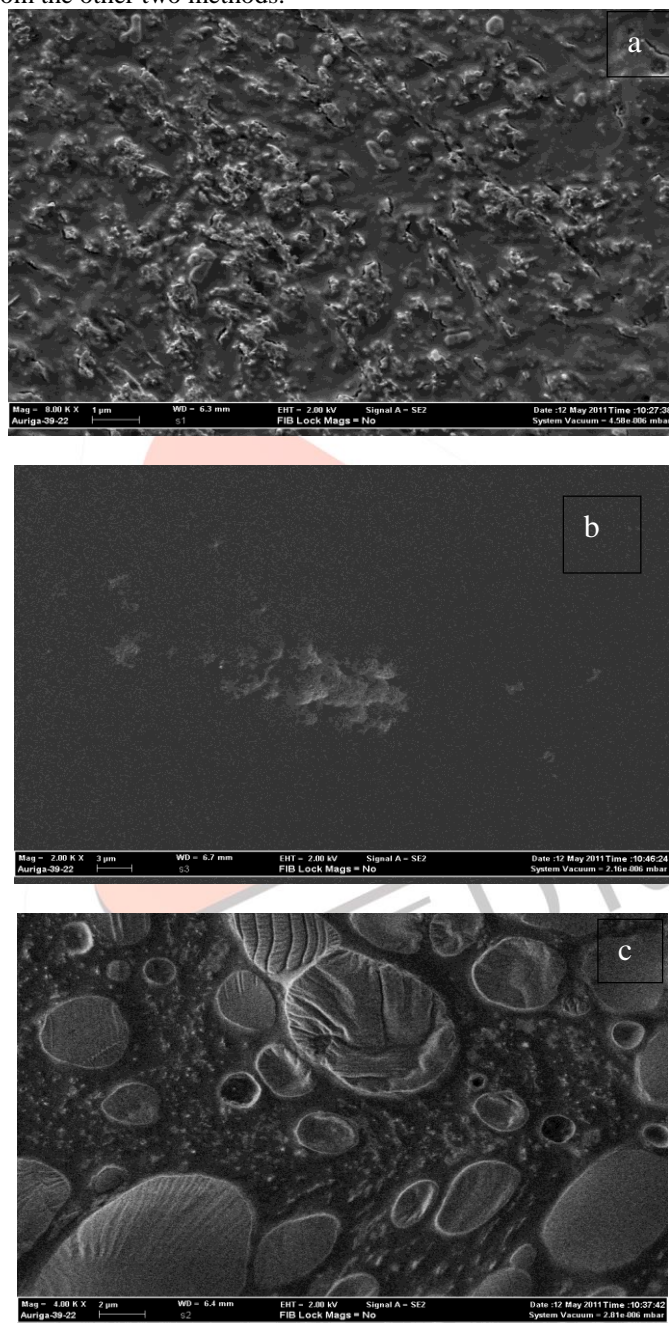
**Table 5** Summary of the parameters extracted from the Nyquist plot of 4.0 M MEA and 4.0 M MEA/ [bmim] [DCA] at CO<sub>2</sub> loading of 0.55 mol/mol and 60 °C.

Parameters	4.0 M MEA+ [bmim][ DCA]			
	0.0	0.1	0.5	1.0
$R_s(\text{Ohm}\times\text{cm}^2)$	3.287	12.81	4.358	10.3
$Q_{dl}(\text{F.s}^{(a-1)})$	$0.945\times10^{-3}$	0.054 59	$1.013\times10^{-3}$	$1.05\times10^{-3}$
$R_{ct}(\text{Ohm}\times\text{cm}^2)$	80.55	10.37	91.96	106.8
$Q_{po}(\text{F.s}^{(a-1)})$	-	$0.8533\times10^{-3}$	-	-
$R_{po}(\text{Ohm}\times\text{cm}^2)$	-	60.38	-	-

## SEM Analysis

Further analysis using SEM analysis was carried out on the surface of carbon steel to study the possible film formation. Fig. 11 shows the images obtained from SEM analysis. These images obtained after immersing the carbon steel sample for 168 hours in carbonated solution of 4.0 M MEA with and without [bmim] [DCA] and [bmim] [BF<sub>4</sub>] at 60 °C. In the absence of both [bmim] [DCA] and [bmim] [BF<sub>4</sub>], the surface seems rough and is covered with non-uniform corrosion products (refer to Fig. 11a). In contrast, with the addition of the 1.0 M [bmim] [BF<sub>4</sub>] to carbonated 4.0 M MEA, the metallic surface is much smoother as shown in Fig. 11b.

On the other hand, when carbon steel specimen is immersed in carbonated 4.0 M MEA+1.0 M [bmim] [DCA], the metallic surface partially covered with corrosion products layers. The layer can be seen much clearer especially for the sample immersed in the carbonated 4.0 M MEA+1.0 M IL (Fig. 11c). This suggests the slowdown of corrosion process, which also supports the corrosion rate results obtained from the other two methods.



**Fig. 11** Surface morphology of carbon steel in carbonated solution of (a) (4.0M MEA), (b) (4.0M MEA+1.0M [bmim][BF<sub>4</sub>]), (c) (4.0M MEA+1.0M [bmim][DCA]) at 60 °C.

#### IV. CONCLUSION

Our study reports the corrosion of carbon steel behavior in aqueous mixture of 4M MEA with and without ([bmim][DCA]) and [bmim][BF<sub>4</sub>] at 60 °C and CO<sub>2</sub> loading of 0.55 mol/mol using polarization curve, EIS measurements. Polarization technique showed that the corrosion rate decreased with increasing the concentration of both [bmim][DCA] and [bmim][BF<sub>4</sub>]. Impedance technique also pointed to the presence of [bmim][DCA] and [bmim][BF<sub>4</sub>] raises both the surface and the charge transfer resistances. The addition of [bmim][DCA] to 4M MEA solution decreased the corrosion rate without change the mechanism of reactions, while adding [bmim] [BF<sub>4</sub>], the data showed different corrosion mechanisms taking place onto the surface of the



specimen. The surface morphology shows that in presence of both [bmim][DCA] and [bmim][BF<sub>4</sub>] in carbonated 4M MEA caused a reduction of corrosion rate. The SEM results obtained are in good agreement with both techniques EIS and polarization curve.

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