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# Experimental and theoretical studies on some selected ionic liquids with different cations/anions as corrosion inhibitors for mild steel in acidic medium



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# ABSTRACT

Inhibition of mild steel corrosion in 1 M HCl solution by some alkylimidazolium-based ionic liquids (ILs) namely 1-ethyl-3-methylimidazolium ethylsulfate [EMIM]<sup>+</sup>[EtSO<sub>4</sub>]<sup>-</sup>, 1-ethyl-3-methylimidazolium acetate [EMIM]<sup>+</sup>[Ac]<sup>-</sup>, 1-butyl-3-methylimidazolium thiocyanate [BMIM]<sup>+</sup>[SCN]<sup>-</sup>, 1-butyl-3-methylimidazolium acetate [BMIM]<sup>+</sup>[Ac]<sup>-</sup> and 1-butyl-3-methylimidazolium dicyanamide [BMIM]<sup>+</sup>[DCA]<sup>-</sup> was investigated using electrochemical, spectroscopic, surface morphology, quantum chemical calculations, quantitative structure activity relationship (QSAR) and Monte Carlo simulation methods. The studied ILs showed appreciable inhibition efficiencies within the range of concentrations considered. Polarization measurements showed that the studied ILs are mixed-type inhibitors, that is, they inhibit both the anodic mild steel dissolution and cathodic hydrogen evolution reactions. The adsorption of the ILs on mild steel affords competitive physisorption and chemisorption processes and obeyed the Langmuir adsorption isotherm. Spectroscopic studies confirmed chemical interactions between the ILs and mild steel, while the scanning electron microscopy (SEM) images revealed the formation of protective film of the inhibitors on mild steel surface. Theoretical quantum chemical calculations, QSAR analyses and Monte Carlo simulations studies were used to correlate experimental results. The best fit QSAR equations are functions of molecular weight, fraction of electrons transferred from the inhibitor to the metal and dipole moment of the ILs.

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# 1. Introduction

The use of corrosion inhibitors to reduce the unwanted metal dissolution process associated with various industrial practices such as cooling water recirculation, acid pickling, acid descaling, oil-well acidizing etc. has been widely studied [1,2]. The use of corrosion inhibitors is one of the most practical and economical methods of protecting metals against corrosion and the initial mechanism involved in any corrosion inhibition process is the adsorption of the inhibitor on the surface of the metal [3–6]. Corrosion inhibitors are often synthesized from relatively cheap and readily available raw materials such as carbonyl compounds,

amines, alcohols etc. Most of these compounds contain  $\pi$ -electrons and functional groups such as -C=C-, -OR, -OH,  $-NR_2$ ,  $-NH_2$  and -SR, and heteroatoms such as S, O and N [7].

lonic liquids (ILs) are among the compounds that have been gaining increasing popularity in corrosion inhibition studies in the recent times. Ionic liquids (ILs) are salts with low melting points, frequently below room temperature [8]. The most common ILs are based on imidazolium, pyridinium, quaternary ammonium and quaternary phosphonium cations, but there is growing interest in some other classes of salts. They usually exhibit diverse chemical and physical properties, as well as phase behavior with other compounds. ILs can be designed for a particular application by selectively choosing the cation, anion and functional groups. Most ILs exhibit extremely low volatility over normal operating temperatures. In addition, they show good thermal stability (473–673 K before noticeable decomposition) and thus, exists as liquids over a rather wide temperature range. This affords the possibility of

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using ILs under many different processing conditions without fear of vapor emissions [9]. A huge number of different ILs can be generated due to the large number of possible permutations of cations and anions as well as variation of the side chain length, nature of ring substituents and/or substituents position on the ring [10,11]. Despite the large number of ILs known, the 1-alkyl-3methylimidazolium based ILs constitute the most commonly used family of ILs in industrial applications [10]. This may be partly due to the availability of quite a number of spectroscopic and physicochemical data on these compounds as compared to other families of ILs [12]. The corrosion inhibition activities of a few number of imidazolium ILs have been documented in the literature [13–16].

The comparative studies on corrosion inhibition properties of IL systems often reported in the literature typically comprise two compounds with the same cations but different anions or vice versa [17–20]. Reports on the effects of alkyl chain length on the inhibition efficiency of ILs are also more common than those on the effects of anions [18,21,22]. Experimental and theoretical investigations on comparative inhibition activities of more than three IL systems are fragmentary. This may be due to the rather complex nature of interactions that exist in IL solutions. Another possible reason is the difficulties in carrying out reliable experimental studies, which is associated with the hygroscopicity of many ILs and presence of impurities [10].

This has motivated us to carry out the present study on the corrosion inhibition properties of five IL systems namely: 1-ethyl-3-methylimidazolium ethylsulfate  $[EMIM]^+[EtSO_4]^-,$ 1-ethyl-3-methylimidazolium acetate [EMIM]<sup>+</sup>[Ac]<sup>-</sup>, 1-butvl-3-methylimidazolium thiocyanate [BMIM]<sup>+</sup>[SCN]<sup>-</sup>, 1-butyl-3-methylimidazolium acetate [BMIM]<sup>+</sup>[Ac]<sup>-</sup> 1-butyland [BMIM]+[DCA]-3-methylimidazolium dicyanamide using electrochemical measurements, spectroscopic techniques, quantum chemical calculations coupled with quantitative structural activities relationship (QSAR) and Monte Carlo simulations approach. The set of ILs considered in the present work comprises those with the same cations but different anions, those with the same anions but different cations and those with different cations and different anions. This kind of composite system will provide undissipated information about the effects of cations, anions and chain length on the corrosion inhibition properties of the ILs. More so, the QSAR analysis generated from such composite systems is expected to be more robust as it takes more factors into consideration. The test material in the present study is mild steel in 1 M HCl solution. To the best of our knowledge, the kind of study reported on the set of ILs considered in this work has not been documented in the literature. The schematic representation of the structures of the studied ILs are presented in Fig. 1.

# 2. Experimental

# 2.1. Mild steel specimens

All experimental procedures were carried out using mild steel specimens of composition (wt%) of C=0.17, Mn=0.46, Si=0.26, S=0.017, P=0.019, and balance Fe. These specimens were carefully prepared prior to each experiment. They were abraded using various grades of emery papers, washed with doubly distilled water, degreased with acetone, air-dried and finally stored in the desic-cators. Each mild steel specimen with prepared shinning surface is used for respective experimental measurements within 1 h.

# 2.2. Inhibitors

The ILs  $[EMIM]^+[EtSO_4]^-$ ,  $[EMIM]^+[Ac]^-$ ,  $[BMIM]^+[SCN]^-$ ,  $[BMIM]^+[Ac]^-$  and  $[BMIM]^+[DCA]^-$  were purchased from Sigma Aldrich with mass fraction purity  $\geq 0.97\%$  and were used without



**Fig. 1.** Schematic representation of the structures of 1-Ethyl-3-methylimidazolium ethyl sulfate [EMIM]<sup>+</sup> [EtSO<sub>4</sub>]<sup>-</sup>, 1-Ethyl-3-methylimidazolium acetate [EMIM]<sup>+</sup> [Ac]<sup>-</sup>, 1-Butyl-3-methylimidazolium thiocyanate [BMIM]<sup>+</sup> [SCN]<sup>-</sup>, 1-Butyl-3-methylimidazolium acetate [BMIM]<sup>+</sup> [Ac]<sup>-</sup>, 1-Butyl-3-methylimidazolium di-cyanamide [BMIM]<sup>+</sup> [DCA]<sup>-</sup>.

any further purification. All the chemicals were stored over 0.4 nm molecular sieves to remove moisture.

#### 2.3. Acid and inhibitor solutions

Aggressive solution of 1 M HCl was prepared by diluting the 37% AR grade HCl solution with distilled water. The stock solutions of ILs were diluted to 100, 300 and 500 ppm and used for the experiments.

# 2.4. Electrochemical measurements

All electrochemical measurements were carried out on Autolab PGSTAT 302 N purchased from Metrohm and controlled by the general-purpose electrochemical software (GPES). A threeelectrode electrochemical setup was used with mild steel as working electrode (WE), platinum rod as counter electrode (CE) and Ag/AgCl in 3 M KCl as reference electrode (RE). All the experiments were performed under atmospheric condition without stirring. Prior to the all electrochemical measurements, a stabilization period of 30 min was allowed for the system to attain a relatively stable value of open circuit potential (OCP). The potentiodynamic polarization curves were recorded in the potential range from -250 to +250 mV (vs Ag/AgCl, 3 M KCl) at a scan rate of 1 mV s<sup>-1</sup>. The electrochemical impedance spectroscopy (EIS) measurements were carried out in a frequency range from 100 kHz to 1 Hz with amplitude of 10 mV peak-to-peak using the AC signal at the OCP.

#### 2.5. UV-visible spectroscopic studies

Mild steel samples with pretreated surfaces as described in Section 2.1 were immersed in acidic solutions of 500 ppm IL solutions for 24 h. The UV-vis spectra of the IL solutions before and after mild steel immersion were recorded on the UViLine 9400 obtained from Schott instruments.

#### 2.6. FTIR spectroscopic studies

Mild steel samples with pretreated surfaces as described in Section 2.1 were immersed in acidic solutions of 500 ppm IL solutions for 24 h. The FTIR spectra for the pure ILs and the resulting

solutions after 24 h of mild steel immersion in the 500 ppm solutions were recorded using the Bruker alpha-P FT-IR spectrometer.

# 2.7. Surface analysis

For the purpose of surface analysis, mild steel specimens with freshly pretreated surface as described in Section 2.1 was utilized. Mild steel specimens with abraded and cleaned surfaces were immersed in 1 M HCl solution without and with 500 ppm concentration of the studied ILs. Samples were removed after 24 h of immersion, rinsed with distilled water, degreased with acetone and finally air-dried. Scanning electron microscopy images of the mild steel samples retrieved from the aggressive solutions as well as plain mild steel surface were taken using the Quanta FEG 250 Environmental Scanning electron microscope.

# 2.8. Quantum chemical calculations and quantitative structure activity relationship (QSAR)

The studied ILs were modelled with GaussView 5.0 to obtain the initial geometry. Gas phase geometry optimizations and vibrational frequency calculations were carried out without symmetry constraint. The Becke's three parameter hybrid functional together with Lee-Yang-Parr correlation functional (B3LYP) was used for the calculations [23,24]. The B3LYP is an hybrid functional that has gained wide popularity in DFT calculations as it produces satisfactory geometries at relatively less computational cost [25-28]. The use of the 6-31++G(d,p) basis set that places diffuse functions on light and non-hydrogenic atoms was necessitated by the presence of anions in the IL systems. Anions generally have a more diffuse electron density than neutral atoms, therefore, diffuse functions must be added to treat them properly [29]. Truhlar and co-workers [29] have described the inclusion of diffuse basis functions as a way of removing the bulk of the errors and improving the accuracy of results especially for DFT calculations. Diffuse functions have been described to work well with quite a number of basis sets in the literature, especially 6-31 G and 6-311 G in minimizing the energies of small anions [30-32]. Optimized geometries of the ILs were confirmed to correspond to their molecular structures at their true energy minima with the absence of imaginary frequency in the calculated vibrational frequencies. Various quantum chemical parameters including the total energy (*TE*), dipole moment ( $\mu$ ), frontier molecular orbital (FMO) energy parameters, i.e. energy of the highest occupied molecular orbital ( $E_{HOMO}$ ) and energy of the lowest unoccupied molecular orbital ( $E_{LUMO}$ ) were obtained from the optimized structures of the ILs. Ionization potential  $(I = -E_{HOMO})$  and electron affinity  $(A = -E_{LUMO})$  were calculated in accordance with the Koopman's theorem [33]. The energy gap  $(\Delta E = E_{LUMO} - E_{HOMO})$  was also calculated. The electronegativity  $(\chi)$ , global hardness  $(\eta)$  and fraction of electrons transferred (N)were calculated respectively as [34,35]:

$$\chi = \frac{1}{2}(l+A) \tag{1}$$

$$\eta = \frac{1}{2}(I - A) \tag{2}$$

$$\Delta N = \frac{\chi_{\rm Fe} - \chi_{inh}}{2(\eta_{\rm Fe} + \eta_{inh})} \tag{3}$$

where  $\chi_{\text{Fe}}$  and  $\eta_{\text{Fe}}$  are the electronegativity and hardness of iron respectively. A value of 7.0 eV was used for the  $\chi_{\text{Fe}}$ , while  $\eta_{\text{Fe}}$  was neglected by assuming that I=A (i.e.  $\eta=0$ ) for a metallic bulk [36]. All quantum chemical calculations were carried out using the Gaussian 09 for Windows [37]. The calculations were carried out in the gas phase with the assumption that effect of solvent will be similar on the compounds and could therefore be safely ignored.

The quantitative structure activity relationships (QSAR) plots and the corresponding equations were derived using the XLSTAT program [38].

#### 2.9. Monte Carlo simulations

Monte Carlo simulations using the Adsorption Locator and Forcite codes implemented in the Material Studio 7.0 software from Accelrys Inc. USA [39], was adopted to compute the low energy configuration and the adsorption energy of the interaction between ionic liquids (ILs)) and clean Fe (110) surface. For the whole simulation procedure, the Universal force field was used to optimize the structures of all components of the system of interest. The universal force field adopted for this simulation has been shown to produce accurate bulk and surface properties for Fe (110) and organic inhibitor molecules [40]. The Fe (110) crystal surface was selected for this simulation, because it is the most stable surface as reported in the literature [41]. The simulation was carried out in a simulation box (17.37 Å  $\times$  17.37 Å  $\times$  38.10 Å) having  $\alpha =$ 90.00°;  $\beta = 90.00^{\circ}$  and  $\gamma = 70.52^{\circ}$  with periodic boundary conditions in order to simulate a representative part of an interface devoid of any arbitrary boundary effects. The Fe (110) plane was next enlarged to a  $(7 \times 7)$  supercell. After that, a vacuum slab of 30 Å thickness was built above the Fe (110) to convert the system to 3D periodicity. The optimized ILs inhibitor using the Forcite code was then added near the surface of Fe (110) and a Monte Carlo simulation annealing procedure was carried out. Detail theoretical procedures using Monte Carlo methodology are well documented elsewhere [42,43].

# 3. Results and discussion

#### 3.1. Potentiodynamic polarization studies

The potentiodynamic polarization curves for mild steel electrode immersed in 1 M HCl solution in the absence and presence of various concentrations of the studied ILs after immersion for 30 min at  $303 \pm 1$  K are presented in Fig. 2. Kinetic parameters such as the corrosion potential ( $E_{corr}$ ), corrosion current density ( $i_{corr}$ ), anodic and cathodic Tafel slopes ( $\beta_a$  and  $\beta_c$  respectively) were obtained and reported in Table 1. The  $i_{corr}$ ,  $\beta_a$  and  $\beta_c$  were obtained by extrapolating the linear segments of the anodic and cathodic linear Tafel plots to the corrosion potential via the use of the Tafel analysis tool incorporated in the GPES software. The percentage inhibition efficiency ( $IE_{PDP}$ %) was evaluated from the measured  $i_{corr}$  values using the relationship [17,18,20]:

$$IE_{PDP}\% = \frac{i^{0}_{corr} - i^{i}_{corr}}{i_{corr}^{0}} \times 100$$
(4)

where  $i^{\circ}_{corr}$  and  $i^{i}_{corr}$  are values of corrosion current density in the absence and presence of inhibitors respectively.

It can be seen from Fig. 2 that the polarization curves in the presence of the IL inhibitors shifted towards the more negative potentials relative to the blank system, indicating the more predominant cathodic inhibition activities of the inhibitors. A compound can only be regarded as either a anodic or cathodic inhibitor when the change in the  $E_{corr}$  value between the inhibited and the blank system is greater than 85 mV [14,44]. The results in Table 1 show that the differences in the  $E_{corr}$  values between the inhibited and the uninhibited systems are generally less than 85 mV, which implies that the studied ILs are mixed-type inhibitors with predominatly cathodic inhibition. In other words, the studied ILs inhibit the anodic dissolution of mild steel in 1 M HCl and also retards the cathodic reduction reaction associated with hydrogen gas evolution. The shift in the polarization curves towards the more negative



**Fig. 2.** Potentiodynamic polarization curves of corrosion inhibition of mild steel in 1 M HCl in the absence and presence of different concentrations of (A) [EMIM]<sup>+</sup> [EtSO<sub>4</sub>]<sup>-</sup>, (B) [EMIM]<sup>+</sup> [Ac]<sup>-</sup>, (C) [BMIM]<sup>+</sup> [SCN]<sup>-</sup>, (D) [BMIM]<sup>+</sup> [Ac]<sup>-</sup> and (E) [BMIM]<sup>+</sup> [DCA]<sup>-</sup>.

values increase with increasing concentration of the ILs. This implies that the mixed-type inhibiting effect of the studied ILs tends to be more predominantly cathodic at higher concentrations.

The change in the values of the anodic Tafel slope,  $\beta$ a in the presence of inhibitors may be attributed to the adsorption of chloride ion (from HCl) or inhibitor molecules on the mild steel

surface, or occurrence of some redox processes that involve Feinhibitor complexes on the active sites of the steel [45–47]. Notable changes in the values of both  $\beta_a$  and  $\beta_c$  as recorded in Table 1 upon addition of inhibitors may imply that the mitigation of both the anodic dissolution and hydrogen evolution reactions is not solely due to surface blocking effect [47]. The values of

Ionic liquids	Concentration of inhibitors (ppm)	$-E_{\rm corr}~({ m mV})$	$i_{\rm corr}~({ m mA~cm^{-2}})$	$\beta_{\rm c}~({\rm mV/dec})$	$\beta_{\rm a}~({\rm mV/dec})$	IE(%)
[EMIM] <sup>+</sup> [EtSO <sub>4</sub> ] <sup>-</sup>	Blank	432	2.928	177	151	-
	100 ppm	433	0.363	97	77	87.58
	300 ppm	436	0.295	82	98	89.92
	500 ppm	539	0.212	156	107	92.75
[EMIM] <sup>+</sup> [Ac] <sup>-</sup>	100 ppm	435	0.683	87	111	68.10
	300 ppm	494	0.358	122	137	81.25
	500 ppm	526	0.274	84	145	87.87
[BMIM] <sup>+</sup> [SCN] <sup>-</sup>	100 ppm	459	0.825	83	95	71.82
	300 ppm	480	0.529	67	129	81.93
	500 ppm	516	0.342	129	73	88.32
[BMIM]+ [Ac] -	100 ppm	436	0.566	65	133	80.66
	300 ppm	468	0.323	150	163	88.96
	500 ppm	493	0.279	177	131	90.47
[BMIM] <sup>+</sup> [DCA] <sup>-</sup>	100 ppm	435	0.683	87	111	76.67
	300 ppm	494	0.358	122	137	87.77
	500 ppm	526	0.274	84	145	90.64

Electrochemical parameters obtained from potentiodynamic polarization curves of  $[EMIM]^+$   $[EtSO_4]^-$ ,  $[EMIM]^+$   $[Ac]^-$ ,  $[BMIM]^+$   $[SCN]^-$ ,  $[BMIM]^+$   $[Ac]^-$ ,  $[BMIM]^+$   $[DCA]^-$ .

Table 2

Electrochemical parameters obtained from Nyquist and Bode plots of  $[EMIM]^+$   $[EtSO_4]^-$ ,  $[EMIM]^+$   $[Ac]^-$ ,  $[BMIM]^+$   $[SCN]^-$ ,  $[BMIM]^+$   $[Ac]^-$ ,  $[BMIM]^+$   $[DCA]^-$ .

Ionic liquids	Concentration of inhibitors (ppm)	$R_{\rm s} (\Omega \ {\rm cm}^2)$	$R_{\rm ct} (\Omega \ {\rm cm}^2)$	n	$C_{\rm dl}~(\mu {\rm F~cm^{-2}})$	IE(%)
[EMIM] <sup>+</sup> [EtSO <sub>4</sub> ] <sup>-</sup>	Blank	0.760	28.2	0.80	571.0	-
	100 ppm	1.718	208.8	0.86	91.84	86.49
	300 ppm	1.395	305.5	0.87	85.12	90.76
	500 ppm	1.758	389.8	0.88	79.44	92.76
EMIM] <sup>+</sup> [Ac] <sup>-</sup>	100 ppm	1.316	87.6	0.87	375.1	67.80
	300 ppm	1.288	145.7	0.82	291.5	80.64
	500 ppm	1.492	217.7	0.81	203.3	87.04
[BMIM] <sup>+</sup> [SCN] <sup>-</sup>	100 ppm	1.565	99.2	0.83	122.61	71.57
	300 ppm	2.305	149.2	0.75	75.12	81.09
	500 ppm	2.415	239.8	0.86	56.34	88.24
[BMIM]+ [Ac]-	100 ppm	2.270	141.4	0.86	230.1	80.05
	300 ppm	2.415	236.8	0.86	136.2	88.09
	500 ppm	2.804	294.4	0.88	122.4	90.42
[BMIM] <sup>+</sup> [DCA] <sup>-</sup>	100 ppm	1.825	121.8	0.89	106.61	76.84
	300 ppm	1.586	219.1	0.90	92.28	87.12
	500 ppm	1.537	307.4	0.90	80.76	90.82

the Tafel slopes also vary with concentrations of the ILs. These observations suggest that inhibitive effect of the studied ILs involves some changes in the mechanism of the corrosion reactions. Similar observations in the literature have been attributed redox process involving intermediates with different redox activities at different concentrations of the inhibitors [47]. Based on these observations and the documented mechanism of Fe corrosion in acidic solution as reported in the literature [20,48–50], it can be assumed that the mechanism of inhibition of steel corrosion by the studied ILs involves; at the anode (adsorption of IL cation, IL<sup>+</sup>):

$$(\text{FeCl}^{-})_{\text{ads}} + \text{IL}^{+} \rightleftharpoons [\text{Fe}(\text{Cl}^{-})(\text{IL}^{+})]_{\text{ads}}$$
(5)

at the anode (adsorption of IL anion, IL<sup>-</sup>):

$$Fe + IL^{-} \rightleftharpoons [FeIL^{-}]_{ads}$$
 (6a)

$$[FeIL^{-}]_{ads} + IL^{+} \rightarrow [FeIL^{-}IL^{+}]_{ads}$$
(6b)

at the cathode:

$$Fe + IL^+ \rightleftharpoons [FeIL^+]_{ads} \tag{7}$$

This implies that anodic Fe dissolution can be mitigated by the intermediate reactions in Eqs. 5 and 6 in the presence of the inhibitors, while cathodic hydrogen evolution is diminished by Eq. 7 in which  $IL^+$  adsorbed on cathodic sites in competition with acidic H<sup>+</sup>.

The inhibition efficiency (%IE<sub>PDP</sub>) values in Table 1 increase with increase in concentration for all the studied ILs with [EMIM]<sup>+</sup>[EtSO<sub>4</sub>]<sup>-</sup> showing the highest values of %*IE*. The higher inhibition efficiency of [EMIM]<sup>+</sup>[EtSO<sub>4</sub>]<sup>-</sup> compared to [EMIM]<sup>+</sup>[Ac]<sup>-</sup> may be as result of more number of electronegative heteroatoms (O and S) present in the [EtSO<sub>4</sub>]<sup>-</sup> anion [51]. The better inhibition efficiency of [EMIM]+[EtSO<sub>4</sub>]<sup>-</sup> compared to the other ILs considered in this work is also in agreement with previous literature reports that organic compounds with S-atom(s) usually show better inhibition efficiency that those containing O and N atoms [19,52,53]. Among the ILs with  $[BMIM]^+$  cation,  $[BMIM]^+[Ac]^$ shows higher inhibition efficiency, though the inhibition efficiencies of [BMIM]<sup>+</sup>[Ac]<sup>-</sup> and [BMIM]<sup>+</sup>[DCA]<sup>-</sup> are almost the same at 500 ppm. The higher inhibition efficiency of [BMIM][Ac] compared to [EMIM][Ac] can be attributed to the longer alkyl chain length in BMIM (butyl) than EMIM (ethyl). Similar observations have been documented in the literature [18,54].

#### 3.2. Electrochemical impedance spectroscopy (EIS)

The EIS measurements were performed on mild steel in 1 M HCl without and with various concentrations of the studied ILs. The Nyquist plots obtained from the EIS measurements are presented in Fig. 3. The Nyquist plots exhibit depressed capacitive loop, which may be attributed to the charge transfer reaction. The depression in semicircle loop is usually attributed to the roughness and other inhomogeneity's of the solid electrode [19]. The diameter of the capacitive loop increases with increasing concentration



Fig. 3. Nyquist plots of corrosion inhibition of mild steel in 1 M HCl in the absence and presence of different concentrations of (A) [EMIM]<sup>+</sup> [EtSO<sub>4</sub>]<sup>-</sup>, (B) [EMIM]<sup>+</sup> [Ac]<sup>-</sup>, (C) [BMIM]<sup>+</sup> [SCN]<sup>-</sup>, (D) [BMIM]<sup>+</sup> [Ac]<sup>-</sup> and (E) [BMIM]<sup>+</sup> [DCA]<sup>-</sup>.

of the IL inhibitors. This is an indication of corrosion inhibition due to the formation of protective film on the mild steel surface.

The Bode phase angle and impedance plots obtained from the EIS measurements are presented in Fig. 4. A new phase angle shift in the higher and middle frequency regions together with a change in the phase angle shift was observed with increase in the concentration of the inhibitors. This is as a result the formation of protective film of the inhibitors on the steel surface leading to change in the electrode interfacial structure.

The impedance kinetic parameters were determined by fitting the impedance data to the equivalent circuit model of the form  $R_s(R_{ct}CPE)$  shown in Fig. 5. This was achieved by using the fit and simulation analysis tool implemented in the GPES software. Excellent fit with this model was obtained for all the experimental data. For the description of a frequency-independent phase shift between an applied ac potential and its current response, a constant phase element (CPE) was used, which is defined in impedance representation as [17]:



**Fig. 4.** Bode plots of mild steel in 1 M HCl in the absence and presence of different concentrations of (A)  $[EMIM]^+$   $[EtSO_4]^-$ , (B)  $[EMIM]^+$   $[Ac]^-$ , (C)  $[BMIM]^+$   $[SCN]^-$  (D)  $[BMIM]^+$   $[Ac]^-$  and (E)  $[BMIM]^+$   $[DCA]^-$ .

$$Z_{CPE} = Q^{-1} (i\omega)^{-n} \tag{8}$$

where *Q* is the proportionality coefficient,  $Y_0$  is the CPE constant,  $\omega$  is the angular frequency (in rad s<sup>-1</sup>), *i* is the imaginary unit ( $i^2 = -1$ ) and *n* is a CPE exponent, which can be used as a gauge of the heterogeneity or roughness of the surface. Depending on the value of n, CPE can represent resistance (n=0,  $Y_0=R$ ), capacitance (n=1,  $Y_0=C$ ), inductance (n=-1,  $Y_0=L$ ), or Warburg impedance (n=0.5,  $Y_0=W$ ). The electrochemical kinetic parameters obtained from the fitting of impedance spectra are listed in Table 2. The impedance value on the real axis at high frequency region corresponds to the solution resistance ( $R_s$ ), while the value at low frequency region corresponds to the charge transfer resistance ( $R_{ct}$ ). The  $R_{ct}$  values for the inhibited systems are generally higher than that of the uninhibited system, which implies that the studied ILs inhibit mild steel corrosion in 1 M HCl. The increased  $R_{ct}$  values with increasing the concentration of the inhibitors correspond to an enhanced impedance to electrochemical corrosion at high inhibitor concentration.

The values of the double layer capacitance  $(C_{dl})$  were calculated from the charge transfer resistance and CPE parameters  $(Y_0 \text{ and } n)$  using the expression [18]:

$$C_{dl} = \left(Y_0 R_{ct}^{1-n}\right)^{1/n}$$
(9)

where  $Y_0$  is the CPE constant and n is the CPE exponent. The value of *n* represents the deviation from the ideal behavior and it lies between 0 and 1.







Fig. 5. Equivalent Circuit Diagram.

The values of the  $R_s$ ,  $R_{ct}$ ,  $C_{dl}$  and n obtained the EIS experiment are listed in Table 2. The inhibition efficiency (%*IE*) was calculated using the following relation [17,18,20]:

$$%IE = 100 \left(\frac{R_{\rm ct} - R_{ct}^0}{R_{ct}}\right) \tag{10}$$

where  $R_{ct}$  and  $R_{ct}^{\circ}$  are the charge transfer resistances in the presence and absence of inhibitors respectively.

The results in Table 2 clearly reveal an increase in  $R_{ct}$  values with the increase in the inhibitor concentrations. This is due to the increase in the surface coverage on the mild steel surface by the adsorption of inhibitor, which also lead to the increase of in-

hibition efficiencies. The decrease in  $C_{dl}$  values can be attributed due to decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, which suggests that the studied ILs inhibit mild steel corrosion by adsorption at the metal/solution interface [55,56] thereby reducing the surface contact between the mild steel and aggressive solution. The values of n range from 0.9 to 0.8 close to unity, suggesting that the CPE is related with the capacitance and the dissolution mechanism of mild steel is controlled by charge transfer process [57,58]. The inhibition efficiency (%IE) values obtained from the EIS measurements are in good agreement with those obtained from the polarization studies. This can be used as a measure of consistency in the observed values of the IE. The inhibition efficiency values derived from Tafel polarization parameters and EIS measurements were plotted against concentration as shown in Fig. 6. The decreasing order of IE for the studied ILs is [EMIM][EtSO4] > [BMIM][DCA] > [BMIM][Ac] > [BMIM][SCN] > [EMIM][Ac].

#### 3.3. Adsorption isotherm

The adsorption of inhibitors on corroding surfaces never reaches the real equilibrium but tends to reach an adsorption steady state. When the corrosion rate is sufficiently decreased in the presence of inhibitor, the adsorption steady state has a tendency to attain a state of quasi-equilibrium. The nature of quasi-equilibrium adsorption of inhibitors can be investigated using appropriate adsorption isotherm. Different adsorption isotherms were tested in order to find the best fitted adsorption



Fig. 6. Relationship between corrosion inhibition efficiency and different concentrations of  $[EMIM]^+~[EtSO_4]^-,~[EMIM]^+~[Ac]^-,~[BMIM]^+~[SCN]^-,~[BMIM]^+~[Ac]^-$  and  $[BMIM]^+~[DCA]^-.$ 

isotherm for adsorption of the ILs on the steel surface. The adsorption of the studied ILs fits well into the Langmuir adsorption isotherm of the form [20]:

$$\frac{C_{inh}}{\theta} = C_{inh} + \frac{1}{K_{ads}} \tag{11}$$

where  $\theta$  is the surface coverage,  $C_{inh}$  is the concentration of the inhibitor and  $K_{ads}$ , is the equilibrium constant for the adsorption/desorption process. The adsorption isotherms for the studied ILs are presented in Fig. 7. It is a known fact that  $K_{ads}$  represents the strength of adsorption or desorption between adsorbate and adsorbent. Large values of  $K_{ads}$  correspond to more efficient ad-

Table 3

Ionic liquids used as inhibitors	$-\Delta G^0_{ads}$ / kJ mol <sup>-1</sup>		$K_{\rm ads}$ (x 10 <sup>3</sup> mol <sup>-1</sup> )		
	Tafel	EIS	Tafel	EIS	
[EMIM] <sup>+</sup> [EtSO <sub>4</sub> ] <sup>-</sup> [EMIM] <sup>+</sup> [Ac] <sup>-</sup> [BMIM] <sup>+</sup> [SCN] <sup>-</sup> [BMIM] <sup>+</sup> [AC] <sup>-</sup> [BMIM] <sup>+</sup> [DCA] <sup>-</sup>	35.85 31.66 31.75 31.76 31.85	35.29 31.74 31.64 31.66 31.74	24.388 5.139 5.332 5.358 5.547	21.771 5.317 5.113 5.138 5.319	

sorption. From the intercepts of the straight lines on the  $C_{inh}/\theta$ -axis (Fig. 7),  $K_{ads}$  can be calculated, which is related to free energy of adsorption,  $\Delta G^{\circ}_{ads}$  as [17,18]:

$$\Delta G_{ads}^0 = -RT \ln(55.55K_{ads}) \tag{12}$$

where *T* is the absolute temperature and the constant value of 55.55 is the molar concentration of water. The negative values of  $\Delta G_{\circ ads}$  implies spontaneity of the adsorption process and stability of the adsorbed film on the mild steel surface. It has been reported that the value of  $\Delta G_{\circ ads}$  around  $-20 \text{ kJ} \text{ mol}^{-1}$  or lower indicates electrostatic interaction between charged metal surface and charged organic molecules in the bulk of the solution (physisorption process), while those around  $-40 \text{ kJ} \text{ mol}^{-1}$  or higher involve charge sharing or charge transfer between the metal surface and organic molecules (chemisorption process) [59]. The calculated values of  $\Delta G^{\circ}$ ads and Kads are presented in Table 3.

The values of  $\Delta G^{\circ}_{ads}$  as shown in Table 3 are negative, which means that the adsorption inhibitors on the metal surface was spontaneous and the values are in-between the two thresholds that correspond to physisorption and chemisorption mechanisms. Thus the studied ILs adsorb onto mild steel surface in 1 M HCl by competitive physisorption and chemisorption processes, though predominantly physisorption [60].



Fig. 7. Langmuir adsorption isotherm plots for the lonic liquids at different concentrations using (A) Tafel and (B) EIS method.



Fig. 8. UV-vis spectra of pure [EMIM]<sup>+</sup> [EtSO<sub>4</sub>]<sup>-</sup>, [EMIM]<sup>+</sup> [Ac]<sup>-</sup>, [BMIM]<sup>+</sup> [SCN]<sup>-</sup> [BMIM]<sup>+</sup> [Ac]<sup>-</sup>, [BMIM]<sup>+</sup> [DCA]<sup>-</sup> and the resulting solution after 24 h of mild steel immersion.

# 3.4. UV-visible spectroscopy

UV-vis spectroscopy is powerful tool used to provide the evidence of interaction between metal and inhibitors. The UV-vis absorption spectra for the 500 ppm solution of the studied ILs and the resulting solutions of the ILs after 24 h of mild steel immersion are shown in Fig. 8. The electronic absorption spectra obtained show the bands in the UV-vis region with a considerable charge transfer character due to  $\pi$ - $\pi^*$  and n- $\pi^*$  transitions. All the studied ILs show UV-vis absorption peak 229 nm. This is attributed to their common  $\pi$ -electrons nucleus (the imidazolium unit). Each of the studied ILs also show some other peaks at different wavelengths, which may be as a results of their different anions and cation-anion interactions. The observed broadening and



Fig. 9. FTIR spectra of pure [EMIM]+ [EtSO<sub>4</sub>]-, [EMIM]+ [Ac]-, [BMIM]+ [SCN]- [BMIM]+ [Ac]-, [BMIM]+ [DCA]- and the resulting solution after 24 h of mild steel immersion.

shift in the change in the wavelength of maximum absorption after 24 h of mild steel immersion is an indication of interactions between the ILs (inhibitors) and iron. The broadening of the absorption peaks observed after mild steel immersion is an evidence of the IL/Fe complex formation [61].

# 3.5. FTIR spectroscopy

The FTIR spectra of pure ILs, and ILs after 24 h of mild steel immersion are shown in Fig. 9. The FTIR spectra show similar fea-

tures due to similar moieties in the studied ILs. A slight differences in the IR spectra were observed in the finger print region due to difference in alkyl chain lengths. The IR spectral bands at above  $3000 \text{ cm}^{-1}$  corresponds to the C-H vibrational modes of the imidazolium ring. The bands between  $2900-2800 \text{ cm}^{-1}$  is due to the aliphatic asymmetric (C–H) stretching vibrations, symmetric and asymmetric stretching modes of CH<sub>2</sub> and CH<sub>3</sub> respectively. The spectral band observed around at  $1700 \text{ cm}^{-1}$  corresponds to ester carbonyl (C=O) group. The IR vibration bands between 1500 and 1400 cm<sup>-1</sup> are due to C–C stretching vibrations and the band at



**Fig. 10.** SEM images of mild steel surface (a) plain mild steel (b) mild steel immersed in 1 M HCl, (c) in the presence of 500 ppm of  $[EMIM]^+$  [EtSO<sub>4</sub>]<sup>-</sup>, (d) in the presence of 500 ppm [EMIM]<sup>+</sup> [Ac]<sup>-</sup>, (e) in the presence of 500 ppm of  $[BMIM]^+$  [SCN]<sup>-</sup>, (f) in the presence of 500 ppm [BMIM]<sup>+</sup> [Ac]<sup>-</sup>, (g) in the presence of 500 ppm of  $[BMIM]^+$  [DCA]<sup>-</sup>.

Quantum chemical parameters (B3LYP/6-31++G\*\*).

Parameters	[EMIM] <sup>+</sup> [EtSO <sub>4</sub> ] <sup>-</sup>	$[EMIM]^+ [Ac]^-$	[BMIM] <sup>+</sup> [SCN] <sup>-</sup>	$[BMIM]^+ [Ac]^-$	[BMIM] <sup>+</sup> [DCA] <sup>-</sup>
Total Energy (a.u)	-1123.10	-573.27	-914.46	-651.91	-663.85
E <sub>HOMO</sub> (eV)	-7.32	-5.38	-4.84	-5.37	-5.46
$E_{LUMO}$ (eV)	-0.92	-0.87	-1.46	-0.83	-1.66
$\Delta E$ (eV)	6.40	4.51	3.38	4.54	3.80
χ (eV)	4.12	3.12	3.15	3.10	3.56
$\eta$ (eV)	3.20	2.25	1.69	2.27	1.90
Dipole moment $(\mu)$	19.95	10.06	13.67	9.96	13.44
$\Delta N$	0.46	0.86	1.14	0.86	0.90
<i>M. wt.</i> (g/mol)	236.08	170.10	197.10	198.14	205.13
%IE (500 ppm)*	92.75	87.87	88.32	90.47	90.64
	(92.76)	(87.04)	(88.24)	(90.42)	(90.82)

\*%IE from Impedance experiments are in the parentheses.

around 1300 cm<sup>-1</sup> is due to C=C stretching vibrations. The inplane bending vibrations around 1200 cm<sup>-1</sup> are due to C–N stretching vibrations. The IR bands seen around at 1100–1000 cm<sup>-1</sup> are due to C–O stretching vibrations. The spectral bands at around 900 cm<sup>-1</sup> are due to aromatic C–H bending vibrations. The spectral IR bands obtained for alkanes at around 750 cm<sup>-1</sup> are due to C–H rocking vibrations and at 600 cm<sup>-1</sup> are due to C–H bending vibrations. The broad band around at 3300 cm<sup>-1</sup> is common to all the studied ILs after 24 h of mild steel immersion which is due to the formation of IL/Fe complex in solution. Also the broad spectral bands observed at around 500–600 cm<sup>-1</sup> are due to the organic metal complex formation [62–64].

#### 3.6. Surface analysis

The surface morphological characterization of plain mild steel surface and mild steel specimens in 1 M HCl without and with 500 ppm of the studied ILs are presented in Fig. 10. It can be seen that the plain mild steel surface exhibit a smooth uniform surface. The mild steel specimens immersed in 1 M HCl show a highly damaged corroded surface due to acid attack. The mild steel specimens retrieved from 1 M HCl solution containing 500 ppm of the studied ILs generally show less damaged surface with minor scratches due to the abrasion of SiC emery sheets which confirms that the ILs form protective films on the steel surface and prevent direct acid attack over the mild steel surfaces [60].

#### 3.7. Quantum chemical calculations

Quantum chemical calculations were carried out on the studied ILs to investigate possible relationship between the experimental inhibition efficiency and some molecular quantum chemical descriptors. The optimized structures, HOMO, LUMO and Fukui indices surfaces of the studied ILs are presented in Fig. 11. The HOMO surfaces provide information about the possible sites or regions in inhibitor molecules where the most loosely bound electron is likely to be forward-donated to the appropriate orbital of the metal atom, while the LUMO surfaces show the prospective



Fig. 11. Optimized structures, HOMO, LUMO, nucleophilic and electrophilic Fukui indices for the studied ILs (B3LYP/6-31++G(d, p).

sites or regions in the inhibitor molecules to which electron from the occupied orbitals of the metal atom may be back-donated. The HOMO surfaces of [BMIM][SCN] and [BMIM][Ac] are essentially of  $\pi$ -type and distributed over the entire imidazole ring. The HOMO surfaces of [EMIM][EtSO<sub>4</sub>], [EMIM][Ac] and [BMIM][DCA] on the other hand are essentially of  $\sigma$ -type and distributed over the anion units. The LUMO surfaces of the five ILs involve contributions from the imidazolium ring.

The Fukui function,  $f(\mathbf{r})$  is often used for analyzing the behavior of different sites in a molecule and predicting relative local reactivity [64]. The nucleophilic and electrophilic Fukui functions,  $f^+$  and  $f^-$  respectively can be calculated [14,65] as:

$$f^+ = q_{(N+1)} - q_N \tag{13}$$

$$f^{-} = q_N - q_{(N-1)} \tag{14}$$

where  $q_{(N+1)}$ ,  $q_N$  and  $q_{(N-1)}$  represent the charges on the atoms in the systems with (N+1), N and (N-1) electrons respectively. The

preferred site for nucleophilic attack is characterized by the highest value of  $f^+$ , while the most susceptible site to electrophilic attack is the atom/region with the highest value of  $f^-$ . The Fukui indices for the studied ILs were calculated using the Mulliken charges on the atoms in the respective systems and the values were visualized as graphic surfaces using the Multiwfn software [66,67].

As shown in Fig. 11, the most probable sites of nucleophilic attacks on the studied ILs are generally located on the imidazolium ring, especially the N1, C2 and N3 atoms in the ring, while the most likely sites of electrophilic attacks are found mainly on the anionic moieties, particularly the electronegative atoms such as S, O and N on such units. Similar local reactivity behaviour had been reported previously for some bis(trifluoromethyl-sulfonyl) imide imidazolium-based ILs, where the susceptibility of C2 atom to nucleophilic attack was attributed to the high positive charge on the C2 atom, a reminiscence of the electron deficiency nature of the N=C bond [64]. The preference of the S, O or N atom in the anion for electrophilic attack is attributable to the fact that these atoms have high electron density around them due to their high electronegativity.

The calculated quantum chemical parameters such as the  $E_{HOMO}$ ,  $E_{IUMO}$ ,  $\Delta E$ ,  $\chi$ ,  $\eta$ ,  $\mu$  and  $\Delta N$  are listed in Table 4. A higher value of E<sub>HOMO</sub> implies better ability of inhibitor molecule to donate electrons to the appropriate vacant orbitals in the metal atom, while a lower value of ELUMO suggests better tendency of an inhibitor to accept electrons from filled orbitals of the metal in a back-donation mechanism. The energy gap,  $\Delta E$  is often used to assess the relative reactivity of inhibitor molecules with the metal atom such that, the lower the  $\Delta E$ , the better the inhibition efficiency and vice versa. It is obvious from the values in Table 4 that the trends of the values obtained for the  $E_{HOMO}$ ,  $E_{LUMO}$  and  $\Delta E$  are not in agreement with the order of the experimental inhibition efficiencies. The same applies to  $\chi$ ,  $\eta$  and  $\Delta N$  which are derivatives of the frontier molecular orbital energies in one way or the other. It is noteworthy that the decreasing order the molecular weights of the studied ILs is [EMIM][EtSO<sub>4</sub>] > [BMIM][DCA] > [BMIM][Ac] > [BMIM][SCN] > [EMIM][Ac], which is in agreement with the order of experimental inhibition efficiencies at 500 ppm.

The nonconformity between unitary quantum chemical parameters and the experimental inhibition efficiencies suggests that the nature of interactions involved in the corrosion inhibition process of the studied ILs is too complex to be correlated to single quantum chemical parameter. In this kind of situation, a more extensive correlation of experimental results with the quantum chemical parameters by using the combination of two or more quantum chemical descriptors called the quantitative structure activity relationship (QSAR) may provide more insights into the relationship between the experimental inhibition efficiencies and quantum chemical parameters [22,64].

#### 3.8. Quantitative structure activity relationships (QSAR)

Another approach for relating the quantum chemical properties of the inhibitors to the observed experimental inhibition efficiencies is to perform quantitative structure activity relationship (QSAR). This approach is better suited for the study of the corrosion inhibitors because there might be multiple inter-related factors contributing to the effectiveness of the studied compounds as corrosion inhibitors. QSAR attempts to develop a relationship in the form of an equation which correlates the quantum chemical parameters to the observed activity. The linear and the nonlinear equations, proposed by Lukovits, are often used in the study of corrosion inhibitors to correlate the quantum chemical parameters with the experimental inhibition efficiency of the inhibitors [68,69]. The linear equation has the form

$$IE_{theor} = AX_iC_i + B \tag{15}$$

where *A* and *B* are the regression coefficients determined through regression analysis,  $X_i$  is a quantum chemical index characteristic of the molecule *i*,  $C_i$  is the experimental concentration of the inhibitor. The non-linear equation has the form:

$$IE_{theor} = \frac{(AX_i + B)C_i}{1 + (AX_i + B)C_i} \times 100$$
(16)

where all the parameters are defined as in the linear equation.

Both equations were utilized to correlate the composite index of quantum chemical parameters with the experimental inhibition efficiency of the studied ILs. The results (Table 5, Fig. 12) show that the linear equation provides a combination of good correlation between quantum chemical parameters and experimental inhibition efficiency. The non-linear equation provides only one possible good correlation between quantum chemical parameters and experimental inhibition efficiency. An optimum of three quantum chemical parameters was sufficient to produce a good corre-



**Fig. 12.** Representative plots of the correlation between experimental inhibition efficiency (%IE) and the predicted inhibition efficiency (pred(%IE)) obtained by utilizing the Lukovits equations of (a) linear and (b) nonlinear multiple regressions. The quantum chemical parameters utilized for the plot are molecular weight (M.wt), number of electrons transferred ( $\Delta N$ ) and dipole moment ( $\mu$ ).

lation with experimentally determined inhibition efficiency. Combinations of the quantum chemical parameters that provided the best correlation are reported in Table 5 together with the equations for the prediction of theoretical inhibition efficiency and the corresponding  $R^2$ , SSE, and RMSE values. Among the linear equations obtained, the  $R^2$  correlation value is in the range of 0.721–0.998. The best equation corresponds to  $R^2$ =0.0998, SSE=0.015 and RMSE=0.122 and has the form

$$\text{\%IE} = 92.18 - 8.15 \times 10^{-2} \text{ * M.wt.} + 5.42 \text{ * } \Delta \text{N} + 0.76 \text{ * } \mu$$
(17)

The combination of other quantum chemical parameters, the derived equations and the corresponding  $R^2$ , SSE and RMSE values are reported in Table 5. Both the SSE values and the RMSE (i.e., the average error of the predicted value to the actual value) are reasonably small to suggest good correlation.

# 3.9. Molecular dynamics simulation

Recently, it has been argued that computing electronic properties is not sufficient to predict the trend of the inhibition

Pair of quantum chemical parameters utilized to derive the linear and the nonlinear multiple regression equation that correlates the theoretically estimated and the experimentally determined inhibition efficiencies.

Quantum chemical parameters		R <sup>2</sup>	SSE	RMSE
Linear regression equations M. wt, $\Delta N$ , $\mu$ $E_{HOMO}$ , $\Delta N$ , $\mu$ $E_{HOMO}$ , $E_{LUMO}$ , $\Delta N$ $E_{HOMO}$ , $E_{LUMO}$ , $\mu$	$\begin{split} & \& IE = 92.18 - 8.15 \times 10^{-02} * M. \text{ wt.} + 5.42 * \Delta N + 0.76 * \mu \\ & \& IE = 8.89 - 9.97 * E_{HOMO} + 35.90 * \Delta N - 0.39 * \mu \\ & \& IE = 42.15 - 5.25 * E_{HOMO} + 0.330 * E_{LUMO} + 22.51 * \Delta N \\ & \& IE = 98.97 + 2.85 * E_{HOMO} + 1.25 * E_{LUMO} + 0.68 * \mu \end{split}$	0.998 0.740 0.735 0.721	0.015 2.554 2.606 2.723	0.122 1.598 1.614 1.650
Non-linear regression equation M. wt, $\Delta N$ , $\mu$	%IE=(0.77* $\mu$ +6.85* $\Delta$ N-7.53 × 10 <sup>-02</sup> *M. wt.+8.84)*100/ (1+(0.77* $\mu$ +6.85* $\Delta$ N-7.53 × 10 <sup>-02</sup> *M. wt.+8.84))	0.978	0.462	0.214

 $R^2$  is the coefficient of determination, and SSE and RMSE are defined as  $SSE = \sqrt{\sum_{i=1}^{N} (IE_{pred} - IE_{exp})^2}$  $RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{N} (IE_{pred} - IE_{exp})^2}$  where  $IE_{pred}$  is the predicted inhibition efficiency and  $IE_{exp}$  is the experimental

determined inhibition efficiency, *n* is the number of observations (compounds) considered.



**Fig. 13.** The most stable low energy configuration for the adsorption of (a)  $[EMIM]^+$   $[EtSO_4]^-$ , (b)  $[EMIM]^+$   $[Ac]^-$ , (c)  $[BMIM]^+$   $[SCN]^-$ , (d)  $[BMIM]^+$   $[Ac]^-$ , and (e)  $[BMIM]^+$   $[DCA]^-$  on Fe (110)/50 H<sub>2</sub>O interface obtained through the Monte Carlo simulation.

performance of the investigated inhibitors in spite of its successes in exploring the mechanism of inhibitors. In fact, in many cases direct correlation between the computed electronic parameters and experimental inhibition efficiencies cannot be established for this set of inhibitors especially in the gas phase. Therefore, it is imperative to carry out rigorous modeling of the direct interaction of the inhibitors with steel in the presence of water to mimic the real experimental condition. Thus, Monte Carlo method to sample possible low energy searches of the configuration space of the inhibitors on clean iron surface in aqueous solution was carried out.

The most stable low energy adsorption configurations of the ILs inhibitors on Fe  $(110)/50 H_2O$  system using Monte Carlo simula-

tions are depicted in Fig. 13. The values for the outputs and descriptors of the Monte Carlo simulations are listed in Table 6. It is evidenced from the Table 6, that the adsorption energies of the investigated ILs on Fe (110) surface are quite close due to the similarity of their molecular structures (the difference between the highest and lowest adsorption energy is -3.28 kcal/mol). This is also the case with the average experimentally determined inhibition efficiency for the ILs inhibitors where the difference between the highest and the lowest inhibition efficiency is only 7.15% using potentiodynamic polarization techniques. In general, all the inhibitors are expected to bind strongly to the steel surfaces since they possess high negative adsorption energy [70].

Outputs and descriptors calculated by the Monte Carlo simulation for the lowest adsorption configurations of (a)  $[EMIM]^+$   $[EtSO_4]^-$ , (b)  $[EMIM]^+$   $[Ac]^-$ , (c)  $[BMIM]^+$   $[SCN]^-$ , (d)  $[BMIM]^+$   $[Ac]^-$ , and (e)  $[BMIM]^+$   $[DCA]^-$  on Fe (110)/50H<sub>2</sub>O Interface (in kcal mol<sup>-1</sup>).

Systems	Total energy	Adsorption energy	Rigid adsorption energy	Deformation energy	$dE_{ad}/dN_i$ inhibitors	$dE_{ad}/dN_i$ 50H <sub>2</sub> O
Fe(110)/[EMIM] <sup>+</sup> [EtSO <sub>4</sub> ] <sup>-</sup>	-52.68	-91.40	-91.53	0.13	-25.41	-1.97
Fe(110)/[EMIM] <sup>+</sup> [AC] <sup>-</sup>	-51.67	-91.40	-91.52	0.12	-24.37	-2.11
Fe(110)/[BMIM] <sup>+</sup> [SCN] <sup>-</sup>	-48.77	-91.12	-91.31	0.18	-27.65	-2.16
Fe(110)/[BMIM] <sup>+</sup> [AC] <sup>-</sup>	-51.78	-91.86	91.19	0.32	-25.27	-2.02
Fe(110)/[BMIM] <sup>+</sup> [DCA] <sup>-</sup>	-50.49	-92.40	-92.58	0.17	-24.87	-2.14

It is generally acknowledged that the primary mechanism of corrosion inhibitor interaction with steel is by adsorption. In all cases, the adsorption energies of the inhibitors are far higher than that of water molecules (Table 6). This indicates the possibility of gradual substitution of water molecules from the surface of iron surface resulting in the formation of a stable layer which can protect the iron from aqueous corrosion. In general, the adsorption process of organic inhibitor molecules can be considered as a result of replacement of water molecules adsorbed on the metal surface according to the following process [71]:

 $Org_{(sol)} + n H_2O_{(ads)} \rightarrow Org_{(ads)} + n H_2O_{(sol)}$ (18)

# 4. Conclusions

Corrosion inhibition properties of imidazolium-based ILs, namely  $[EMIM]^+$   $[EtSO_4]^-$ ,  $[EMIM]^+$   $[Ac]^-$ ,  $[BMIM]^+$   $[SCN]^-$ ,  $[BMIM]^+$   $[Ac]^-$  and  $[BMIM]^+$   $[DCA]^-$  on mild steel in 1 M HCl have been investigated using electrochemical methods, spectroscopic techniques, quantum chemical calculations, QSAR and Monte Carlo simulations approaches. The following conclusions were drawn:

- (a) Potentiodynamic polarization results showed that all the studied ILs exhibit mixed-type inhibition activities with predominant cathodic inhibitive effect.
- (b) The EIS results revealed the formation of protective film on the mild steel surface.
- (c) Adsorption process involves both physisorption and chemisorption mechanisms and conforms to the Langmuir adsorption isotherm.
- (d) FTIR and UV-vis spectroscopic studies revealed the occurrence of chemical interactions between the ILs and iron in the mild steel.
- (e) SEM images confirmed the formation of protective film by ILs on mild steel surface.
- (f) Experimental, quantum chemical calculations and Monte Carlo simulations results showed that the order of decreasing inhibition efficiency of the studied ILs is [EMIM]<sup>+</sup> [EtSO4]<sup>-</sup> > [BMIM]<sup>+</sup> [DCA]<sup>-</sup> > [BMIM]<sup>+</sup> [AC]<sup>-</sup> > [BMIM]<sup>+</sup> [SCN]<sup>-</sup>> [EMIM]<sup>+</sup> [AC]<sup>-</sup> and corresponds to the order of decreasing molecular weights.
- (g) The results of theoretical quantum chemical calculations, Monte Carlo simulations and QSAR analyses corroborate experimental observations. Based on the QSAR analyses, the inhibitive effects of the studied ILs appear to depend strongly on composite descriptors involving the molecular weight, fraction of electrons transferred from the inhibitor to the metal and dipole moment of the ILs.

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