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Density functional treatment and electro analytical measurements of liquid phase interaction of 2-ethylbenzimidazole (EBI) and ethyl (2-ethylbenzimidazolyl) acetate (EEBA) on mild steel in hydrochloric acid



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ABSTRACT

DFT calculations on the liquid phase interaction and corrosion inhibition properties of 2-ethylbenzimidazole (EBI) and its derivative ethyl (2-ethylbenzimidazolyl)acetate (EEBA) on mild steel in hydrochloric acid (0.5, 5 and 1.5 M) at three different temperatures (303, 308 and 313 K) have been studied using EIS, polarization, adsorption measurements and computational calculations. Results show that EBI and EEBA act as effective inhibitors for the corrosion of mild steel in hydrochloric acid media. Polarization studies showed that both the inhibitors behave as mixed type inhibitors with respect to the electrode reactions. EEBA offers better inhibition efficiency than EBI. The inhibition efficiency found to decrease with increase in temperature in either of the cases. The mechanism involves adsorption phenomenon and in the case of EEBA, the adsorption obeyed Langmuir adsorption isotherm. For EBI, the adsorption obeyed Langmuir adsorption isotherm except for 313 K in 1.5 M HCl, for which the best fit adsorption isotherm was Temkin adsorption isotherm.

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1. Introduction

Mild steel is widely used as structural material in automobiles, pipes and chemical industries [1]. Acid solutions are generally used for removal of undesirable scale and rust on the metals, cleaning of boilers and heat exchangers, oil-well acidizing in oil recover and so on [2-6]. However the rate of metal dissolution caused by the acidic media is quite high. A most efficient solution to the problems caused by corrosion is the use of corrosion inhibitors. The use of organic inhibitors is one of the most practical methods for protection of metals against corrosion, and is becoming increasingly popular according to recent studies [7]. Most common inhibitors are organic compounds containing functional electronegative groups, π electrons in triple or conjugated double bonds and hetero atoms like N, S and O [8]. These organic compounds can adsorb on the metal surface and thereby reduce the corrosion rate [9]. The researches show that these molecules adsorb on the metal surface by displacing water molecules on the surface and forming a protective film [10–12]. Especially, the studies show that chloride containing acidic medium plays an important role because chloride ions easily adsorb on the inner Helmholtz plane [13]. It is very well known that HCl_(aq) is one of the most widely used acid for descaling, degreasing, pickling, etc. Therefore the protection efficiency of the inhibitor in this medium is very important [14]. In recent years, there is considerable amount of effort devoted to studying inhibition properties of benzimidazole and its derivatives for metallic corrosion. Benzimidazole and its derivatives have received considerable attention on their inhibition properties of metallic corrosion over the past years [15-16]. Benzimidazole is a heterocyclic organic compound, and the nitrogen atom and the aromatic ring in the molecular structure are likely to facilitate the adsorption of the compounds on the metal surface [17]. Some derivatives of benzimidazoles have been demonstrated as excellent inhibitors for metals and alloys in acidic solution, and exhibit different inhibition performance with the difference in substituent groups and substituent positions on the imidazole ring [18-24]. J. Alijourani et al. investigated the corrosion inhibition of carbon steel in hydrochloric acid and sulphuric acids in the presence of some benzimidazole derivatives such as benzimidazole (BI), 2-methylbenzimidazole (2-CH₃-BI) and 2-mercaptobenzimidazole (2-SH-BI). In both the media 2-SH-BI showed highest efficiency and 2-BI showed lowest efficiency [25]. X. Wang et al. had conducted studies on the influences of a benzimidazole derivative namely 1,8-bis(1-chlorobenzyl-benzimidazolyl)-octane (CBO) on the corrosion behaviour of mild steel in different concentrations of HCl. The studies showed that the inhibitor is an excellent mixed type inhibitor [26]. Y. Tang et al. conducted studies on three novel benzimidazole derivatives, 2-aminomethylbenzimidazole (2-ABI), bis(2-benzimidazolylmethyl)amine (BBIA) and tris(2benzimidazolylmethyl)amine (TBIA) as inhibitors for mild steel in 1 M

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HCl. The inhibition efficiency was found to depend on the concentration of the inhibitor, temperature and concentration of the acid solution [27]. A. Dutta et al. tested the different bis-benzimidazole derivatives as potential corrosion inhibitors for mild steel in 1 M HCl and the inhibitors were proved to be mixed type inhibitors [28]. M. Yadav et al. studied the inhibitive action of synthesised benzimidazole derivatives namely 2-((1-morpholinomethyl)1H-benzo[d]imidazole-2-yl)phenol (MBP), 2-((1-piperazine-1-yl)methyl-1H-benzo[d]imidazole-2yl)phenol (PzMBP) and 2-(1-((piperazine-1-yl)methyl)-1H-benzo[d]imidazole-2-yl)phenol (PMBP) on corrosion of N80 steel in 15% HCl solution. It was found that the inhibition efficiency of all the inhibitors increased with increase in concentration of inhibitors and decreased with increase in temperature. The studies also found out that the inhibitors were mixed type [29]. All the studies revealed that the benzimidazole derivatives inhibited the corrosion by getting adsorbed on to the metal surface. Another remarkable feature is that during the adsorption on to the metal surface, benzimidazole molecules show two anchoring sites suitable for surface bonding: the nitrogen atom with its lonely sp² electron pair and the aromatic rings [30].

The aim of the present investigation is to examine the inhibitive properties of 2-ethylbenzimidazol (EBI) (Fig. 1a) and its derivative ethyl(2-ethylbenzimidazolyl)acetate (EEBA) (Fig. 1b) on mild steel in different concentrations of HCl (0.5, 1 and 1.5 M). The study has been





Fig. 1. Optimized geometries of (a)EBI (b) EEBA.

conducted using EIS and potentiodynamic polarization techniques. Quantum chemical parameters were also calculated.

2. Experimental

2.1. Inhibitor

2.1.1. 2-Ethylbenzimidazole

A mixture of *o*-phenylenediamine (10 g, 0.092 mol) and propionic aid (0.11 mol) was dissolved in 4 M HCl (10 ml) and refluxed at 100 °C for 12 h. Completion of the reaction was monitored using TLC. The contents were cooled to room temperature and neutralized with saturated solution of NaHCO₃ [31].

2.1.2. Ethyl (2-ethylbenzimidazolyl)acetate

The solution of 2-ethylbenzimidazol (0.062 mol) in acetone (20 ml) was mixed with ethylchloroacetate (7.9 ml, 0.074 mol) and potassium carbonate (16.5 g, 0.12 mol) and refluxed for 6 h. Completion of the reaction was monitored by TLC. The reaction mixture was filtered. From the clear filtrate, excess acetone was removed by distillation and then was added to water. The solid product separated was collected by filtration and dried. Further purification was done by crystallization from ethyl acetate to give ethyl(2-methylbenzimidazolyl)acetate [31].

2.2. Medium

The medium of the study was made from reagent grade HCl (E. Merck) and doubly distilled water. All tests were performed in aerated medium under different temperatures (303, 308 and 313 K) and atmospheric pressure.

2.3. Materials

The mild steel specimen used was of the following composition (wt.): C (0.20%), Mn (1%), P (0.03%), S (0.02%) and Fe (98.75%). The mild steel specimens used were cut in 4.8×1.9 cm² coupons and polished as recommended by ASTM (0–4 grit of 1200 mesh). During the electrochemical measurements only 1 cm² area was exposed. Before measurements, the samples were polished using buffing machine and different grades of emery paper (6–1200 grade) followed by washing with ethanol, acetone and finally with distilled water for achieving mirror bright finish.

2.4. Electrochemical measurements

Electrochemical tests were carried out in a conventional three electrode corrosion cell with platinum sheet (1 cm² surface area) as auxiliary electrode and saturated calomel electrode (SCE) as the reference electrode. The working electrode was first immersed in the test solution and after establishing a steady state open circuit potential (OCP), the electrochemical measurements were carried out in a Gill AC computer controlled electrochemical work station (ACM, UK, Model No: 1475). Electrochemical impedance spectroscopy (EIS) measurements were carried out with amplitude of 10 mV (RMS) AC Sine wave with frequency range of 10 kHz–0.1 Hz. The polarization curves were obtained in the potential range from -250 mV to +250 mV (vs. SCE) with a sweep rate of 60 mV/min.

2.5. Computational study

The theoretical calculations were carried out using B3LYP. It is a version of DFT method which uses Beck's three parameter functional (B3) and it includes a mixture of HF with DFT exchange terms associated with the gradient corrected correlation functional of Lee, Yang and Parr (LYP) [32]. It has much less convergence problems than those found for pure DFT methods [33]. The full geometry optimization of



Fig. 2. Randle's circuit.



Fig. 3. Nyquist plots for mild steel corrosion in (a) 0.5 M HCl(b) 1 M HCl and (c) 1.5 M HCl in the absence and presence of EBI at 303 K.

the inhibitor was carried out at the B3LYP/6-31G* level using Gaussian 03 program package. The quantum chemical parameters calculated were $E_{HOMO},\,E_{LUMO},\,\chi$ (electro negativity), η (global hardness), etc. Fukui indices were also determined.

3. Results and discussion

3.1. Electrochemical measurements

3.1.1. Electrochemical impedance spectroscopy (EIS)

The EIS study was done for mild steel in various concentrations of HCl ranging from 0.5 M to 1.5 M in the presence and absence of the inhibitors EBI and EEBA. The study was done in the absence and presence



Fig. 4. Nyquist plots for mild steel corrosion in (a) 0.5 M HCl (b) 1 M HCl and (c) 1.5 M HCl in the absence and presence of EEBA at 303 K.

Table 1a

Charge transfer resistance	(R.,)	corrosion rate	CR	and	nercentage	inhibition	efficiency	of FBI	obtained from	FIS study
charge transfer resistance	(IAct)	, comosion rate	C.N	anu	percentage	minipition	CHICKENCY		obtained non	I LIS SLUUY.

Conc. Of HCL(M)	Conc. Of	Temperature (K)							
HCl (M)	EBI (ppm)	303			308			313		
		$R_{ct} (\Omega cm^2)$	C.R (mm/yr)	%IE	$R_{ct} (\Omega cm^2)$	C.R (mm/yr)	%IE	$R_{ct} (\Omega cm^2)$	C.R (mm/yr)	%IE
0.5	Blank	8.24	36.67	-	86.20	3.51	-	67.42	4.49	-
	50	37.92	7.97	78.38	171.20	1.77	49.65	114.00	2.65	40.86
	100	97.35	3.10	91.58	227.50	1.33	62.11	226.80	1.33	70.27
	150	199.3	1.52	95.89	539.00	0.56	84.01	345.40	0.88	80.48
	200	426.3	0.71	98.08	633.00	0.48	86.41	441.80	0.68	84.74
1	Blank	6.05	49.96	-	13.00	23.26	-	7.79	38.33	-
	50	14.84	20.37	59.2	22.16	13.64	41.34	12.84	23.55	39.06
	100	35.65	8.48	83.02	40.11	7.54	67.59	16.22	18.64	51.9
	150	39.41	7.67	84.64	46.38	6.52	71.97	26.32	11.49	70.36
	200	118.10	2.56	94.88	64.47	4.69	79.8	34.06	8.88	77.09
1.5	Blank	9.79	30.90	-	6.53	46.29	-	4.65	65.02	-
	50	22.48	13.45	56.44	9.61	31.46	32.00	5.14	58.82	9.5
	100	25.77	11.73	62.01	9.75	31.02	33.03	5.97	50.62	21.19
	150	56.59	5.34	82.69	10.31	29.33	36.66	6.52	46.34	28.68
	200	175.60	1.72	94.42	11.99	25.22	45.54	6.84	44.23	32.01

of various concentrations of inhibitors ranging from 50 to 200 ppm (ppm by weight) at temperatures 303, 308 and 313 K.

The equivalent circuit proposed to fit and interpret the EIS data was Randle's circuit (Fig. 2) in which there is charge transfer resistance (R_{ct}) parallel with double layer capacitance (C_{dl}) in series with solution resistance (R_s). Nyquist plots obtained from the study were shown in Figs. 3 and 4 (only the representative figures are given).

Nyquist plots are electrochemical impedance spectra in a complex plane. The existence of a single semi-circle showed the single charge transfer process during dissolution which is unaffected by the presence of inhibitor molecules. The addition of inhibitor molecules causes an increase in R_{ct} values [34]. The increase in R_{ct} values is attributed to the formation of a protective film on the metal-solution interface [35,36]. Thus it can be concluded that the inhibitor molecules function by adsorption on to the metal surface and thereby causing an increase in R_{ct} value [37].

All the Nyquist plots had a depressed semi-circle shape in the complex plane with centre under the real axis. This behaviour is a characteristic of solid electrodes. The depressed semi-circle shape is due to the non-ideal behaviour of double layer as a capacitor. This in turn is due to the surface heterogeneity resulting from surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitors, etc. The high frequency part of the impedance and phase angle reflects the behaviour of heterogeneous surface layer whereas the low frequency part shows the kinetic response for the charge transfer reaction [38]. Thus the parallel combination of double layer capacitance and charge transfer resistance which are in series with solution resistance, particularly in the presence of an efficient inhibitor, is found to be an inadequate approach for modelling the metal-acid solution interface [39]. Thus to account for the non-ideal behaviour, it is necessary to use a constant phase element, CPE instead of double layer capacitance [40]. The CPE can be modelled as follows:

$$Z_{CPE} = (j\omega c)^{-\alpha} \tag{1}$$

where Z_{CPE} is the impedance, j is the square root of -1, c is the capacitance and α is the measure of non-ideality of the capacitor and has a value in the range of $0 < \alpha < 1$ [41].

The charge transfer resistance values were calculated from the difference in impedance at lower and higher frequencies. The double layer capacitance, C_{dl} and the frequency at which the imaginary component of the impedance maximum were obtained from the equation given below:

$$C_{dl} = \frac{1}{\omega X R_{ct}}$$
(2)

where $\omega = 2\pi f_{max}$ and f_{max} is the frequency at which the imaginary component of impedance is maximum.

Table 1b

Charge transfer resistance (R_{ct}), Corrosion rate (C.R) and percentage inhibition efficiency of EEBA obtained from EIS study.

Conc. Of O	Conc. Of EEBA	Temperature (K)								
HCl (M)	(ppm)	303			308			313			
		$R_{ct} (\Omega cm^2)$	C.R (mm/yr)	%IE	$R_{ct} (\Omega cm^2)$	C.R (mm/yr)	%IE	$R_{ct} \left(\Omega \ cm^2\right)$	C.R (mm/yr)	%IE	
0.5	Blank	36.54	8.27	-	21.34	14.17	-	19.03	15.89	-	
	50	787.60	0.38	95.4	160.60	1.88	86.7	90.23	3.35	78.9	
	100	841.90	0.36	95.7	215.60	1.40	90.1	135.10	2.24	85.9	
	150	1285.0	0.24	97.2	270.00	1.12	92.1	228.70	1.32	91.7	
	200	1388.0	0.22	97.4	438.10	0.69	95.1	328.10	0.92	94.2	
1	Blank	34.96	8.65	-	9.22	32.78	-	5.49	54.98	-	
	50	477.10	0.63	92.7	65.46	4.62	85.9	33.28	9.09	83.5	
	100	673.10	0.45	94.8	96.50	3.13	90.4	49.20	6.15	88.8	
	150	846.60	0.36	95.9	146.10	2.07	93.7	53.02	5.70	89.6	
	200	898.10	0.34	96.1	160.00	1.89	94.2	70.88	4.27	92.2	
1.5	Blank	18.74	16.13	-	8.24	36.68	-	5.19	58.2	-	
	50	211.1	1.43	91.1	66.18	4.57	87.5	22.58	13.39	76.9	
	100	443.8	0.68	95.8	73.33	4.12	88.8	25.25	11.97	79.4	
	150	573.3	0.53	96.7	77.16	3.92	89.3	30.87	9.79	83.2	
	200	665.1	0.45	97.2	83.92	3.60	90.2	45.35	6.67	88.5	

Percentage inhibition efficiencies were calculated from charge transfer resistance values as follows:

IE (%) =
$$\frac{R_{ct}^* - R_{ct}}{R_{ct}^*} \times 100$$
 (3)

where R_{ct}^* and R_{ct} denote charge transfer resistance in the presence and absence of the inhibitors.

Result obtained from EIS study for the inhibitor, EBI has been summarized in Table 1a and that for EEBA in Table 1b. From the thorough analysis of the result, it can be seen that for both the inhibitors, at all the three temperatures, the charge transfer resistance values as well as the inhibition efficiency increased with increase in concentration of the inhibitor. The inhibition efficiency decreased with acid concentration. Another observation made from EIS study was that the efficiency of the inhibitors decreased with increase in temperature. This leads to the conclusion that inhibition was achieved by the adsorption of the inhibitors on the mild steel surface. As the temperature was increased, the adsorption of the inhibitor on to the mild steel surface became difficult which caused the inhibition efficiency to decrease. Thus maximum efficiency was obtained for 200 ppm concentration of the inhibitor in 0.5 M HCl at 303 K for both the inhibitors. It was also found that EEBA is a more efficient inhibitor than EBI.



Fig. 5. Polarization curves for mild steel corrosion in (a) 0.5 M HCl (b) 1 M HCl and (c) 1.5 M HCl in the absence and presence of EBI at 303 K.



Fig. 6. Polarization curves for mild steel corrosion in (a) 0.5 M HCl (b) 1 M HCl and (c) 1.5 M HCl in the absence and presence of EEBA at 303 K.

Table 2a

Corrosion current density (icorr), corrosion rate (C.R) and percentage inhibition efficiency (%IE) of EBI in 0.5 M HCl obtained from potentiodynamic polarization study.

Conc. Of EBI	Temperature (K)												
(ppm)	303				308			313					
	$-E_{corr}(mV)$	i_{corr} (mA/cm ²)	C.R (mm/yr)	%IE	$-E_{corr}(mV)$	i_{corr} (mA/cm ²)	C.R (mm/yr)	%IE	$-E_{corr}(mV)$	i_{corr} (mA/cm ²)	C.R (mm/yr)	%IE	
Blank	445.23	3.99	46.33	-	470.49	0.46	5.37	-	432.85	0.36	4.21	-	
50	475.09	0.79	9.21	80.1	442.84	0.24	2.83	47.3	439.85	0.22	2.49	40.6	
100	474.36	0.31	3.62	92.5	442.91	0.18	2.05	61.8	462.65	0.11	1.29	69.3	
150	478.35	0.16	1.87	95.9	457.02	0.07	0.88	83.6	445.56	0.069	0.80	80.9	
200	485.00	0.08	0.98	97.9	455.99	0.065	0.76	85.8	458.4	0.057	0.067	84.2	

Table 2b

Corrosion current density (icorr), corrosion rate (C.R) and percentage inhibition efficiency (%IE) of EBI in 1 M HCl obtained from potentiodynamic polarization study.

Conc. Of EBI	Temperature (K)												
(ppm)	303				308			313					
	$-E_{corr}(mV)$	$i_{corr}(mA/cm^2)$	C.R (mm/yr)	%IE	$-E_{corr}(mV)$	$i_{corr}(mA/cm^2)$	C.R (mm/yr)	%IE	$-E_{corr}(mV)$	$i_{corr}(mA/cm^2)$	C.R (mm/yr)	%IE	
Blank	484.00	1.55	18.01	-	498.88	1.03	11.99	-	547.29	4.29	49.78	-	
50	447.37	0.67	7.77	56.9	422.48	0.59	6.83	43.0	406.79	2.63	30.49	38.8	
100	457.32	0.25	2.92	83.8	530	0.36	4.15	65.4	489.39	2.18	25.24	49.3	
150	452.87	0.23	2.70	85.2	414.34	0.29	3.33	72.3	477.75	1.22	14.13	71.6	
200	472.16	0.10	1.22	93.2	413.96	0.22	2.59	78.4	420.85	1.05	12.13	75.6	

Table 2c

Corrosion current density (i_{corr}), corrosion rate (C.R) and percentage inhibition efficiency (%IE) of EBI in 1.5 M HCl obtained from potentiodynamic polarization study.

Conc. Of EBI	Temperature (K)												
(ppm)	303				308			313					
	$-E_{corr}(mV)$	$i_{corr}(mA/cm^2)$	C.R (mm/yr)	%IE	$-E_{corr}(mV)$	$i_{corr}(mA/cm^2)$	C.R (mm/yr)	%IE	$-E_{corr}(mV)$	$i_{corr}(mA/cm^2)$	C.R (mm/yr)	%IE	
Blank	448.8	2.32	26.85	-	401.93	3.19	37.04	-	399.21	4.63	53.63	-	
50	457.65	1.00	11.68	56.5	399.82	2.21	25.56	30.9	387.98	4.21	48.78	9.0	
100	457.56	0.86	10.00	62.7	479.7	2.14	24.80	33.1	398.5	3.59	41.69	22.3	
150	466.24	0.40	4.69	82.5	399.96	2.04	23.67	36.1	395.98	3.36	38.93	27.4	
200	469.05	0.17	1.99	92.6	398.72	1.83	21.16	42.9	399.86	3.09	35.80	33.2	

Table 3a

Corrosion current density (icorr), corrosion rate (C.R) and percentage inhibition efficiency (%IE) of EEBA in 0.5 M HCl obtained from potentiodynamic polarization study.

Conc. Of EEBA	Temperature (K)												
(ppm)	303				308			313					
	-E _{corr} (mV)	i _{corr} (mA/cm ²)	C.R (mm/yr)	%IE	-E _{corr} (mV)	i _{corr} (mA/cm ²)	C.R (mm/yr)	%IE	-E _{corr} (mV)	i _{corr} (mA/cm ²)	C.R (mm/yr)	%IE	
Blank	510.83	0.657	7.61	-	455.13	1.163	13.47	-	420.31	1.253	14.53	-	
50	457.54	0.041	0.48	93.7	467.43	0.162	1.87	86.1	480.11	0.269	3.12	78.5	
100	497.40	0.032	0.38	95.1	481.61	0.113	1.31	90.3	489.56	0.180	2.09	85.6	
150	476.45	0.031	0.36	95.2	478.64	0.091	1.05	92.2	491.25	0.107	1.24	91.5	
200	479.74	0.027	0.31	95.9	490.85	0.055	0.64	95.2	485.98	0.076	0.88	93.9	

Table 3b

Corrosion current density (icorr), corrosion rate (C.R) and percentage inhibition efficiency (%IE) of EEBA in 1 M HCl obtained from potentiodynamic polarization study.

Conc. Of EEBA	Temperature	(K)										
(ppm)	303				308			313				
	$-E_{corr}(mV)$	i_{corr} (mA/cm ²)	C.R (mm/yr)	%IE	$-E_{corr}(mV)$	i_{corr} (mA/cm ²)	C.R (mm/yr)	%IE	$-E_{corr}(mV)$	i_{corr} (mA/cm ²)	C.R (mm/yr)	%IE
Blank	489.12	0.728	8.44	-	494.7	2.534	29.37	-	490.25	3.884	45.01	-
50	485.25	0.057	0.65	92.2	466.6	0.394	4.57	84.4	466.56	0.647	7.50	83.3
100	456.33	0.043	0.49	94.1	469.7	0.240	2.79	90.5	484.33	0.473	5.49	87.8
150	435.14	0.039	0.44	94.7	484.2	0.167	1.94	93.4	502.47	0.407	4.72	89.5
200	463.86	0.029	0.34	95.9	476.2	0.155	1.81	93.9	472.14	0.302	3.50	92.2

Table 3c

Corrosion current density (icorr), corrosion rate (C.R) and percentage inhibition efficiency (%IE) of EEBA in 1.5 M HCl obtained from potentiodynamic polarization study.

Conc. Of EEBA	Temperature (K)												
(ppm)	303				308			313					
	$-E_{corr}(mV)$	i_{corr} (mA/cm ²)	C.R (mm/yr)	%IE	$-E_{corr}(mV)$	i_{corr} (mA/cm ²)	C.R (mm/yr)	%IE	$-E_{corr}(mV)$	i_{corr} (mA/cm ²)	C.R (mm/yr)	%IE	
Blank	486.41	1.269	14.72	-	438.38	3.032	35.14	-	442.43	4.987	57.79	-	
50	479.84	0.114	1.32	91.0	444.50	0.367	4.25	87.9	431.19	1.142	13.24	77.1	
100	474.3	0.058	0.67	95.4	459.08	0.351	4.06	88.4	447.33	1.031	11.95	79.3	
150	448.65	0.041	0.47	96.8	458.90	0.317	3.67	89.5	444.55	0.839	9.73	83.2	
200	469.62	0.038	0.44	97.0	452.27	0.281	3.25	90.7	443.65	0.573	6.65	88.5	

3.1.2. Potentiodynamic polarization study

This method involves the monitoring of the current that is produced as a function of time or potential by varying the potential of the working electrode [42]. Both anodic and cathodic polarization curves for mild steel in various concentrations of HCl ranging from 0.5 to 1.5 M HCl in the presence and absence of different concentrations of the inhibitors, EBI and EEBA, ranging from 50 to 200 ppm at temperatures 303, 308 and 313 K are shown in Figs. 5 and 6. The result obtained from the study for EBI is shown in Tables 2a–2c and that for EEBA in Tables 3a–3c.The percentage inhibition efficiency was calculated in each case using the following equation:

$$E(\%) = \frac{i_{corr} - i_{corr}^*}{i_{corr}} \times 100$$
(4)



Fig. 8. Langmuir adsorption isotherms for the interaction of 2-EBI on mild steel in (a) 0.5 M (b) 1 M (c) 1.5 M HCl and (d) Temkin adsorption isotherm for 2-EBI-mild steel interaction in 1.5 M HCl at 313 K.

where i_{corr} and i_{corr}^* denote corrosion current density in the absence and presence of the inhibitor. The corrosion current densities were determined by the extrapolation of anodic and cathodic tafel lines to the corrosion potential, E_{corr} .

From the result obtained from the study, it is clearly evident that for both the inhibitors, at all the three temperatures 303, 308 and 313 K, the corrosion current density decreased with increase in concentration of the inhibitor. Therefore, the percentage inhibition efficiency also increased with increase in concentration of the inhibitor. Increase in temperature as well as increase in acid concentration caused an increase in corrosion current density thereby decreasing the inhibition efficiency. The maximum efficiency was obtained for 200 ppm concentration of the inhibitors in 0.5 M HCl at 303 K. From potentiodynamic polarization study also, it was seen that EEBA was more efficient inhibitor than EBI. The result obtained from the potentiodynamic polarization study was in perfect agreement with that obtained from EIS study.

On analyzing the tafel plots it could be understood that the addition of the inhibitors, EBI and EEBA, didn't cause the corrosion potential to shift towards anodic or cathodic region. Also there was change on both anodic and cathodic polarization curves after inhibitor addition. This observation leads to the conclusion that the inhibitors, EBI and EEBA act as mixed type inhibitors. A comparison of percentage inhibition efficiencies of the two inhibitors were given in Fig. 7 in the online version at http://dx.doi.org/10.1016/j.molliq.2016.04.113. (Please refer in the supplementary materials).

3.2. Adsorption study

As known, the adsorption isotherms provide important information on interaction between the inhibitor and metal surface [43]. The interaction of the inhibitor and steel iron surface is described on the model followed by adsorption isotherms. Adsorption of inhibitor molecules on surface is a substitution process where an exchange of adsorbed water molecules with organic molecules occurred. The degree of surface covered (θ) by inhibitor on steel is dependent on inhibitor concentration at constant temperature, this way adsorption isotherm is evaluated at equilibrium conditions [44]. The inhibition efficiencies of organic molecules mainly depend on their adsorption ability on the metal surface. Therefore, it is of utmost importance to determine the relation between adsorption and corrosion inhibition. Several adsorption isotherms were attempted to fit the degree of surface coverage values, θ (%IE/100) to adsorption isotherms including Frumkin, Temkin, Freundlich and Langmuir isotherms. The values for various concentrations of inhibitors in acidic media have been evaluated from EIS measurements. In the case of EBI, when C_{inh}/ vs. C_{inh} was plotted, a straight line with R² value close to unity was obtained in all the cases and thus obeyed Langmuir adsorption isotherm (Fig. 8a-c), except value at 313 K in 1.5 M HCl which gave straight line with R² value close to unity when vs. Log C_{inh} was plotted and in this case Temkin adsorption isotherm was obeyed as represented in Fig. 8d. The θ values for EEBA obeyed Langmuir adsorption isotherm at all the three temperatures in different acid concentrations which are represented in Fig. 9.

Langmuir adsorption isotherm can be represented using the following equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}.$$
(5)

Temkin adsorption isotherm can be represented using the following equation:

$$\exp(f\theta) = K_{ads}C_{inh} \tag{6}$$

where C_{inh} is the concentration of inhibitor in ppm, K_{ads} is the equilibrium constant for adsorption-desorption process which is obtained from the following equation:

$$K_{ads} = \frac{\theta}{C_{inh}(1-\theta)}.$$
(7)

The free energy of adsorption ΔG_{ads} was calculated using the equation:

$$\Delta G_{ads} = -RTln(55.5 \text{ K}_{ads}). \tag{8}$$



Fig. 9. Langmuir adsorption isotherms for EEBA-mild steel interaction in (a) 0.5 M (b) 1 M and (c) 1.5 M HCl.

Table 4a	
Adsorption parameters obtained for different concentrations of EBI at different acid concentration and tempe	ratures.

Conc. of	Conc. Of	Temperature (K)	Temperature (K)									
HCl (M)	EBI (ppm)	303		308		313						
		$K_{ads} (10^4 M^{-1})$	$-\Delta G_{ads} (kJ/mol)$	$K_{ads} (10^4 M^{-1})$	$-\Delta G_{ads} (kJ/mol)$	$K_{ads} (10^4 M^{-1})$	$-\Delta G_{ads} (kJ/mol)$					
0.5	50	1.06	33.47	0.28	30.68	0.20	30.25					
	100	1.59	34.49	0.24	30.21	0.35	31.65					
	150	2.28	35.39	0.51	32.15	0.40	32.04					
	200	3.77	36.66	0.46	31.90	0.41	32.07					
1	50	0.42	31.16	0.21	29.82	0.18	30.06					
	100	0.71	32.47	0.30	30.82	0.15	29.61					
	150	0.53	31.75	0.25	30.32	0.23	30.61					
	200	1.35	34.08	0.29	30.69	0.245	30.77					
1.5	50	0.38	30.88	0.14	28.79	0.03	25.35					
	100	0.238	29.71	0.07	27.13	0.0392	25.99					
	150	0.46	31.39	0.05	26.50	0.0391	25.98					
	200	1.24	33.85	0.06	26.71	0.03	25.65					

From Tables 4a and 4b, it can be seen that K_{ads} values are relatively high. This shows the high adsorption ability of inhibitor on mild steel surface [45]. It can also be seen from the table that ΔG_{ads} values are negative. This indicates the spontaneity of adsorption and the stability of adsorbed layer on mild steel surface [46,47]. It is said that the values of ΔG_{ads} obtained around -20 kJ/mol or lower indicate physisorption whereas the values around -40 kJ/mol indicate chemisorption [48–50]. The adsorption phenomena of an organic molecule cannot be considered as purely physical or chemical adsorption phenomena [51, 52]. The adsorption of inhibitor on to the mild steel surface may involve both physisorption and chemisorption. From electrochemical studies it was found that %IE decreased with increase in temperature. This can be explained by considering the point that the adsorption of inhibitor on mild steel surface is not effective at higher temperatures.

3.3. Computational study

To investigate the effect of molecular structure on inhibition efficiency, some quantum chemical calculations were performed. Various quantum chemical parameters of the two inhibitors were calculated using Gaussian 03 program package. In the case of EBI, the energy of highest occupied molecular orbital (E_{HOMO}) is -5.8762 eV. For EEBA, the value of E_{HOMO} is -5.798 eV. The energy of the lowest unoccupied molecular orbital (E_{LUMO}) obtained for EBI is -0.2313 eV. For EEBA, the value of E_{LUMO} is -0.205 eV. In the case of EBI, the energy gap (ΔE), $E_{LUMO}-E_{HOMO}$ is 5.6449 eV and the energy gap for EEBA is 5.593 eV. An idea about the inhibition efficiency of the molecule will be obtained from ΔE value. A small ΔE value indicates more efficient

inhibition [14]. The HOMO and LUMO of the two inhibitor molecules were given in Fig. 10 in the online version at http://dx.doi.org/10. 1016/j.molliq.2016.04.113. (please refer in the supplementary materials). The Δ E value for EEBA is smaller than that of EBI which shows that EEBA is more efficient inhibitor than EBI. Thus the theoretical study is in perfect agreement with the electrochemical studies.

The optimized molecular geometries of EBI and EEBA were determined and shown in Fig. 1. Condensed Fukui indices of EBI and EEBA were calculated and the results are given in Tables 5 in the online version at http://dx.doi.org/10.1016/j.molliq.2016.04.113.a and b (please refer in the supplementary materials). The local reactivity of the inhibitor molecule had been investigated using the condensed Fukui indices which give an indication about the reactive centres of molecules (nucleophilic and electrophilic centres). The molecular regions where the Fukui function is large are chemically softer than the regions where the Fukui function is small. The site of nucleophilic attack will be the one with maximum f⁺ value and the site of electrophilic attack will be the one with maximum f⁻ value. From the table we can see that in the case of EBI, f^+ value is the highest for C (3). Hence this is the site for nucleophilic attack. The f⁻ value is the highest for C (5). Hence this is the site for electrophilic attack. In the case of EEBA, f⁺ value is the highest for C (7) and hence this is the site for nucleophilic attack. The f⁻ value is highest for C (5). Hence this is the site for electrophilic attack.

4. Conclusions

Electrochemical measurements such as EIS and potentiodynamic polarization were used to study the corrosion inhibition efficiency of

Table 4b

Adsorption parameters obtained for different concentrations of EEBA in different acid concentration and temperatures.

Conc. of	Conc. Of	Temperature (K)	Temperature (K)									
HCl (M)	EEBA (ppm)	303		308		313						
		$K_{ads} (10^4 \text{M}^{-1}) -\Delta G_{ads} (kJ/mol)$		$K_{ads} (10^4 M^{-1})$	$-\Delta G_{ads} (kJ/mol)$	$K_{ads} (10^4M^{-1})$	$-\Delta G_{ads} (kJ/mol)$					
0.5	50	8.63	38.75	2.71	36.42	1.56	35.58					
	100	4.63	37.18	1.89	35.49	1.27	35.04					
	150	4.81	37.28	1.62	35.11	1.53	35.53					
	200	3.89	36.74	2.02	35.67	1.69	35.79					
1	50	5.28	37.51	2.25	35.95	2.11	36.36					
	100	3.79	36.68	1.95	35.58	1.65	35.72					
	150	3.24	36.28	1.96	35.59	1.19	34.87					
	200	2.56	35.69	1.60	35.07	1.23	34.96					
1.5	50	4.26	36.97	2.91	36.61	1.39	35.28					
	100	4.74	37.24	1.65	35.15	0.802	33.85					
	150	4.06	36.85	1.16	34.25	0.69	33.45					
	200	3.61	36.55	0.95	33.74	0.80	33.84					

different concentrations of EBI and EEBA in various concentrations of HCl ranging from 0.5 to 1.5 M at temperatures 303, 308 and 313 K. Based on this study it can be concluded that

- (i) In the presence of EBI and EEBA there is effective reduction in corrosion of mild steel exposed to HCl.
- (ii) The inhibition efficiency of EBI and EEBA increases with increase in its concentration. The efficiency was found to decrease with increase in temperature as well as increase in acid concentration. In the case of both the inhibitors, maximum efficiency was observed in 0.5 M HCl at 303 K. EEBA was found to be more efficient inhibitor than EBI.
- (iii) The mode of inhibition of EBI and EEBA was through adsorption on to the mild steel surface. The mode of adsorption was believed to be both physisorption and chemisorption. For EBI, the adsorption obeyed Langmuir adsorption isotherm except for 313 K in 1.5 M HCl, for which the best fit adsorption isotherm was Temkin adsorption isotherm. For EEBA, the adsorption obeyed Langmuir adsorption isotherm.
- (iv) Various quantum chemical parameters as well as optimized geometry of the inhibitor were calculated. Theoretical study also showed that EEBA was more efficient inhibitor than EBI. The Fukui indices were also calculated.

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.molliq.2016.04.113.

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