

INFLUENCE OF ANIONS ON THE INHIBITION OF CORROSION OF ZINC IN ACIDIC SOLUTIONS BY N-HETEROCYCLICS

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The influence of anions such as chloride and sulphate on the corrosion of zinc in 1 N HCl and 1 N H₂SO₄ by N-heterocyclics such as imidazole (Im), 2-methyl imidazole (M Im) and benzimidazole (B Im) has been studied using weight loss and gasometric measurements potentiodynamic polarization studies, a.c. impedance measurements and UV reflectance studies. Imidazoles are found to be more inhibitive in 1 N HCl than in 1 N H₂SO₄. The inhibition of corrosion of zinc by these compounds is found to be under mixed control, but predominantly under cathodic control. Trends in the increase of charge transfer resistance (R_t) and decrease in double layer capacitance (C_{dl}) values also indicate the adsorption of these compounds on the metal surface. UV spectral studies were also carried out to establish the actual mechanism of inhibition of corrosion. The adsorption of these compounds from both the acids on the surface of zinc obeys Temkin's adsorption isotherm.

Keywords: N-heterocyclics, corrosion inhibition, adsorption isotherm, impedance spectroscopy, UV reflectance studies

INTRODUCTION

Heterocyclic compounds are well known for their efficacy as corrosion inhibitors and those containing nitrogen have been frequently referred to in the literature [1-5]. Nitrogen containing heterocyclic compounds are considered to be excellent complex or chelate forming substances with metals of transition series [6].

Such complexes of substances or their salts with transition metals are strongly adsorbed forming a thin, adherent film providing a barrier between the metal surface and the corrosive medium, thereby bringing down the rate of corrosion.

Imidazoles have been proved to be potentially effective corrosion inhibitors and their remarkable efficiency for copper and its alloys [7-13] as well as for iron [14-18] and mild steel [19] has been well established. The efficacy of imidazoles and their derivatives as inhibitors for the corrosion of zinc in acidic solutions has also been reported by a few authors [20,21], but the information provided is very little. The extensive application of imidazoles as inhibitors for the corrosion of

different metals in different media is based on the two following considerations.

First, these compounds are industrially important and are commercially available. Second, the electron cloud on the aromatic ring is expected to induce greater adsorption of the compound on the metal surface.

In the present study the influence of imidazole (Im), 2-methyl imidazoles (M Im) and benzimidazole (B Im) on the inhibition of corrosion of zinc in 1 N HCl and 1 N H₂SO₄ has been investigated using weight loss and gasometric studies, potentiodynamic polarization studies, a.c. impedance measurements and UV reflectance measurements.

EXPERIMENTAL

Rectangular zinc specimens of the composition 1.03% Pb, 0.04% Cd, 0.01% Fe and the remainder Zn procured from Cominco Binani Zinc Ltd, Aluva, Kerala and of size 5 x 2 x 0.13 cm were used for weight loss and gasometric studies. These strips were given mechanical polishing and

degreased with acetone before use. For potentiodynamic polarization studies and a.c. impedance measurements a cylindrical rod of zinc of the same composition as above and axially embedded in Teflon with an exposed area of 0.44 cm^2 and provided with an electrical contact was used.

The electrode was polished using a sequence of emery papers and then degreased with acetone. HCl and H_2SO_4 of AR grade were used for preparing solutions. Imidazoles were of high purity Loba Chemie make. Triply distilled water was used to prepare all experimental solutions.

Weight loss and gasometric measurements were carried out as described elsewhere [22]. Potentiodynamic polarization studies were carried out as described earlier [23] at a temperature of $305 \pm 1 \text{ K}$. A platinum foil of large surface area was used as the auxiliary electrode and $\text{Hg}/\text{Hg}_2\text{Cl}_2/1 \text{ N HCl}$ and $\text{Hg}/\text{Hg}_2\text{SO}_4/1 \text{ N H}_2\text{SO}_4$ were used as reference electrodes. Impedance measurements were carried out at the open circuit potential after immersing the zinc specimen in the experimental solution using Electrochemical System (EG & G PAR) which includes a digital potentiostat model 273 and a lock-in-amplifier model 5208 and IBM PC in the frequency range 100 MHz to 100 KHz. The applied voltage of the sinusoidal wave was 5 mV.

UV reflectance studies were carried out on the surfaces of polished, corroded and corrosion inhibited zinc specimens in the range of 200-700 nm using normal incident angle (40°) using UV visible NIR spectrophotometer (Model U 3400, Hitachi, Japan).

RESULTS AND DISCUSSION

Weight loss and gasometric studies

The structural and molecular formulae of imidazoles used are shown in Table I. Tables II(a), II(b), III(a) and III(b) give the values of inhibition efficiency for different concentrations of imidazoles in 1 N HCl and 1 N H_2SO_4 obtained from weight loss and gasometric measurements. Imidazoles are found to inhibit the corrosion of

zinc in both the acids in the order $\text{B Im} > \text{M Im} > \text{Im}$.

They are found to be more effective as corrosion inhibitors in 1 N HCl than in 1 N H_2SO_4 . It has already been reported that nitrogen containing compounds are more effective in HCl [24-25] than in H_2SO_4 . It can be seen from these tables that there is fairly very good agreement between the values of inhibition efficiency obtained by both the methods in both the acids.

The inhibitive effect of imidazoles can be due to the interaction between the π -electrons of the imidazole ring with the positively charged metal surface [26], resulting in the adsorption of the compound on the metal surface. The interaction of lone pairs of electrons of the nitrogen atom in the imidazole ring with the metal surface may also favour the adsorption of these compounds on the metal surface. The electrostatic interaction of positively charged imidazolium cation (Im H^+) formed in the acidic solution [27] by its combination with hydrogen ions, with the negatively charged metal surface may also be responsible for the adsorption of these compounds on the metal surface [28]. 2-methyl imidazole (M Im) gives more inhibition in both the acids. This can be attributed to the presence of an electron releasing $-\text{CH}_3$ group which enhances the electron density at the anchoring point. This leads to more

Table I: Formulae of imidazoles

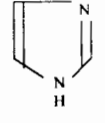
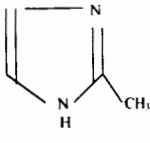
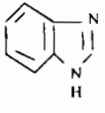
No.	Name of the Compound	Molecular formulae	Structure
1.	Imidazole (Im)	$\text{C}_3\text{H}_4\text{N}_2$	
2.	2-Methyl Imidazole (M Im)	$\text{C}_4\text{H}_6\text{N}_2$	
3.	Benzimidazole (B Im)	$\text{C}_7\text{H}_6\text{N}_2$	

TABLE II(a): Values of inhibition efficiency (%) for different concentrations of imidazoles from weight loss measurements for zinc in 1 N HCl

Inhi- bitor used	Values of inhibition efficiency (%) for different concentrations (mM) of imidazoles				
	10	20	30	40	50
A	45.8	47.7	52.6	59.8	71.7
B	52.4	60.2	66.4	72.4	77.6
C	59.9	68.2	72.4	78.9	82.5

A = Imidazole (Im); B = 2-methyl imidazole (M Im)
C = Benzimidazole (B Im)

TABLE III(a): Values of inhibition efficiency (%) for different concentrations of imidazoles from gasometric measurements for zinc in 1 N HCl

Inhi- bitor used	Values of inhibition efficiency (%) for different concentrations (mM) of imidazoles				
	10	20	30	40	50
A	49.0	50.2	51.3	56.9	68.6
B	51.8	58.8	67.8	69.8	74.9
C	57.3	68.2	74.1	75.3	78.8

A = Imidazole (Im); B = 2-methyl imidazole (M Im)
C = Benzimidazole (B Im)

adsorption, thereby more corrosion inhibition. The structural change from imidazoles (Im) to benzimidazole (B Im) with the addition of a benzene ring has greater influence on the inhibitive property of the resulting compound, namely benzimidazole (B Im). The additional effect is due to the mobile π -electrons of the benzene ring, which can interact with the positively charged metal surface resulting in an enhanced surface coverage of the metal surface. In the case of imidazole (Im) and 2-methyl imidazole (M Im) the adsorption occurs through the lone pairs of electrons of the nitrogen atom and π -electrons of the imidazole ring only. But in the case of benzimidazole there is an additional effect of π -electrons of the benzene ring. Quantum mechanical calculations also reveal the fact that electron density of the benzimidazole is more than that for imidazoles [29].

TABLE II(b): Values of inhibition efficiency (%) for different concentrations of imidazoles from weight loss measurements for zinc in 1 N H₂SO₄

Inhi- bitor used	Values of inhibition efficiency (%) for different concentrations (mM) of imidazoles				
	10	20	30	40	50
A	34.9	39.5	44.0	51.6	58.2
B	47.6	54.2	60.1	68.6	76.2
C	54.2	64.5	72.4	74.6	82.2

A = Imidazole (Im); B = 2-methyl imidazole (M Im)
C = Benzimidazole (B Im)

The better performance of imidazoles in HCl can be explained as follows.

Imidazoles can exist either as neutral molecules or in the form of cations in aqueous acidic solutions. As neutral molecules they can adsorb through sharing of electrons between the nitrogen atom in the heterocyclic ring and the metal surface. They can also adsorb through the electrostatic interaction between the positively charged imidazolium cation (Im H^+) and the negatively charged metal surface. The extent of adsorption is also influenced by the nature of anions present in an acidic solution [30].

The specific adsorption of anions is expected to be more pronounced and significant with anions having a smaller degree of hydration such as chloride ions. Being specifically adsorbed they created an excess negative charge towards the solution phase and favour more adsorption of

TABLE III(b): Values of inhibition efficiency (%) for different concentrations of imidazoles from gasometric measurements for zinc in 1 N H₂SO₄

Inhi- bitor used	Values of inhibition efficiency (%) for different concentrations (mM) of imidazoles				
	10	20	30	40	50
A	35.2	39.2	41.6	51.5	56.9
B	48.5	56.4	62.9	69.8	75.2
C	60.9	65.3	73.3	79.2	81.7

A = Imidazole (Im); B = 2-methyl imidazole (M Im)
C = Benzimidazole (B Im)

TABLE IV: Potentiodynamic parameters for the corrosion of zinc in 1 N HCl and 1 N H₂SO₄ containing different concentrations of imidazoles

Inhibitor concn (mM)	1 N HCl					1 N H ₂ SO ₄				
	E_{corr} (mV)	Tafel slope (mV.dec ⁻¹)		I_{corr} (mA . cm ⁻²)	IE (%)	E_{corr} (mV)	Tafel slope (mV.dec ⁻¹)		I_{corr} (mA . cm ⁻²)	IE (%)
		b_a	b_c				b_a	b_c		
Blank	-1075	45	120	3.40	—	-1034	60	125	2.80	—
A										
10	-1070	48	124	1.80	47.10	-1028	62	130	1.80	35.70
30	-1062	50	130	1.60	52.90	-1019	65	135	1.50	46.40
50	-1056	53	135	0.90	73.50	-1005	68	140	1.20	57.10
B										
10	-1067	50	127	1.58	53.50	-1025	65	132	1.48	47.10
30	-1060	55	135	1.15	66.10	-1010	70	140	1.10	60.70
50	-1060	57	138	0.83	75.60	-1000	70	145	0.65	76.80
C										
10	-1065	52	130	1.48	56.50	-1020	70	135	1.08	61.40
30	-1055	58	140	0.92	72.90	-1005	75	145	0.75	73.20
50	-1047	60	142	0.68	80.00	-996	78	150	0.55	80.40

A = Imidazole (Im); B = 2-methyl imidazole (M Im) C = Benzimidazole (B Im)

imidazolium cations (Im H⁺) leading to enhanced adsorption and corrosion inhibition [31]. It is also possible that stronger adsorption of organic molecules is not always a direct combination of organic molecules with the metal surface. In some cases the adsorption occurs through the already adsorbed chloride or sulphate ions which interfere with the adsorbed organic molecules. The lesser interference by sulphate ions results in lower adsorption and lesser inhibition of corrosion.

Potentiodynamic polarization studies

Table IV gives different corrosion kinetic parameters such as corrosion current (I_{corr}), corrosion potential (E_{corr}) and Tafel slopes (b_a and b_c) for different concentrations of imidazoles. It is found that imidazoles bring down the values of I_{corr} of zinc in both the acids. This decrease is more in 1 N HCl than in 1 N H₂SO₄, because

they are more effective as inhibitors in 1 N HCl. Among imidazoles the decrease in I_{corr} values follows the order B Im > M Im > Im which is

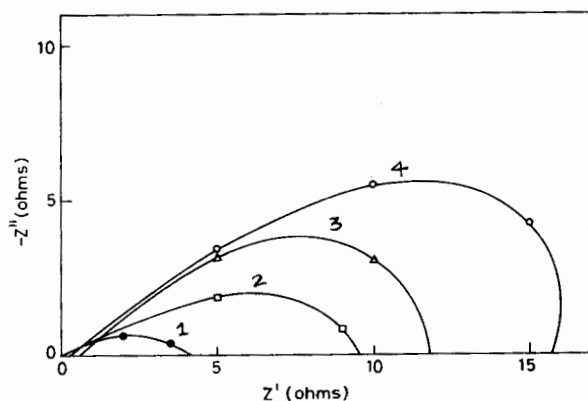


Fig. 1: Nyquist plot for zinc in 1 N HCl containing different concentrations of imidazole (Im)
(1) Blank (2) 10 mM Im (3) 30 mM Im (4) 50 mM Im

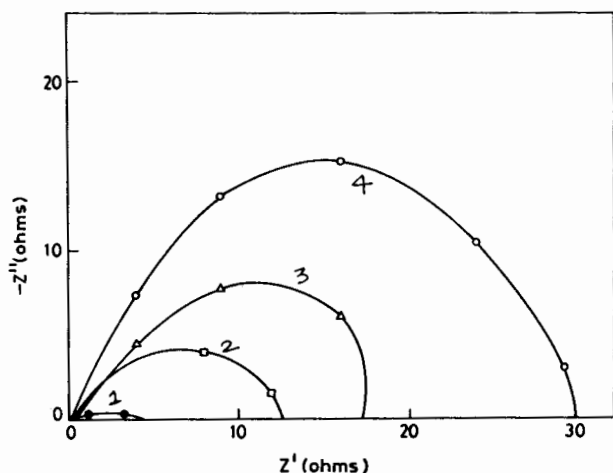


Fig. 2: Nyquist plot for zinc in 1 N HCl containing different concentrations of 2-methyl imidazole (M Im)
(1) Blank (2) 10 mM Im (3) 30 mM Im (4) 50 mM Im

the same as that obtained for inhibition efficiency values for imidazoles.

In the absence of imidazoles under study the potentiodynamic polarization behaviour of zinc in 1 N HCl showed an anodic Tafel slope (b_a) of 45 mV and a cathodic Tafel slope (b_c) of 120 mV. These values are similar to those reported earlier [32]. Similarly an anodic Tafel slope (b_a) of 60 mV and a cathodic Tafel slope (b_c) of 125 mV were obtained for zinc in 1 N H_2SO_4 . These values are in agreement with those reported earlier [33]. The presence of imidazoles in acidic solutions is found to enhance both the Tafel slopes, in both the acids but the anodic Tafel slope (b_a) to a lesser extent

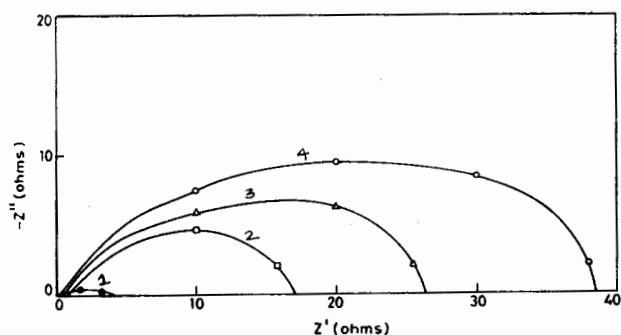


Fig. 3: Nyquist plot for zinc in 1 N HCl containing different concentrations of benzimidazole (B Im)
(1) Blank (2) 10 mM Im (3) 30 mM Im (4) 50 mM Im

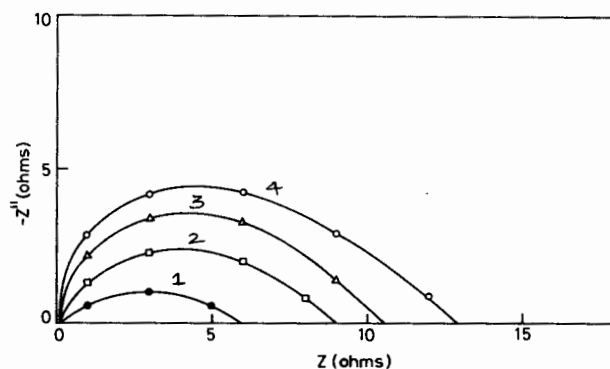


Fig. 4: Nyquist plot for zinc in 1 N H_2SO_4 containing different concentrations of imidazole (Im)
(1) Blank (2) 10 mM Im (3) 30 mM Im (4) 50 mM Im

than the cathodic Tafel slope (b_c). So the inhibition of corrosion of zinc by N-heterocyclics in both the acids, is under mixed control, but predominantly under cathodic control.

A C impedance measurements

Impedance diagrams obtained for the frequency range 100 MHz to 100 KHz at the open circuit potential for zinc in 1 N HCl and 1 N H_2SO_4 in the presence and absence of different concentrations of imidazoles are shown in Figs. 1-6. It can be seen from these figures that impedance diagrams in most of the cases are not perfect semicircles. The difference has been attributed to frequency dispersion [34-35]. Charge transfer resistance (R_t) and double layer

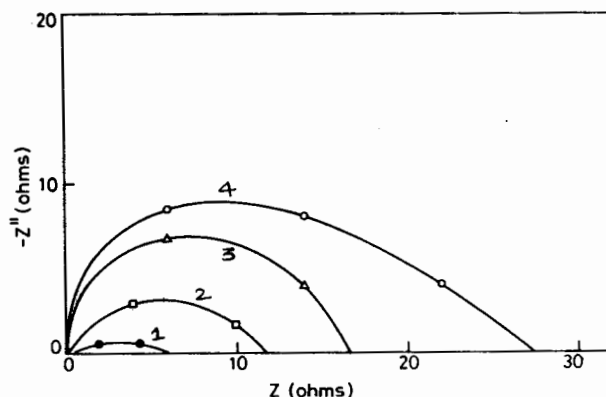


Fig. 5: Nyquist plot for zinc in 1 N H_2SO_4 containing different concentrations of 2-methyl imidazole (M Im)
(1) Blank (2) 10 mM Im (3) 30 mM Im (4) 50 mM Im

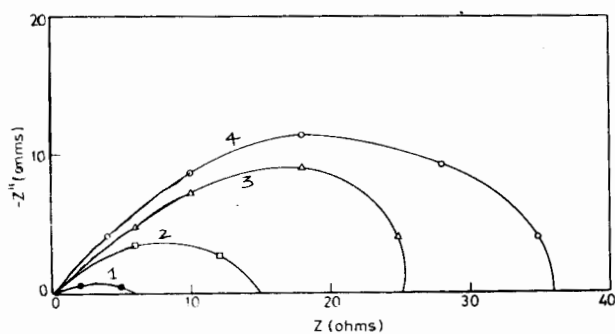


Fig. 6: Nyquist plot for zinc in 1 N H_2SO_4 containing different concentrations of benzimidazole (B Im)
(1) Blank (2) 10 mM Im (3) 30 mM Im (4) 50 mM Im

capacitance (C_{dl}) values were derived from Nyquist plots as reported earlier [23]. Table V gives values for R_t , I_{corr} and C_{dl} for zinc in 1 N HCl and 1 N H_2SO_4 in the presence of imidazoles (50 mM). It can be seen from this table that I_{corr} for zinc in 1 N HCl is more than that in 1 N H_2SO_4 . This observation is in agreement with that observed earlier in potentiodynamic polarization studies. It can also be seen from the table that maximum value of R_t is shown by benzimidazole (B Im) followed by 2methyl imidazoles (M Im) and imidazole (Im) in the decreasing order. Values of I_{corr} also follow a similar order.

It can be clearly seen from the table that the value C_{dl} is more for 1 N HCl than 1 N H_2SO_4 . All the compounds bring down the values of C_{dl} in both the acids by getting adsorbed on the surface of zinc. Maximum decrease in the value of double layer capacitance (C_{dl}) is found in the

case of benzimidazole followed by 2-methyl imidazole and imidazole in the decreasing order. All these observations bring out the fact that the effectiveness of the imidazoles as inhibitors for the corrosion of zinc in both the acids follows the order B Im > M Im > Im. Values of inhibition efficiency obtained from this method agree fairly well with those reported for other methods used in this study.

UV reflectance studies

The fact that the formation of a strongly adsorbed insoluble film on the metal surface is responsible for the inhibition of corrosion of zinc in both the acids is also supported by reflectance studies using different specimens under similar conditions. Fig. 7 shows the reflectance curves for polished zinc specimen and polished specimens dipped in 1 N HCl alone and in the presence of 50 mM imidazoles.

It can be seen from this figure that the reflectance is maximum for the polished specimen and it is brought down considerably in the case of specimen dipped in 1 N HCl. This clearly shows that there is a change in the surface characteristics due to corrosion of zinc in HCl alone. However, in the case of specimens dipped in HCl containing different imidazoles reflectance is decreased only to a very little extent. This observation clearly brings out the fact that surface characteristics are not very much changed in the presence of imidazoles due to the formation of a film on the surface of zinc.

TABLE V: Impedance parameters for the corrosion of zinc in 1 N HCl and 1 N H_2SO_4 in the presence of imidazoles (50 mM)

Inhibitor	1 N HCl				1 N H_2SO_4			
	R_t ($\Omega \text{ cm}^2$)	C_{dl} ($\mu \text{ F} \cdot \text{cm}^{-2}$)	I_{corr} ($\text{mA} \cdot \text{cm}^{-2}$)	IE (%)	R_t ($\Omega \text{ cm}^2$)	C_{dl} ($\mu \text{ F} \cdot \text{cm}^{-2}$)	I_{corr} ($\text{mA} \cdot \text{cm}^{-2}$)	IE (%)
Blank	4.04	262	3.52	—	5.91	198	2.98	—
A	15.65	205	0.84	76.14	13.07	163	1.52	49.0
B	29.71	192	0.59	83.24	26.95	158	0.78	73.8
C	38.42	176	0.48	86.30	36.20	142	0.62	79.2

A = Imidazole (Im); B = 2-methyl imidazole (M Im) C = Benzimidazole (B Im)

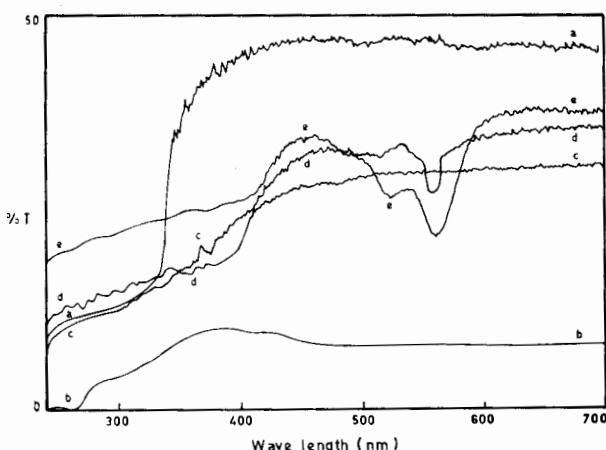


Fig. 7: UV reflectance curves for zinc specimens with different conditions
 (a) polished (b) dipped in 1 N HCl
 (c) 50 mM imidazole (Im)
 (d) 50 mM 2-methyl imidazole (M Im)
 (e) 50 mM Benzimidazole (B Im)

CONCLUSION

The main conclusions obtained from this study are the following

- Imidazoles inhibit the corrosion of zinc in both the acids, but more effectively in 1 N HCl.
- The extent of corrosion inhibition in both the acids follows the order B Im > M Im > Im.
- The inhibition of corrosion by imidazoles is due to the process of adsorption.
- Imidazoles act as mixed, but predominantly as cathodic inhibitors.
- The adsorption of imidazoles from both the acids on the surface of zinc obeys Temkin's adsorption isotherm.

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Adsorption isotherm

The nature of interaction of imidazoles with the metal surface which enables the adsorption of these compounds on the metal surface leading to the inhibition of corrosion can be deduced from the adsorption characteristic of inhibiting compounds. The coverage of the metal surface (θ) by the compound is very useful for discussing adsorption characteristics. For any concentration it can be calculated using the equation

$$\theta = \frac{W_0 - W}{W} \quad (1)$$

where W and W_0 are metal losses in the presence and absence of the organic compound. Surface coverage (θ) data for imidazoles were tested graphically for finding a suitable adsorption isotherm. A straight line relationship was obtained when surface coverage (θ) was plotted against $\log C$, thereby proving that the adsorption of imidazoles on the surface of zinc from both the acids obeys Temkin's adsorption isotherm.

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