

Research Article

Inhibition of Mild Steel Corrosion in Sulphuric Acid Using Esomeprazole and the Effect of Iodide Ion Addition

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The inhibition of the corrosion of mild steel in 1 M H_2SO_4 solution by the pharmaceutically active compound esomeprazole (ESP) has been investigated by using weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy measurements. The effect of temperature on the corrosion behavior with the addition of different concentrations of ESP was studied in the temperature range of 30–60°C. Results obtained revealed that the inhibition efficiency increased with the increase in concentration of the inhibitor but decreased with the increase in temperature. The addition of KI increased the inhibition of ESP to a considerable extent. The experimental results suggest that the presence of iodide ions in the solution stabilized the adsorption of the ESP molecule on the mild steel surface, thereby improving the inhibition efficiency. Polarization curves indicated that the ESP belonged to a mixed-type inhibitor. Adsorption of the inhibitor on the mild steel surface is found to obey the Langmuir adsorption isotherm. Some thermodynamic functions of dissolution and adsorption processes were also determined. Surface analysis via scanning electron microscope (SEM) and atomic force microscope (AFM) shows a significant improvement in the surface morphology of the mild steel plate.

1. Introduction

The environmental consequence of corrosion is enormous, and its inhibition has been deeply investigated. It has been found that one of the best methods of protecting metals against corrosion involves the use of inhibitors which are substances that slow down the rate of corrosion [1]. Therefore, the development of corrosion inhibitors based on organic compounds containing nitrogen, sulphur, and oxygen atoms is of growing interest in the field of corrosion and industry [2]. The corrosion inhibition is a surface process, which involves adsorption of the organic compounds on a metal surface. The adsorption depends mainly on the electronic structure of the molecule [3]. The inhibition efficiency of organic compounds depends on the mode of interaction with the metal surface and molecular structure. However, there is an increasing concern about the toxicity of most corrosion inhibitors. The toxic effects not only affect living organisms but also poison the environment [4]. Due to the toxicity of some corrosion inhibitors, there has been increasing search

for green corrosion inhibitors. Inhibitors in this class are those that are environmentally friendly and nontoxic.

Recently, several studies have been carried out on the inhibition of corrosion of metals by drugs. Moreover, the pharmaceutically active compound esomeprazole (ESP) is big enough (molecular mass –345.417 g/mol) and likely to effectively cover more surface areas (due to adsorption) of the mild steel. Furthermore, ESP is very cheap, easily available, environmentally friendly, and, most importantly, nontoxic. In view of these favorable characteristics, ESP was chosen for the corrosion studies. The IUPAC name of ESP is [S]-5-methoxy-2-[(4-methoxy-3,5-dimethylpyridin-2-yl)methylsulfinyl]-3H-benzimidazole.

The main objective here is to find out the synergistic effect with halide ions and also to investigate the temperature dependence of the corrosion rate with the aim to obtain the apparent activation energies of the corrosion process of steel in 1 M H_2SO_4 solution in the absence and presence of different concentrations of ESP. It was also the purpose of the present work to test the experimental data with several

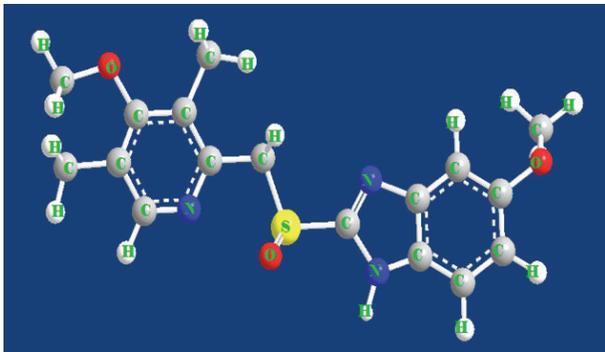


FIGURE 1: Structure of esomeprazole.

adsorption isotherms at different temperatures, in order to determine the standard free energies of the adsorption process and gain more information on the mode of adsorption of the inhibitor on the electrode surface.

2. Experimental Technique

Rectangular steel coupons in the size of $3.5 \times 1.5 \times 0.2$ cm were cut with a small hole of 2 mm diameter at the upper edge of the specimen for weight loss studies. For the electrochemical studies, the size of the electrodes was 1 cm^2 of exposed area with a 4 cm long tag for electrochemical contact. The mild steel sample used for the present study was analyzed in the IIT campus, Chennai, India and was found to have the composition (in wt.%) 0.104% C, 0.58% Mn, 0.035% P, 0.026% S, and the rest Fe. The corrosive solution was 1 M H_2SO_4 obtained by dilution of sulphuric acid with triple distilled water. The ESP compound was separated from the drug (brand name Sompraz, Sun Pharma, Sikkim, India) by recrystallization with ethanol. The molecular structure of the used inhibitor is presented in Figure 1.

The inhibitor concentration in weight loss and electrochemical study was in the range 50–300 ppm. The test coupons were mechanically polished with different grades of emery papers 1/0, 2/0, 3/0, 4/0, 5/0, and 6/0, cleaned with acetone, washed with distilled water, and finally dried in dry air before every experiment. After weighing accurately, the specimens were immersed in 100 mL of 1 M H_2SO_4 with and without the addition of different concentrations of inhibitors. After 2 h of immersion the coupons were taken out, washed, dried, and weighed accurately. Duplicate experiments were performed in each, and the mean value of weight loss was reported. The corrosion rate (CR) and the percentage of inhibition efficiency (IE%) were calculated by the following equation:

$$\text{IE} (\%) = \left[\frac{W_o - W_i}{W_o} \right] \times 100, \quad (1)$$

where W_o is the corrosion rate in the absence of the inhibitor and W_i is the corrosion rate in the presence of the inhibitor.

Two electrochemical techniques, namely, DC-Tafel slope and AC electrochemical impedance spectroscopy (EIS), were used to study the corrosion behavior. All electrochemical

measurements were carried out using a CHI 760D electrochemical impedance analyzer model. For these studies a three-electrode cell assembly with 1 cm^2 of mild steel as a working electrode, a saturated calomel electrode (SCE) as the reference electrode, and platinum foil as the counter electrode was used. The working electrode was polished before use. Before starting the electrochemical experiments, the test sample was allowed to reach steady-state value of OCP. The EIS measurements were carried out by using an ac signal of 0.1 V amplitude for the frequency spectrum from 100 kHz to 0.01 Hz in the potential range ± 200 mV. The inhibition efficiency is calculated from the electrochemical impedance spectra by the following equation:

$$\text{IE} (\%) = \left[\frac{R_{ct}^i - R_{ct}^o}{R_{ct}^i} \right] \times 100, \quad (2)$$

where R_{ct}^i and R_{ct}^o are the charge transfer resistance values with and without esomeprazole, respectively. The inhibition efficiency is calculated from the polarization curves by the following equation:

$$\text{IE} (\%) = \left[\frac{I_{corr}^o - I_{corr}^i}{I_{corr}^o} \right] \times 100, \quad (3)$$

where I_{corr}^o and I_{corr}^i are the corrosion current densities in the absence and presence of inhibitor, respectively.

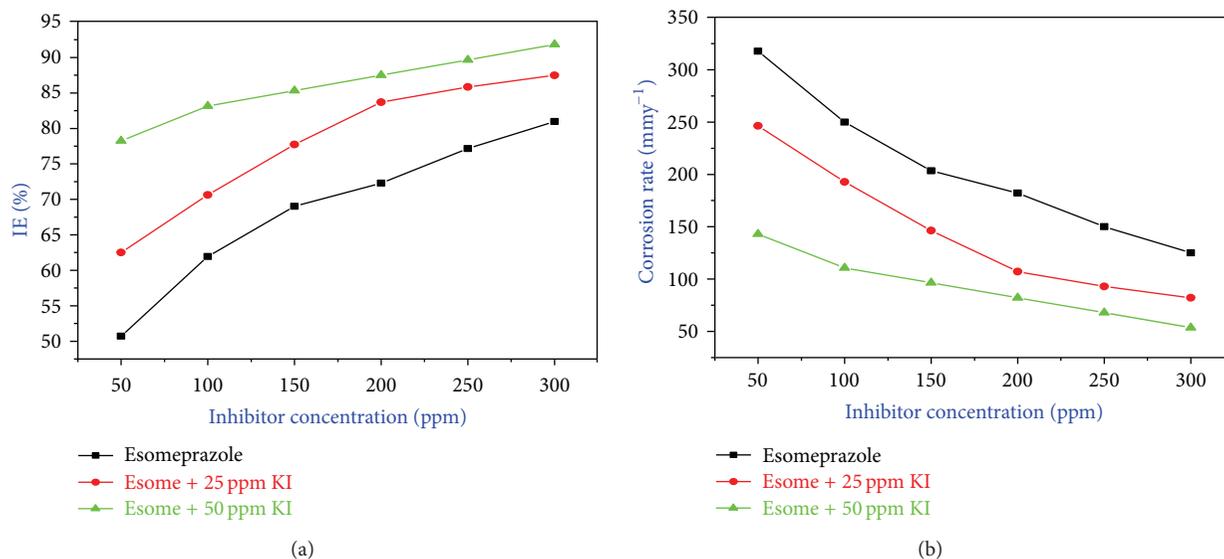
For the morphological study, surface features of carbon steel were examined after exposure to 1 M H_2SO_4 solutions in the absence and presence of the optimum concentration of ESP was examined by JEOL/EO JSM-6390 model scanning electron microscope (SEM) and atomic force microscopy model Nanosurf EZ2-AFM.

3. Results and Discussion

3.1. Weight Loss Measurements. Table 1 shows the results obtained from weight loss measurements for mild steel in 1 M H_2SO_4 solutions in the absence and presence of different concentrations of ESP. It has been observed from the results that the IE% of ESP increases from 50.72% to 80.97% with the increase in inhibitor concentration from 50 to 300 ppm. Indeed, corrosion rate values of mild steel decreases from 107.1 mmy^{-1} to 40.8 mmy^{-1} on the addition of 50 ppm to 300 ppm of ESP. The increase in efficiency from 50.72% to 80.97% may be due to the blocking effect of the surface by both adsorption and film formation mechanisms, which decreases the effective area of corrosion attack [5]. The results confirm that ESP is an efficient corrosion inhibitor, which gives efficiency values as high as 80.97% in room temperature. The inhibiting performance exhibited by the compound may be due to the presence of protonated form of nitrogen and sulphur atoms of the compound which makes it adsorb quickly on the mild steel surface, thus forming an insoluble stable film on the surface of the mild steel. It is clear that ESP showed good inhibition for mild steel corrosion in 1 M H_2SO_4 solutions because the inhibitor molecule is made of planar aromatic rings of benzimidazole and a pyridine ring and also contains S and N atoms and π -electrons [6].

TABLE 1: Weight loss values of various concentrations of esomeprazole in 1 M H₂SO₄ solution.

Concentration (ppm)	Weight loss (mg cm ⁻²)	Corrosion rate (mm y ⁻¹)	Surface coverage (θ)	IE η (%)
blank	184	657.1	—	—
50	89	317.8	0.5072	50.72
100	70	250	0.6195	61.95
150	57	203.5	0.6903	69.03
200	51	182.1	0.7229	72.29
250	42	150	0.7716	77.17
300	35	125	0.8097	80.97

FIGURE 2: (a) Variation of corrosion rate in 1 M H₂SO₄ on mild steel with ESP with the addition of KI solution at room temperature, (b) variation of inhibition efficiency in 1 M H₂SO₄ on mild steel with ESP with the addition of KI solution at room temperature.

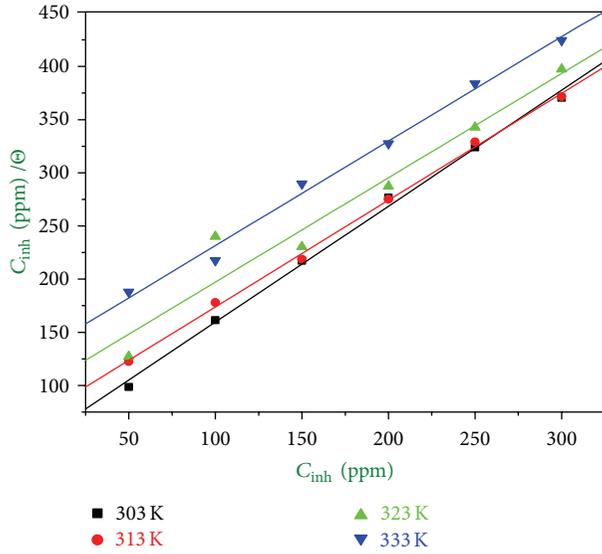
3.1.1. Synergistic Effect. Figures 2(a) and 2(b) show the values of corrosion rate (CR) and inhibition efficiency (IE%) for various concentrations of ESP without and with the addition of 25 and 50 ppm of potassium iodide. It is evident from the figure that the addition of KI decreases the corrosion rate and improves the inhibition efficiency of esomeprazole significantly. It is thought that the halide ions are able to improve adsorption of the organic cations by forming the intermediate bridges between the positively charged metal surface and the positive end of the inhibitor. The synergistic ability of the halide increases in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$ [7] and is initiated by the specific adsorption of the anion onto the metal surface. The greater influence of the iodide ion is often attributed to its large ionic radius, high hydrophobicity, and low electronegativity compared to the other halide ions [8, 9]. The synergistic effect between ESP and I^- ions can be explained by the fact that the addition of the KI component stabilized the adsorption of ESP on mild steel surface [10, 11]. This stabilization may be caused by the interaction between the ESP and I^- ion. Thus, the interaction enhances the inhibition efficiency to a considerable extent due to the increase of the surface coverage in the presence of iodide ions.

3.1.2. Influence of Temperature. The loss in the weight of the steel samples in 1 M H₂SO₄ in the absence and presence of various concentrations of esomeprazole drug at different temperatures was determined. The effect of temperature on the inhibition efficiency of the ESP is shown in Table 2. In all cases, an increase in ESP concentration leads to a decrease in the corrosion rate of samples indicating that the presence of esomeprazole drug retards the general corrosion of samples in 1 M H₂SO₄. On the other hand, an increase in temperature from 303–333 K resulted in an increase in the corrosion rate for all the concentration of ESP, probably as a result of desorption of inhibitor molecules from the metal surface.

3.1.3. Adsorption Isotherm. The efficiency of the organic compound ESP as a corrosion inhibitor depends not only on the characteristics of the environment in which it acts, the nature of the metal surface and electrochemical potential at the interface, but also on the structure of the inhibitor itself, which includes the number of adsorption active centers in the molecule, their charge density, the molecule size, the mode of adsorption, the formation of metallic complexes, and the projected area of the inhibitor on the metallic surface [12]. The phenomenon of interaction between the metal surface and

TABLE 2: Weight loss values of esomeprazole at various temperatures in 1 M H₂SO₄ solution.

Concentration of inhibitor (ppm)	Corrosion rate (mm y ⁻¹)				Inhibition efficiency (%)			
	303 K	313 K	323 K	333 K	303 K	313 K	323 K	333 K
Blank	657.1	659.7	735	821.5	—	—	—	—
50	317.8	390.2	446	603	50.72	40.85	39.32	26.60
100	250	289.1	318.2	444.2	61.95	56.18	41.68	45.93
150	203.5	207.3	256.5	396.3	69.03	68.58	65.10	51.76
200	182.1	180	223	320	72.29	72.71	69.65	61.05
250	150	158.5	198.8	286.5	77.17	75.97	72.95	65.12
300	125	127.2	180.1	241	80.97	80.71	75.50	70.66

FIGURE 3: The langmuir adsorption isotherm plots for the adsorption of esomeprazole in 1 M H₂SO₄ on the surface of mild steel.

the inhibitor can be better understood in terms of adsorption isotherm. The plots of C_{inh}/θ against C_{inh} (Figure 3) yield a straight line with approximately unit slope, indicating that the inhibitor under study obeys Langmuir adsorption isotherm. Assumptions of Langmuir relate the concentration of the adsorbate in the bulk of the electrolyte (C_{inh}) to the degree of surface coverage (θ) as (5):

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}, \quad (4)$$

where K_{ads} is the equilibrium constant of adsorption and θ is the surface coverage and expressed by IE%/100. By plotting values of C_{inh}/θ versus values of C_{inh} , straight line graphs were obtained (see Figure 3), which proves that the Langmuir adsorption isotherm is obeyed. Comparing the degree of linearity of the Langmuir adsorption isotherms as measured by values of R^2 (Table 3), it is seen that the Langmuir adsorption isotherm is best applicable at room temperature (303 K) than at higher temperatures. This confirms that the adsorption behavior of the inhibitor is strongly influenced by temperature. Also, values of the slope at room temperature (303 K) are greater than the values obtained at 313 K–333 K,

TABLE 3: Thermodynamic adsorption parameters for mild steel in 1 M H₂SO₄ in the presence of optimum concentrations of esomeprazole at different temperatures.

Temperature (K)	R^2	K_{ads} (10^4 M ⁻¹)	ΔG_{ads}° (KJ mol ⁻¹)
303	0.9966	46.58	-19.79
313	0.9882	73.23	-21.62
323	0.9419	101.13	-23.18
333	0.9904	135.59	-24.71

indicating that the strength of the attractive behavior of the inhibitor decreases with temperature. The slope of the C_{inh}/θ versus C_{inh} plots shows deviation from unity, which means nonideal simulating [13] and being unexpected from the Langmuir adsorption isotherm. It might be the results from the interactions between the adsorbed species on the mild steel surface [14, 15]. Adsorption equilibrium constant (K_{ads}) and free energy of adsorption (ΔG_{ads}°) were calculated using the relationships:

$$\Delta G_{ads}^{\circ} = -RT \ln (55.5K_{ads}), \quad (5)$$

where 55.5 is the concentration of water in solution in mol L⁻¹ and R is the universal gas constant. Calculated values of ΔG_{ads}° and K_{ads} were calculated from the plot of the isotherms in Figure 6 and recorded in Table 3. The ΔG_{ads}° values are negative, and the values are -19.79, -21.62, -23.18, and -24.71 kJ/mol from 303 K to 333 K, respectively, for the Langmuir isotherm plot. The negative values of ΔG_{ads}° ensure that the adsorption of the inhibitor molecule on to the steel surface is a spontaneous process. Generally, values of ΔG_{ads}° up to -20 kJ mol⁻¹ are consistent with physisorption, while those around -40 kJ mol⁻¹ or higher values are associated with chemisorption as a result of the sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate type of metal bonds [16]. In the present study, the calculated values of ΔG_{ads}° range between -19.79 and -24.71 kJ mol⁻¹ (Table 3), indicating that the adsorption mechanism of ESP on mild steel in 1 M H₂SO₄ solution at the studied temperatures may be a combination of both physisorption and chemisorption (comprehensive adsorption). However, physisorption was the major contributor, while chemisorption only slightly contributed to the

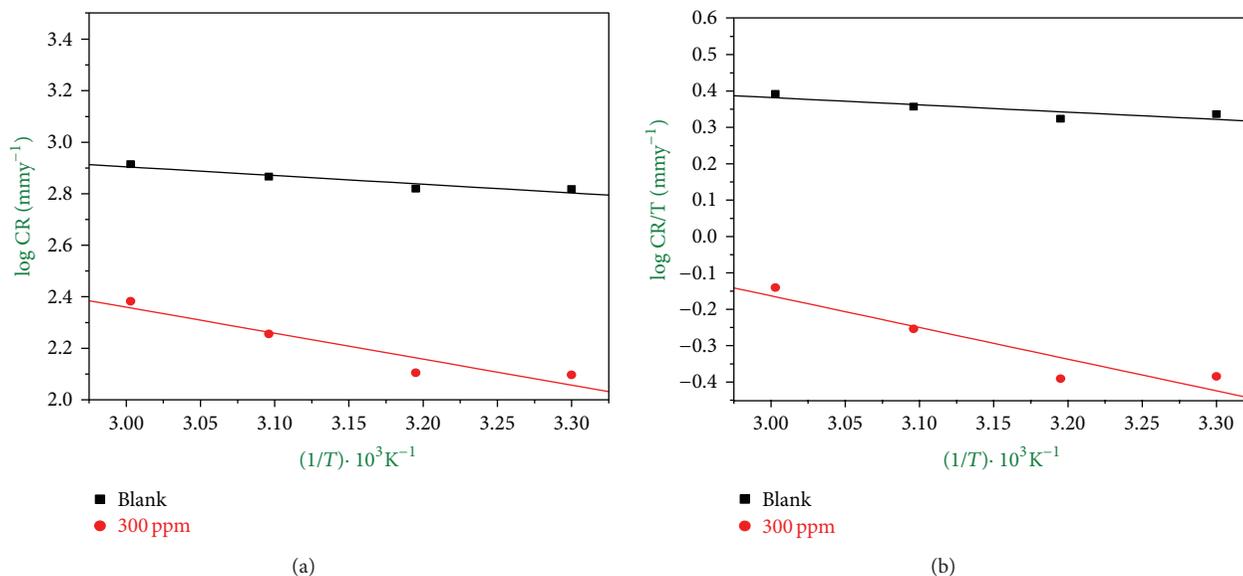


FIGURE 4: (a) Adsorption isotherm plots for log CR versus $1/T$. (b) Adsorption isotherm plot for $\log CR/T$ versus $1/T$.

TABLE 4: Thermodynamic activation parameters for mild steel in 1 M H_2SO_4 in the absence and presence of different concentrations of esomeprazole.

Concentration of Inhibitor (ppm)	E_a° (KJ mol $^{-1}$)	$-\Delta H_a^\circ$ (KJ mol $^{-1}$)	$-\Delta S_a^\circ$ (KJ mol $^{-1}$)
1 M H_2SO_4	75.05	18.837	201.45
300 ppm	103.1	46.879	214.28

adsorption mechanism judging from the decrease of IE % with increase in temperature.

3.1.4. Thermodynamic Parameters. Thermodynamic parameters are important to understand the inhibition mechanism. The thermodynamic functions for dissolution of mild steel without and with the addition of optimum concentration of ESP at various temperatures were calculated from the logarithm of corrosion rate (CR) of metal in acidic H_2SO_4 solution by using the Arrhenius equation:

$$\log CR = \frac{-E_a^\circ}{2.303RT} + A, \quad (6)$$

where CR is the corrosion rate, E_a° is the apparent activation energy, and A is the preexponential factor. The arrhenius plots of log CR versus $1/T$ for the blank and different concentrations of ESP give a straight line and a slope equal to $-(E_a^\circ/2.303R)$ shown in Figure 4, from which the values of E_a° for the inhibited corrosion reaction of mild steel have been calculated and recorded in Table 4. It was observed for the H_2SO_4 solution that E_a° , 75.05 kJ mol $^{-1}$. In the presence of the inhibitor is the activation energies are increased up to 103.1 kJ mol $^{-1}$ compared to the acid solution revealing the retardation of the corrosion reaction. The marked changes in E_a° suggest that the inhibitor may either participate in

the electrode or may change the potential difference of the metal-solution interface by adsorption.

From the transition state equation:

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a^\circ}{R}\right) \exp\left(-\frac{\Delta H_a^\circ}{RT}\right), \quad (7)$$

where ΔH_a° is the enthalpy of activation, ΔS_a° is the entropy of activation, h is Planck's constant, N is the Avogadro number, and R is the universal gas constant, the plot of $\log (CR/T)$ versus $1/T$ gives straight lines with a slope equal to $-(\Delta H_a^\circ/2.303R)$ and an intercept $(\log(R/Nh) + (\Delta S_a^\circ/2.303R))$ from which ΔH_a° and ΔS_a° values were calculated and listed in Table 4. The negative sign of ΔH_a° indicates that the adsorption process is exothermic [17]. This indicates that IE % decreases when the temperature increases. Such behavior can be interpreted on the basis that increasing the temperature resulted in desorption of the adsorbed inhibitor molecules from the metal surface. The negative values of ΔS_a° might be explained in the following way: before the adsorption of inhibitors onto the metal surface, inhibitor molecules might freely move in the bulk solution, but with the progress in the adsorption, inhibitor molecules were orderly adsorbed onto the metal surface, and as a result, there was a decrease in entropy [18].

3.2. Electrochemical Impedance Spectroscopy. The corrosion behavior of mild steel in 1 M H_2SO_4 with different concentrations of ESP and its synergistic effect with potassium iodide solution were studied by AC impedance spectroscopy. In general, the impedance spectra exhibit one single depressed semicircle, and the diameter of the semicircle increases with the increase of inhibitor concentration. The semicircle can be attributed to the charge transfer that takes place at electrode/solution interface, and the transfer process controls the corrosion reaction of mild steel. The existence of a single

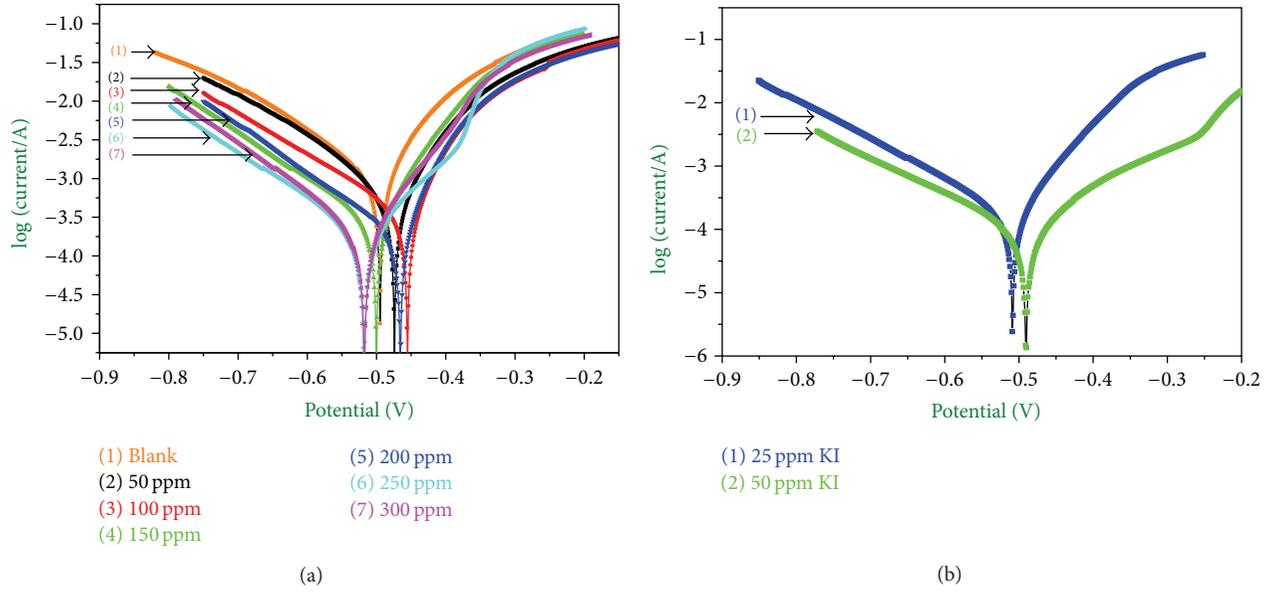


FIGURE 5: (a) Nyquist plots of mild steel in 1M H₂SO₄ with various concentrations of esomeprazole. (b) Nyquist plots of mild steel in 1M H₂SO₄ with various concentrations of esomeprazole with the addition of KI.

TABLE 5: Electrochemical impedance parameters for mild steel in 1M H₂SO₄ containing different concentrations of esomeprazole with the addition of KI.

Inhibitor concentration (ppm)	R_{ct} ($\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F cm}^{-2}$)	I.E η (%)
Blank	13.67	1656.9	—
50	44.746	153.8	69.45
100	48.623	134.58	71.89
150	53.798	110.93	74.59
200	56.90	96.86	75.98
250	59.582	87.18	77.06
300	66.291	71.77	79.38
25 ppm KI	68.499	66.6	80.04
50 ppm KI	86.567	41.83	84.21

semicircle shows the single charge transfer process during dissolution which is unaffected by the presence of inhibitor molecules [19, 20]. The impedance spectra observed are depicted in Figure 5. In the diagrams, imaginary component Z'' was plotted against real component Z' . It indicates that the mechanism of mild steel corrosion in the absence and presence of ESP is purely controlled by the charge transfer process. It is also observed that the R_{ct} values of mild steel in 1M H₂SO₄ with different concentrations of ESP are higher than the uninhibited solution. The impedance parameters obtained from the curves are given in Table 5.

Inspection of the results in Table 5 indicated that the charge transfer resistance increased with an increase in the concentration of ESP and KI. The change of R_{ct} values can be related to the gradual replacement of water molecules and/or hydroxyl ions by ESP molecule on the surface and

consequently leads to a decrease in the number of active sites necessary for the corrosion reaction. The increase in R_{ct} value is attributed to the formation of a protective film on the metal/solution interface. Moreover, the values of double-layer capacitance, C_{dl} , decreased with increasing ESP concentration. The decrease in C_{dl} is probably due to a decrease in local dielectric constant and/or an increase in the thickness of a protective layer at electrode surface, enhancing therefore the corrosion resistance of the studied steel. The interfacial double-layer capacitance (C_{dl}) values have been estimated from the impedance value using the Nyquist plot by the formula

$$C_{dl} = (2\pi f_{\max} R_{ct})^{-1}. \quad (8)$$

The maximum inhibition efficiency (79.38%) is obtained for 300 ppm of ESP, and the inhibition efficiency is increased (84.21) when adding 50 ppm of KI solution. The values of AC impedance corroborates the results obtained from weight loss and polarization studies.

3.3. Tafel Polarization. Potentiodynamic polarization curves for mild steel in 1M H₂SO₄ with and without ESP with shown in Figures 6(a) and 6(b). The important parameters of corrosion current densities (I_{corr}), cathodic Tafel slope (β_c), anodic Tafel slope (β_a), and the inhibition efficiency (IE %) as functions of ESP concentrations are derived from polarization curves that are presented in Table 6. From Table 6, it is clear that the corrosion current density (I_{corr}) values decreases from 1.4060 mAcm⁻² to 0.2142 mAcm⁻² and 0.1120 mAcm⁻² with the addition of optimum concentration (300 ppm) of ESP and ESP with 50 ppm of KI, respectively. The cathodic and anodic Tafel slope values are almost the same with and without inhibitors. It conforms that esomeprazole adsorbs on metal surfaces by simply blocking the active sites, and the

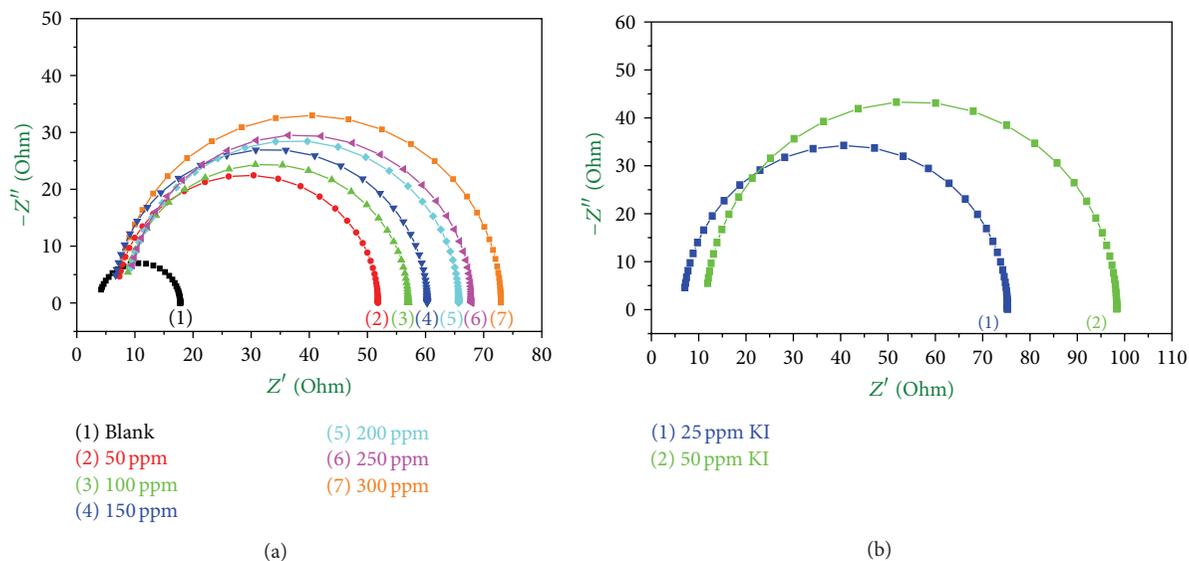


FIGURE 6: Tafel polarization behavior of mild steel in (a) 1M H_2SO_4 with different concentrations of esomeprazole and (b) 1M H_2SO_4 with different concentrations of esomeprazole with the addition of KI.

TABLE 6: Tafel polarization for the corrosion of mild steel in 1M H_2SO_4 in the absence and presence of different concentrations of esomeprazole with the addition of KI.

Inhibitor concentration (ppm)	β_a (mV)	β_c (mV)	$-E_{corr}$ (mV/SCE)	I_{corr} (mA/cm ²)	Linear polarization (R)	IE (%)
Blank	8.6330	6.463	494.2	1.4060	20.5	—
50	10.168	6.951	473.9	0.6035	42.1	57.08
100	9.9790	5.516	454.9	0.4942	56.8	64.85
150	11.854	5.897	502.3	0.3493	70.1	75.16
200	11.232	5.891	465.1	0.2826	89.9	79.90
250	8.0010	6.316	516.4	0.2264	134.1	83.90
300	10.955	6.847	517.8	0.2142	114	84.76
25 ppm KI	13.094	6.757	508.1	0.1778	122.5	87.35
50 ppm KI	7.5050	5.898	490.0	0.1120	289.7	92.03

mechanisms of anodic and cathodic reactions are unaffected [21]. The shift of the corrosion potential (E_{corr}) shows a slight shift towards the cathodic side region as concentrations of the inhibitor increased from 50 to 300 ppm, suggesting that the effect of the inhibitor is more pronounced at the cathodic side. However, according to Ferreira and others [7, 22] if the displacement in corrosion potential is more than 85 mV with respect to the corrosion potential of the uninhibited solution, the inhibitor can be seen as a cathodic or anodic type. In the present study, the maximum displacement was 23 mV, indicating that ESP belonged to mixed type. These results suggest that the studied inhibitor was first adsorbed onto the metal surface and impeded by merely blocking the metal surface without affecting the anodic and cathodic reaction mechanism [23].

3.4. Scanning Electron Microscopy. The SEM images were recorded (Figures 7(a), 7(b), 7(c), and 7(d)) to establish the interaction of inhibitor molecules with the metal surface. The SEM images show the features of mild steel surface after 2 h in 1M H_2SO_4 in absence and presence of optimum

concentration of esomeprazole (300 ppm) (Figure 7(c)) and adding 50 ppm of KI solution (Figure 7(d)) at room temperature. The SEM images revealed that the mild steel specimen immersed in inhibited solutions (Figures 7(c) and 7(d)) is in better conditions having smooth protective film coating, while the metal surface immersed in blank acid solutions (Figure 7(b)) is roughly covered with corrosion products and appeared to be full of pits and cavities. The polishing stretches are also visible on the surface in Figure 7(a). This indicated that the ESP molecules hinder the dissolution of iron by forming protective film on mild steel surface and thereby reduce the corrosion rate. The surface analysis results suggest higher adsorption of ESP on the surface of mild steel, which support the weight loss, EIS, and polarization results.

3.5. Atomic Force Microscopy. An atomic force microscope (AFM) was used to image the mild steel specimen, and it was used mainly for measuring three-dimensional topography. Analysis of the images allowed quantification of surface roughness over area scales $2 \mu m \times 2 \mu m$. The three dimensional AFM images are shown in Figures 8(a)–8(c). As can

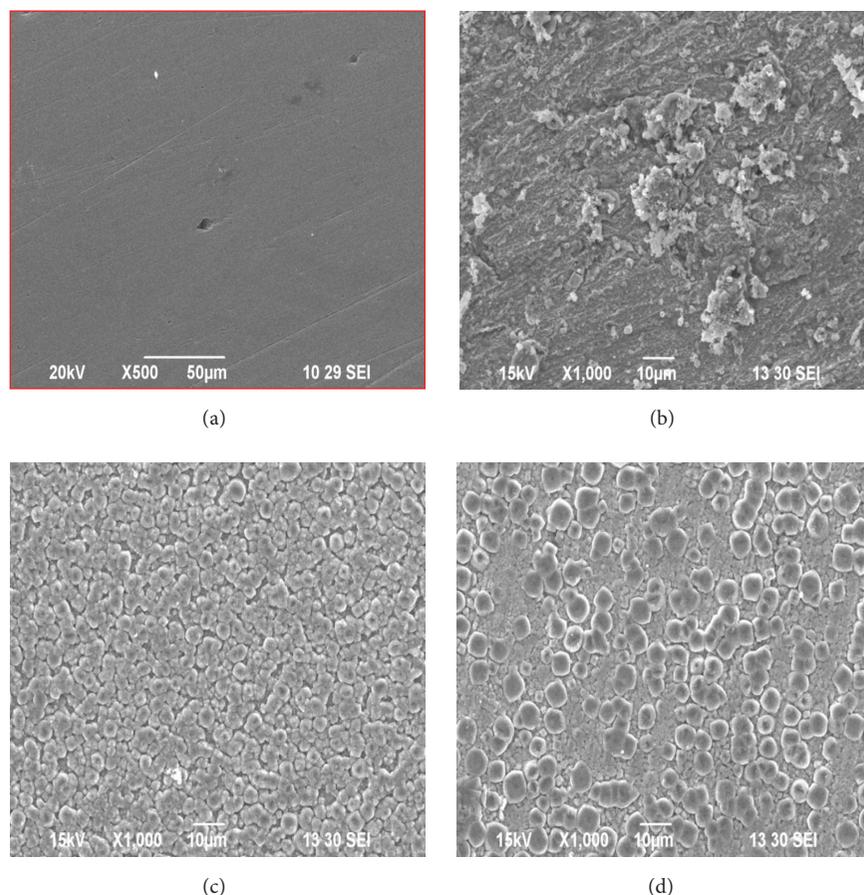


FIGURE 7: SEM images of mild steel: (a) polished metal, (b) 1 M H_2SO_4 solution without esomeprazole, (c) 0.5 M H_2SO_4 solution with optimum concentration of esomeprazole, and (d) 1 M H_2SO_4 solution with optimum concentration of esomeprazole + KI.

be seen from Figures 8(a)–8(c), the average roughness of polished mild steel (Figure 8(a)) and mild steel in 1 M H_2SO_4 without inhibitor (Figure 8(b)) was calculated to be 759 nm and 129 nm, respectively. The mild steel surface in the free acid solution is getting cracked due to the acid attack on the surface (Figure 8(b)). However, in the presence of 300 ppm concentration of esomeprazole drug, the average roughness was reduced to 276 nm (Figure 8(c)).

4. Inhibition Mechanism

The ESP can be easily protonated in the sulphuric acid solution because the molecule is made of a planer of benzimidazole, pyridine ring, and also contains S, N, and O atoms with lone pair electrons and π electrons. Thus, they become cations, existing in equilibrium with the corresponding molecular form



Physical adsorption may take place due to electrostatic interaction between protonated molecule and FeSO_4^{2-} species. Coordinate covalent bond formation between electron pairs of unprotonated S atom and N atoms of aromatic rings with metal surface can take place [24]. In addition, ESP molecules are chemically adsorbed due to the interaction of

π -orbitals with metal surface. This phenomenon is associated with the deprotonation of physically adsorbed protonated molecules. In the present study, the value of $\Delta G_{\text{ads}}^{\circ}$ is from $-19.79 \text{ kJ mol}^{-1}$ to $-24.71 \text{ kJ mol}^{-1}$, hence, showing that adsorption of ESP molecules on the surface of mild steel takes place through both physical as well as chemical processes.

5. Conclusion

- (i) Esomeprazole acts as a good inhibitor for the corrosion of mild steel in 1 M H_2SO_4 .
- (ii) The inhibition efficiency and corrosion rate of esomeprazole increased with adding potassium iodide and decreased with temperature.
- (iii) The EIS measurements suggest that ESP molecules function by adsorption at metal surface thereby causing the decrease in C_{dl} values and increasing in R_{ct} values.
- (iv) Potentiodynamic polarization curve reveals that ESP belonged to mixed-type inhibitor, and the effect of the inhibitor is more pronounced at the cathodic side.
- (v) The adsorption of ESP obeys the Langmuir adsorption isotherm. The adsorption process is a

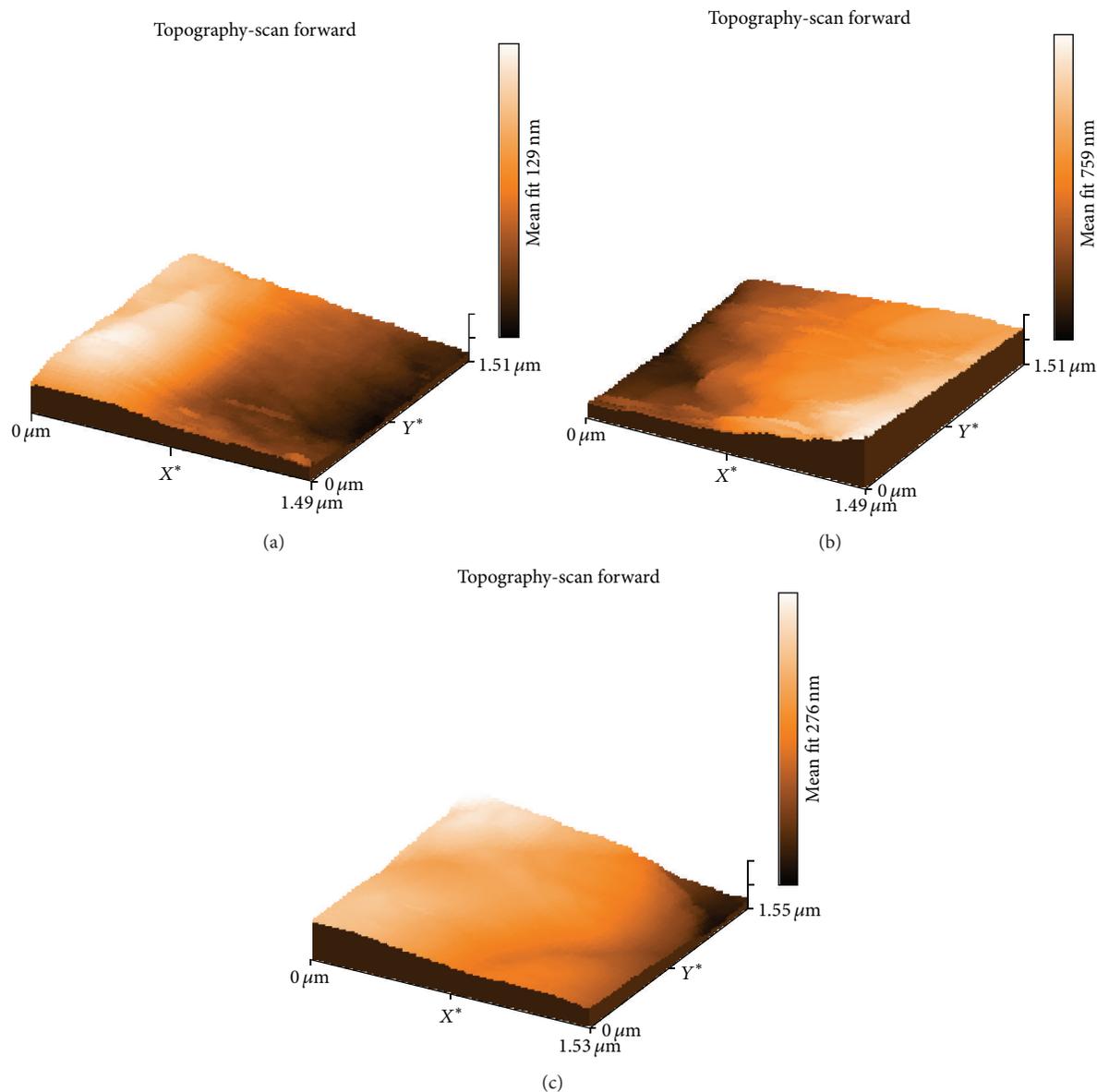


FIGURE 8: AFM images of mild steel: (a) polished metal, (b) 1M H_2SO_4 solution without esomeprazole, and (c) 1M H_2SO_4 solution with optimum concentration of esomeprazole.

spontaneous and exothermic process accompanied by an increase of entropy.

- (vi) The surface analysis indicated that the ESP molecules hinder the dissolution of iron by forming protective film on mild steel surface and thereby reduce the corrosion rate.
- (vii) The results obtained from weight loss, impedance, and polarization studies are in good agreement.

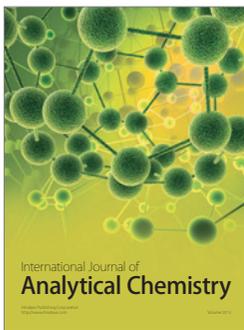
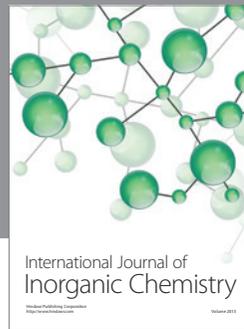
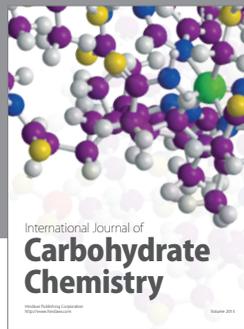
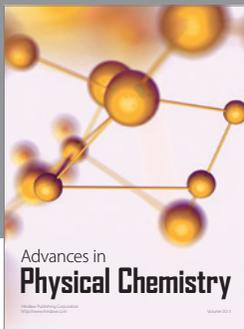
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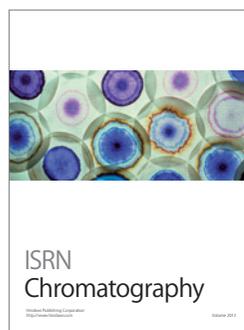
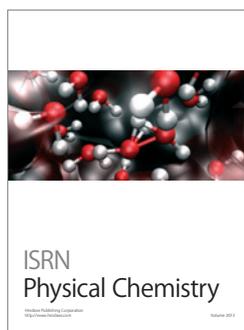
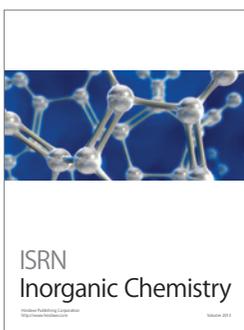
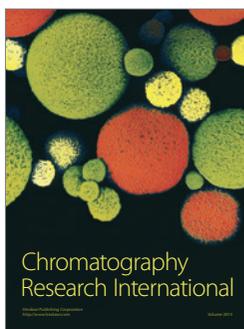
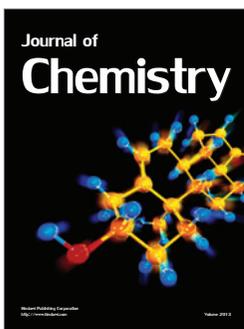
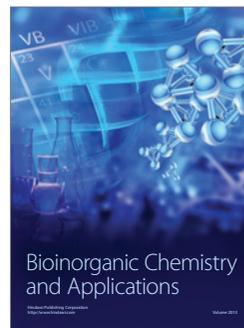
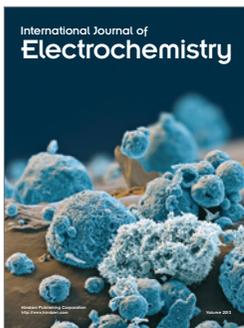
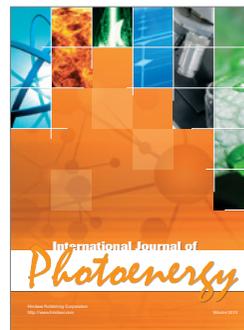
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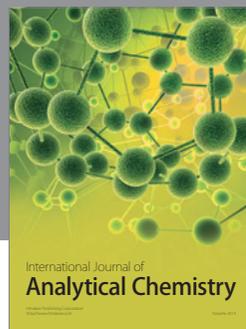
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