

Inhibition effects of acetyl coumarines and thiazole derivatives on corrosion of zinc in acidic medium

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Abstract. The corrosion inhibition characteristics of acetyl coumarine (AC), bromo acetyl coumarine (BAC) and thiazole derivatives (BTMQ and BTCQ) on the corrosion of zinc in 0.1 M HCl solution were investigated by weight loss, potentiodynamic polarization and impedance techniques. The inhibition efficiency increased with increase in inhibitor concentration upto 5×10^{-4} M, then gave almost same inhibition efficiency. The polarization measurements indicated the mixed nature of inhibitors. The adsorption of compounds obeyed Langmuir's adsorption isotherm. The thermodynamic functions for adsorption processes were evaluated.

Keywords. Acetyl coumarines; adsorption isotherm; corrosion inhibition; impedance; zinc.

1. Introduction

White rust formation on zinc and galvanized products due to corrosion remains a serious commercial problem in spite of many available control methods. Also zinc gets corroded when exposed to different industrial environment and aqueous media. To inhibit the corrosion reaction of zinc in aqueous media, the inhibitors play a key role. The earlier research work revealed the use of a large number of organic compounds of different nature as corrosion inhibitors for zinc (Rodney and Leroy 1978; El-Mahdy and Mohmoud 1995; Gad Allah *et al* 1998). Most of these organic compounds are adsorbed on the metal surface and provide a barrier between metal and environment, thereby reducing the rate of corrosion. The effectiveness of inhibition depends on the nature and surface charge of the metal, the nature of the medium, the nature and chemical structure of the inhibitor molecule such as functional groups, aromaticity, the π orbital character of the donating electron, steric factor, and electron density at the donor atoms (Stupnisek-Lisac and Metikos-Hukovia 1993; Tamil Selvi *et al* 2003).

Large numbers of inhibitors are available in literature but these types of inhibitors are generally toxic in nature (Aramaki 2002; Bellezze *et al* 2002; Arenas and Damborenea 2004; Ferreira *et al* 2004; Swiatowska-Mrowiecka *et al* 2008). The use of chemical inhibitors has been limited because of the environmental threat, recently, due to environmental regulations. The toxic effects of most corrosion inhibitors have led to the use of inhibitors which are eco-friendly and harmless. The use of green corrosion

inhibitors is well documented (Raja and Sethuraman 2008). However, most of these compounds are not only expensive, but also toxic to living beings. It is needless to point out the importance of cheap and safe inhibitors of corrosion (Bentiss *et al* 1999; Bouyanzer *et al* 2010).

In the present investigation an attempt has been made to evaluate the inhibiting action of acetyl coumarine (AC), bromo acetyl coumarine (BAC) and thiazole derivatives (BTMQ and BTCQ) on the corrosion of zinc in 0.1 M HCl solution. Chemical and electrochemical methods were used to determine the rate of corrosion and corrosion inhibition efficiencies. The structures of organic additives used as inhibitors are shown in figure 1.

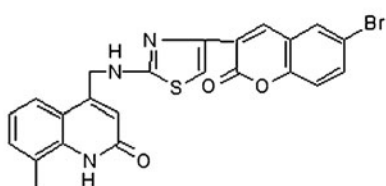
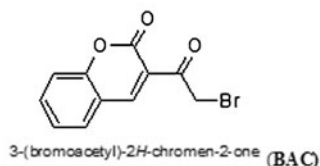
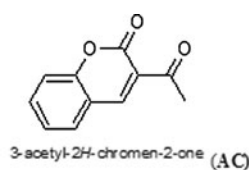
2. Experimental

2.1 Preparation of inhibitors

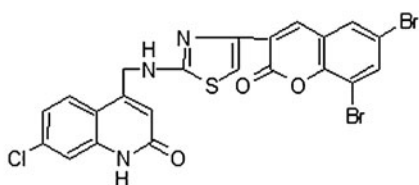
2.1a Acetyl coumarine: A mixture of substituted salicylaldehyde (0.004 mol) and ethylacetoacetate (0.004 mol) in 10 cm³ of ethyl alcohol was stirred at room temperature with few drops of piperidine for 8 h. The resulting yellow coloured solid obtained was filtered, washed with excess of chilled alcohol, dried and crystallized (Knoevenagel 1898; Buu-Hoi *et al* 1957).

2.1b Bromo-acetyl coumarine: 3-acetyl coumarine (0.004 mol) in 10 cm³ of chloroform (alcohol free) was treated dropwise with bromine (0.004 mol) in 10 cm³ of chloroform. The mixture was stirred for 10 h at room temperature. The separated solid was filtered, dried and crystallized (Koelsch 1950).

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4-[[4-(6-bromo-2-oxo-2H-chromen-3-yl)thiazol-2-ylamino]-methyl]-8-methyl-1H-quinoline-2-one (BTMQ)



4-[[4-(6,8-bromo-2-oxo-2H-chromen-3-yl)thiazol-2-ylamino]-methyl]-7-chloro-1H-quinoline-2-one (BTCQ)

Figure 1. Chemical structures of inhibitors.

2.1c *Triheterocyclic thiazoles*: 4-amino methyl carbostyryl hydrochloride (0.003 mol–630 mg) in methanol (20 cm³) was taken in a 100 cm³ RB flask and potassium thiocyanate (0.006 mol–580 mg) was added to it. The reaction mixture was refluxed on a water bath for 3 h. After cooling, separated solid of potassium chloride was filtered off. To the mother liquor, 3-bromo acetyl coumarin (0.003 mol–800 mg) was added and refluxing was continued for further 4 h. The reaction mixture was left overnight. Yellow crystals of thiazole obtained were filtered and washed with more water.

2.2 Weight loss studies

Zinc sheets having rectangular shape with an exposed area of 2 × 4 × 1 cm were used for the corrosion rate measurements. The samples were first degreased with trichloroethylene, grounded with different grades of emery papers, washed with water and rinsed with alcohol. The dried and weighed samples were placed in 50 cm³ of 0.1 M HCl solutions with and without inhibitors for 2 h at 303 K. Multiple experiments were performed in each case and the mean value of

the weight loss was noted. Corrosion rate and inhibition efficiency (% IE) were calculated.

2.3 Potentiodynamic polarization studies

The potentiodynamic polarization studies were carried out with zinc strips having an exposed area of 1 cm². A conventional three electrode cell consisting of zinc as working electrode, platinum foil as counter electrode, and a saturated calomel electrode (SCE) as reference was used. Potentiodynamic polarization studies were carried out using an Autolab Potentiostat-Galvanostat and the data was analyzed using General purpose electrochemical system software. At a constant scan rate of 2 mV s⁻¹ from open-circuit potential (OCP), anodic and cathodic polarization curves were obtained. The inhibition efficiencies were calculated from corrosion currents determined using the Tafel extrapolation method.

2.4 Electrochemical impedance studies

Electrochemical impedance measurements were carried out using an electrochemical system frequency response analyser (FRA). The electrochemical impedance spectra (EIS) were acquired in the frequency range 10 kHz to 10 mHz at the rest potential by applying 5 mV sine wave AC voltage. The double layer capacitance (CPE) and the charge transfer resistance (R_p) were determined from Nyquist plots (Raghavan 2000). The inhibition efficiencies were calculated from R_p values.

3. Results and discussion

3.1 Weight loss measurements

Corrosion parameters obtained from weight loss measurements for various inhibitors on the corrosion rate of zinc metal in 0.1 M HCl are recorded in table 1. Figures 2 and 3 show the variation of dissolution rates and percentage inhibition (% IE) efficiencies for BAC and BTCQ as representative compounds. It was observed that a significant decrease in dissolution rate occurred over the concentration range from 0.63×10^{-4} M to 5×10^{-4} M and corresponding increase in %IE in case of AC, BAC, BTMQ and BTCQ. The highest %IE of 97% was observed with BAC having the concentration of 5×10^{-4} M. The concentration of inhibitor at 5×10^{-4} M is taken as optimum concentration in our studies because above this concentration almost same %IE was observed.

3.2 Polarization studies

The anodic dissolution of zinc and the cathodic evolution of hydrogen were carried out potentiodynamically in

Table 1. Corrosion parameters obtained from weight loss, polarization and impedance measurements for zinc in 0.1 M HCl containing various concentrations of inhibitors at 303 K.

Inhibitor	Concentration (M) × 10 ⁻⁴	Corrosion rate (mg cm ⁻² hr ⁻¹)		-E _{corr} (mV)	Tafel polarization			Impedance			% IE (Weight)	% IE (Tafel)	% IE (Imp)
		Weight loss			I _{corr} (mA cm ⁻²)	b _a (V/dec)	b _c (V/dec)	R _s (ohm)	R _p (ohm)	CPE (F cm ²) × 10 ⁻³			
Blank	0	1.25		1.007	0.0215	0.276	0.245	1.45	0.65	28.6	-	-	-
AC	0.63	0.73		1.009	0.0133	0.271	0.253	1.98	1.08	17.5	42	38	39
	1.25	0.53		0.998	0.0103	0.296	0.268	1.76	1.56	13.1	58	52	58
	2.5	0.41		0.992	0.0065	0.278	0.273	1.93	2.73	7.7	72	70	76
	5	0.19		0.974	0.0037	0.263	0.281	1.83	5.95	5.15	85	83	89
BAC	0.63	0.54		1.008	0.0097	0.252	0.224	1.8	1.29	14.9	57	55	49
	1.25	0.3		1.005	0.0060	0.238	0.210	1.89	2.18	8.42	76	72	71
	2.5	1.3		0.996	0.0028	0.221	0.196	2.01	4.09	5.42	90	87	81
	5	0.04		0.998	0.0013	0.197	0.179	1.86	9.34	3.05	97	94	89
BTMQ	0.63	0.7		0.997	0.0123	0.273	0.242	1.64	1.15	16.5	44	43	43
	1.25	0.49		0.985	0.0093	0.330	0.260	1.54	1.87	10.9	61	57	65
	2.5	0.26		1.006	0.0050	0.375	0.295	1.67	3.27	6.6	79	77	80
	5	0.1		1.018	0.0026	0.333	0.293	1.59	4.67	4.3	92	88	86
BTCQ	0.63	0.64		0.974	0.0114	0.278	0.258	1.57	1.07	17.1	49	47	39
	1.25	0.34		0.992	0.0069	0.324	0.248	1.72	1.45	13.2	73	68	55
	2.5	0.19		1.008	0.0032	0.275	0.293	1.91	2.26	7.63	85	82	71
	5	0.11		1.012	0.0022	0.318	0.270	1.88	3.63	4.87	91	90	82

acidic chloride solution containing various concentrations of inhibitors. Figures 4 and 5 show the effects of BAC and BTCQ on the cathodic and anodic polarization of zinc in acidic chloride solution. Similar curves were obtained for AC and BTMQ. The presence of the inhibitors in the solution shifted the anodic polarization curves to more positive values and cathodic polarization curves to more negative potentials. The corrosion current densities were determined by extrapolating the anodic and cathodic Tafel lines to the free corrosion potentials.

Electrochemical corrosion parameters like corrosion potential, corrosion current density, cathodic and anodic Tafel slopes values and inhibition efficiencies (%IE) are given in table 1. Addition of inhibitors reduced the corrosion current of zinc in acid chloride solution. Thus the results in the table 1 indicated that the inhibition efficiency increased with the inhibitor concentration.

The anodic and cathodic Tafel slopes in the presence of AC, BAC, BTMQ and BTCQ indicated that the inhibitors interfered with the cathodic and anodic reactions. Table 1

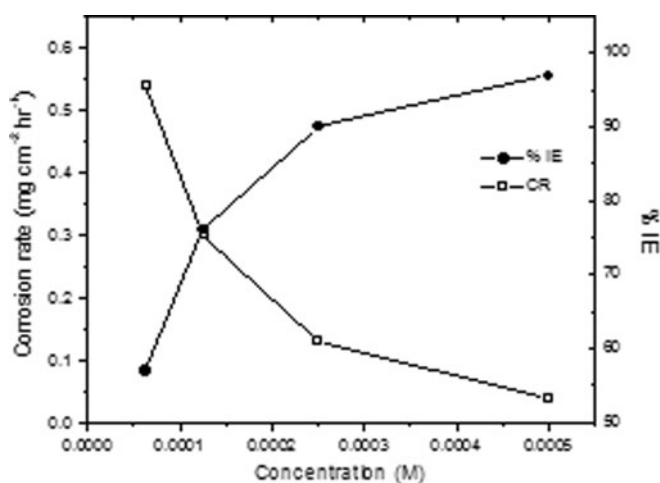


Figure 2. Variation of CR and %IE with concentration of BAC obtained from weight loss method.

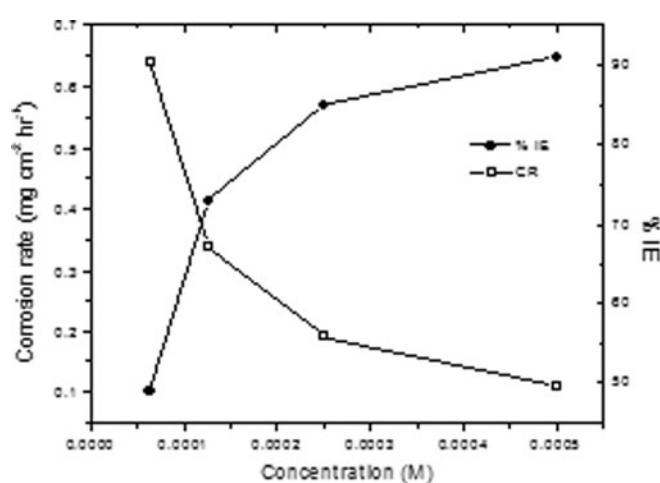


Figure 3. Variation of CR and %IE with concentration of BTCQ obtained from weight loss method.

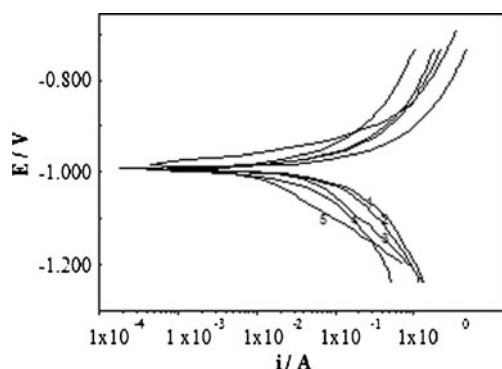


Figure 4. Polarization curves of zinc in 0.1 M HCl in the presence of different concentrations of BAC at 303 K. (1) HCl blank, (2) 0.63×10^{-4} M, (3) 1.25×10^{-4} M, (4) 2.5×10^{-4} M, (5) 5×10^{-4} M.

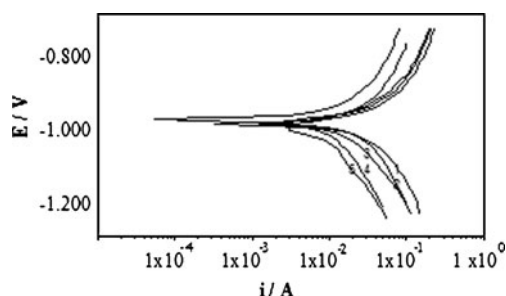


Figure 5. Polarization curves of zinc in 0.1 M HCl in the presence of different concentrations of BTCQ at 303 K. (1) HCl blank, (2) 0.63×10^{-4} M, (3) 1.25×10^{-4} M, (4) 2.5×10^{-4} M, (5) 5×10^{-4} M.

shows that the values of the anodic (b_a) and cathodic (b_c) Tafel slopes obtained in the absence and presence of inhibitors are approximately the same. This indicated the mixed type of control by the inhibitors (Rudresh and Mayanna 1977).

3.3 Electrochemical impedance spectroscopy (EIS)

Impedance measurements of zinc immersed in 0.1 M HCl solutions without and with BAC and BTCQ are presented in the form of Nyquist plots in figures 6 and 7, respectively. Equivalent circuit is shown in figure 8. Inhibitors AC and BTMQ also gave plots of similar nature.

It was observed that as the concentration of inhibitor increased, the diameter of capacitive loop and consequently the values of charge transfer resistance (R_p) increased, which was an indication of the inhibiting action. Values of EIS parameters corresponding to the impedance spectra recorded in the presence of the investigated compounds are listed in table 1.

The value of the electrolyte resistance (R_s) obtained in the pure medium increased in the presence of the investigated

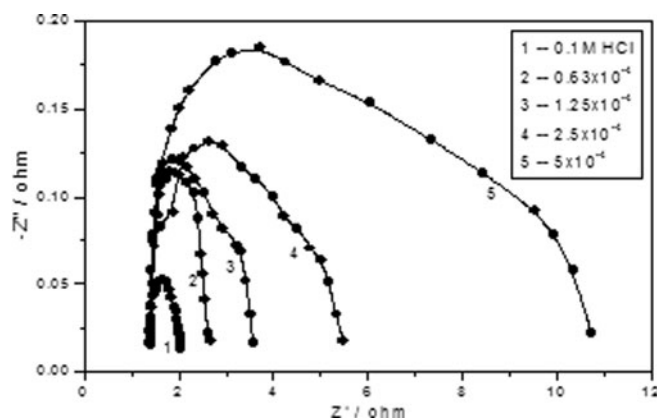


Figure 6. Nyquist plots for zinc in 0.1 M HCl in the absence and presence of different concentrations of BAC.

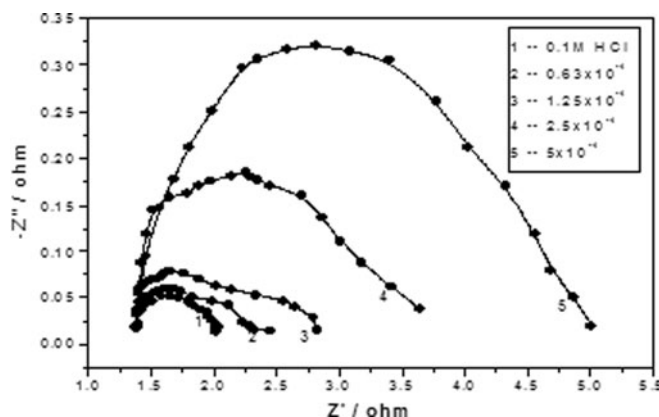


Figure 7. Nyquist plots for zinc in 0.1 M HCl in the absence and presence of different concentrations of BTCQ.

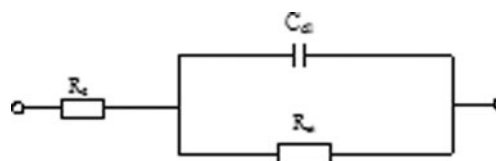


Figure 8. Equivalent circuit for the electrochemical impedance measurements.

compounds. This was attributed to the change in the conductivity of the medium. Besides the increase in value of R_p , the value of CPE obtained in the blank solution is drastically decreased in the presence of inhibitor. This was correlated to the decrease in the area on zinc surface exposed to corrosive solution (increase in the area covered with the inhibitor) as

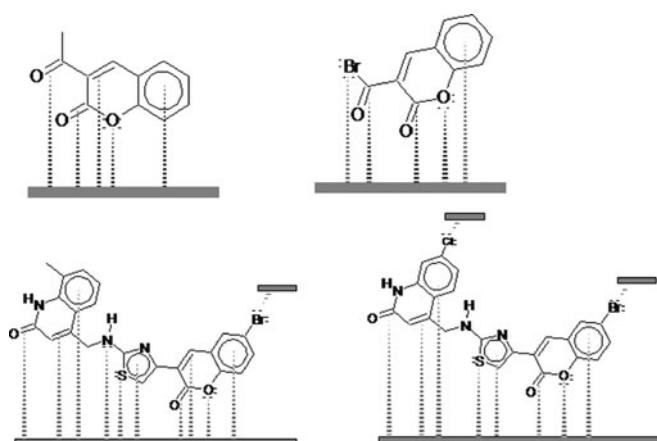


Figure 9. Skeletal representation of the lone pair and π electron interactions of the inhibitor molecules with steel surface.

a result of adsorption. Hence the corrosion rate was appreciably decreased in the presence of the inhibitors. Figure 9 shows the possible skeletal interaction of the lone pair and π electron of the inhibitor molecules with zinc surface.

3.4 Adsorption isotherms

The nature of inhibitor interaction with the corroding surface during corrosion inhibition of metal was deduced in terms of adsorption characteristics of the inhibitors. The surface coverage (θ) data was generally employed to explain adsorption characteristics. Although the weight loss and cur-

rent density measurements are correlated to surface coverage, they did not represent the same magnitude of corrosion rate (table 2). The θ values generated from direct measurement of weight loss were greater than polarization measurements. This was probably because of slight etching of the surface during corrosion.

The values of θ and C (concentration of the inhibitor solution) were tested by fitting to the various isotherms. Attempts were made to fit the values of θ and C of the studied inhibitor from mass loss experiments with several adsorption isotherms like Langmuir, Temkin, Freundlich and Flory–Huggins. However, the best fit was obtained with Langmuir isotherm plots of $\log \theta/1 - \theta$ versus $\log C$ gave straight lines with a slope of nearly unity for the investigated compounds (figure 10), indicating that the adsorption of inhibitors on zinc obeyed Langmuir adsorption isotherm.

3.5 Thermodynamic parameters

The surface coverage (θ) was calculated using the equation $1 - \theta = i^*/i$, where i^* and i are the corrosion currents with and without inhibitors. The apparent free energy of adsorption (ΔG^0) was calculated from the relation

$$\Delta G^0 = -2.303 RT \log 55.5 K, \quad \text{where } K = \theta/C(1 - \theta).$$

Values of surface coverage (θ), equilibrium constant (K) and free energy of adsorption (ΔG^0) at different concentrations of AC, BAC, BTMQ and BTCQ are given in table 2. The negative values of ΔG^0 indicated the spontaneous adsorption of the inhibitor and revealed strong interaction between inhibitor molecules and metal surface. The values of

Table 2. Adsorption parameters for the inhibitors tested on zinc in 0.1 M HCl solution at 303 K.

Inhibitor	Concentration (M) $\times 10^{-4}$	θ		$10^{-3} \times K$	$-\Delta G$
		Weight loss	Polarization		
AC	0.63	0.42	0.38	9.8	33.28
	1.25	0.58	0.52	8.67	32.97
	2.5	0.72	0.70	9.33	33.15
	5	0.85	0.83	9.76	33.24
BAC	0.63	0.57	0.55	19.56	35.02
	1.25	0.76	0.72	20.57	35.14
	2.5	0.90	0.87	26.77	35.81
	5	0.97	0.94	31.33	36.2
BTMQ	0.63	0.44	0.43	12.07	33.8
	1.25	0.61	0.57	10.6	33.47
	2.5	0.79	0.77	13.39	34.06
	5	0.92	0.88	14.67	34.29
BTCQ	0.63	0.49	0.47	14.19	34.2
	1.25	0.73	0.68	17.0	34.66
	2.5	0.85	0.82	17.78	34.78
	5	0.91	0.90	18.0	34.81

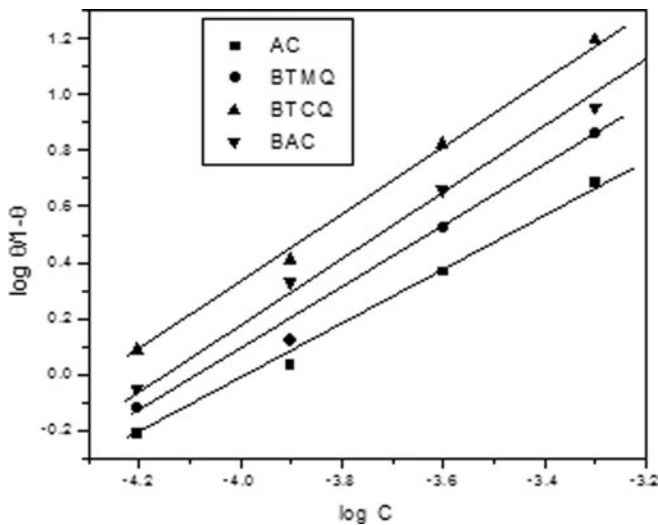


Figure 10. Langmuir adsorption isotherm for zinc in 0.1 M HCl containing various concentrations of inhibitor from polarization study.

equilibrium constant for BAC is highest and that of AC being lowest, AC provided the poorest protection and BAC the highest against zinc corrosion. This is also supported by higher negative ΔG^0 values for BAC.

4. Conclusions

Addition of AC, BAC, BTMQ and BTCQ inhibited the corrosion of zinc in HCl solution. The %IE was maximum for BAC and was in the order BAC > BTMQ > BTCQ > AC. Inhibition efficiency increased with inhibitor concentra-

tion. The investigated compounds inhibited both anodic and cathodic reaction by adsorption. The adsorption of molecules was found to obey Langmuir adsorption isotherm. The %IE obtained from weight loss, polarization and impedance methods were in good agreement.

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