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Corrosion Inhibition Studies of Mild Steel in Acid Medium Using Chloroquine Phosphate

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In this investigation, attempts have been made to study the inhibitive effect of chloroquine phosphate for mild steel in 1 M HCl in the concentration range of 5×10^{-6} M to 1×10^{-2} M by weight loss, DC polarization methods and AC impedance spectroscopy. Results indicate that the addition of chloroquine phosphate to the acid reduce the rate of metal attack. Inhibition efficiency increases with the concentration of chloroquine phosphate. Thermodynamic parameters have also been evaluated. Surface coverage values have been tested graphically for suitable adsorption isotherm. Chloroquine phosphate yielded a maximum of 98.69 % in 1 M HCl, electro chemical studies are carried out with the various concentrations of chloroquine phosphate to find out the nature of the action of chloroquine phosphate. From these results, chloroquine phosphate is found to behave as a mixed type inhibitor.

Key Words: Corrosion, Inhibition, Mild steel, Chloroquine phosphate.

INTRODUCTION

Corrosion of metals in different environments is one of the serious problems faced by the industries and its prevention has been approached from various angles like surface coating plating and alloying. Technological and financial considerations may sometimes favour the addition of certain inhibitors to reduce the corrosion rate. In general, organic compounds have been used as inhibitors in industries. Due to the presence of hetero atoms such as O, N and S with lone pair of electrons inhibitors gets chemisorbed on the metal surface. Many organic compounds were investigated as corrosion inhibitors for mild steel in acid medium[1-3]. The present work is undertaken to study the inhibitive effect of chloroquine phosphate on mild steel in HCl acid medium.

EXPERIMENTAL

The mild steel specimens were cut into 5 cm × 1 cm pieces for immersion studies and were lacquered so as to expose an area of 1 cm^2 for all electrochemical studies. The specimens were mechanically polished, degreased and dried in acetone, stored in a dessicator and used for all the studies. Their edges were abraded with fine grade of emery papers. Stock solutions of chloroquine phosphate were prepared and diluted to appropriate concentrations (1×10^{-2} to 5×10^{-6} M) with 1 M HCl. Weight loss measurements were carried out in triplicate and from the data, corrosion rate and inhibitor efficiency were determined.

Electrochemical studies were carried out using conventional three electrode cell with larger area platinum foil as counter electrode, mild steel as working electrode and saturated calomel electrode (SCE) as reference electrode. Solatron Electrochemical Analyzer model (1280B) inter-faced with an IBM computer were used. Zplot and Corrware softwares were used for data acquisition and analysis.

RESULTS AND DISCUSSION

Effect of concentration: Values of corrosion rate and percentage inhibition efficiency for the corrosion of mild steel in 1 M HCl in the presence of different concentration of inhibitor for different immersion times are depicted in Table-1. The inhibition efficiency increases with increase in concentration of the inhibitor for all the periods of immersion (Fig. 1). In HCl medium the maximum efficiency (98.69 %) was noticed for 1 × 10^{-2} M concentration at 24 h. This infers that there is a strong correlation between inhibition efficiency (IE) and concentration of the inhibitors and the enhanced IE at higher concentration can be attributed to increased surface area coverage of the inhibition.

TABLE-1
INHIBITION EFFICIENCY (IE) AS THE FUNCTION OF TIME OF IMMERSION AND CONCENTRATION OF CHLOROQUINE PHOSPHATE

Concentration of the inhibitor (M)	Immersion time (h)					
	0.5	1	3	6	12	24
	IE (%)	IE (%)	IE (%)	IE (%)	IE (%)	IE (%)
Blank						
5 × 10^{-6}	16.90	21.62	48.81	58.60	61.02	62.08
1 × 10^{-5}	23.94	41.44	66.38	66.48	71.99	75.29
5 × 10^{-5}	53.52	57.65	82.14	85.18	90.09	93.12
1 × 10^{-4}	80.28	80.48	89.17	90.91	93.59	95.54
5 × 10^{-4}	81.69	81.98	93.92	95.52	96.64	97.45
1 × 10^{-3}	83.09	84.68	95.15	96.78	97.40	98.02
5 × 10^{-3}	88.73	89.18	95.92	97.63	98.17	98.42
1 × 10^{-2}	94.36	94.59	96.77	98.18	98.56	98.69

Effect of immersion: For a given time of immersion, inhibition efficiency increases with increase in concentration. For a particular concentration, the inhibition efficiency increases with an increase in immersion time. This may be due to the formation of barrier film which prevents the attack of acid on metal surface.

It is evident from the study that longer periods of immersion results indicate the greater stability of adsorbed chloroquine phosphate. This behaviour can be discussed on the basis that prolonged immersion of steel in acidic solutions. (a) Allows the cathodic or hydrogen evolution kinetics to increase presumably as more cathodic or carbon containing sites are exposed by the corrosion process[1]. (b) Increases the concentration of ferrous ions which decreases the corrosive nature of the acid[2].

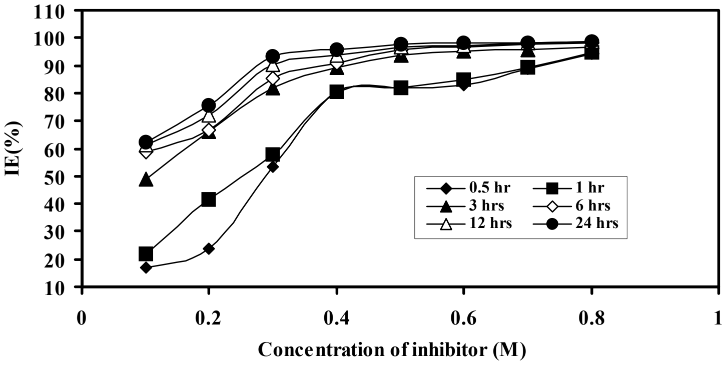

Fig. 1.

Effect of temperature: Temperature studies were carried out in presence of varying concentration of the inhibitor at 303, 313, 323, 333 and 343 K are presented in Table-2. The percentage of inhibition efficiency increases upto 333 K, further increase in temperature shows a decrease in efficiency. The same trend was observed for inhibitor efficiency and for all concentrations in all the temperatures studied. The maximum inhibition efficiency (98.7 %) was noticed for 1 × 10^{-2} M at 333 K. The decreased protection efficiency with respect to increase of temperature might be explained by the fact that increase of temperature affected the rate of adsorption/desorption ratio and if the rate of corrosion was faster than the rate of adsorption, there might be decrease in inhibition rate with temperature[3].

TABLE 2
INHIBITION EFFICIENCY (IE) AS THE FUNCTION OF TEMPERATURE

Concentration of the inhibitor (M)	Temperature (K)				
	303	313	323	333	343
	IE (%)	IE (%)	IE (%)	IE (%)	IE (%)
Blank					
5 × 10^{-6}	16.90	22.50	26.26	28.20	2.54
1 × 10^{-5}	23.94	25.83	30.06	30.66	12.03
5 × 10^{-5}	53.52	54.99	57.59	58.62	35.12
1 × 10^{-4}	80.28	80.80	81.64	82.54	56.58
5 × 10^{-4}	81.69	84.58	87.03	90.41	73.65
1 × 10^{-3}	83.09	89.58	94.62	95.58	83.21
5 × 10^{-3}	88.73	92.50	96.36	96.44	89.51
1 × 10^{-2}	94.36	95.41	97.94	98.71	92.77

Adsorption isotherms: It is generally accepted that organic molecules inhibit corrosion by adsorption at the metal/solution interface and that the degree of adsorption depends on the chemical structure of the molecules, the solutions of chemical composition, the nature of the metal surface, temperature and the electrochemical potential at the metal/solution interface[4]. Adsorption provides information about the interaction among the adsorbed molecules themselves as well as their interaction with the electrode surface[5]. A useful method that assists in the understanding of the mechanism of organo electrochemical reactions in the adsorption processes is the adsorption isotherm. A plot of log (θ/1-θ) *vs.* log C could give a straight line indicating that the chloroquine phosphate under study obey Langmuir adsorption isotherm. Examination of straight line obtained by plotting surface coverage *vs.* log C, reveal that the adsorption of chloroquine phosphate could be fitted with Temkin adsorption isotherm also.The experimental data fitted with both Langmuir adsorption isotherm and Temkin adsorption isotherm. This indicates that the main process of inhibition is by adsorption. This may also infer that there is a molecular interaction among the adsorbed particles and the metal surface.

Kinetic and thermodynamic parameters: The Arrhenius plots log (C.R) *vs.* 1/T for both uninhibited and inhibited systems are rectilinear. The activation energies calculated from the slopes of the curves are tabulated in Table-3. The marked change in energy of activation suggest that the inhibitor may either participate in the electrode process or may change the potential difference of the metal solution interface by adsorption. The free energy values are found to be negative which shows strong interaction of inhibitor molecules and a spontaneous adsorption of the inhibitor on the metal surface (Table-3). The free energy of adsorption increases with temperature indicates increase in inhibitor efficiency with temperature[6]. The large negative values of ΔG and positive values of ΔS are also characteristic of strong interaction. These observations coupled with increase in inhibition efficiency and decreases in free energy of adsorption with temperature are suggestive of chemisorption of the inhibitors on the surface of mild steel[7].

TABLE-3
TABULATION OF ACTIVATION ENERGY AND THERMODYNAMIC PARAMETERS

Conc. of the inhibitor (M)	Activation energy (E_a = KJ/mol)	Change in free energy of adsorption (-ΔG KJ/mol)					Change in enthalpy (-ΔH KJ/mol)	Change in entropy (-ΔS J/mol)
		303 K	313 K	323 K	333 K	343 K		
Blank	51							
5×10^{-6}	53	36	38	40	42	35	18	181
1×10^{-5}	53	36	37	39	40	38	10	153
5×10^{-5}	56	35	36	38	39	37	6	136
1×10^{-4}	63	36	38	39	40	38	4	135
5×10^{-4}	53	33	34	36	38	36	20	176
1×10^{-3}	43	31	34	37	38	35	43	246
5×10^{-3}	42	28	30	33	34	32	37	218
1×10^{-2}	44	28	30	33	35	31	45	243

Polarization studies: To find out the nature of the inhibitor, mode of action, mechanism of the reaction, polarization studies such as Tafel, linear and impedance measurements were carried out. The corrosion kinetic parameters such as E_{corr}, I_{corr}, Tafel constants b_a and b_c are given in Table-4.

TABLE-4
POLARIZATION DATA OF MILD STEEL IN THE PRESENCE OF CHLOROQUINE PHOSPHATE

Conc. of the inhibitor (M)	$-E_{corr}$ (mV/s)	$I_{corr} \times 10^{-4}$ (mA/dec)	b_a (mV/dec)	b_c (mV/dec)	IE (%)
Control	473	17.00	112	151	
10^{-5}	491	8.07	83	52	52
10^{-4}	488	6.71	74	106	60
10^{-3}	494	3.40	70	154	80
5×10^{-3}	498	3.00	90	110	82
10^{-2}	486	1.58	91	162	90

I_{corr} was found to decrease as the concentration of the inhibitor increased and R_p was found to increase with concentration. The active species of chloroquine phosphate effectively inhibited the acid corrosion of mild steel. The value of b_a and b_c did not vary predominantly with that of blank indicating the mixed mode of inhibition (Fig. 2). A maximum of 96.76 % was obtained using I_{corr} values (10^{-2} M solution) and from linear polarization it was found to be 96.67 % (10^{-2} M solution).

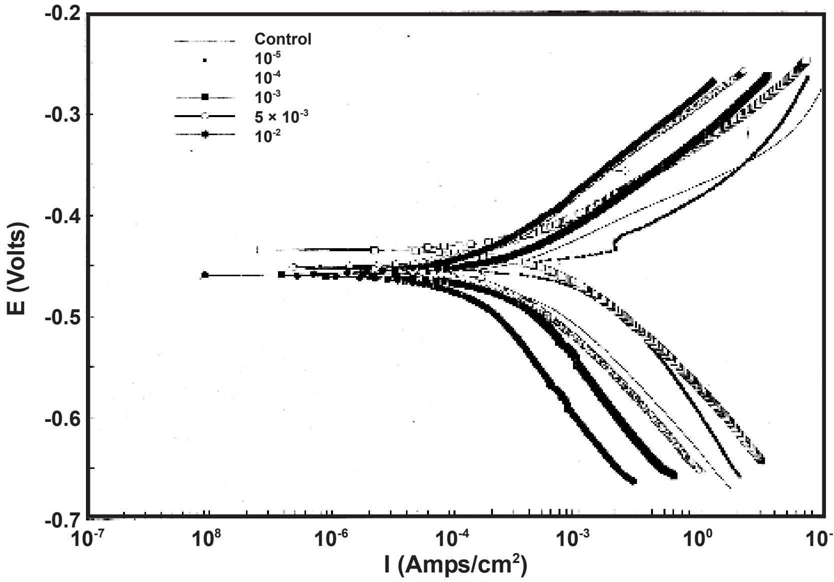

Fig. 2. Polarization curves for mild steel in 1 M HCl with chloroquine phosphate

Impedance studies: From Table-5, it can be seen that R_{ct} gradually increases with increase in chloroquine phosphate concentration inferring that a protective barrier on the metal surface results thereby enhancing the inhibition.The C_{dl} value was found to decrease with increase in concentration of chloroquine phosphate revealing that the probable mechanism is adsorption of the active species on the metal surface (Fig. 3).

TABLE-5
TABULATION OF R_{ct} AND C_{dl} AS A FUNCTION OF CONCENTRATION OF CHLOROQUINE PHOSPHATE

Concentration (M)	R_{ct} (Ohm/cm^2)	IE (%)	C_{dl} (µF/cm^{-2})	θ	R_p (Ohm/cm^2)	IE (%)
Control	14.3	–	56.50	–	16.1	–
10^{-5}	31.0	53.87	27.12	0.52	34.0	52.47
10^{-4}	36.0	60.27	22.89	0.59	40.0	59.60
10^{-3}	78.0	81.67	10.46	0.81	82.0	80.29
5×10^{-3}	103.0	86.12	9.33	0.83	95.0	82.98
10^{-2}	182.0	92.14	4.81	0.91	176.0	90.82

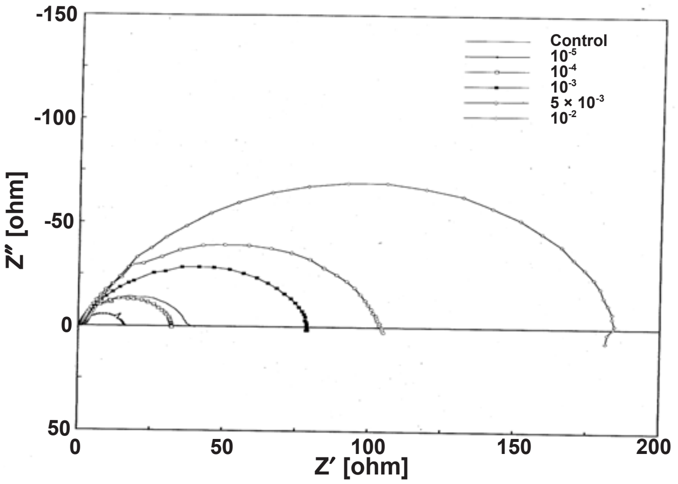

Fig. 3. Nyquist plots for mild steel in 1 M HCl with chloroquine phosphate

Conclusion

Chloroquine phosphate was found to be a good inhibitor for mild steel in 1 M HCl from various parameter such as immersion time, temperature variation and effect of concentration. It is found to obey Langmuir and Temkin isotherms. Kinetic and thermodynamic parameters revealed a strong interaction between the metal surface and the inhibitor. Electrochemical studies confirmed the mixed mode of inhibition.

REFERENCES

1. S.J. Keny, A.G. Kumbhar, C. Thinaharan and G. Venkateswaran, *Corrosion Sci.*, **50**, 411 (2007).
2. K.S. Parikh and K.J. Joshi, *Trans. SAEST*, **39**, 29 (2004).
3. S. Ali, H.A.A. Al-Muallem, M.T. Saeed and S.U. Rahman, *Corrosion Sci.*, **50**, 664 (2008).
4. S.J. Zakvi and G.N. Mehta, *Trans. SAEST*, **23**, 407 (1988).
5. G. Schmith, *Br. Corros. J.*, **19**, (1984).
6. O.L. Riggs, in ed.: C.C. Nathan, Corrosion Inhibitors, NACE, Houstan, TX, pp. 7-27 (1973).
7. B.B. Damaskin, O.A. Petrill and V.V. Batrakov, Adsorption of Organic Compounds on Electrodes (1971).

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