Studies on the influence of iodide ions on the synergistic inhibition of the corrosion of mild steel in an acidic solution

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The synergistic action caused by iodide ions on the corrosion inhibition of mild steel in 0.5 M H_2SO_4 in the presence of dicyclohexylamine (DCHA) has been investigated using potentiodynamic polarization, linear polarization and a.c. impedance techniques. DCHA inhibits the corrosion of mild steel in 0.5 M H_2SO_4 even at lower concentrations. The inhibition efficiency decreases with increase in the concentration of the amine. The addition of iodide ions enhances the inhibition efficiency to a considerable extent. The adsorption of this compound is also found to obey Langmuir's adsorption isotherm, thereby indicating that the main process of inhibition is by adsorption. The increase in surface coverage values in the presence of iodide ions indicates that DCHA forms an insoluble complex at lower amine concentrations by undergoing a joint adsorption. The synergism parameter (S) is defined and calculated both from inhibition efficiency and surface coverage values. This parameter in the case of DCHA is found to be more than unity, indicating that the enhanced inhibition efficiency caused by the addition of iodide ions is only due to synergism and there is a definite contribution from the inhibitor molecule. Thus, DCHA is then adsorbed by coulombic attraction on the metal surface where the I^- is already chemisorbed and thus reduces the corrosion rate.

1. Introduction

Although the synergistic effects of halide ions with amines on steel are well known, the mechanism for their beneficial action is little known, and there exists a limited number of attempts to explain the nature of the synergism. Halide ions are known both to stimulate and inhibit the corrosion of metals [1]. The aim of the present investigation is the study of the synergistic effect of halide ions, in particular iodide ions, on the corrosion inhibition of mild steel in 0.5 M H_2SO_4 in the presence of dicyclohexylamine (DCHA) using electrochemical measurements.

2. Experimental details

Mild steel rod of the following composition was used: 0.1–0.2 wt % C, 0.02–0.03 wt % Si, 0.4–0.5 wt % Mn, 0.3–0.8 wt % P and the remainder Fe. The working electrode was a mild steel rod embedded in a Teflon rod with an exposed area of 0.268 cm²; it was provided with a screw type stem for the electrical contact. The electrode was polished using different grades of emery paper and finally degreased with trichloroethylene before use. All solutions were prepared using triple distilled water. The sulphuric acid used was of Excellar grade (BDH), dicyclohexylamine (DCHA) was of AnalaR grade (Fluka) and potassium iodide was of AnalaR grade (BDH). All the experiments were carried out at a constant temperature of 35 ± 1 °C.

Potentiodynamic and linear polarization studies were made using a corrosion measurement system (PAR EG&G). The potential of the working electrode was varied by a PAR universal programmer (model 175) through a PAR potentiostat (model 173). Tafel plots were made on a PAR X–Y recorder (model RE 0074). A platinum foil was used as the auxiliary electrode and a saturated calomel electrode served as the reference electrode.

The sweep rate was 1 mV s⁻¹. A.c. impedance measurements were carried out at the open circuit potential using an electrochemical interface (1186 Solartron) and a frequency response analyser (1174 Solartron) from 10 kHz to 1 mHz by applying 5 mV a.c. voltage. Nyquist plots were made from these experiments. R_t and C_{dl} values were obtained from the Nyquist plots as described earlier [2].

All the experiments were performed in deaerated solutions. Purified nitrogen gas was used for deaeration, which was carried out for 30 min for each experiment.

3. Results

Figure 1 gives the potentiodynamic polarization plots of mild steel for various concentrations of dicyclohexylamine (DCHA). The corrosion kinetic parameters derived from these curves are given in Table 1. The concentration of DCHA was varied from 1×10^{-6} M to 1×10^{-2} M. It can be seen from Table 1 that DCHA inhibits the corrosion of mild steel
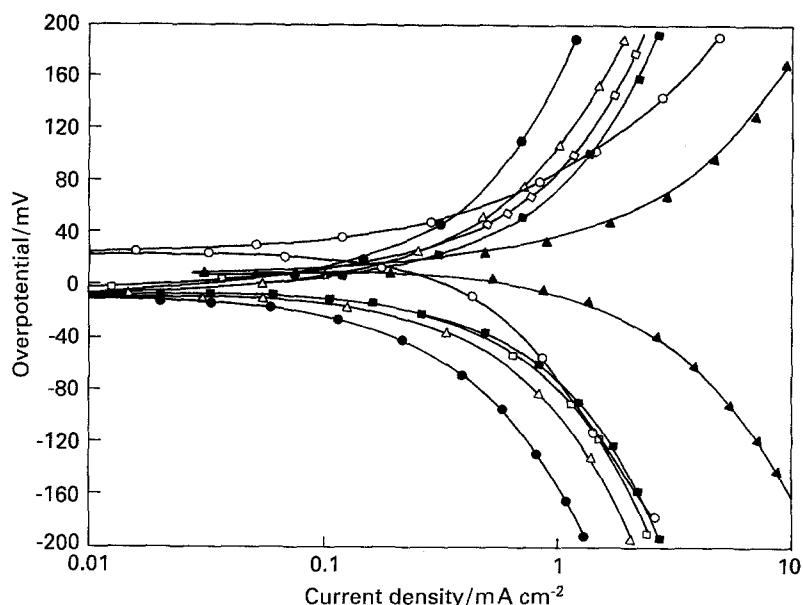
Fig. 1. Potentiodynamic polarization of mild steel in 0.5 M H_2SO_4 containing various concentrations of DCHA. Key: (■) 1×10^{-3}, (□) 1×10^{-4}, (△) 1×10^{-5}, (●) 1×10^{-6}, (○) 1×10^{-2} and (▲) 0.5 M H_2SO_4.

more effectively only at lower concentrations. The inhibition efficiency decreases with increase in concentration of DCHA. The value of I_{corr} is least in the presence of the lowest concentration of DCHA and it is found to increase with increase in the concentration of the compound. E_{corr} is shifted to more negative values in the presence of lower concentrations of DCHA and then shifts to less negative values in the presence of increasing concentrations of DCHA.

The potentiodynamic polarization plots for mild steel in 0.5 M H_2SO_4 containing 1×10^{-3} M DCHA and various concentrations of KI are shown in Fig. 2 and the corresponding corrosion kinetic parameters are given in Table 2. It is evident that KI gives maximum synergistic effect at a concentration of 1×10^{-4} M and a decrease in the concentration of iodide ions decreases inhibition efficiency.

Table 3 gives the values of inhibition efficiency for DCHA of various concentrations in the presence and absence of KI. The inhibition efficiency decreases with increase in the concentration of DCHA. Addition of KI enhances the efficiency by about 20%. The synergistic effect also increases with decreasing DCHA concentration. Tafel slopes are not affected to any great extent. It appears that the inhibitor affects both anodic and cathodic reactions to the same negligible extent. Surface coverage values (θ) also follow the same trend as the inhibition efficiency.

Figures 3 and 4 show the linear polarization plots for the corrosion of mild steel in 0.5 M H_2SO_4 for various concentrations of DCHA alone and in the presence of KI. Values of polarization resistance (R_P) and inhibition efficiency are given in Table 4. The polarization resistance decreases with increase

Table 1. Potentiodynamic polarization parameters for mild steel in 0.5 M H_2SO_4 containing various concentrations of DCHA

Conc. of DCHA/M	E_{corr} /mV	Tafel slopes		I_{corr} /$\mu A\,cm^{-2}$	I.E. /%
		b_c /mV dec^{-1}	b_a /mV dec^{-1}		
Blank	−555	120	80	540	−
1×10^{-2}	−520	120	82	230	58
1×10^{-3}	−565	100	82	82	85
1×10^{-4}	−588	125	90	135	75
1×10^{-5}	−640	110	82	31	94
1×10^{-6}	−600	125	90	7	99

Table 2. Potentiodynamic polarization parameters for mild steel in 0.5 M H_2SO_4 + 1×10^{-3} DCHA for various I^- concentrations

Conc. of KI/M	E_{corr} /mV	Tafel slopes		I_{corr} /$\mu A\,cm^{-2}$	I.E. /%
		b_c /mV dec^{-1}	b_a /mV dec^{-1}		
1×10^{-4}	−580	120	84	52	90.4
1×10^{-5}	−586	114	82	82	84.8
1×10^{-6}	−600	110	80	123	77.2
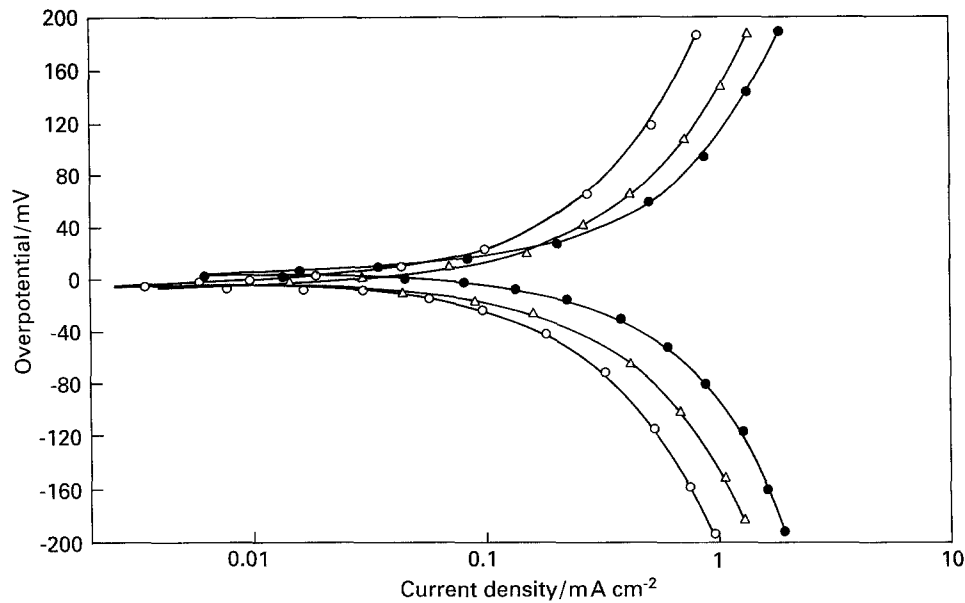
Fig. 2. Potentiodynamic polarization of mild steel in 0.5 M H_2SO_4 + 1 × 10^{-3} M DCHA for various I^- concentrations. Key: (O) 1 × 10^{-4}, (△) 1 × 10^{-5} and (●) 1 × 10^{-6} M.

Table 3. Potentiodynamic polarization parameters for mild steel in 0.5 M H_2SO_4 for various concentrations of DCHA in the presence and absence of KI

Conc. of DCHA/M	Conc. of KI/M	E_{corr} /mV vs SCE	I_{corr} /μA cm^{-2}	Tafel slopes		I.E. /%	θ
				b_c /mV dec^{-1}	b_a /mV dec^{-1}		
1 × 10^{-3}	–	−565	82	100	82	84.8	0.85
1 × 10^{-3}	1 × 10^{-4}	−579	32	100	80	94.1	0.94
4 × 10^{-3}	–	−542	160	100	90	70.4	0.70
4 × 10^{-3}	1 × 10^{-4}	−532	46	125	80	91.5	0.91
6 × 10^{-3}	–	−516	205	100	82	62.0	0.62
6 × 10^{-3}	1 × 10^{-4}	−530	135	100	82	75.0	0.75
8 × 10^{-3}	–	−525	220	110	80	59.3	0.59
8 × 10^{-3}	1 × 10^{-4}	−550	140	110	80	74.1	0.74
1 × 10^{-2}	–	−520	230	120	82	57.4	0.57
1 × 10^{-2}	1 × 10^{-4}	−522	180	120	90	66.6	0.66

in DCHA concentration. Addition of iodide ions further decreases the R_P values. The inhibition efficiency is found to increase with decreasing concentration of DCHA. The synergistic effect also increases with the addition of more KI to the DCHA solutions.

Nyquist plots for mild steel in 0.5 M H_2SO_4 for various concentrations of DCHA alone and in the presence of KI are shown in Figures 5 and 6. Table

Table 4. Data obtained from linear polarization of mild steel in 0.5 M H_2SO_4 for various concentrations of DCHA in the presence and absence of KI

Conc. of DCHA/M	Conc. of KI/M	$1/R_P$ /Ω^{-1}	I.E. /%
1 × 10^{-3}	–	0.111	85.3
1 × 10^{-3}	1 × 10^{-4}	0.330	93.5
4 × 10^{-3}	–	0.071	83.4
4 × 10^{-3}	1 × 10^{-4}	0.250	91.3
6 × 10^{-3}	–	0.066	69.4
6 × 10^{-3}	1 × 10^{-4}	0.083	73.6
1 × 10^{-2}	–	0.050	56.1
1 × 10^{-2}	1 × 10^{-4}	0.066	66.8

5 gives the values of charge transfer resistance (R_t), double layer capacitance (C_{dl}) and inhibition efficiency obtained from the above plots. Values of R_t increase, while values of C_{dl} decrease with decrease in DCHA concentration. The addition of iodide ions further increases the (R_t) values.

The inhibition efficiency obtained by the above three methods in the presence and absence of KI are

Table 5. Impedance parameters for mild steel in 0.5 M H_2SO_4 for various concentrations of DCHA in the presence and absence of KI

Conc. of DCHA/M	Conc. of KI/M	R_t /Ω	C_{dl} /μF	I.E. /%
1 × 10^{-3}	–	105	7.6	86.7
1 × 10^{-3}	1 × 10^{-4}	116	6.9	87.9
4 × 10^{-3}	–	83	9.6	83.1
4 × 10^{-3}	1 × 10^{-4}	96	8.3	85.4
6 × 10^{-3}	–	49	16.2	68.6
6 × 10^{-3}	1 × 10^{-4}	66	12.1	78.8
8 × 10^{-3}	–	41	19.6	67.3
8 × 10^{-3}	1 × 10^{-4}	51	15.6	72.5
1 × 10^{-2}	–	31	26.1	54.2
1 × 10^{-2}	1 × 10^{-4}	46	17.3	69.5
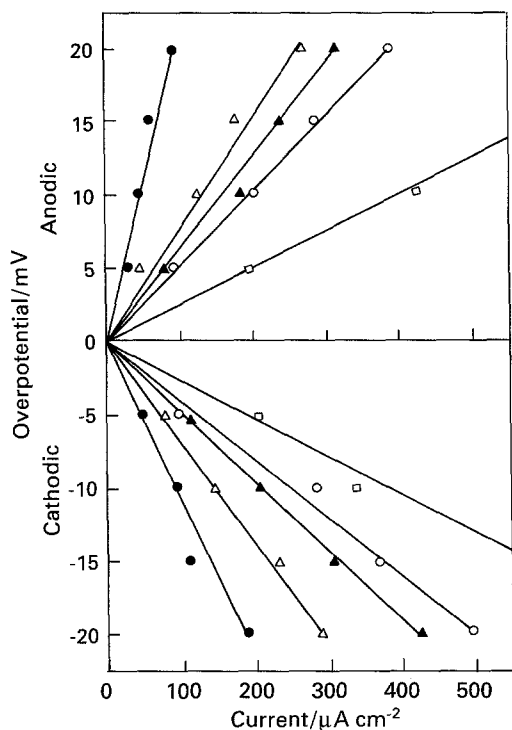
Fig. 3. Linear polarization plots of mild steel in 0.5 M H_2SO_4 for various concentrations of DCHA. Key: (O) 1×10^{-2}, (●) 1×10^{-3}, (△) 4×10^{-3}, (▲) 6×10^{-3} and (□) 0.5 M H_2SO_4.

given in Table 6. All the three techniques give almost identical values of inhibition efficiency for mild steel by DCHA in 0.5 M H_2SO_4.

The synergism parameter (S) was calculated using the relationship given by Aramaki and Hackermann [3]

$$S_I = \frac{(1 - I_{1+2})}{(1 - I'_{1+2})} \quad (1)$$
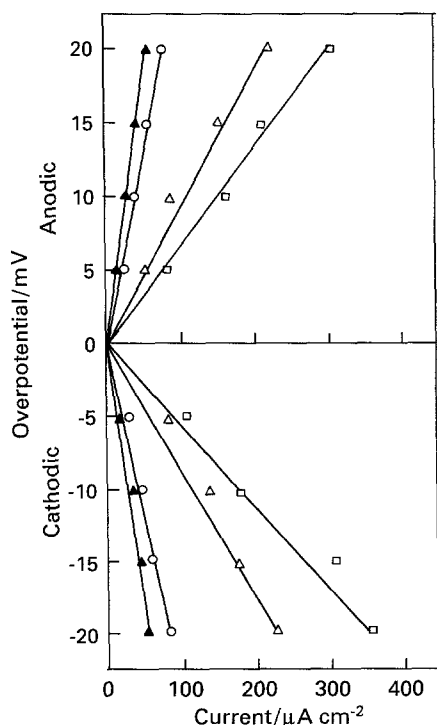
Fig. 4. Linear polarization plots of mild steel in 0.5 M H_2SO_4 + 1×10^{-4} M KI containing various concentration of DCHA. Key: (□) 1×10^{-2}, (▲) 1×10^{-3}, (O) 4×10^{-3} and (△) 6×10^{-3} M.
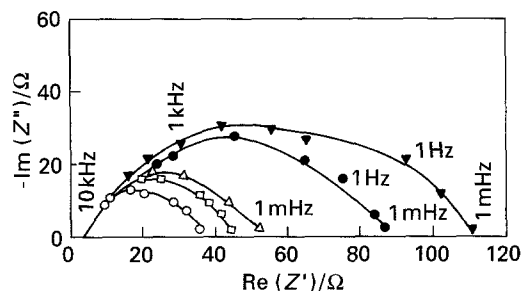
Fig. 5. Nyquist plots of mild steel in 0.5 M H_2SO_4 containing various concentration of DCHA. Key: (▼) 1×10^{-3}, (●) 2×10^{-3}, (△) 4×10^{-3}, (□) 8×10^{-3} and (O) 1×10^{-2} M.
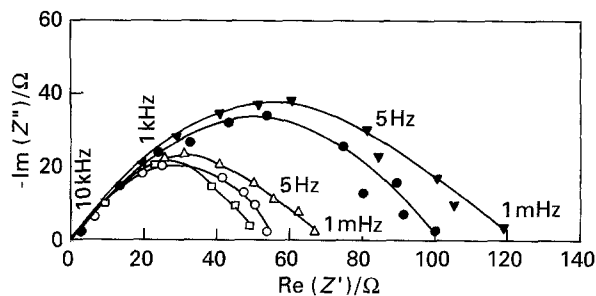
Fig. 6. Nyquist plots of mild steel in 0.5 M H_2SO_4 + 1×10^{-4} M KI containing various concentration of DCHA. Key: (▼) 1×10^{-3}, (●) 2×10^{-3}, (△) 4×10^{-3}, (□) 8×10^{-3} and (O) 1×10^{-2} M.

$$S_\theta = \frac{(1 - \theta_{1+2})}{(1 - \theta'_{1+2})} \quad (2)$$

where

$$I_{1+2} = (I_1 + I_2) - (I_1 I_2)$$

I_1 = inhibition efficiency of the anion
I_2 = inhibition efficiency of the cation
I'_{1+2} = measured inhibition efficiency for the cation in combination with anion
$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \theta_2)$
θ_1 = surface coverage by anion
θ_2 = surface coverage by cation
θ'_{1+2} = measured surface coverage by both anion and cation

This parameter was calculated both from the values of inhibition efficiency and from the degree of surface coverage (θ) i.e., S_I and S_θ. These values are given in

Table 6. Comparison of inhibition efficiencies obtained by different methods

Conc. of DCHA/M	Conc. of KI/M	Inhibition efficiency/%		
		Tafel	Linear polarization	Impedance
1×10^{-3}	–	84.8	80.3	86.7
1×10^{-3}	1×10^{-4}	94.1	93.5	87.9
4×10^{-3}	–	70.4	83.0	83.1
4×10^{-3}	1×10^{-4}	91.5	91.3	85.4
6×10^{-3}	–	62.0	69.4	68.6
6×10^{-3}	1×10^{-4}	75.0	73.6	78.8
8×10^{-3}	–	59.3	–	67.3
8×10^{-3}	1×10^{-4}	74.1	–	72.5
1×10^{-2}	–	57.4	56.1	54.2
1×10^{-2}	1×10^{-4}	66.6	66.8	69.5

Table 7. Synergism parameters S_I and S_θ for various concentrations of DCHA

Conc. of DCHA/M	S_I	S_θ
1×10^{-3}	1.95	2.08
4×10^{-3}	2.80	2.60
6×10^{-3}	1.18	1.18
8×10^{-3}	1.21	1.22
1×10^{-2}	1.16	0.99

Table 7. The values are calculated for various concentrations of DCHA. Figure 7 shows the plot of synergism parameter (S_I) against various concentrations of the amine. The S_I values given in Table 7 are more than unity and this suggests that the enhanced inhibition efficiency caused by the addition of iodide ions to DCHA is only due to a synergistic effect.

The plot of c/θ against c is linear in nature, as shown in Fig. 8, which shows that DCHA obeys the Langmuir adsorption isotherm.

4. Discussion

The synergistic inhibitive effect brought about by the combination of DCHA and iodide ions for the corrosion of mild steel in 0.5 M H_2SO_4 can be explained as follows. The strong chemisorption of iodide ions on the metal surface is responsible for the synergistic effect of iodide ions, in combination with the DCHA cation. The $DCHA^+$ is then adsorbed by coulombic attraction at the metal surface, where iodide ions are already adsorbed by chemisorption. Stabilization of adsorbed iodide ions by means of electrostatic interaction with $DCHA^+$ leads to greater surface coverage and, thereby, greater inhibition [4].

The inhibition efficiency for the corrosion of mild steel in 0.5 M H_2SO_4 in the presence of DCHA decreases with increase in inhibitor concentration. This shows that adsorption of amine decreases with increase in amine concentration. The adsorbed intermediate formed at the metal surface by the interaction with DCHA is probably a complex. Frignani et al. [5] have reported that an organic compound formed is a more or less stable complex which has a definite oxidative property [6]. At lower concentrations of DCHA the adsorbed intermediate formed, may be an insoluble complex leading to very high values of inhibition efficiency. Higher
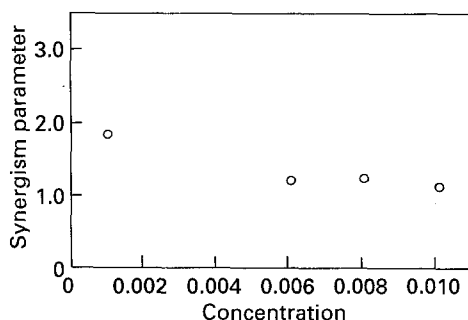
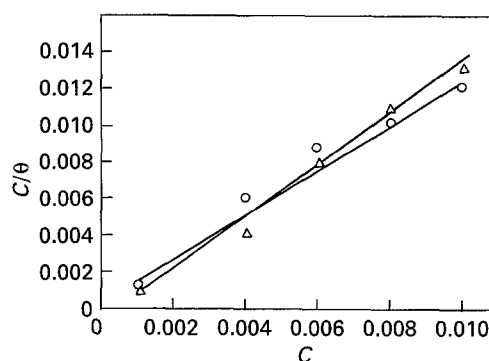Fig. 7. Plot of synergism parameter S_I against C for DCHA.

Fig. 8. Plot of C/θ against C for DCHA. Key: (○) DCHA and (△) DCHA + KI.

values of inhibition efficiency due to this complex arise from the blocking of most of the active sites on the metal surface due to increased coverage. But at higher concentrations of the amine, the complex formed is soluble, which leads to less inhibition. In the case of coverage also, it is found to decrease with increase in the concentration of DCHA, thereby supporting the fact that an insoluble complex formed at lower concentrations of the amine becomes soluble at higher concentrations. This is due to the accumulation of a large number of molecules at higher concentrations which makes the complex soluble.

The above observation is supported by values of C_{dl} in the presence of different concentrations of DCHA. Usually the values of C_{dl} decrease with increase in inhibitor concentration [7–10]. But in the case of DCHA the reverse is observed, i.e., C_{dl} values increase with increasing the amine concentration. The addition of iodide ions to DCHA is found to increase R_t values, supporting the fact that the inhibition of corrosion of mild steel by DCHA in 0.5 M H_2SO_4 is only due to synergism caused by iodide ions. It has also been observed that, as the concentration of the amine increases, the adsorption of the amine decreases, leading to less inhibition and thereby the enhancement of C_{dl} values.

The synergistic effect obtained by the addition of iodide is greater at lower concentrations and considerably less at higher concentrations of DCHA. It is due to the fact that iodide acts more effectively at lower concentrations of the amine enhancing the efficiency more than in the case of higher concentrations. Variation of coverage (θ) in the presence of iodide and different concentration of DCHA follows the same trend. A plot of c/θ against c, gives a straight line, indicating the fact that the adsorption of the inhibitor obeys a Langmuir isotherm. It is also seen from Table 7 that most of the values of S_I and S_θ are greater than unity, clearly showing that the corrosion inhibition brought out by DCHA and iodide in combination is synergistic in nature. Thus it can be concluded that the iodide ion is initially chemisorbed on the metal surface. DCHA ions are then adsorbed by coulombic attraction on the metal surface, where the anion is already chemisorbed and thus suppresses the self corrosion rate by the stabilization of the adsorbed anion and by the increase in surface coverage.

5. Conclusions

(i) DCHA inhibits the corrosion of mild steel in 0.5 M H_2SO_4 more at lower concentrations in the presence of iodide ions. This is probably caused by the formation of an insoluble complex at lower concentrations due to joint adsorption.

(ii) Addition of iodide ions enhances the inhibition efficiency.

(iii) DCHA and iodide ions in combination inhibit the corrosion of steel in 0.5 M H_2SO_4 by affecting both cathodic and anodic reactions.

(iv) Values of the synergism parameters (S_I and S_θ) clearly show that the corrosion inhibition produced by DCHA and iodide combination is synergistic in nature.

(v) The observed variations in R_t and C_{dl} also indicates that the inhibition is only due to synergism.

(vi) The adsorption of DCHA on the steel surface from 0.5 M H_2SO_4 obeys a Langmuir isotherm, indicating that the main inhibition process is through adsorption.

Acknowledgement

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