Asian Journal of Chemistry; Vol. 24, No. 8 (2012), 3675-3678

ASIAN JOURNAL OF CHEMISTRY

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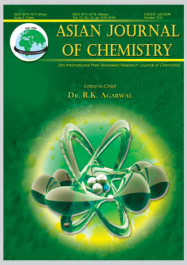

Cysteine as Inhibitor on the Corrosion of Mild Steel in Sulphuric Acid and Hydrochloric Acid Solutions

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(*Received*: 6 September 2011; *Accepted*: 21 March 2012) AJC-11215

The corrosion inhibition of mild steel in 0.5 M H_2SO_4 and 1 M HCl by L-cysteine (Cys) has been studied using potentiodynamic polarization measurements. Inhibition efficiency was found to increase with increasing concentration of L-cysteine in both acids and the higher inhibition efficiency is obtained in 1 M HCl. The activation energy as well as other electrochemical parameters for the inhibition process was calculated. The results suggest that the L-cysteine could serve as an effective inhibition of the corrosion of mild steel in hydrochloric acid and sulphuric acid.

Key Words: Cysteine, Mild steel, Polarization, Interface, Acid inhibition.

INTRODUCTION

Acid solutions are generally used for the removal of undesirable scale and rust in several industrial processes. Hydrochloric acid and sulphuric acid are widely used in the pickling processes of metals. Use of inhibitors is one of the most practical methods for protection against corrosion especially in acid solutions to prevent metal dissolution and acid consumption[1]. A number of organic compounds have been reported as effective corrosion inhibitors[2-7]. But, most of them are highly toxic to both human being and environment. The toxic effects of these inhibitors have led to the use of naturally occurring products as corrosion inhibitors[8]. Compounds containing sulphur and nitrogen are more effective as corrosion inhibitors in acid media[9].

Amino acids as non-toxic, environmentally friendly, biodegradable and other characteristics, is the most promising green corrosion inhibitor material. Cysteine is a thiol amino acid, but as an organic adsorbent, the interfacial inhibit corrosion behaviour of cysteine at mild steel/sulfuric acid and/or hydrochloric acid has rarely been studied. In the present work, L-cysteine (Cys), has been studied as corrosion inhibitor for mild steel in 0.5 M H_2SO_4 and 1 M HCl by electrochemical polarization methods.

EXPERIMENTAL

The electrolyte was 0.5 M H_2SO_4 and 1 M HCl with vatious concentrations of L-cysteine. Reagent-grade H_2SO_4 and HCl were used and the aggressive solution were made up with double-distilled water. A traditional three-electrode cell was used for electrochemical measurements. A platium sheet electrode was used for the auxilliary electrode and the reference electrode was a saturated calomel electrode (SCE) with a Luggin capillary. All potentials were measured with respect to the saturated calomel electrode. The working electrode is A_3 mild steel rod (C, 0.17 %; Si, 0.20 %; Mn, 0.37 %; S, 0.03 %; P, 0.01 % and reminder iron). The rod specimen was embedded in Teflon holder using epoxy resin with an exposed area of 0.29 cm^2. Before each experiment, the electrode was first mechanically polished with various grades of sandpaper (up to 1200 grit) and then ultrasonically cleaned in acetone for 2 min, followed by a rinse in double-distilled water.

Detection method: Electrochemical experiments were carried out using a CHI660B electrochemical workstation. Potentiodynamic polarization curves were recorded at a sweep rate of 1 mV s^{-1}. Electrochemical data were obtained after 1 h of immersion with the working electrode at the rest potential and all tests have been performed in non-de-aerated solutions under unstirred conditions.

RESULTS AND DISCUSSION

Potentiodynamic polarization: Fig. 1 shows potentiodynamic polarization curvess of mild steel in 0.5 M H_2SO_4 and 1 M HCl in the absence and presence of L-cysteine. It is clear from Fig. 1, that both anodic and cathodic reactions of mild steel corrosion were suppressed in the presence of L-cysteine in both acids. Electrochemical kinetic parameters, *i.e.*, corrosion potential (E_{corr}), cathodic and anodic Tafel slope (b_c

TABLE-1
POTENTIODYNAMIC POLARIZATION PARAMETERS FOR THE CORROSION OF MILD STEEL IN BOTH ACIDS CONTAINING DIFFERENT CONCENTRATION OF L-CYSTEINE

Acids	C_{corr} (M)	E_{corr} (V)	i_{corr} ($\times 10^{-3}$ A cm^{-2})	b_a (mV dec^{-1})	b_c (mV dec^{-1})	η (%)
0.5 M H_2SO_4	Blank	-0.504	2.15	136	161	-
	0.005	-0.491	0.448	94.3	113	79.2
	0.01	-0.481	0.476	98.0	123	77.9
	0.02	-0.480	0.357	102	117	83.4
	0.06	-0.482	0.469	104	115	78.2
	0.1	-0.485	0.465	109	113	78.4
1.0 M HCl	Blank	-0.494	1.03	117	119	-
	0.005	-0.512	0.732	143	116	28.9
	0.01	-0.510	0.313	112	93.3	69.6
	0.02	-0.509	0.226	106	93.8	78.0
	0.06	-0.507	0.0939	118	82.2	90.9
	0.1	-0.487	0.0720	100	81.8	93.0

and b_a) and corrosion current density (i_{corr}), obtained by extrapolation of the Tafel lines, are presented in Table-1. The inhibition efficiencies (η %) of L-cysteine in both acids are also given in Table-1. The inhibition efficiency is defined as:

$$\eta(\%) = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100 \quad (1)$$

where, i^0_{corr} and i_{corr} are the corrosion current density values without and with inhibitor, respectively.

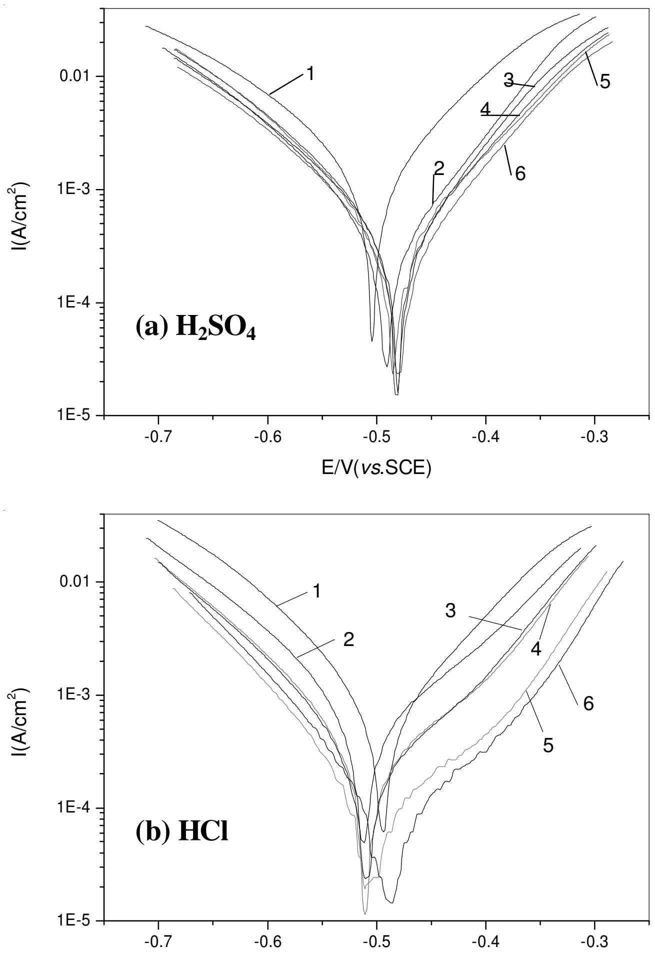

Fig. 1. Polarization curves for mild steel in (a) 0.5 M H_2SO_4 and (b) 1.0 M HCl with different concentrations of L-cysteine. 1: blank; 2: 0.005 M; 3: 0.01 M; 4: 0.02 M; 5: 0.06 M; 6: 0.1 M

The slight shifts of E_{corr} values towards positive direction are found in the presence of various concentrations of L-cysteine in 0.5 M H_2SO_4, whereas inverse effect is observed in 1 M HCl, indicating that the adsorption of the anions has an effect on the behaviour of L-cysteine inhibitor. No distinct change is observed in the slopes of the cathodic Tafel lines in the presence of various concentrations of L-cysteine in both acids, which indicates that L-cysteine does not change the mechanism of the hydrogen evolution reaction. In 1.0 M HCl, the slopes of the anodic Tafel lines have an decreasing trend with the increase of the concentration of L-cysteine, while not obviously in 0.5 M H_2SO_4. This result suggests that the addition of L-cysteine changes the anodic metal dissolution reaction in both acid solutions and the effect on anodic dissolution reaction in the presence of SO_4^{2-} is different from that in the presence of Cl^-.

As it can be seen from Table-1, corrosion current densities decrease and the inhibition efficiencies increase with the increase of inhibitor concentrations. But the inhibition ability of the compound to mild steel corrosion in 1.0 M HCl is higher than that in 0.5 M H_2SO_4, suggesting that the adsorption of the anions may influence the adsorption of the compound onto the mild steel surface.

Effect of temperature: The activation energy of corrosion process can be obtained by investigating the influence of temperature on corrosion inhibition, consequently some information about adsorption mechanism of the inhibitor can be obtained from the activation energy values. Polarization curves of mild steel in 0.5 M H_2SO_4 and 1.0 M HCl at different temperatures (30-50 ºC) in the absence and presence of 0.02 M of L-cysteine are given in Fig. 2. Electrochemical parameters and inhibition efficiencies are presented in Table-2. The corrosion current density increases with the increase of temperature both in uninhibited and inhibited solutions, but inhibition efficiency of L-cysteine decreases with increasing temperature, thus the inhibition efficiency of L-cysteine is temperature-dependent in both acids.

In order to calculate the activation energy of the corrosion process, Arrhenius equation was used:

$$I_{corr} = k\exp(-\frac{E_a}{RT}) \quad (2)$$

where, k is the pre-exponential factor and Ea is the activation energy. Fig. 3 presents the Arrhenius plots of the natural logatithm of the corrosion current density *vs.* 1/T in both acids.

TABLE-2
POTENTIODYNAMIC POLARIZATION PARAMETERS FOR THE CORROSION OF MILD STEEL IN BOTH ACIDS CONTAINING DIFFERENT CONCENTRATION OF L-CYSTEINE

T(°C)	0.5 M H_2SO_4		0.5 M H_2SO_4 + 0.02 M L-Cysteine			1.0 M HCl		1.0 M HCl + 0.02 M L-Cysteine		
	E_{corr} (V)	i_{corr} (×10^{-3}A cm^{-2})	E_{corr} (V)	i_{corr} (×10^{-3} A cm^{-2})	η (%)	E_{corr} (V)	i_{corr} (×10^{-3} A cm^{-2})	E_{corr} (V)	i_{corr} (×10^{-3} A cm^{-2})	η (%)
30	-0.504	2.15	-0.480	0.357	83.4	-0.494	1.03	-0.509	0.226	78.0
40	-0.502	3.01	-0.493	0.431	78.0	-0.492	1.28	-0.494	0.330	74.4
50	-0.500	3.68	-0.494	0.642	58.2	-0.489	1.78	-0.495	0.592	66.9
60	-0.498	4.22	-0.495	0.997	37.7	-0.488	1.96	-0.496	0.893	54.5

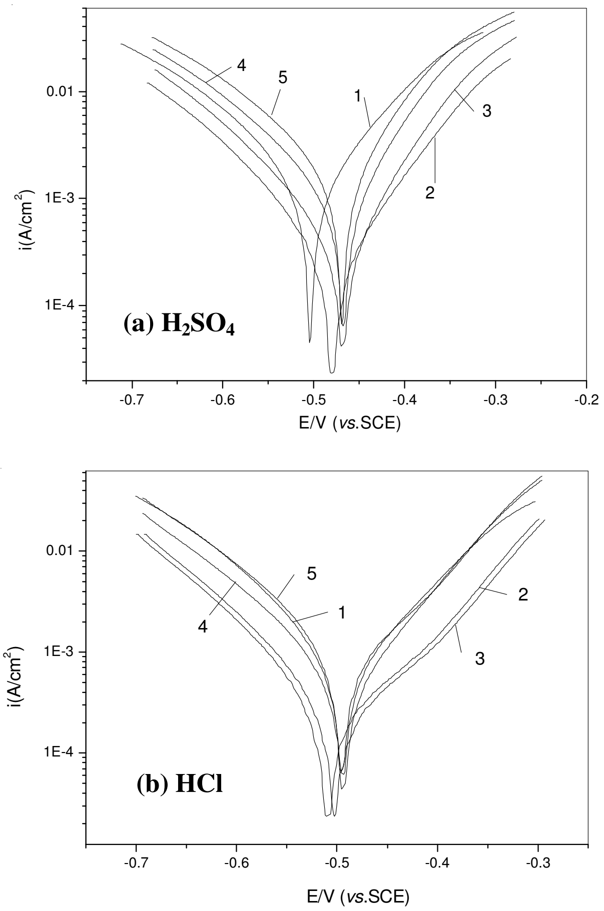

Fig. 2. Polarization curves for mild steel in (a) 0.5 M H_2SO_4 and (b) 1.0 M HCl containing 0.02 M L-cysteine at different temperature. 1: blank; 2: 30 °C; 3: 40 °C; 4: 50 °C; 5: 60 °C

The calculated values of activation energy are given in Table-3. Table-3 shows that the value of E_a obtained in 0.5 M H_2SO_4 containing L-cysteine is higher than that obtained without L-cysteine, which may be interpreted as physical adsorption that occurs in the first stage[6]. The increase in activation energy can be attributed to an appreciable decrease in the adsorption of the inhibitor on the steel surface with the increase in temperature[3]. On the other hand, the value of E_a obtained in 1 M HCl containing L-cysteine is lower than that in the uninhibited solution, which can be attributed to its chemisorption on the steel surface[5]. The decrease of E_a value can be interpreted as slow rate of inhibitor adsorption with a resultant closer approach to equilibrium during the experiments at high temperature[2]. But Behpour *et al.*[6] explained the change of the activation energy from energetic heterogeneity of the surface. If energetic surface heterogeneity is assumed, active centers of the surface have different energy. There are two possibilities *i.e.*, in the first case the inhibitor is adsorbed on the most active adsorption sites (having the lowest energy) and the corrosion process takes place predominantly on the active sites of higher energy (resulting in the higher activation energy). In the second case a smaller number of more active sites remain uncovered which take part in the corrosion process (resulting in the lower activation energy). In addition, Vracar and Drazic[4] argued that the criteria, adsorption type obtained from the change of activation energy, can not be taken as decisive due to competitive adsorption with water whose removal from the surface requires also some activation energy. On the other word, the so-called chemisorption process may contain physical simultaneously and *vice versa*. The results show that the L-cysteine could serve as an effective inhibition of the corrosion of mild steel in hydrochloric acid and sulphuric acid.

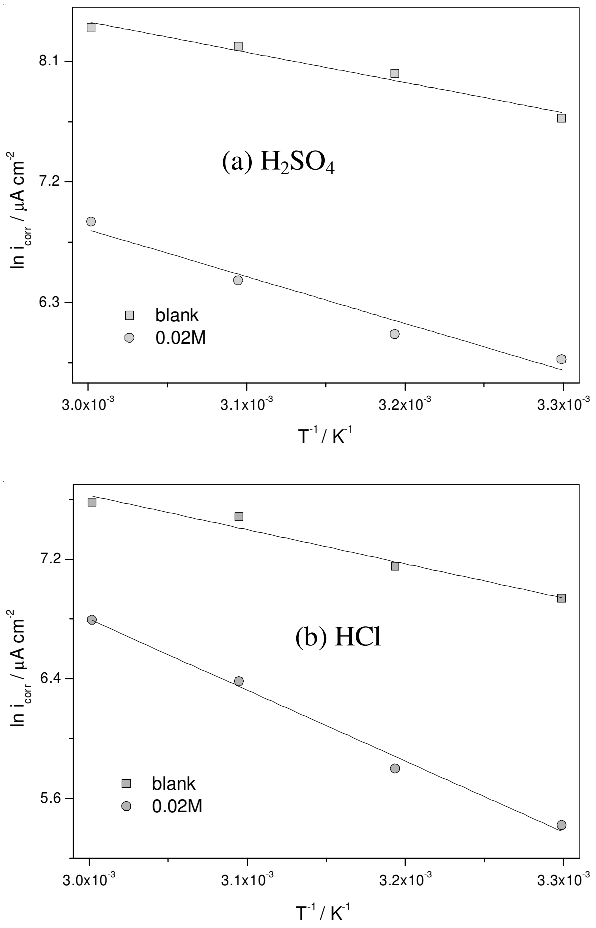

Fig. 3. Arrhenius plots for mild steel in (a) 0.5 M H_2SO_4 (b) 1 M HCl with and without 0.02M L-cysteine

TABLE-3
ACTIVATION ENERGY FOR THE CORROSION OF MILD STEEL IN BOTH ACIDS WITHOUT AND WITH 0.02 M L-CYSTEINE

Systems	E_a (kJ mol^{-1})
0.5 M H_2SO_4	18.69
0.5 M H_2SO_4 + 0.02 M L-Cysteine	40.75
1.0 M HCl	91.36
1.0 M HCl + 0.02 M L-Cysteine	52.54

Conclusion

The examined L-cysteine inhibits the corrosion of mild steel in 0.5 M H_2SO_4 and 1 M HCl but the efficiency is slightly better in HCl solution than in H_2SO_4. Polarization curves indicated that L-cysteine acts as mixed type inhibitor in both acid solutions. The L-cysteine inhibits the corrosion of mild steel in acid media by adsorption mechanism.

ACKNOWLEDGEMENTS

This work was funded by the Applied Basic Research Project of Yancheng Institute of Technology of Chian, Jiangsu (Grant no. XKR2011005).

REFERENCES

1. L.R. Chauhan and G. Gunasekaran, *Corros. Sci.*, **49**, 1143 (2007).
2. T.P. Hoar and R.D. Holliday, *J. Appl. Electrochem.*, **3**, 502 (1953).
3. T. Szauer and A. Brandt, *Electrochim. Acta*, **26**, 209 (1981).
4. L.M. Vracar and D.M. Drazic, *Corros. Sci.*, **44**, 1669 (2002).
5. A. Popova, E. Sokolova, S. Raicheva and M. Christov, *Corros. Sci.*, **45**, 33 (2003).
6. M. Behpour, S.M. Ghoreishi, N. Soltani and M. Salavati-Niasari, *Corros. Sci.*, **51**, 1073 (2009).
7. Y.M. Tang, X.Y. Yang and W.Z. Yang, *Corros. Sci.*, **52**, 1801 (2010).
8. A.A. Ec Hosary, R.M. Saleh and A.M. Shams El-Din, *Corros. Sci.*, **12**, 897 (1972).
9. S. Muralidharan, K.L.N. Phani, S. Pitchumani, S. Ravichandran and S.V.K. Iyer, *J. Electrochem. Soc.*, **142**, 1478 (1995).