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Effect of 2-amino-3-mercaptopropanoic acid (cysteine) on the corrosion behaviour of low carbon steel in sulphuric acid

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Abstract

The effect of cysteine (cys) on the corrosion of low carbon steel (LCS) in sulphuric acid solution was investigated using electrochemical and scanning electron microscopy (SEM) techniques. Electrochemical impedance spectroscopy (EIS) results reveal that the presence of cys at low concentrations (0.1–0.5 $\mathrm{mmol\,L^{-1}}$) promoted the LCS corrosion process, whereas an inhibiting effect was observed at higher concentrations (1.0–5.0 $\mathrm{mmol\,L^{-1}}$), which was enhanced on deaeration of the test solution. Polarization results revealed that cys actually inhibited the cathodic process at all concentration but exerted a stimulating effect on the anodic metal dissolution reaction. Despite the cathodic inhibiting effect, the polarization resistances at low cys concentrations were less than that in the blank acid. This suggests that the anodic reaction was the predominant influence determining the corrosion rates in the presence of cys. This has been discussed vis-à-vis the catalytic effect of the Fe–cys complex, which turns the Fe surface more electrochemically active.

Keywords: Low carbon steel; Corrosion; Cysteine; Anodic reaction; Cathodic reaction

1. Introduction

The corrosion of metals at the solid–liquid interface by acids is a major dilemma encountered in numerous industrial processes. A significant method to protect the metals from corrosion is addition of species to the solution in contact with the surface in order to inhibit the corrosion reaction and reduce the corrosion rate. To this end, the use of organic compounds containing nitrogen, oxygen, or sulphur as inhibitors to reduce corrosion attack has received detailed attention [1–5]. These compounds act at the interphase created by corrosion product between the metal and aqueous aggressive solution and their interaction with the corroding metal surface, usually via adsorption, often leads to a modification in either the mechanism of the electrochemical process at the double layer or in the surface available to the process. Subsequent categorization of cathodic or anodic inhibition is derived from experimental evidence of the predominant influence of an additive on one of the two partial reactions that constitute the corrosion phenomenon.

A number of studies have been undertaken to relate the modes inhibitor adsorption with various molecular parameters [6,7]. In most cases parameters connected with the chemical and electronic structures of the molecule often act simultaneously to influence the adsorption process; making it difficult to indisputably isolate the predominant effect. Some fundamental correlations can however be proposed from examination of available literature. For instance it has been shown that N-containing compounds tend to preferentially adsorb on cathodic sites on Fe in acidic solution whereas S-containing compounds mainly function by chemisorption on anodic sites [8]. Interestingly the presence of functional groups containing both N and S in a compound has been shown to often result in enhanced inhibition effectiveness. This has been attributed to an adsorption mechanism involving both the N and S atoms of the molecule and has been highlighted in studies

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using mercaptotriazole derivatives [9] and S-containing amino acids (methionine, cysteine, cystine, *N*-acetylcysteine) [10] as non-toxic inhibitors for iron in acidic solutions. Badawy et al. also observed that cysteine [$HSCH_2CH$ $(CO_2H)NH_2$] displayed outstanding protective efficiency on Cu–Ni alloys in neutral chloride solutions [11]. Recently however, Silva et al. [12] reported somewhat contrary observations on the effect of cysteine on the corrosion of 304 L stainless steel in sulphuric acid. The compound did not affect the corrosion behaviour of the steel specimen at low concentrations (10^{-6} to 10^{-5} M) and at higher concentrations turned the metal surface active, promoting the anodic dissolution reaction. We thus thought it worthwhile to investigate how this compound affects the corrosion of low carbon steel in sulphuric acid, particularly since we had observed remarkable inhibitive efficiency in an earlier study [13] using methionine [CH_3–S–CH_2–CH_2–CH–$CO_2H)NH_2$], a related S-containing amino acid. AC and DC electrochemical techniques were used all through this investigation. EIS was used to provide insight into the kinetics of electrode processes as well as the surface characteristics of each electrochemical system, whereas the polarization technique was used to monitor the effect of the additive on both the cathodic and the anodic reactions. Also, since cysteine is known to be oxidized to cystine and cysteic acid experimental data obtained in aerated solutions have been compared with those in deaerated solutions. Morphological changes on the corroding steel surface were visualized by scanning electron microscopy (SEM).

2. Experimental

Electrochemical experiments were performed in a conventional three-electrode glass cell of 400 ml capacity using a PARC Parstat-2273 Advanced Electrochemical System. Test coupons of 1 cm^2 surface area, fabricated from an A3 low carbon steel specimen, with percentage composition C: 0.22; Si: 0.1–0.3; Mn: 0.6; P: 0.045, were used as working electrode. These were wet-polished with silicon carbide abrasive paper (from grade #400–#1000), degreased in acetone, rinsed with distilled water and dried in warm air. A platinum foil was used as counter electrode and the reference electrode was a saturated calomel electrode (SCE). The aggressive solution was 0.5 M H_2SO_4 solution, prepared from analytical reagent grade sulphuric acid and distilled water. Cysteine (cys) was obtained from SCRC, China and dissolved in the test corrodent to obtain the desired concentrations. 0.005 M solutions of KI were prepared in the blank corrodent and in 0.005 M cys solution.

All experiments were undertaken in stagnant aerated solutions at 30 ± 1 °C. Prior to each measurement, the working electrode was immersed in a test solution for 30 min until a stable open circuit potential was attained. Polarization studies were carried out in the potential range ±250 mV versus corrosion potential (E_{corr}) at a scan rate of 0.333 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were made at corrosion potentials over a frequency range of 100 kHz–10 mHz, with a signal amplitude perturbation of 5 mV. Spectra analyses were performed using Zsimpwin software, also supplied by PARC. Measurements at two cys concentrations (0.0005 and 0.005 M) were also repeated under deaerated conditions. The test solutions were bubbled with a stream of nitrogen for 30 min prior to electrode immersion and during electrochemical measurements. Each test was run in triplicate to verify the reproducibility of the results.

SEM examinations of electrode surfaces exposed to different test solutions for 2 h were achieved using a Shimadzu SSX-550 scanning electron microscope.

3. Results and discussion

3.1. Open circuit potential measurements

The evolution of the open circuit potential (OCP) with time for low carbon steel in 0.5 M H_2SO_4 solution without and with different concentrations of cys (0.05–5.0 mM) after 30 min of immersion is illustrated in Fig. 1 . A slight shift of potential towards negative values is observed in the presence of cys. Such potential shift can be attributed to adsorption of cys and/or deposition of reaction products on the electrode surface [11]. The magnitude of the OCP displacements suggest that cys simultaneously affects the cathodic and anodic reactions, since precise categorization of a compound as an anodic or cathodic inhibitor requires an OCP displacement of up to 85 mV with respect to the blank corrodent.

3.2. Electrochemical impedance spectroscopy measurements

The key objective of EIS experiments is to provide insight into the characteristics and kinetics of electrochemical processes occurring at the Fe/H_2SO_4 interface in absence and presence of cys. The impedance response of these systems is presented in Fig. 2a–c , which exemplify, respectively, the Nyquist, Bode and phase angle plots. The Nyquist plots for all systems generally have the form of only one depressed semicircle, corresponding to one time constant in the Bode plots. The results however clearly show a distinct concentration dependence of the effect of cys on

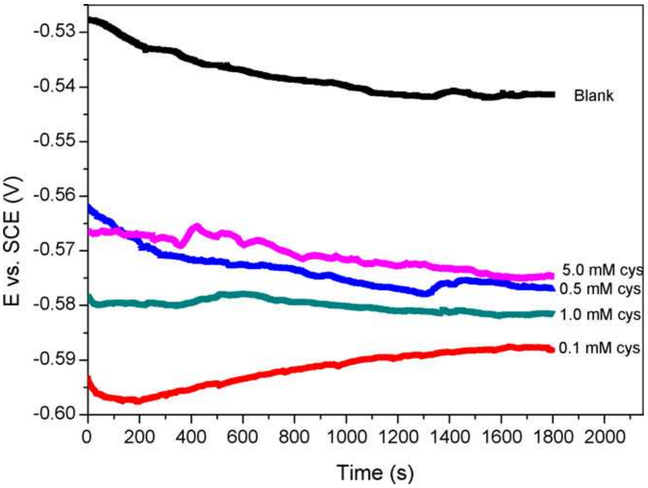

Fig. 1. Variation of open circuit potential (OCP) with time for LCS in 0.5 M H_2SO_4 without and with different concentrations of cys.

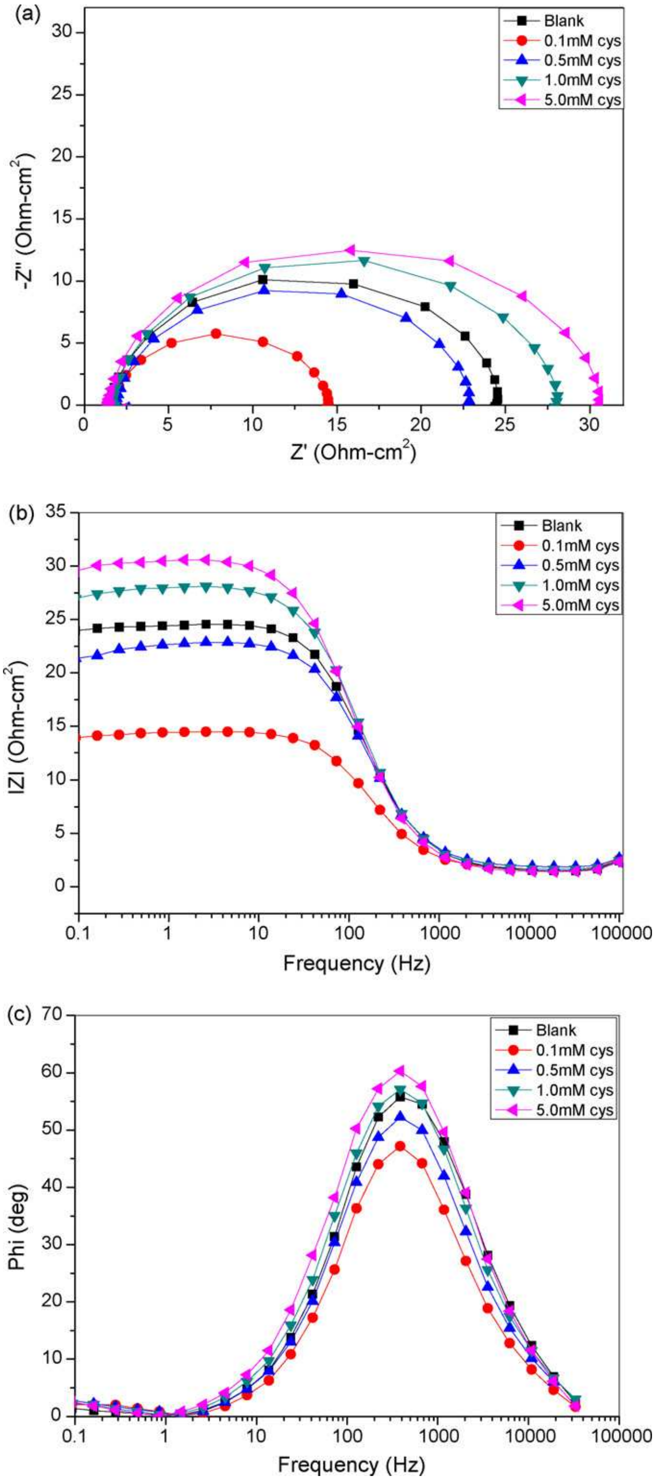

Fig. 2. Electrochemical impedance plots of LCS in 0.5 M H_2SO_4 in the absence and presence of cys; (a) Nyquist, (b) Bode and (c) phase angle plots.

Table 1
Electrochemical impedance parameters for LCS in 0.5 M H_2SO_4 in absence and presence of cys

System	R_{ct} (Ω cm^2)	C_{dl} (μF cm^{-2})	n
Blank	23.1	54.3	0.93
0.1 mM cys	13.0	96.6	0.91
0.5 mM cys	21.3	88.9	0.91
1.0 mM cys	26.6	82.4	0.92
5.0 mM cys	29.2	74.9	0.92

the corrosion behaviour of the LCS specimen. Compared to the blank acid, the size of the semi circle in Fig. 2a, the impedance of the interface in Fig. 2b and the maximum phase angle in Fig. 2c all decreased in the presence of cys at low concentrations (0.1–0.5 mM) and increased at higher concentrations. This indicates that the compound catalyzed the corrosion reaction at low concentrations but functioned as a corrosion inhibitor at higher concentrations.

The impedance spectra were appropriately analyzed by fitting to the equivalent circuit model $R_s(Q_{dl}R_{ct})$, which was previously used to model the steel/acid interface [13] and the values of the impedance parameters given in Table 1 . A constant phase element (CPE), represented by the terms Q_{dl} and n and with impedance given by $Z_{CPE} = Q^{-1}(j\omega)^{-n}$, where j is an imaginary number and ω is the angular frequency in rad s^{-1} is used in place of a capacitor to compensate for the deviations from ideal dielectric behaviour associated with the non-homogeneity of the electrode surface [7]. The values of the double layer capacitance, C_{dl}, were obtained at the frequency (f_{max}) at which the imaginary component of the impedance is a maximum by $C_{dl} = 1/(2\pi f_{max} R_{ct})$.

Table 1 shows that the presence of cys at 0.01 and 0.05 mM concentrations reduced charge transfer resistance (R_{ct}) values from 23.1 Ω cm^2 in the blank acid to 13.0 and 21.3 Ω cm^2, respectively, indicating stimulation of the corrosion reaction. R_{ct} values however increased at higher cys concentrations, up to 26.7 and 29.2 Ω cm^2 at [cys] = 1.0 mM and 5.0 mM, respectively, signifying a reduction in the corrosion rate. The corresponding percentage inhibition efficiencies (η%) were, respectively, 13 and 20%, as calculated from [$\eta\% = (1 - R_{ct}/R'_{ct}) \times 100$], where R_{ct} and R'_{ct} represent the values in absence and presence of cys. The results also show that the presence of cys, at any concentration, modified the interfacial capacitance, which suggests that cys was adsorbed on the electrode surface at all concentrations. The increase in C_{dl} values may be considered in terms of the Helmholtz model ($C_{dl} = \varepsilon\varepsilon_o A/\delta$), to suggest that the presence of cys at the Fe/solution interface rendered the Fe surface more electrochemically active, probably diminishing the stability and thickness of the protective layer of reaction products on the electrode surface, where ε is the dielectric constant of the medium, ε_o the vacuum permittivity, A the electrode area and δ is the thickness of the protective layer. Although the parameter n does not vary greatly, its value can be seen to decline at low cys concentrations due to increased surface roughness resulting from both cys adsorption and enhanced corrosion rates.

Fig. 3 compares the impedance response in inhibited solution under aerated and deaerated conditions. Removal of oxygen from the solution increased the R_{ct} more than twofold to give values of 50.8 and 74.9 Ω cm^2 for 0.5 and 5.0 mM cys, respectively. This suggests that the degree of cys influence on the corrosion of LCS in 0.5 M H_2SO_4 depends on the presence of oxygen in the solution and the possibility of cys oxidation.

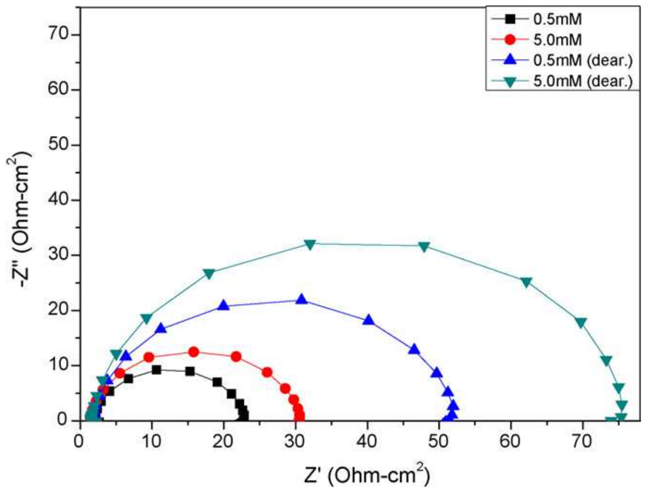

Fig. 3. EIS Nyquist plots of LCS in aerated and deaerated 0.5 M H_2SO_4 solutions containing 0.5 and 5.0 mM cys.

3.3. Polarization measurements

Polarization experiments were undertaken specifically to separate the different effects of cys on the anodic and cathodic partial reactions of the corrosion process. Fig. 4 illustrates typical anodic and cathodic polarization curves of low carbon steel in 0.5 M H_2SO_4 without and with different concentrations of cys. The corrosion potential (E_{corr}) is shifted to the negative direction in the presence of cys, which is in agreement with the OCP results and indicates inhibition of the cathodic process of the corrosion reaction. The plots also show that cys at the same time exerted a stimulating effect on the anodic reaction. The cathodic inhibiting effect is observed at all cys concentrations and increased steadily with concentration. The acceleration of the anodic reaction, which also takes place at all cys concentrations, is however more pronounced at low concentrations.

Polarization resistances (R_p) for the LCS electrode in the different test solutions were determined from the polarization curves in the vicinity of E_{corr}. Straight lines were obtained in the potential range E_{corr} −20 mV and E_{corr} +10 mV. Despite the fact that cys inhibited the cathodic process of LCS corrosion at all concentrations, Table 2 shows that the polarization resistance at low concentrations are lower than that in the blank acid, which is in agreement with the EIS results. This suggests that the anodic dissolution process is the predominant influence in determining the corrosion rate in solutions containing cys. R_p values were used to calculate the inhibition efficiency ($\eta_R\%$) at [cys] exhibiting a corrosion inhibiting effect by [$\eta_R\% = (1 - R_p/R'_p) \times 100$], where R_p is the polarization resistance value in 0.5 M H_2SO_4 solution without cys and R'_p is the polarization resistance in the presence of cys. $\eta_R\%$ values of 7.7 and 18.5% were obtained for 0.001 and 0.005 M cys, respectively, which are in agreement with those from EIS measurements.

Table 2
Corrosion potential and polarization resistance values for LCS in 0.5 M H_2SO_4 in absence and presence of cys

System	E_{corr} (mV)	R_p (Ω cm^2)
Blank	−553	33.4
0.1 mM cys	−568	18.7
0.5 mM cys	−562	29.5
1.0 mM cys	−564	36.2
5.0 mM cys	−560	41.0

Fig. 5 compares the polarization curves obtained in the presence of 0.005 M cys under aerated and deaerated conditions. The plots reveal that the inhibiting effect of cys on the cathodic reaction is enhanced by removal of oxygen from the solution, while the catalytic effect on the anodic reaction is reduced although not completely eliminated. Consequently, R_p values increased from 41 to 106.3 Ω cm^2.

Fig. 6 shows the SEM images of the LCS surface after 2 h immersion in 0.5 M H_2SO_4 in the absence of any additive (Fig. 6a) and the presence of 0.005 M cys under aerated (Fig. 6b) and deaerated (Fig. 6c) conditions. The LCS electrode presents a very rough surface in the absence of cys as expected, due to corrosive attack of the acid solution. The slight inhibiting effect

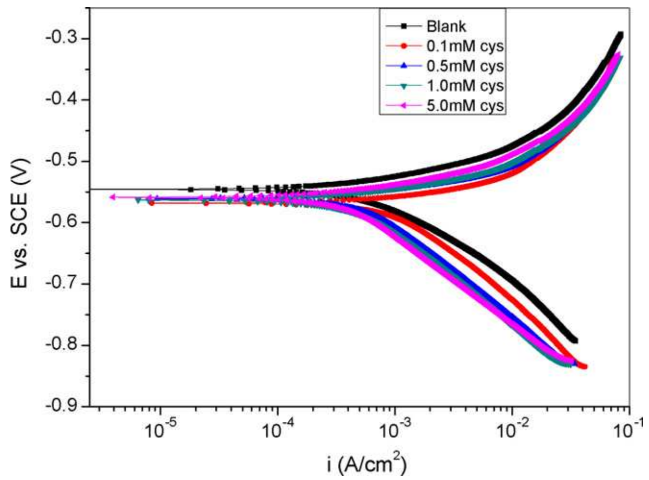

Fig. 4. Polarization curves of LCS in 0.5 M H_2SO_4 in the absence and presence of cys.

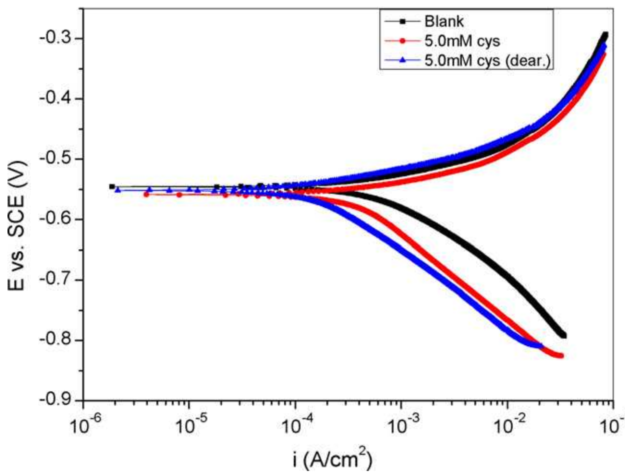

Fig. 5. Polarization curves of LCS in aerated and deaerated 0.5 M H_2SO_4 containing 0.005 M cys.

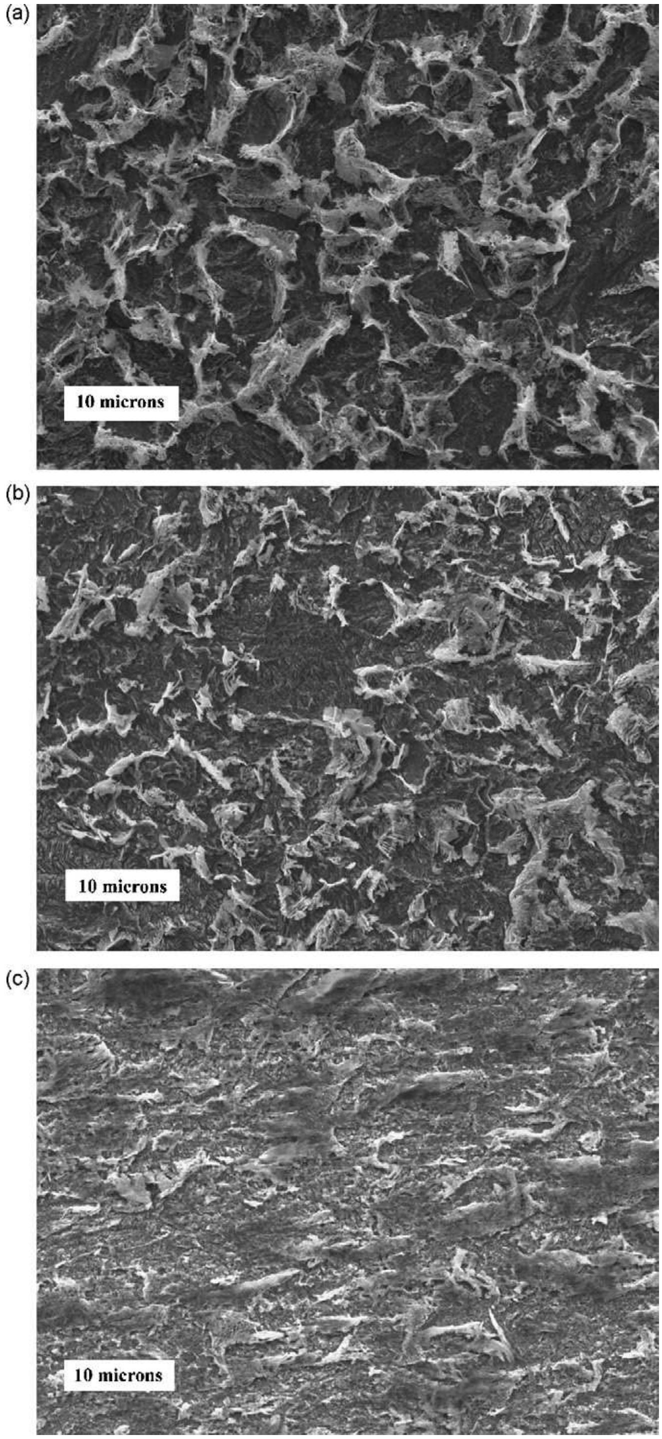

Fig. 6. SEM images of the LCS surface after 2 h immersion in 0.5 M H_2SO_4; (a) without additive, (b) with 0.005 M cys (aerated) and (c) with 0.005 M cys (deaerated).

afforded by cys at 0.005 M concentrations reduced the roughness of the metal surface. This inhibiting action of cys is obviously more pronounced in deaerated conditions, which is in agreement with our electrochemical results.

The pertinent issue now is why the results obtained in this study with cys deviate so markedly from those reported elsewhere and for other amino acids and related compounds. An important factor could be the differences in experimental conditions, particularly since most of the other studies were conducted in deaerated solutions using different corrodent and electrode compositions. For instance studies on the electrochemical behaviour of cys using solid electrodes [14,15] have shown that the molecule undergoes oxidation, with formation of a disulphide bridge, to cystine, which is poorly soluble in aqueous solution. Further oxidation to cysteic acid is also possible in the presence of strong oxidizing agents and the net oxidation sequence corresponds to: $RSH \rightarrow RSSR \rightarrow RSO_2H \rightarrow RSO_3H$. The possibility of these oxidation products interfering with the protective effect of cys is attested to by the difference in our experimental results in aerated and deaerated solutions. This however does not adequately account for the poor performance of cys in comparison to methionine [13]. Differences in the reactivity of cys and methionine have been ascribed to the methyl substituent of the S atom in the latter, which hinders the formation of S-bridged dimeric species [16]. According to Berthon [17], cys, with three ionizable protons, is prone to protonated complex formation and the size of the S atom of the thiol group will facilitate the formation of polynuclear complexes. The molecule will be protonated at the amino function in acidic solutions ($HSCH_2CH(CO_2H)NH_3^+$) and the cationic species can then be adsorbed on cathodic sites and retard the rate of the hydrogen evolution reaction. This is responsible for the observed cathodic inhibiting effect. As shown in an earlier study using methionine [13], adsorption on anodic sites will be facilitated by the lone pairs of electrons on the S atom, leading to the formation of Fe–cys complexes on the metal surface. The resulting complex could, depending on its chemical stability and relative solubility, either inhibit or catalyze further metal dissolution. Indeed, the low inhibiting properties of cys in sulphuric acid solution could be due to the formation of a non adherent and/or soluble Fe(II)–cys–SO_4 complex that desorbs easily from the LCS surface. Our experimental results further show that the resulting complex actually exerted a catalytic effect on the anodic Fe electro-dissolution reaction. To further confirm this, experiments were conducted in the presence of iodide ions, which are strongly chemisorbed on the surface of iron in acidic solutions and are known to facilitate the adsorption of some organic inhibitors by forming intermediate bridges between the positively charged metal surface and the positive end of the compound. Adsorption of iodide ions on the metal surface leads to a recharging of the electrical double layer and the inhibitor is then drawn into the double layer by electrostatic interaction with the adsorbed anions, forming ion-pairs on the metal surface:

$$I_s^- \rightarrow I_{ads}^- \qquad (1a)$$

$$I_{ads}^- + Inh_s^+ \rightarrow (I^- - Inh^+)_{ads} \qquad (1b)$$

I_s^- and Inh_s^+ represent the iodide ion and inhibitor, respectively, in the bulk of the solution while I_{ads}^-, Inh_{ads}^+ refer to the same species in the adsorbed stat, while and $(I^- - Inh^+)_{ads}$ represents the adsorbed ion-pair.

Fig. 7 illustrates the polarization curves for LCS in 0.5 M H_2SO_4 containing 0.005 M of KI, 0.005 M cys as well as 0.005 M KI in combination with 0.005 M cys. Interestingly, all

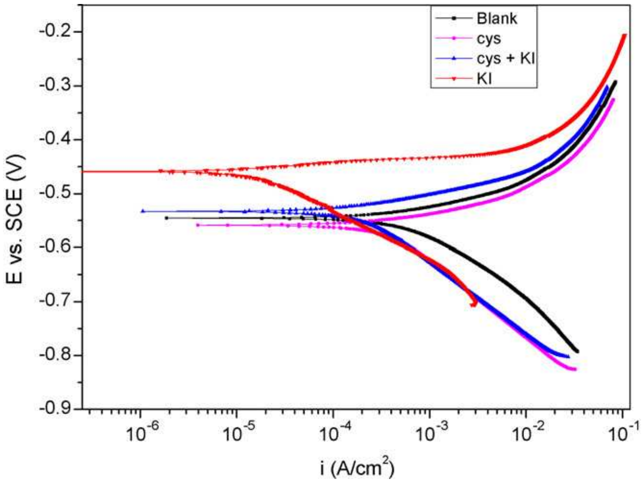

Fig. 7. Polarization curves for LCS in 0.5 M H_2SO_4 containing 0.005 M KI, 0.005 M cys and 0.005 M KI + 0.005 M cys.

the additives exerted analogous inhibitive effects on the cathodic reaction but retarded the anodic reaction kinetics to different extents. Adsorption of I-ions on the electrode surface (Eq. (1a)) led to a marked reduction in the magnitude of the anodic current density, signifying an inhibition of the anodic process. Although the cys + KI combination (Eq. (1b)) actually inhibited the Fe dissolution reaction as opposed to cys alone, this was more subdued than the effect of KI. This is further evidence that cys renders the LCS surface more electrochemically active, even diminishing the inhibitive effect of KI on the anodic metal dissolution and thus confirming that the Fe–cys complex stimulates the anodic reaction.

4. Conclusions

The effect of cysteine on the corrosion of low carbon steel in 0.5 M H_2SO_4 was studied in the concentration range of 0.0001–0.005 M. The compound exerted an inhibiting effect on the cathodic reaction and at the same time catalyzed the anodic reaction at all concentrations. Cys was found to accelerate the LCS corrosion process at low concentrations because the catalytic effect of the Fe–cys complex on anodic reaction surpassed the cathodic inhibiting effect. The protective effect was further enhanced by removal of oxygen from the solution.

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References

[1] G. Mu, X. Li, J. Coll. Interface Sci. 289 (2005) 184.
[2] Y. Feng, K.S. Siow, W.K. Teo, A.K. Hsieh, Corros. Sci. 41 (1999) 829.
[3] L. Larabi, Y. Harek, O. Benali, S. Ghalem, Prog. Org. Coat. 54 (2005) 256.
[4] E.E. Oguzie, C. Unaegbu, C.N. Ogukwe, B.N. Okolue, A.I. Onuchukwu, Mater. Chem. Phys. 84 (2004) 363.
[5] E.E. Oguzie, G.N. Onuoha, A.I. Onuchukwu, Mater. Chem. Phys. 89 (2004) 305.
[6] K.F. Khaled, Electrochim. Acta 48 (2003) 2493.
[7] A. Popova, M. Christov. Corros. Sci. 48 (2006) 3208.
[8] A. Fragnani, G. Trabanelli, Corrosion 55 (1999) 653.
[9] H.L. Wang, R.B. Liu, J. Xin, Corros. Sci. 46 (2004) 2455.
[10] M.S. Morad, A. El-Hagag, A. Hermas, M.S. Abdel Aal, J. Chem. Technol. Biotechnol. 77 (2002) 486.
[11] W.A. Badawy, K.M. Ismail, A.M. Fathi, Electrochim. Acta 51 (2006) 4182.
[12] A.B. Silva, S.M.L. Agostinho, O.E. Barcia, G.G.O. Cordeiro, E. D'Elia, Corros. Sci. 48 (2006) 3668.
[13] E.E. Oguzie, Y. Li, F.H. Wang, J. Coll. Interf. Sci. 310 (2007) 90.
[14] J. Reynaud, B. Malfoy, J. Electroanal. Chem. 114 (1980) 195.
[15] T. Ralph, M. Hitchman, J. Millington, F. Walsh, J. Electroanal. Chem. 375 (1994) 1.
[16] E. Farkas, I. Sovago, Amino Acids, Peptides and Proteins, vol. 33, The Royal Society of Chemistry, 2002, p. 318.
[17] G. Berthon, Pure Appl. Chem. 67 (1995) 1117.