

Inhibiting effect of thiosemicarbazide on cold rolled carbon steel

S. A. Hossain* and A. I. Almarshad

The inhibitive effect of thiosemicarbazide on the corrosion of cold rolled carbon steel in acidic media has been studied. For this investigation, a standard potentiodynamic polarisation technique was used to determine the corrosion rate and the inhibition efficiency and also to find out which adsorption isotherm governs the inhibition process. For this purpose, thiosemicarbazide was added to 0.5M H₂SO₄ in four concentrations ranging between 1×10^{-4} M and 1×10^{-2} M. Analysis of the experimental data shows that concentration has a strong influence on the efficiency of inhibition. Thermodynamics studies confirm that the inhibitor adsorption follows the Langmuir adsorption isotherm.

Keywords: Cold-rolled carbon steels, Potentiodynamic polarisation, Corrosion inhibition, Thiosemicarbazide, Adsorption

Introduction

The corrosion of iron and steel is a fundamental academic and industrial concern that has received a considerable amount of attention.¹ The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media.² Progress in this field has been phenomenal in recent years as shown by the literature.³

The corrosion of carbon steels, especially of thinner sections and in more severe conditions such as marine and industrial environments, justifies attention because of their use in automobiles, offshore structures, ship-building, oil and natural gas transportation and general engineering applications.

Acid solutions are widely used in industry, in applications such as acid pickling, acid cleaning, acid descaling and oil well acidising. Because of the severe aggressivity of acid solutions, a considerable amount of effort has been expended on the study of organic compounds as corrosion inhibitors⁴ and these are commonly used to reduce the corrosive attack on metallic materials. The best known inhibitors of corrosion in acids are organic compounds containing N and S atoms in their molecular structure through which they adsorb on the metal.⁵⁻⁸ Several authors⁹⁻¹⁴ have investigated the influence of organic compounds containing sulphur as inhibitors for the corrosion of steel in acidic solutions. The data show that most organic inhibitors act by adsorption on the metal surface. The most important prerequisites for compounds to be efficient inhibitors are that the substances should form compact barrier films, should be chemisorbed on the metal surface, and that the barrier layer thus formed should increase the inner layer thickness.¹⁵

In the present investigation, a detailed study has been conducted on the corrosion characteristics of EN10130 cold rolled carbon steel, Grade FeP01, in 0.5M H₂SO₄ solution. The effects of thiosemicarbazide on this steel have also been investigated in order to determine its efficiency as a corrosion inhibitor and to learn more about the mechanism of inhibition in this steel. Moreover, attempts have been made to establish which adsorption isotherm is followed in its action as an inhibitor.

Experimental

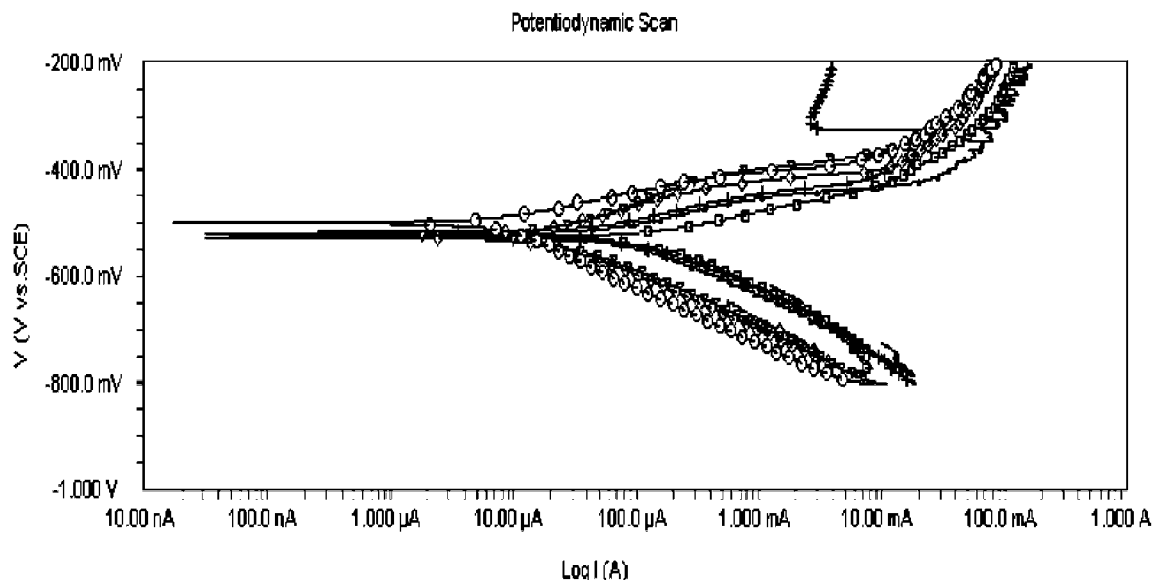
Cold-rolled carbon steel to the EN10130 specification, Grade FeP01, was obtained from the Saudi Iron and Steel Company (Hadeed) with the following chemical composition (wt-%): 0.050 C; 0.20 Mn; 0.02 S; 0.006 P; 0.023 Si; 0.046 Al; 0.04 Cu; 0.02 Ni; 0.02 Cr; 0.002 Mo; 0.005 B; 0.006 (Nb + V + Ti); balance Fe.

Samples with dimensions of 10 mm × 10 mm × 5 mm were cut from the source material and were prepared as working electrodes by mechanical grinding into the form of a cuboid. An insulated copper wire was attached to one surface of each specimen using low melting point solder. The specimens were mounted in epoxy resin in such a way that only the surface opposite the electrical connection, with an exposed surface area of 1 cm², was in contact with the solution. This surface was polished mechanically using progressively finer grades of emery paper to a 600 grit finish, followed by final polishing using alumina powder. Before use, the polished surface was thoroughly washed and degreased in ethanol then dried at room temperature.

For polarisation studies, the test solution was 0.5M H₂SO₄ prepared from laboratory grade H₂SO₄ and distilled water. The inhibitor used was thiosemicarbazide at concentrations ranging from 1×10^{-4} to 1×10^{-2} M. The electrochemical cell consisted of a 600 mL glass beaker fitted with a Perspex lid having openings for the electrodes. A conventional three-electrode assembly

Corrosion Research Group, AERI, King Abdulaziz City for Science and Technology, P.O. Box 6086, Riyadh – 11442, Saudi Arabia

*Corresponding author, email asiful_s@yahoo.co.in



1 Potentiodynamic polarisation curves for carbon steel in 0.5M H_2SO_4 solution containing various concentrations of thiosemicarbazide: (\square) 0.5M H_2SO_4 ; (+) $5 \times 10^{-4}\text{M}$ thiosemicarbazide + 0.5M H_2SO_4 ; (∇) $5 \times 10^{-3}\text{M}$ thiosemicarbazide + 0.5M H_2SO_4 ; (\blacktriangle) $1 \times 10^{-4}\text{M}$ thiosemicarbazide + 0.5M H_2SO_4 ; (\diamond) $1 \times 10^{-3}\text{M}$ thiosemicarbazide + 0.5M H_2SO_4 ; (\circ) $1 \times 10^{-2}\text{M}$ thiosemicarbazide + 0.5M H_2SO_4

was used, with the carbon steel sample as the working electrode, a graphite rod as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode to which all potentials were referred. The potentiostat was made by Gamry Instruments and was used with that company's Windows-based Framework version 4.21 (2002) corrosion software.

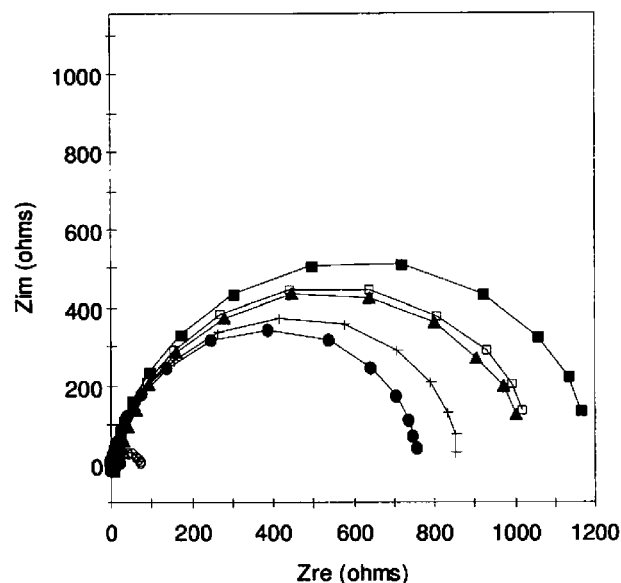
Before each experiment, the electrochemical cell was thoroughly cleaned then washed with distilled water. The quantity of electrolyte used for each polarisation experiment was 250 mL. Freshly polished samples (working electrodes) were placed in the electrochemical cell and immersed in the test solution for 60 min, by which time the steady-state open-circuit potential had been obtained. Then potentiodynamic cathodic and anodic polarisation curves were determined using a scan rate of 0.2 mV s^{-1} . The curves that were obtained are shown in Fig. 1. Values of I_{corr} were calculated from these curves using the Tafel extrapolation method.

Electrochemical impedance measurements were carried out at the open circuit potential using an EG&G Princeton Applied Research Model 263A Potentiostat/Galvanostat, a Model 5210 Lock-in Amplifier, the Power Suite 2.35.2 corrosion software and the Power sine 2.20.0 impedance software from the same company. Again, a conventional three-electrode assembly was used, with a graphite rod as the auxiliary electrode and a saturated calomel reference electrode. Following initial immersion of the specimen, a stabilisation period of 20 h was allowed for the open circuit potential to stabilise before the impedance measurements were commenced. A 10 mV peak-to-peak sine wave over an ac frequency range extending from 100 kHz to 100 MHz was used for the impedance measurements. The results obtained are shown as Nyquist impedance diagrams in Fig. 2.

Results and discussion

The potentiodynamic polarisation curves of Fig. 1 display shifts towards lower values of I_{corr} as the

concentration of thiosemicarbazide inhibitor added to the 0.5M H_2SO_4 was increased progressively to 10^{-2}M . Some tendency for the E_{corr} value to shift towards more noble values with increasing inhibitor concentration is also evident. The results summarised in Table 1 show, for example, that the E_{corr} value for steel increases from -528 mV in uninhibited acid to -503 mV in acid containing 10^{-2}M thiosemicarbazide. This shift indicates that addition of the inhibitor mainly affects the anodic process. From Table 1, it is also apparent that the I_{corr} values for uninhibited acid and for acid containing 10^{-2}M thiosemicarbazide are 195 and 12.70 mA cm^{-2} , respectively. This implies that the addition of thiosemicarbazide reduces the corrosion rate of carbon steel in sulphuric acid.



2 Nyquist impedance diagrams of carbon steel in 0.5M H_2SO_4 solution containing various concentrations of thiosemicarbazide: (\circ) 0; (\bullet) $1 \times 10^{-4}\text{M}$; (\times) $5 \times 10^{-4}\text{M}$; (\blacktriangle) $1 \times 10^{-3}\text{M}$; (\square) $5 \times 10^{-3}\text{M}$; (\blacksquare) $1 \times 10^{-2}\text{M}$

Values of inhibitor efficiency were calculated using the expression

$$\text{Inhibitor efficiency, } \eta(\%) = 100 \times \theta \quad (1)$$

where θ is the surface coverage, expressed as^{16–20}

$$\theta = (I_0 - I)I_0 \quad (2)$$

where I_0 is the corrosion rate of the uninhibited system, i.e. without inhibitor; and I is the corrosion rate of the inhibited system, i.e. with inhibitor.

The results are included in Table 1 and show that even a very low concentration of inhibitor provides an appreciable degree of protection, the inhibitor efficiency being 64.82% for a thiosemicarbazide concentration of 10^{-4} M, rising to 93.48% with a concentration of 10^{-2} M. Thus, the level of protection can be correlated with the increasing degree of surface coverage, supporting the conclusion that thiosemicarbazide inhibits the corrosion process through surface adsorption.

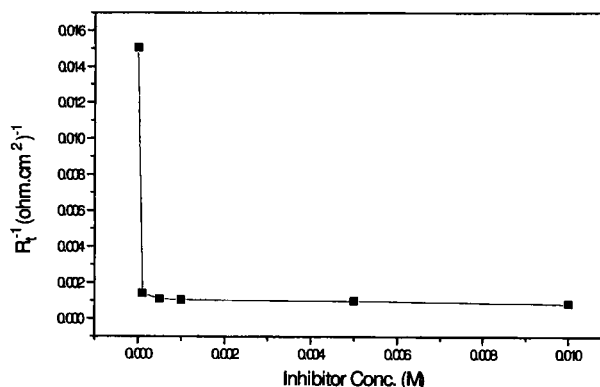
The corrosion behaviour of the carbon steel in acidic solutions containing thiosemicarbazide was also investigated by electrochemical impedance spectroscopy at room temperature after immersion for 20 h. Nyquist plots for the carbon steel in uninhibited acid solution and in inhibited solutions containing various concentrations of thiosemicarbazide are shown in Fig. 2. The impedance diagrams obtained are not perfect semicircles and this is attributed to frequency dispersion.^{21,22} The charge transfer resistance (R_t) values were calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru *et al.*²³ To obtain the double layer capacitance (C_{dl}), the frequency at which the imaginary component of the impedance was maximum, ($-Z''_{max}$), was identified and C_{dl} values were obtained from the equation

$$f(-Z''_{max}) = 1/2\pi C_{dl} R_t \quad (3)$$

The inhibition efficiency of the corrosion of steel was calculated from the charge transfer resistance as follows

$$\eta(\%) = [(R_{t \text{ corr}}^{-1} - R_{t \text{ corr (inh)}}^{-1})/R_{t \text{ corr}}^{-1}] \times 100 \quad (4)$$

where $R_{t \text{ corr}}$ and $R_{t \text{ corr (inh)}}$ are the charge transfer resistance values in the absence and presence of



3 Reciprocal charge transfer resistance for carbon steel in 0.5M H_2SO_4 containing different concentrations of thiosemicarbazide

inhibitor, respectively. The impedance parameters determined in this way are given in Table 2. They show that as the thiosemicarbazide concentration increases, the R_t values increase, but the C_{dl} values tend to decrease. This decrease in C_{dl} values is due to the adsorption of thiosemicarbazide on the metal surface. As observed previously, the corrosion potential shifts in the positive direction when the concentration of inhibitor increases, which is indicative of anodic control.

From the results of the electrochemical impedance spectroscopy study, curves can be established for R_t^{-1} and C_{dl} versus the concentration of the thiosemicarbazide inhibitor, as shown in Figs. 3 and 4, respectively. It is evident that the shape of these two curves is the same, so it can be concluded that the more the concentration of inhibitor increases, the more the charge transfer resistance increases and the more the double layer capacitance decreases.

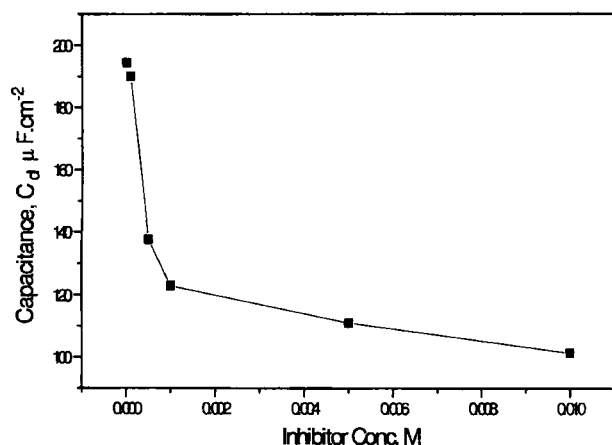
From Fig. 5, it can be seen that inhibition efficiencies obtained from electrochemical impedance spectroscopy studies were higher than those determined from the potentiodynamic polarisation measurements. This is attributed to the fact that the impedance measurements were undertaken following immersion of the carbon steel samples in the test environment for 20 h, whereas the period allowed for stabilisation of the potential

Table 1 Potentiodynamic polarisation parameters for corrosion of carbon steel in 0.5M H_2SO_4 containing different concentrations of thiosemicarbazide

Concentration, M	E_{corr} , Mv	I_{corr} , $\mu A \text{ cm}^{-2}$	Surface coverage, θ	Inhibitor efficiency, η , %
0	-528	195
1×10^{-4}	-522	68.60	0.6482	64.82
5×10^{-4}	-519	49.90	0.7441	74.41
1×10^{-3}	-517	28.50	0.8538	85.38
5×10^{-3}	-514	19.70	0.8989	89.89
1×10^{-2}	-503	12.70	0.9348	93.48

Table 2 Impedance parameters for corrosion of carbon steel in 0.5M H_2SO_4 containing different concentrations of thiosemicarbazide

Concentration, M	E_{corr} , mV	R_t , $\Omega \text{ cm}^2$	C_{dl} , $\mu F \text{ cm}^{-2}$	Inhibitor efficiency, η , %
0	-528	66.44	194.3	...
1×10^{-4}	-522	710.19	189.9	90.64
5×10^{-4}	-519	914.19	137.8	92.73
1×10^{-3}	-517	952.11	122.9	93.02
5×10^{-3}	-514	1003.40	111.0	93.37
1×10^{-2}	-503	1189.36	101.4	94.41



4 Double layer capacitance for carbon steel in 0.5M H₂SO₄ containing different concentrations of thiosemicarbazide

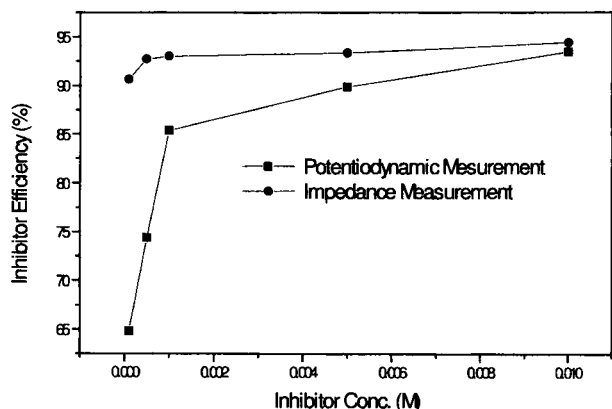
before the polarisation measurements was only 1 h. It is concluded that adsorption equilibrium was achieved in the impedance case due to the longer exposure time.

The quality of fit of the surface coverage values (θ) was tested graphically against various adsorption isotherms, including the Bockris–Swinkel isotherm,²⁴ the Flory–Huggins isotherm,²⁵ the Langmuir isotherm²⁶ and the Temkins isotherm,²⁷ in order to establish which one best fits the experimental data. The data failed to fit the Bockris–Swinkel isotherm, the Flory–Huggins isotherm and the Temkins isotherm. However, a plot of C_{inh}/θ versus C_{inh} yielded a straight line, as shown in Fig. 6, providing clear evidence that the adsorption process of thiosemicarbazide in 0.5M H₂SO₄ solution follows the Langmuir adsorption isotherm, which can be expressed as

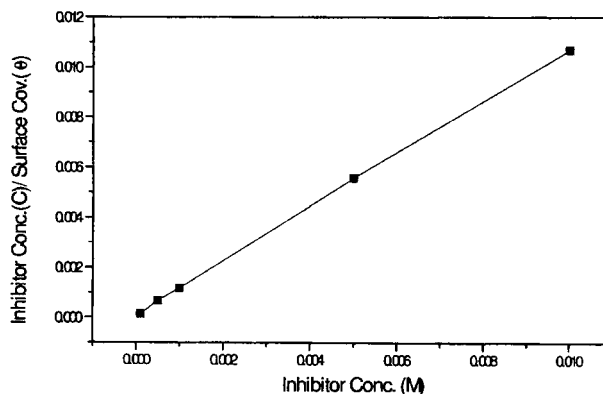
$$\frac{C_{inh}}{\theta} = C_{inh} + \frac{1}{K} \quad (5)$$

where C_{inh} is the concentration of inhibitor and K is the adsorption coefficient. This is consistent with earlier work²⁸ showing that the inhibition of thiosemicarbazide derivatives on mild steel obeys the Langmuir adsorption isotherm.

From the Langmuir adsorption isotherm plot of C_{inh}/θ versus C_{inh} , the free energy of adsorption (ΔG_{ads}^0) was calculated from the intercept ($1/K$) of the straight line.



5 Inhibitor efficiency for carbon steel in 0.5M H₂SO₄ containing different concentrations of thiosemicarbazide: (■) potentiodynamic measurement; (●) impedance measurement



6 Langmuir adsorption plot for carbon steel in 0.5M H₂SO₄ containing different concentrations of thiosemicarbazide

The adsorption coefficient K is temperature dependent and is related to the Gibbs free energy of the process by

$$K = \exp(-\Delta G_{ads}^0/RT)$$

The value of ΔG_{ads}^0 characterises the spontaneity of the adsorption process under the experimental conditions used. Generally, values of ΔG_{ads}^0 of up to -20 kJ mol^{-1} are consistent with electrostatic interaction between the charged molecules and the charged metal (physical adsorption), while those more negative than -40 kJ mol^{-1} involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption).^{29,30} The ΔG_{ads}^0 value calculated from the above equation was $-11.102 \text{ kJ mol}^{-1}$. This indicates that the adsorption is of the physical type. The low and negative value of ΔG_{ads}^0 indicates the spontaneous adsorption of inhibitor on the surface of metal, as has been reported in the literature for the case of mild steel.³¹

Conclusions

1. Polarisation curves for cold rolled carbon steel in 0.5M H₂SO₄ solutions containing additions of thiosemicarbazide display shifts to lower values of corrosion current I_{corr} which increase as the concentration of inhibitor increases. This shows that thiosemicarbazide additions decrease the corrosion rate of carbon steel.

2. The addition of thiosemicarbazide to 0.5M H₂SO₄ solution shifts the corrosion potential E_{corr} to more noble values. This indicates that thiosemicarbazide is an anodic inhibitor.

3. The inhibitor efficiency and degree of surface coverage increased with increasing concentration of thiosemicarbazide up to the maximum concentration investigated of 10^{-2} M .

4. The adsorption of thiosemicarbazide on the carbon steel in 0.5M H₂SO₄ solution followed the Langmuir adsorption isotherm.

5. The free energy of adsorption (ΔG_{ads}^0) displayed a negative value indicative of spontaneous physical adsorption of the inhibitor on the steel surface.

References

1. H. H. Uhlig and R. W. Revie: 'Corrosion and corrosion control'; 1995, New York, Wiley.
2. G. Trabacelli: *Corrosion*, 1991, **47**, 410.
3. G. Schmitt: *Br. Corros. J.*, 1984, **19**, 165.

4. B. G. Clumpley: 'Chemical inhibitors for corrosion control'; 1990, Cambridge, Royal Society of Chemistry.
5. M. A. Quraishi, M. A. Wajid Khan and M. Ajmal: *Anti-Corros. Methods Mater.*, 1996, **43**, 5.
6. S. Muralidharan and S. V. Iyer: *Anti-Corros. Methods Mater.*, 1997, **44**, 100.
7. N. Al-Andis *et al.*: *Corros. Prev. Control*, 1995, **42**, 13.
8. B. Hammonite *et al.*: *Corrosion*, 1995, **51**, 41.
9. A. E. Makrides and N. Hackerman: *Ind. Eng. Chem. Part 1*, 1955, **47**, 1773.
10. L. Felloni: *Metall. Ital.*, 1953, **46**, 70.
11. L. Cavallaro and L. Felloni: *Metall. Ital.*, 1952, **44**, 356.
12. L. Cavallaro, L. Felloni and G. Trabanelli: Proc. 1st Eur. Symp. on 'Corrosion inhibitors', Ferrara, Italy, 1960, 111.
13. L. Cavallaro, L. Felloni, G. Trabanelli and F. Pullidori: *Electrochim. Acta*, 1964, **9**, 485.
14. R. Driver and R. J. Meakins: *Br. Corros. J.*, 1974, **9**, 233.
15. S. Muralidharan *et al.*: *J. Electrochem. Soc.*, 1995, **142**, 1478.
16. L. I. Antropov: *Prot. Met.*, 1977, **13**, 323.
17. H. Fischer: Proc. 1st Eur. Symp. on 'Corrosion inhibitors', Ferrara, Italy, 1960, University of Ferrara, Suppl. No. 3.
18. T. V. Malysheva *et al.*: *Prot. Met.*, 1976, **12**, 300.
19. D. Altura and K. Nobe: *Corrosion*, 1973, **29**, 433.
20. A. R. Silveira *et al.*: *Bras. Eletroquim. Eletroanal.*, Brazil, 1984, 271.
21. F. Mansfeld, M. W. Kendig and S. Tsai: *Corrosion*, 1981, **37**, 301.
22. F. Mansfeld, M. W. Kendig and S. Tsai: *Corrosion*, 1982, **38**, 570.
23. T. Tsuru, S. Haruyama and G. Gijutsu: *J. Jpn Soc. Corros. Eng.*, 1978, **27**, 573.
24. J. O'M. Bockris and D. A. J. Swinkel: *J. Electrochem. Soc.*, 1964, **111**, 736.
25. H. P. Dhar, B. E. Conway and K. M. Joshi: *Electrochim. Acta*, 1973, **18**, 789.
26. R. A. Alberty and R. J. Silbey: 'Physical chemistry', 2nd edn, 845; 1997, New York, John Wiley & Sons.
27. A. N. Frumkin: *J. Phys. Chem.*, 1925, **166**, 466.
28. S. Sayed Azim *et al.*: *Br. Corros. J.*, 1998, **33** (4), 297–301.
29. E. Kamis, F. Bellucci, R. M. Latanision and E. S. H. El-Ashry: *Corrosion*, 1991, **47**, 677.
30. F. Donahue and K. Nobe: *J. Electrochem. Soc.*, 1965, **112**, 886.
31. A. E. Stoyanova, E. I. Sokolova and S. N. Raicheva: *Corros. Sci.*, 1997, **39**, 1595.