Inhibiting Properties of Morpholine as Corrosion Inhibitor for Mild Steel in 2N Sulphuric Acid and Phosphoric Acid Medium

K. JAYANTHI¹, M. SIVARAJU², AND K. KANNAN^{3*}

¹Department of Chemistry, Queen Mary's College, Chennai 600004, Tamilnadu, India

jayanthi.goutham@gmail.com

²Department of Chemistry, Muthayammal Technical Campus, Rasipuram 637408, Tamilnadu, India

Sivarajuviji06@gmail.com

³Department of Chemistry, Government College of Engineering, Salem 636 011, India

kannan_k2002@yahoo.co.in

Received 11 October 2011; Accepted 25 December 2011

Abstract: The inhibition effect of morpholine on the corrosion of mild steel in 2N sulphuric acid and phosphoric acid has been studied by mass loss and polarization techniques between 302K and 333K. The inhibition efficiency increased with increase in concentration. The corrosion rate increased with increase in temperature and decreased with increase in concentration of inhibitor compared to blank. The adsorption of inhibitor on the mild steel surface has been found to obey Temkin's adsorption isotherm. Potentiostatic polarization results reveal that morpholine act as mixed type inhibitor. The values of activation energy (E_a), free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH), and entropy of adsorption (ΔS) were also calculated.

Keywords: Mild Steel; Sulphuric acid; phosphoric acid; Corrosion inhibition; Temkin's adsorption isotherm; Potentiostatic polarization; Morpholine.

Introduction

Phosphoric acid is a major chemical product, which has many important uses, especially in the production of fertilizers. Most of the acid is produced from phosphate rock by wet process. Generally nickel-base alloys and stainless steel are frequently used in many parts of the wet process and a considerable quantity of data has been published about the resistance of these materials to corrosion by phosphoric acid solution¹⁻⁴. Most of the previous studies were focused on the inhibition of stainless steel or chromium-nickel steel in hydrochloric acid or sulphuric acid solutions using organic compounds containing nitrogen, sulphur and oxygen atoms as corrosion inhibitors^{5,6}.

Organic inhibitors are widely used in various industries. Among them, heterocyclic compounds comprise a potential class of inhibitors. There is wide consideration in the literature regarding corrosion inhibition studies by nitrogen containing heterocycles⁷⁻¹⁰. Heterocyclic compounds containing nitrogen and sulphur atoms are of particular

importance as they often provide excellent inhibition compared with compounds containing only nitrogen or sulphur¹¹⁻¹². The corrosion inhibiting property of these compounds is attributed to their molecular structure. These compounds contain π electrons and heteroatom, which induce greater adsorption of the inhibition molecules onto the mild steel surface.

So, in this investigation, the corrosion of mild steel in 2N phosphoric acid and 2N sulphuric acid solutions in the absence and presence of morpholine at 302 K to 333K has been studied by mass loss method and polarization techniques. It is aimed to predict the corrosion rate, inhibition efficiency on mild steel corrosion and the thermodynamic feasibility of inhibition via surface coverage on mild steel by adsorbed morpholine at various temperatures. The adsorption characteristic of morpholine was studied in order to access the adsorption isotherm(s).

Experimental Methods

Mass loss measurement

Mild steel specimens were cut to size of 5 cm x 1 cm from the mild steel sheets having the following percentage composition as shown below. The surface of specimens were polished with emery papers ranging from 110 to 410 grades and degreased with trichloroethylene specimens were dried and stored in vacuum desiccators containing siligal and then initially weighed in an electronic balance. After that the specimens were suspended with the help of PTFE, threads and glass rod in 100ml beaker containing acid in the presence and absence of inhibitors. The specimens were removed after 4 hours exposure period, washed with water to remove any corrosion products and finally washed with acetone. After that they were dried and reweighed. Mass loss measurements were carried out in 2N phosphoric acid and 2N sulphuric acid with Morpholine in the concentration range of 1 % to 5% as inhibitors and the temperature between 302 K and 333 K for an immersion period of 4 hours. All the solutions were prepared with AR grade chemicals in double distilled water. Mass loss measurements were performed as per ASTM method described previously¹³⁻¹⁵.

Composition of mild steel

Element	Fe	Ni	Mo	Cr	S	P	Si	Mn	C
Composition (%)	99.686	0.013	0.015	0.043	0.014	0.009	0.007	0.196	0.017

Potentiostatic Polarization measurements

Polarization measurements were carried out in a conventional three-electrode cell. Mild steel strips coated with lacquer except for an exposed area of 1 cm² were used as the working electrode. The saturated calomel electrode and the platinum foil were used as reference and counter electrodes respectively. The potentiostatic polarization measurement was carried out using BAS – 100 a model instrument. The potential of the test electrode was measured with respect to SCE and platinum electrode was used as auxiliary electrode and the experiment were carried out at 302K to 333K.

Table 1 Corrosion parameters of *Morpholine* on mild steel in 2N sulphuric acid and 2N phosphoric acid by weight loss method.

Temp. (K)	Conc. of Inhibitor (%)	2N Sulphuric acid			2N Phosphoric acid		
		CR (mmpy)	SC (θ)	IE (%)	CR (mmpy)	SC (θ)	IE (%)
302	Blank	63.7496	-----	-----	15.6031	-----	-----
	1	34.4753	0.4592	45.92	15.1573	0.9029	90.29
	2	29.4229	0.5385	53.85	12.2595	0.9212	92.12
	3	28.0112	0.5606	56.06	08.1730	0.9476	94.76
	4	25.7822	0.5956	59.56	06.5384	0.9581	95.81
	5	20.0611	0.6853	68.53	04.9038	0.9686	96.86
313	Blank	114.8682	-----	-----	53.7934	-----	-----
	1	35.6641	0.6895	68.95	27.1196	0.4959	49.59
	2	30.5374	0.7342	73.42	21.8443	0.5939	59.39
	3	22.1415	0.8072	80.72	19.3924	0.6395	63.95
	4	17.5349	0.8474	84.74	14.7858	0.7251	72.51
	5	15.0087	0.8693	86.93	07.3557	0.8633	86.33
323	Blank	143.6223	-----	-----	72.8142	-----	-----
	1	60.7033	0.5773	57.73	52.4559	0.2776	27.76
	2	46.2148	0.6782	67.82	38.2646	0.4745	47.45
	3	36.7786	0.7439	74.39	31.5776	0.5663	56.63
	4	32.6178	0.7729	77.29	21.9185	0.7040	70.40
	5	28.3826	0.8024	80.24	16.5689	0.7724	77.24
333	Blank	300.9160	-----	-----	89.0860	-----	-----
	1	158.7053	0.4726	47.26	68.4305	0.2316	23.16
	2	140.9476	0.5316	53.16	52.0844	0.4078	40.78
	3	98.4478	0.6728	67.28	38.7847	0.5646	56.46
	4	85.7425	0.7151	71.51	32.1501	0.6305	63.05
	5	64.8641	0.7844	78.44	22.5129	0.7472	74.72

Results and Discussion

Mass loss Studies

Table 1 shows the value of inhibition efficiency [IE%] surface coverage (θ) and corrosion rate obtained at different concentration of the inhibitors in 1N hydrochloric acid solutions for an immersion period of 3 hours. From the mass value, the inhibition efficiency [IE%] and surface coverage (θ) were calculated using the following equation¹⁶⁻¹⁸.

Inhibitor efficiency

$$(I \%) = \frac{W_b - W_i}{W_b} \times 100 \quad [1]$$

Surface coverage

$$(\theta) = \frac{W_b - W_i}{W_b} \quad [2]$$

Where W_u and W_i are the corrosion rates for mild steel in the absence and presence of inhibitor respectively at the same temperature.

It could be seen from the table that the addition of inhibitor to the acid has reduced the corrosion rate. The inhibition efficiency increased with increase in concentration of inhibitors and increased with temperature from 302 K to 313 K and then decreased in 2N sulphuric acid. The inhibition efficiency increased with increase in concentration of inhibitors and decreased with temperature from 313 K to 333 K in 2N phosphoric acid. The values of the corrosion rate and inhibition efficiency of the inhibitors are known to depend on the molecular structure of the inhibitors.

The maximum inhibition efficiency of morpholine was found to be 86.93% and 96.86% in 2N sulphuric acid and 2N phosphoric acid with 5% of inhibitor concentration respectively at 313K and 302K and then decreased. Inhibition efficiency of morpholine in 2N phosphoric acid solution was found to be greater than 2N sulphuric acid solution because in 2N phosphoric acid solution phosphate ions probably form a bridge between the protonated molecules of inhibitors and facilitate the adsorption of inhibitor molecules, while in 2N sulphuric acid this bridge is not formed due to Low charge to mass ratio, as such that adsorption of molecules on the surface of the metal is mostly physical and gives low inhibition efficiency¹⁹⁻²⁰

Thermodynamic Consideration

Table 2 shows that the calculated values of activation energy (E_a) and free energy of absorption (ΔG_{ads}) for mild steel corrosion in 2N sulphuric acid and 2N phosphoric acid with and without inhibitors at 313K to 333K. Energy of activation (E_a) was calculated from the slopes of plots of $\log p$ versus $1/T$ in Fig. 1&2 and also calculated from Arrhenius equation²¹⁻²².

$$\log P_2/P_1 = E_a/2.303 R [1/T_1 - 1/T_2] \quad [3]$$

where P_1 and P_2 are the corrosion rates at temperatures T_1 and T_2 respectively. E_a value was found to be 41.73KJ/mole and 21.86 in 2N sulphuric acid and 2N phosphoric acid at 313K to 333 K. The E_a values for 2N sulphuric acid and 2N phosphoric acid containing inhibitors are found to be higher than that of without inhibitors. These higher values of E_a indicate the physical adsorption of the inhibitors on metal surface²³⁻²⁴ and also indicate that besides, adsorption of these inhibitors increases the activation energy of the corrosion process. The E_a values are calculated from the slopes of Arrhenius plot and by using equation-3 are approximately almost similar.

Figure 1. Arrhenius Plot for Corrosion in 2N Sulphuric acid with Morpholine.

Figure 2. Arrhenius Plot for Corrosion in 2N Phosphoric acid with Morpholine.

Table 2. Thermodynamic parameters for mild steel in 2N sulphuric acid and 2N phosphoric acid with *Morpholine*.

Inhibitor	Conc of Inhibitor (%)	Ea (from eqn,1) KJ/Mol	Ea (from plot) KJ/	ΔG_{ads} KJ/Mole				ΔH KJ/mol	ΔS KJ/mol/k
				302K	313K	323K	333K		
Inhibitor+ 2N H_2SO_4	Blank	41.73	40.21	-----	-----	-----	-----	36.75	-----
	1	64.69	62.10	-9.6738	-12.5278	-11.6227	-10.8159	59.71	0.2058
	2	66.27	65.78	-8.7314	-11.2920	-10.9263	-9.5509	61.29	0.2069
	3	64.66	64.23	-7.9377	-11.3191	-10.6990	-10.0738	37.68	0.1336
	4	68.78	68.90	-7.5758	-11.3055	-10.3519	-10.2338	37.00	0.1306
	5	63.42	61.25	-7.9974	-11.1943	-10.2269	-10.2394	58.44	0.1954
Inhibitor + 2N H_3PO_4	Blank	21.86	22.20	-----	-----	-----	-----	16.88	-----
	1	40.10	41.46	-15.6832	-10.4091	-8.2174	-7.7993	35.12	0.1288
	2	37.65	37.30	-14.5176	-9.6372	-8.6501	-8.1677	32.67	0.1245
	3	30.03	30.56	-14.5949	-9.0845	-8.5578	-8.7974	25.05	0.1016
	4	33.66	34.12	-14.4617	-9.3682	-9.3896	-8.7609	28.68	0.1124
	5	48.47	49.15	-14.6532	-11.0595	-9.7450	-9.6642	43.49	0.1596

The free energy of adsorption (ΔG_{ads}) at different temperatures was calculated from the following equation ²⁵.

$$\Delta G_{(ads)} = -RT \ln (55.5 K) \quad [4]$$

where K is given by

$$K = \theta / C(1 - \theta) \quad [5]$$

K = equilibrium constant

θ = Surface coverage;

where θ is surface coverage on the metal surface, C is concentration of inhibitor in mole/lit and K is equilibrium constant. 55.5 is concentration of water (mol/lit).

The negative values of (ΔG_{ads}) indicated the spontaneous adsorption of the inhibitors. This is usually characteristic of strong interaction with the metal surface. It is found that the ΔG_{ads} values are more positive than (-40 KJ/mole⁻¹) indicating that inhibitors is physically adsorbed on the metal surface ²⁶⁻²⁷.

The free energy of adsorption (ΔG_{ads}) of Morpholine in 2N sulphuric acid and 2N phosphoric acid can be calculated from the equation (4) at 303K to 333K, while the

enthalpy of adsorption (ΔH) and entropy of adsorption (ΔS) were also calculated from the following equations (28).

$$\Delta H^0 = E_a - RT \quad [6]$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad [7]$$

Table 2 shows thermodynamic data obtained in this study. It could be seen from the table the activation energy increases linearly with increasing efficiency of the inhibitor.

Ideally, a corrosion inhibitor is a substance that greatly increases the activation energy of corrosion. The negative values of (ΔG_{ads}) indicate the spontaneous adsorption of the inhibitor on the surface of mild steel. It's also observed that (ΔS) increases with increasing efficiency of the inhibitors. This is opposite to that we expect, since the adsorption is an exothermic process and is always accompanied by a decrease in entropy. Ateya et. Al.²⁹ have described this situation as due to the adsorption of the organic compound, which is accompanied by desorption of water molecules from the surface. While the adsorption process is believed to be exothermic and associated with a decrease in entropy of the solute, the opposite is true for the solvent. Therefore, this gain in entropy that accompanied the substitutional adsorption process is attributed to the increase in solvent entropy.

Adsorption isotherms

The electrochemical process on the metal surface are likely to be closely to the adsorption of the inhibitors³⁰ and the adsorption is known to depend on the chemical structure of the inhibitors^{31, 32}. The adsorption of the inhibitors molecules from aqueous solutions can be regarded as quasi-substitution process³³ between the organic compound in the aqueous phase, org (aq) and water molecules at the electrode surface, H₂O (s).

Where x (the size ratio) is the number of water molecules displaced by one molecule of inhibitor.

Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions. The most frequently used are those of Langmuir, Frumkin, Parsons, Temkin, Flory –huggins and Bockris –Swinkels^{34,35}. All these isotherms are of the general form:

$$f(\theta, x) \exp(-a\theta) = K C$$

Where f (θ,x) is the configurational factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm³⁶.

The mechanism of inhibition of corrosion is generally believed to be due to the formation and maintenance of a protective film on the metal surface. The plot of surface coverage (**θ**) obtained by mass loss method versus **log C** at different concentrations of the inhibitors

shows a straight line indicating that the adsorption of the inhibitor from acid on mild steel surface follows the Temkin's adsorption isotherm²⁵. This also points out that the corrosion inhibition by these compounds being a result of their adsorption on the metal surface. Fig.3 and 4 show the Temkin's adsorption isotherm plots for Morpholine with 2N sulphuric acid and 2N phosphoric acid.

Figure 3. Temkin's adsorption isotherm for corrosion behaviour of mild steel in 2N Sulphuric acid with Morpholine.

Potentiostatic Polarization studies

The Polarization behavior of mild steel functioning as cathode as well as anode in the test solution is shown in Fig.5 and 6 for 2N sulphuric acid and 2N phosphoric acid with Morpholine at room temperature (302K). The electrochemical data obtained are shown in Table 3. It is evident that Morpholine bring about considerable polarization of cathode as well as anode. It was therefore inferred that the inhibitive action is of a mixed type and the cathodic and anodic Tafel slopes increased with increasing inhibitor concentration and the increase is predominant in the case of the former indicating that the cathodic inhibition is dominating through the inhibitive action is of mixed nature. The non-constancy of Tafel slopes for different inhibitor concentration reveals that the inhibitor act through their interference in the mechanism of the corrosion processes at the cathode as well as anode.

The corrosion Parameters deduced from Tafel polarization such as corrosion current I_{corr} , corrosion potential E_{corr} , Tafel constant b_a and $-b_c$ and inhibition efficiency are given in Table 3. The i_{corr} values were decreased with increasing concentration of the inhibitors. The inhibition efficiency values were determined from the values of corrosion current.

Figure 4. Temkin's adsorption isotherm for corrosion behavior of mild steel in 2N Phosphoric acid with Morpholine.

Figure 5. Typical Potentiostatic curves for mild steel in 2N Sulphuric acid with Morpholine.

Figure 6. Typical Potentiostatic curves for mild steel in 2N Phosphoric acid with Morpholine

Reasons for inhibition

It has already been reported by many workers³⁷⁻⁴¹ that most of the organic inhibitors work by way of adsorption on the metal surface as has been established in the present work. Adsorption bond strength depends upon the electron density available at the point of adsorption. The point of adsorption may be any electron-donating element such as N, O, S, P, etc. present in the molecular structure of the inhibitor. If there is more than one electron-donating element present then which atom will have a higher tendency to become point of adsorption depends upon the distribution of electrons on the overall structure of the molecule.

In the presence of an inhibitor, a thin black film has always been observed on the surface of the specimens. This shows that the inhibition is due to the formation of some complex film with the metal ions. The organic compounds used as inhibitors like Morpholine have the following structure.

This inhibitor acts as a proton acceptor in an acidic medium. It forms an organo-metallic complex layer with the metal ions on the surface of the metal, thus inhibiting corrosion. The N and O atoms act as the reaction centers in the complexation reaction with the metal ions. The adsorption of the inhibitors over mild steel surface may be through N and O, which is supposed to be the active center for adsorption of inhibitor molecule due to the presence of charge on it.

Table 3. Polarization parameters for the corrosion behaviour of mild steel in 2N sulphuric acid and 2N phosphoric acid with and without *Morpholine*.

Temp (K)	Conc. of inhibitor (%)	2N sulphuric acid					2N Phosphoric acid				
		- E _{corr} Vs SCE (mv)	I _{corr} $\mu\text{A}/\text{cm}^2$	Tafel constant mv/decade		IE (%)	- E _{corr} Vs SCE (mv)	I _{corr} $\mu\text{A}/\text{cm}^2$	Tafel constant mv/decade		IE (%)
				b _a	-b _c				b _a	-b _c	
302	Blank	572	310	80	95	-----	540	250	30	90	----
	1	560	220	75	85	40.95	560	120	40	80	52.00
	2	550	188	72	90	43.80	582	110	45	75	56.00
	3	565	180	70	85	46.66	592	100	52	63	60.00
	4	570	175	75	80	55.23	600	82	40	75	67.20
	5	565	160	67	93	60.95	630	60	60	80	76.00
313	Blank	572	1050	140	95	-----	620	590	60	70	----
	1	570	620	135	85	44.38	570	330	40	80	44.06
	2	575	590	120	80	53.38	640	290	60	65	50.84
	3	580	560	110	70	61.88	625	270	40	85	54.23
	4	575	470	100	73	67.50	640	240	40	85	59.32
	5	580	410	95	70	70.94	640	190	35	90	67.79
323	Blank	570	1800	110	70	-----	600	880	50	70	-----
	1	580	1120	110	85	40.00	565	510	55	65	42.04
	2	575	1080	100	80	37.77	630	450	60	70	48.86
	3	565	1050	85	70	41.66	615	420	45	65	52.27
	4	573	880	83	65	51.11	620	380	60	80	56.81
	5	563	780	70	60	56.66	775	320	45	55	63.63
333	Blank	570	2600	90	85	-----	600	1400	20	80	-----
	1	563	1920	90	70	26.15	585	900	50	65	35.71
	2	570	1700	85	65	33.33	630	820	40	70	41.42
	3	565	1550	85	55	40.35	645	740	55	75	41.14
	4	560	1400	80	55	45.38	690	720	60	70	48.57
	5	570	1250	80	50	51.92	655	620	55	75	55.71

Conclusion

Corrosion rates of mild steel in 2N sulphuric acid and 2N phosphoric acid decreased with increasing concentration of Morpholine. The inhibition efficiency increased with respect to the concentration of inhibitors as it is assumed that the inhibition efficiency is equal to surface coverage. The inhibition efficiency of Morpholine in 2N sulphuric acid and 2N phosphoric acid increased with rise in temperature respectively up to 313K and then decreased. The adsorption of Morpholine on mild steel surface from the acid solution follows Temkin's adsorption isotherm. The low and negative value of ΔG_{ads} indicated that the Morpholine is physically adsorbed and spontaneous adsorption of inhibitor on the surface of mild steel. The inhibition efficiency obtained from mass loss studies and

polarization measurement shows fairly good agreement. Morpholine shows the better inhibition in 2N phosphoric acid than 2N sulphuric acid. It is found that the Morpholine acting as mixed type inhibitor. Energy of activation (E_a) values indicates physical adsorption of the inhibitor on metal surface.

References

1. Hart A C, *Br Corros. J.*, 1971, **6**, 205.
2. Hart A C, *Br Corros. J.*, 1973, **8**, 66.
3. Saleh R M, Badran M M, Alhosary A A, and El Dahan H A, *Br Corros. J.*, 1988, 105.
4. Smith F and Van Droffeleaar N H, *Br Corros. J.*, 1991, **26**, 265.
5. Al –Mayot A M, Al-Suhybani A A, and Al –Ameer A K, *Desalination.*, 1998, **25**, 116 and references therein.
6. Bilgic S and Caliskan N, *J. Appl. Electrochem.*, 2001, **31**, 79.
7. Granese S L, Rosales B M, Oviedo C, and Zerbino J O, *Corros. Sci.*, 1990, **33**, 1439.
8. Subramaniam G, Balasubramaniam K, and Shridhar P, *Corros. Sci.*, 1990, **30**, 1019.
9. Stupnisek-lisac E, Metikos-Hukovic M, Lencic D, Vorkapic-Furac J, and Borkovic K, *Corrosion*, 1992, **48**, 924.
10. Raicheva S N, Aleksiev B V, and Sokolov E J, *Corrosion Sci.*, 1993, **3**, 343.
11. Quraishi M A, Khan M A W, Ajmal M, Muralitharan S, and Iyer S V, *Br. Corros. J.*, 1997, **32**, 72.
12. Quraishi M A, Khan M A W, Ajmal M, Muralitharan S, and Iyer S V, *Br. Corros. J.*, 1997, **53**, 475.
13. Mathur P M and Vasudevan T, *Corrosion*, 1982, **38**, 17.
14. ASTM G 31 – 72, “*Standard Practice for laboratory Immersion Corrosion Testing of Metals*”, West Conshohocken, PA; ASTM, 1990.
15. Ajmal M, Mideen A S and Quraishi M A, *Corros. Sci.*, 1994, **36**, 79.
16. Talati I D and Modi R M, *Trans. SAEST*, 1986, **11**, 259.
17. Al-Shamma L A, Saleh J M and Hikmat N A, *Corros. Sci.*, 1987, **27**, 221.
18. Chandrasekaran V et al., *Orient J. Chem.*, 2005, **21**, 81.
19. Okafor P C, Ekpe U J, Ebenso E E, Umoren E M, and Leizou K E, *Bull. of Electrochem.*, 2005, **21**, 347.
20. Ebenso E E, Okafor P C, Offiong O E, Ita B I, Ibook U J and Ekpe U J, *Bull. Electrochem.*, 2001, **17**, 459.
21. Ebenso E E, *Bull. Electrochem.*, 2003, **19**, 209.
22. Okafor P C, Ebenso E E, Ibook U J, Ekpe U J and Ikpi M I, *Trans. SAEST*, 2003, **38**, 91.
23. Putilova I N, Barannik V P and Balezin S S, *Metallic Corrosion Inhibitors*, Pergamon Press, Oxford **30**, 1960.
24. Chandrasekaran V, Kannan K and Natesan M *Corrosion Science and Tech.*, 2005, **4**, 191-200.
25. Quraishi M A and Rana Sardar, *Bull. Electrochem.*, 2002, **18**, 515.
26. Brinic S, Grubac A, Babic R and Metikos-Hukovic M, *8th European Symposium on Corrosion Inhibitors*, 1995, **1**, 197.
27. Gomma G K and Wahdan M H, *Indian J. Chem. Technol.*, 1995, **2**, 107.

28. Chandrasekaran V, Kannan K and Natesan M, *Journal of metallurgy and material Science.*, 2004, **46**, 253.
29. Ateya B, Callow L and Dawson J, *Br.corros. J.*, 1980 **15**, 20.
30. Hackerman N, *Corrosion*, 1962, **18**, 332.
31. Atya B G, El-Anadouli B E and El-Nizamy F M, *Corros. Sci.*, 1984, **24**, 497.
32. Cheng X L, Ma.Ma H Y, ChenS H, Yu R, Chen X and Yao Z M, *Corros. Sci.*, 1999, **41**, 321.
33. Bouayed M, Rabaa H, Srhiri A, Saillard J Y, Bachir A B and Beuze L A, *Corros. Sci.*, 1999, **41**, 501.
34. Lkeda O, Jimbo H and Jaumura H, *J. Electroanal. Che.*, 1982, **137**, 127.
35. Pearsons R, *J. Electroanal. Chem.*, 1964, **7**,136.
36. Bockris J O M and D Swinkkels A J, *J. Electrochem. Soc.*, 1964, **11**, 736.
37. Hackerman N and Hurd R M, 1st *International Congress, Metallic Corrosion*, Butterworths, London, 1962.
38. Meakins R J, *J.Appl. Electrochem.*,1963, **13**, 339.
39. Meakins R J, *Brit. Corros. J.*, 1971, **6**, 111.
40. Walker R, *Corrosion*, 1976, **32**, 414.
41. Raicheva S N, Aleksive B V and Sokolova E I, *Corros. Sci.*, 1993, **34**, 351.