Indian Journal of Chemical Technology
Vol. 17, January 2010, pp. 50-55

Efficiency of xylenol orange as corrosion inhibitor for aluminium in trichloroacetic acid

P S Desai* & R T Vashi[1]

Department of Chemistry, Arts, Science and Commerce College Kholwad, Kamrej Char Rrasta, Surat 394 185, India
[1]Department of Chemistry, Navyug Science College, Rander Road, Surat 395 009, India
Email: psdesai69@yahoo.co.in

Received 2 March 2009; revised 3 September 2009

The corrosion of aluminium in trichloroacetic acid (TCA) containing xylenol orange has been studied. In TCA, the corrosion rate increases with the increase in acid concentration. At constant acid concentration, the inhibition efficiency of xylenol orange increases with the inhibitor concentration. At constant inhibitor concentration, the inhibition efficiency decreases with the increase in the acid concentration. As temperature increases, percentage of inhibition decreases. Plot of log (θ/1-θ) versus log C results in a straight line, suggesting that the inhibitor cover both the anodic and cathodic regions through general adsorption following Langmuir isotherm. The polarization curves show very little anodic but significant cathodic polarization.

Keywords: Corrosion, Aluminium, Trichloroacetic acid, Xylenol orange

Aluminium and its alloys are remarkable and attractive materials for engineering applications owing to its light weight and high thermal and electrical conductivity[1]. The corrosion of the metal has been reported to depend on processes associated with the passivating surface oxide film such as metal ion transfer to the metal/oxide interface, metal ion and oxygen ion transfer to the oxide/solution interface, ion migration in the oxide film, and electron transfer from the metal to acceptor species in solution[2]. The use of chloro substituted acetic acid in cellulose industry brings in serious corrosion problem. To prevent the attack of acid, it is very important to add a corrosion inhibitor to decrease the rate of aluminium dissolution in such solution. Thus, many studies concerning the inhibition of aluminium corrosion using organic substance have been conducted in acidic and basic solutions[3-7]. Mishra *et al.*[8] studied the inhibition capacity of anisidine on aluminium alloy in TCA. Many researchers used dyes as corrosion inhibitors *viz.* methlthymolblue complexon[9], xanthenes and azo dyes[10] for aluminium in TCA. Different kinds of dyes are known *viz*., heterocyclic, xanthenes, anthraquinone, azo and TPM. Literature related to prevention of corrosion of metals shows that the information about the inhibition of corrosion of aluminium is scanty[11,12]. Methlthymolblue complexon is a class of TPM dye and this dyestuff has triaryl structure, and xylenol orange belongs to the same class, therefore, xylenol orange is chosen as corrosion inhibitor. The present article reports the inhibitive action of xylenol orange on the corrosion of aluminium in TCA solutions using gravimetric as well as polarization methods.

Experimental Procedure

Rectangular specimens of size 0.5×0.2×0.018 dm having an area of 0.2414 sq.dm of 2S grade aluminium (Al = 98.02, Mg = 0.37, Si = 0.49, Fe = 0.68, Mn = 0.16 and Cu = 0.082%) with small hole of about 5 mm diameter near the upper edge, were used for the corrosion study. The specimens were polished by a line buffing wheel using first the Tripoli composition and then jeweler's rouge[13,14], the direction of final polishing being perpendicular to that of the first one. The method gave a mirror-like finish. The specimens were degreased by immersion in A. R. grade acetone and dried in warm air using air dryer and preserved in desiccater till use. The test specimens were immersed in 0.01, 0.05 and 0.10 M TCA solution with and without inhibitor. Xylenol orange was used as inhibitor in 1, 2, 3 and 4 mM concentration. One specimen was suspended by a glass hook in each beaker containing 230 mL of the test solution and was exposed in the air at room temperature for 24 h. After the tests, the specimens were cleaned with chromic-phosphate mixture solution[15]. Triplicate experiments were performed in each case and the mean value of the weight loss data are presented.

To study the effect of temperature on corrosion rate, the specimens were immersed in 230 mL in 0.05 M TCA, with 1, 2, 3 and 4 mM inhibitor concentration at solution temperatures of 313, 323 and 333 K for a period of 2 h. For the temperature effect study, thermostat assembly with accuracy of ± 0.5°C was used[16,17]. Form the data, inhibition efficiency, energy of activation (E_a), heat of adsorption (Q_{ads}) and free energy of adsorption (ΔG^0_{ads}), were calculated.

Inhibition efficiency (η%) in percentage has been calculated using the following relation:

$$\eta\% = \left(\frac{W_u - W_i}{W_i}\right) \times 100 \quad \ldots (1)$$

where W_u is the weight loss of the metal in uninhibited acid and W_i is the weight loss of a metal in inhibited acid solution i.e. containing inhibitor. Energy of activation (E_a) has been calculated from the slopes of log P versus $1/T$ (P = corrosion rate, T = absolute temperature) and also with the help of Arrhenius equation[18].

$$Log\frac{P_2}{P_1} = \frac{E_a}{2.303R}\left[\left(\frac{1}{T_1}\right) - \left(\frac{1}{T_2}\right)\right] \quad \ldots (2)$$

where P_1 and P_2 are the corrosion rates at temperature T_1 and T_2 respectively.

The values of heat of adsorption (Q_{ads}) were calculated by the following equation.

$$Q_{ads} = 2.303R\left[Log\left(\frac{\theta_2}{1-\theta_2}\right) - Log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \left[\left(\frac{T_1 T_2}{T_2 - T_1}\right)\right] \quad \ldots (3)$$

where θ_1 and θ_2 [$\theta = \left(\frac{W_u - W_i}{W_i}\right)$] are the fraction of the metal surface covered by the inhibitor at temperature T_1 and T_2, respectively.

The values of the free energy of adsorption (ΔG^0_{ads}) were calculated with slope of the following equation[19].

$$LogC = Log\left(\frac{\theta}{1-\theta}\right) - LogB \quad \ldots (4)$$

where $LogB = -1.74 - \left(\frac{\Delta G^0_{ads}}{2.303RT}\right)$ and C is the inhibitor concentration.

The enthalpy of adsorption (ΔH^0_{ads}) and entropy of adsorption (ΔS^0_{ads}) were calculated using the following Eqs (5) and (6).

$$\Delta H^0_{ads} = E_a - RT \quad \ldots (5)$$

$$\Delta S^0_{ads} = \frac{\Delta H^0_{ads} - \Delta G^0_{ads}}{T} \quad \ldots (6)$$

Open Circuit potential was measured by immersing aluminium specimen having an area of 0.0675 dm^2 in 0.01 M TCA with and without 1 mM inhibitor concentration and the potentials were recorded against the saturated calomel electrode after every 2 min till a constant potential was attained.

For polarization study, metal specimens of rectangular design having an area of 0.02585 dm^2 were exposed to corrosive solutions. Aluminium metal was used as the working electrode, Ag/AgCl was used as reference electrode and an auxiliary platinum electrode that was placed in a 100 mL corrosive media through which external current was supplied automatically from computerized polarization instrument. The change in potential was measured by potentiostat/galvanostat (Autolab Model -273). Galvanostatic polarization studies were done with and without inhibitor in 0.01 M TCA.

All chemicals and reagents used were of analytical grade and used as such without further purification.

Results and Discussion

The *p*H of the 0.01 M solution of TCA was found to be 2.02 while with the inhibitor (0.01 M TCA + 1 mM inhibitors) it was found to be 2.27.

The results of the determination of corrosion rate of aluminium in TCA without inhibitor are shown in Fig. 1. The corrosion rate increases with the acid concentration. The effect of acid concentration on the corrosion inhibition efficiency of inhibitor xylenol orange for the corrosion of aluminium is depicted in Fig. 2. It may be seen from the figure that the inhibitive efficiency of the xylenol orange in different concentrations (1, 2, 3 and 4 mM) decreases with the increase in acid concentration. It is also evident from the figure that at constant acid concentration, the inhibition efficiency of the xylenol orange increases with the inhibitor concentration e.g. in 0.10 M TCA the inhibition efficiency was found to be 87.10, 94.49, 95.61 and 96.60% with respect to 1, 2, 3 and 4 mM inhibitor concentration respectively (Fig. 2).

The plot of Log (θ/1- θ) versus log C (inhibitor concentration) shows straight line (Fig. 3), which indicate that the inhibition action appears to be the chemisorptions and inhibitors cover both anodic and cathodic region through general adsorption following Langmuir isotherm.

Effect of temperature

Temperature has significant influence on the metal corrosion rates. The results of the study of effect of change in temperature on the corrosion rates of aluminium in 0.05 M TCA solution showed that the corrosion of aluminium increases with increasing temperatures (Fig. 4). It showed that the increases of corrosion rate may be due to thermal activated kinetic[20]. A similar trend in the decrease in the inhibition efficiency xylenol orange was observed (99.10, 98.82 and 96.12%) with 313, 323 and 333 K respectively with 4 mM inhibitor concentration (Fig. 5). The above observation can be explained with respect to the characteristic features of the cathodic process of hydrogen evolution, where the decrease of the reaction over potential with rise in temperature leads to an increase in the rate of cathodic reaction[21].

The mean value of the energy of activation E_a calculated by using Eq. (2) for aluminium in pure acid solution was found to be 33.83 kJ.mol^{-1} while in acid solution containing inhibitor, the mean E_a values were found to be higher than that of uninhibited system (Table 1). The higher values of mean in presence of

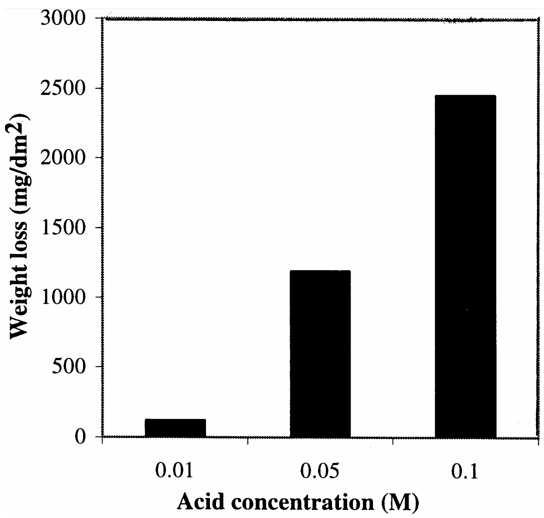


Fig. 1 — Weight loss of aliminium in various concentrations of TCA at 301 K

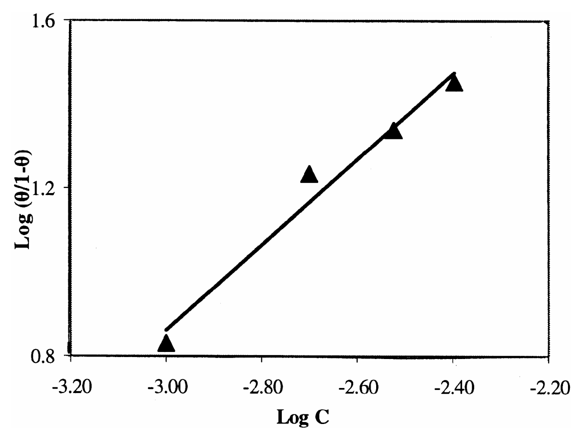


Fig. 3 —Plot of Log (θ/1- θ) versus log C for xylenol orange in 0.05 M TCA

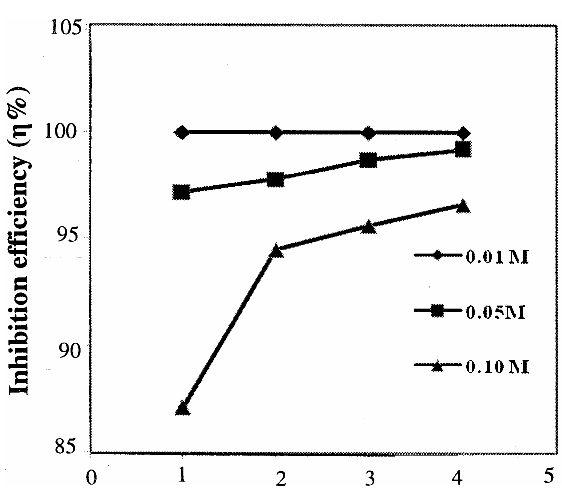


Fig. 2 — Variation of inhibition efficiency of xylenol orange in different TCA concentrations at 303 K

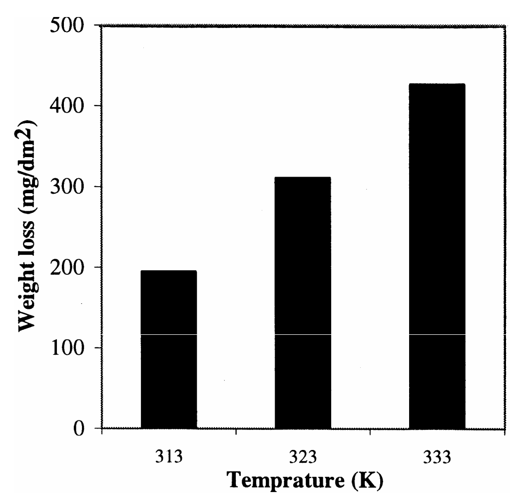


Fig. 4 — Weight loss of aluminium in 0.05 M at different temperatures

inhibitor E_a indicate physical adsorption of the inhibitor molecules on metal surface[22], which leads to an increase in the energy barrier for the corrosion process. The values of E_a calculated from the slope of Arrhenius plot (Fig. 6) and using Eq. (2) are almost similar.

From Table 1, it is also evident that among the thermodynamic parameters the values of Q_{ads} were negative in all the cases ranging from - 37.5 to - 66.0 kJ.mol^{-1}. The negative values showed that the adsorption, and hence the inhibition efficiency, decreases with a rise in temperature[24].

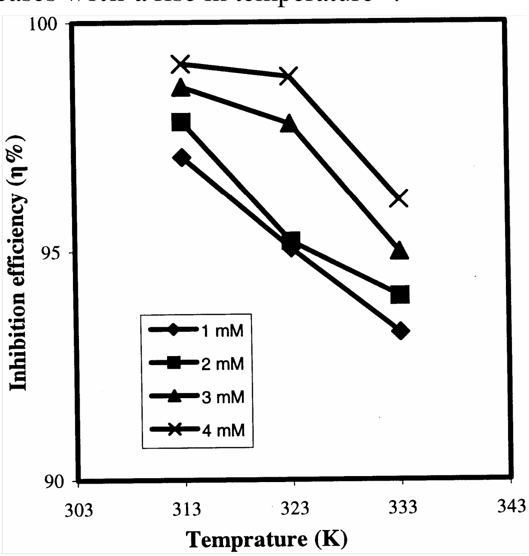


Fig. 5 — Inhibitor efficiency against corrosion of aluminium in 0.05 M TCA at different temperatures

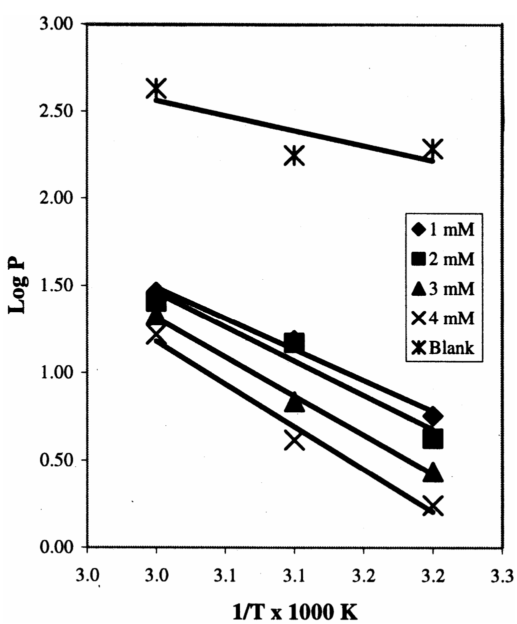


Fig. 6 — Arrhenius plots for corrosion of aluminium in 0.05 M TCA with different concentrations of xylenol orange

Similarly the mean ΔG^0_a values were found to be negative almost in all cases and lie in the range of -37.4 to -35.9 kJ.mol^{-1} (Table 1). The negative value of ΔG^0_{ads} suggests that the inhibitor molecules are strongly adsorbed on the metal surface; the values also indicate a spontaneous adsorption of the inhibitor molecules usually characterized by the strong interactions with the metal surface. It is found that the $\Delta G_a°$ values are more positive than -40 kJ.mol^{-1} indicating that inhibitor molecules are physically adsorbed on the metal surface[25,26].

The enthalpy changes (ΔH^0_a) are positive indicating the endothermic nature of the reaction[27] suggesting that higher temperature favours the corrosion process. The entropy (ΔS^0_a) values are positive confirming that the corrosion process is entropically favourable[28].

Open circuit potential

A specimen of aluminium when immersed in 0.01 M TCA developed a steady state potential of -689 mV versus SCE. In the presence of xylenol orange the corrosion potentials was found to be -651 mV. Xylenol orange had slightly increased the corrosion potential, suggesting slight polarization of local anodes.

Polarization behaviour

The polarization behaviour of aluminium in acid solution at 1 mM inhibitor concentration under galvanostatic conditions at different current densities in presence and absence of inhibitors is shown in Fig. 7. The values of corrosion current densities in the presence and absence of inhibitor were obtained from the plot while percentage of inhibition efficiency was calculated using the relation:

$$\eta(\%)=\left[\frac{i_{corr}(u)-i_{corr}(i)}{i_{corr}(u)}\right]\times100 \qquad ...(7)$$

Table 1 —- Energy of activation (E_a), heat of adsorption (Q_{ads}) and free energy of adsorption (ΔG^0a) for aluminium in 0.05 M TCA contain xylenol orange.

Inhibitor concn. (mM)	E_a (kJ/mol) from Arrhenius plot	E_a (kJ/mol) from Eq. (2)	Mean values (kJ/mol) $-Q_{ads}$	$-\Delta G_a$	ΔH_a	ΔS_a
Blank	32.61	33.83	-	-	-	-
1	67.46	69.93	37.5	37.4	54.0	0.28
2	74.83	77.14	44.7	35.9	45.8	0.25
3	85.61	89.65	57.5	36.1	99.0	0.41
4	93.43	98.22	66.0	36.8	121.3	0.49

*E_a calculated

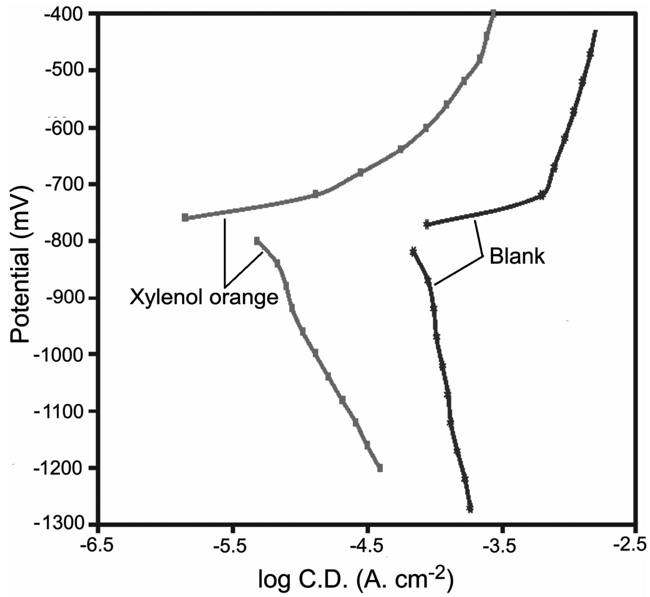


Fig. 7 — Polarization curves for corrosion of aluminium in 0.01 M TCA containing 1 mM xylenol orange.

The curves show polarization of both, the cathodes as well as anodes. Thus the open circuit potentials and galvanostatic polarization data suggest that the inhibitor functions through general adsorption on cathodic as well as anodic sites on the metal surface. Inhibition efficiency calculated from corrosion current obtained by extrapolation of the cathodic and anodic Tafel lines are given in Table 2. The inhibition efficiencies from Tafel plots also agree well (within $\pm$ 5%) with the values obtained from weight loss data.

Mechanism

Generally, aluminium dissolves in acid solutions due to hydrogen evolution type of attack. The reaction-taking place at the microelectrodes of the corrosion cell being represented as under,

$$Al \rightarrow Al^{+3} + 3e^{-} \text{ (Anode)} \quad \ldots (8)$$

$$H^{+} + e^{-} \rightarrow H \text{ (Cathode)} \quad \ldots (9)$$

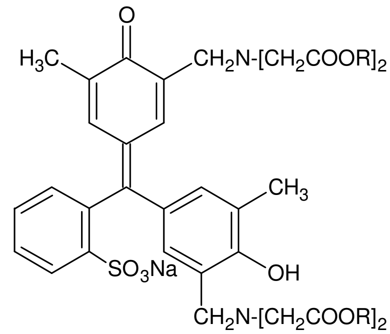
Followed by the reaction

$$H + H \rightarrow H_2 \uparrow \quad \ldots (10)$$

In the case of dissolution of aluminium in TCA the reaction in the initial stages appear to be[29]:

$$3CCl_3COOH + Al \rightarrow [CCl_3COO]_3\, Al + 3H \quad \ldots (11)$$

Xylenol orange acts as indicator[30] by making complexes with.specific metal cations. According to Talati *et al.*[31] corrodibility may be explained in the following manner, if the metal-colourants complex is more stable at lower *p*H values; is insoluble and formed *in situ* on the metal surface, the extent of corrosion decreases. Usually, corrosion inhibitors containing atoms of nitrogen, sulphur or oxygen have electron donating ability and their action is attributed to the adsorption of the inhibitor molecules on the metal surface through an unshared pair of electrons belonging to the functional atom[32,] similar mechanism may exist in the present case.



Xylenol orange

Table 2 — Polarization data and inhibition efficiency (IE) for aluminium in 0.01 M TCA at 1 mM xylenol orange.

System	E_{corr} (mV)	I_{corr} (A/cm²)	Tafel slope (mV/decade)			IE (%)	
			$+\beta_a$	$-\beta_c$	β	Wt. loss method	Pol. Method
Blank	-755	0.082	6250	231	96	_	_
xylenol orange	-760	0.010	2000	156	63	95	99

Conclusions

The corrosion of aluminium increases with the thricholoroacetic acid concentration and decreases with increasing inhibitor concentration. The inhibiting efficiency of the inhibitor with the rise in temperature of the system. The presence of inhibitor in the solution increases the energy of activation of the system (E_a). The results indicate physical adsorption of the inhibitor on metal surface. The values of ΔG^0_{ads} suggest that the inhibitor molecules may be strongly adsorbed on the metal surface.

Acknowledgement

The authors are thankful to Department of Chemistry, Navyug Science College, Surat and Department of Chemistry, Arts, Science and Commerce College, Kamrej Char Rasta, Surat for providing laboratory facilities.

References

1 Elewady GY, El- said I A & Fouda A S, *Int J Electrochem Sci,* 3 (2008) 177.

2 Hurlen T, Liam H, Odegard O S & Valand T, *Electrochim Acta,* 29 (1984) 579.

3 Stern M & Geary A I J, *J Electrochem Soc*, 104 (1957) 56.

4 Maayta A K & Al-Rawashdeh N A F, *Corros Sci,* 46 (2004) 1129.

5 Ebenso E E, Okafor P C & Ekpe U J, *Anti-Corros Methods Maters*, 37 (2003) 381.

6 Bereket G, Pinarbasi A & Ogretir C, *Anti-Corros Methods Mater*, 51 (2004) 282.

7 Fouda A S, Moussa M N, Taha F I & Elneanaa A I, *Corros Sci,* 26 (1986) 719.

8 Mishra A, Sanja D, Sangani A & Godhani D R, *Asian J Exp Chem,* 3(1-2) (2008) 36.

9 Desai P S & Vashi R T, *J Indian Chem Soc*, 85(1) (2008) 92.

10 Talati J D & Gandhi D K, *Indian J Technol,* 20 (1982) 312.

11 Mears R B, *The Corrosion Handbook* edited by H H Uhlig (John Willey & Sons Inc, New York), 1948, 45.

12 Tomashor N D, *Theory of Corrosion and Protection of Metals* edited by B H Tytel, I Geld & H S Preser (Macmillan & Co., New York), 1966, 618.

13 Trivedi A M & Desai M N, *Indian J Appl Chem,* 21 (1958) 137.

14 Talati J D, Desai M N & Trivedi A M, *Werkstoffe Korros*, 10 (1959) 26.

15 Uhlig H H, *The Corrosion Hand Book* (John Willey & Sons Inc., New York), 1948, 41.

16 Wesley, *Corrosion* (International Nickel Company), 1956, 51.

17 *Am Soc Testing Materials*, (Spec Tech Publ) 1950, 93.

18 Subramanian N & Ramkrishnaiah K, *Indian J Technol*, 8 (1970) 369.

19 Abdel A M S & Saied A E L, *Trans SAEST*, 16 (1981) 197.

20 Sanyal B & Nigam R S, *Labdev J Sci Technol,* 8 (1970) 120.

21 Harek Y & Larabi L, *Kem Ind,* 53 (2004) 55.

22 Putilova I N, Barannik V P & Balezin S A, *Metallic Corrosion Inhibitors* (Pergamon Press, Oxford), 1960, 30.

23 Noor E A, *Egyp J Chem*, 47 (2004) 305.

24 Bhajiwala H M & Vashi R T, *Bull Electrochem,* 17 (2001) 441.

25 Brinic S, Grubac A, Babic R & Metikos-Hukovic M, *8th European Symposium on Corrosion Inhibitors*, 1 (1995) 197.

26 Gomma G K & Wahdan M H, *Indian J Chem Technol,* 2 (1995) 107.

27 Agrawal D, Gupta K D & Saxena K K, *Trans SAEST,* 38 (2003) 111.

28 Issa R M, El-Sonbati A Z, El-Bindary A A & Kera H M, *Eur Polym J*, 38 (2002) 561.

29 Talati J D & Patel B M, *Indian J Technol*, 8 (1970) 230.

30 Vogel I, *A Text Book of Quantitative Inorganic Analysis*, 3rd edn (Longman, Green & Co. Ltd., London), 1961, 428.

31 Talati J D & Patel S A, *Indian J Technol*, 26 (1988) 284.

32 Talati J D & Joshi N H, *Denki Kagaku*, 45 (1977) 722.