CORROSION BEHAVIOUR OF CARBON STEEL IN THE PRESENCE OF POLYVINYLPYRROLIDONE

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ABSTRACT

The inhibition efficiency of polyvinyl pyrrolidone (PVP) in controlling corrosion of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^-, in the absence and the presence of Zn^{2+} has been evaluated by weight loss method. Influence of pH, immersion period, N-cetyl-N,N,N-trimethyl ammonium bromide and sodium dodecyl sulphate on the inhibition efficiency of the inhibitor system has also been investigated. The nature of the protective film has been analysed by FTIR and fluorescence spectroscopy. In the presence of PVP, the protective film consists of Fe^{2+} - PVP complex; the film is found to be uv-fluorescent. In the presence of PVP and Zn^{2+}, the protective film consists of Fe^{2+} - PVP complex and $Zn(OH)_2$; it is found to be uv-fluorescent.

Keywords: Carbon steel, corrosion inhibition, fluorescence, polymers, polyvinyl pyrrolidone.

INTRODUCTION

Several polymers have been used as corrosion inhibitors /1-8/. They function as corrosion inhibitors (i) by increasing the resistance to the rate of diffusion of the corrosive agent and (ii) by absorbing on the surface of the metal through their functional groups, thus protecting the metal against the corrosive environment. Polymers such as polyacrylamide /1-5/, carboxymethyl cellulose /6/, poly-N, vinylimidazole /7/ and phosphonic acid derivatives of polyamides /8/ have been used as inhibitors. Polyvinyl pyrrolidone has been used to inhibit corrosion of carbon steel in ground water /9/. The present work is undertaken (i) to evaluate the inhibition efficiency of polyvinyl pyrrolidone (PVP) (M.wt 40,000), in controlling corrosion of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^-, (ii) to investigate the influence of Zn^{2+}, pH, immersion period, N-cetyl-N,N,N-trimethyl ammonium bromide and sodium dodecyl sulphate on the inhibition efficiency of the PVP system, and (iii) to analyse the protective film by means of FTIR spectra and fluorescence spectra.

EXPERIMENTAL

Preparation of the specimens

Carbon steel specimens (0.026% S, 0.06% P, 0.4% Mn, 0.1% C and the rest iron) of the dimensions 1.0x4.0x0.2 cm were polished to a mirror finish and degreased with trichloroethylene, and used for the weight-loss method and surface examination studies.

Weight-loss method

Carbon steel specimens, in triplicate, were immersed in 100 ml of the solutions containing various concentrations of the inhibitor in the absence and presence of Zn^{2+}, for one hour. The weight of the specimens before and after immersion were determined using a Mettler balance, AE-240. The corrosion products were cleaned with Clarke's solution /10/. The corrosion inhibition efficiency (IE) was then calculated using the equation.

$$IE = 100\,[1 - (W_2 / W_1)]\,\%$$

Where W_1 = Corrosion rate in the absence of inhibitor,

W_2 = Corrosion rate in the presence of inhibitor

Surface examination study

The carbon steel specimens were immersed in various test solutions for a period of one hour. After one hour, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimens was analysed by various surface analysis techniques.

FTIR spectra

These spectra were recorded in a Perkin Elmer – 1600 spectrophotometer. The film was carefully removed, mixed thoroughly with KBr and made into pellets, and the FTIR spectra were recorded.

Fluorescence spectra

Fluorescence spectra were recorded in a Hitachi F-4500 fluorescence spectrophotometer.

RESULTS AND DISCUSSION

Weight loss study

Corrosion rates of carbon steel immersed in an aqueous solution containing 60 ppm of chloride ion, for 1 hour, in the absence and presence of polyvinyl pyrrolidone (PVP) are given in Table I. The inhibition efficiencies are also given in this Table. It is found that PVP has good inhibition efficiency at pH 7.

Table I

Corrosion rates (CR) [mg/dm^2 hour] of carbon steel immersed in an aqueous solution containing 60 ppm of Cl$^-$. Immersion period = 1 hour pH = 7

PVP, ppm	Corrosion rate m/d^{2}h	IE %
0	6.00	--
50	0.48	92
100	0.30	95
150	0.18	97
200	0.18	97
250	0.12	98

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Influence of pH on the inhibition efficiency of PVP

When the pH of the solution in lowered from 7 to 3, (addition of dil.H_2SO_4) the IE decreases to a great extent (Table II). When the pH is increased from 7 to 10 (addition of NaOH solution), the IE decreases to some extent at lower concentrations of PVP, namely, 50 ppm and 100 ppm. However at higher concentrations of PVP (150, 200, 250 ppm) there is no change in the IE (Table III).

Table II

Corrosion rates of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^-. Immersion period = 1 hour pH = 3

PVP, ppm	Corrosion rate m/d^2h	IE %
0	6.00	--
50	4.50	25
100	3.60	40
150	3.30	45
200	3.00	50
250	2.10	65

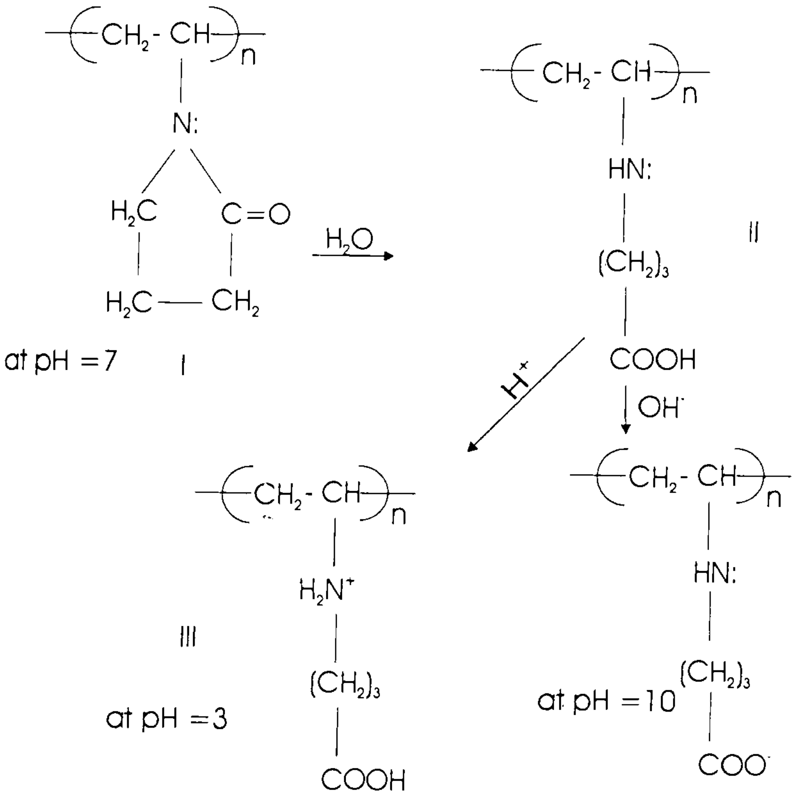
Table III

Corrosion rates of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^-. Immersion period = 1 hour pH = 10

PVP, ppm	Corrosion rate m/d^2h	IE %
0	6.00	--
50	1.32	78
100	1.02	83
150	0.30	95
200	0.18	97
250	0.12	98

When PVP is hydrolysed in the presence of acids (lower pH) or alkalies (higher pH), there is a change of functional group /11/ (*cf* Scheme 1).

The very high inhibition efficiency at pH 7 may be due to the fact that PVP is coordinated to Fe^{2+} on the metal surface through the N atom and the



Scheme 1

oxygen atom resulting in the formation of Fe^{2+} - PVP complex on the anodic sites of the metal surface.

At lower pH value of 3 (structure III), the N atom is protonated. The lone pair of electrons is not available. Nitrogen has attained a positive charge. The C=O group has been converted into COOH group. Therefore coordination with Fe^{2+} is very difficult. Hence a decrease in IE is noticed.

At higher pH value of 10 (structure IV), a lone pair of electrons is available on N and a carboxylate anion is formed. Coordination with Fe^{2+} can take place through the N atom and O^- of the carboxylate anion. The resulting Fe^{2+}-PVP complex is a 7 membered ring system. This is a strainless complex. Hence the stability of the complex increases. This accounts for the higher IE of PVP at higher pH value (say 10) than at lower pH value (say 3).

Influence of Zn^{2+} on the IE of PVP

The influence of Zn^{2+} on the IE of PVP is given in Table IV. At pH 7, when 5 ppm of Zn^{2+} is added to PVP, the IE decreases to a great extent. This may be due to the fact that a Zn^{2+}-PVP complex is formed in solution. The transport of PVP from the bulk of the solution towards the metal surface is restricted in the presence of Zn^{2+}. The coordination is through the N atom and the O atom of the C = O group with Zn^{2+}. When this complex diffuses from the bulk of the solution towards the metal surface, it is not easily broken to form Fe^{2+} - PVP complex on the metal surface.

Table IV

Influence of 5 ppm of Zn^{2+} on the inhibition efficiency of PVP

Immersion period : 1 hour

PVP, ppm	pH = 3	pH = 7	pH = 10
50	20	26	75
100	25	30	80
150	30	38	92
200	40	42	95
250	50	60	97

At pH 3, PVP cannot form a complex either with Zn^{2+} or with Fe^{2+}, because N has attained a +ve charge (structure III). Hence a decrease in IE is noticed.

At pH 10, (structure IV) high inhibition efficiency is observed. Lone pair of electrons is available on nitrogen; carboxylate anion $-COO^-$ is present. The transport of PVP towards the metal surface is facilitated by the presence of Zn^{2+}. Zn^{2+} - PVP complex is formed and transported towards the metal surface. On the metal surface, Zn^{2+} - PVP complex is converted into Fe^{2+} - PVP complex at the anodic sites. Zn^{2+} is released. It is deposited at the cathodic sites as $Zn(OH)_2$. This accounts for the high IE at pH 10.

Influence of CTAB on the IE of PVP

The influence of N-cetyl-N,N,N-trimethyl ammonium bromide (CTAB), a cationic surfactant, on the IE of PVP is given in Table V. It is observed that 50 ppm of PVP has 92% IE. When 50 ppm of CTAB is added the IE decreases to 40%. As the concentration of CTAB increases, the IE increases, reaches a maximum (98%) and then decreases. The maximum IE is obtained at 200 ppm of CTAB. Upto 200 ppm of CTAB, it exists as a monomer. Above this critical value, there may be formation of micelles. The transport of PVP towards the metal surface is not facilitated. Hence a decrease in IE after this critical concentration is observed.

Table V

Influence of CTAB on the IE of PVP

Immersion period = 1 hour pH = 7

PVP, ppm	CTAB ppm	IE %
50	0	92
50	50	40
50	100	90
50	150	95
50	200	98
50	250	95

Influence of SDS on the IE of PVP

The influence of sodiumdodecyl sulphate (SDS) an anionic surfactant, on the IE of PVP is given in Table VI. It is found that when SDS is added, the IE first decreases and then increases. A maximum IE is reached at 200 ppm of SDS. Afterwards the IE decreases. There may be formation of micelles after this critical concentration. The transport of PVP to the metal surface is not facilitated; hence a decrease in IE after this critical concentration.

Table VI

Influence of SDS on the IE of PVP

Immersion period = 1 hour pH = 7

PVP, ppm	SDS, ppm	IE %
50	0	92
50	50	50
50	100	85
50	150	92
50	200	98
50	250	50

Influence of immersion period on the IE

It is observed from Fig. 1 that, as the immersion period increases, the IE decreases. For a 1-hour period the IE is very high, i.e. 92%; but for a 3-hour period it decreases to 85%; for a 5-hour period it decreases further to 70%. This may be due to the fact that as the period of immersion increases, the protective film formed on the metal surface, namely, Fe^{2+}-PVP complex, is broken by the aggressive chloride ion and hence the IE decreases. Further there is a competition between the formation of $FeCl_2$ (and also $FeCl_3$) and formation of Fe-PVP complex. It seems that as the immersion period increases the formation of $FeCl_2$ is more favoured than the formation of Fe-PVP complex at the anodic sites of the metal. Hence a decrease in inhibition efficiency is noticed as the period of immersion increases.

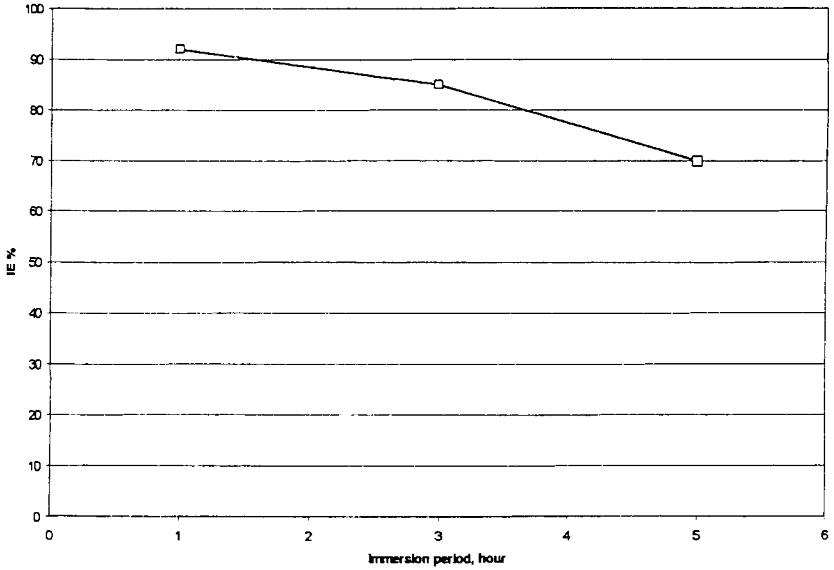


Fig.. 1: Influence of immersion period on the IE of the PVP system.

Surface analysis

The protective film formed on the surface of the metal in the presence of PVP system and also the PVP-Zn^{2+} system has been analysed by FTIR spectroscopy and fluorescence spectroscopy.

Analysis of FTIR spectra

The FTIR spectrum (KBr) of pure PVP is shown in Fig. 2a. The C=O stretching frequency appears at 1654 cm^{-1}. The C-N stretching frequency appears at 1291.8 cm^{-1}. The FTIR spectrum (KBr) of the film formed on the surface of the metal after immersion in the solution, containing 100 ppm of PVP is shown in Fig. 2b. It is found that the C=O stretching frequency of PVP has decreased from 1654 cm^{-1} to 1632 cm^{-1}. The C-N stretching frequency of PVP has decreased from 1291.8 cm^{-1} to 1081 cm^{-1}. It is inferred that PVP has coordinated with Fe^{2+} through the oxygen atom and nitrogen atom resulting in the formation of Fe^{2+}-PVP complex on the anodic sites of the metal surface /12/.

The FTIR spectrum (KBr) of the film formed on the surface of the metal after immersion in the solution containing 100 ppm of PVP and 5 ppm of

Zn^{2+} is shown in Fig. 2c. The C=O stretching frequency of PVP has decreased from 1654 cm^{-1} to 1596 cm^{-1}. The C-N stretching frequency of PVP has decreased from 1291.8 cm^{-1} to 1080 cm^{-1}. It is inferred that PVP has coordinated with Fe^{2+} through oxygen and nitrogen. The band at 1382 cm^{-1} is due to $Zn(OH)_2$ formed on the cathodic sites of the metal surface /2,12/.

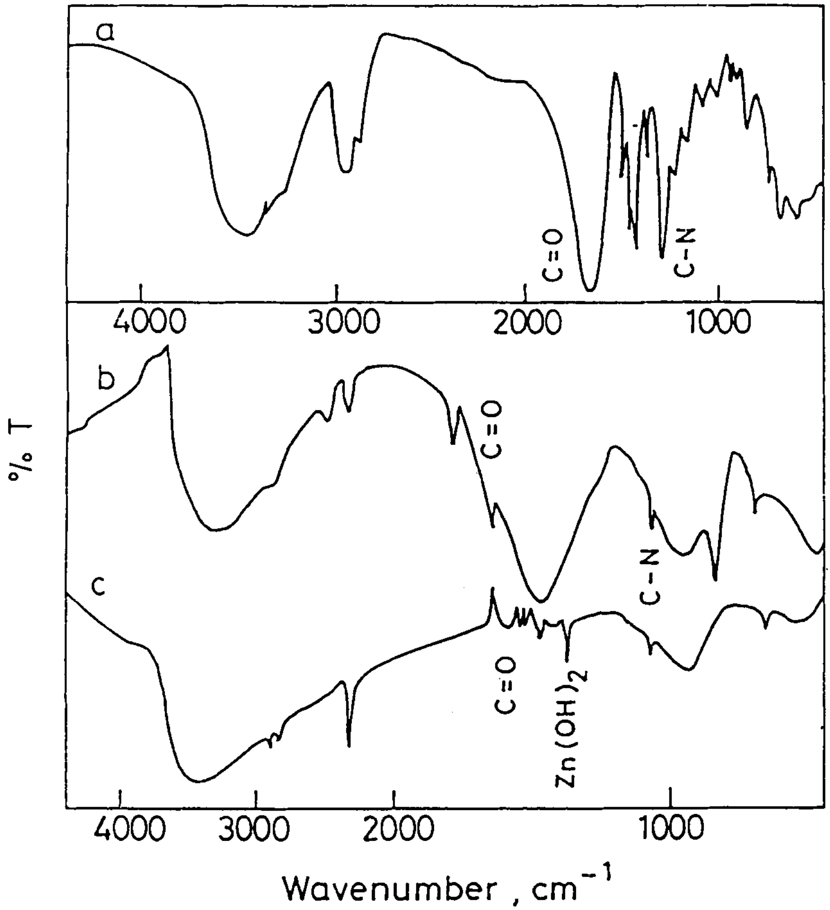


Fig. 2: FTIR spectra of pure PVP (a) and of film formed on surface of carbon steel after immersion in various solutions

(a) Cl^- 60 ppm + PVP 100 ppm

(b) Cl^- 60 ppm + PVP 100 ppm + Zn^{2+} 5 ppm

Fluorescence spectra

The emission spectrum (λ_{ex} = 363 nm) of the film formed on the surface of the metal after immersion in the solution containing 100 ppm of PVP is shown in Fig. 3a. Peaks appear at 468, 481 and 518 nm. This emission spectrum is due to Fe^{2+}-PVP complex formed on the metal surface. The corresponding excitation spectrum (λ_{em} = 468 nm) is shown in Fig.3c. Peaks

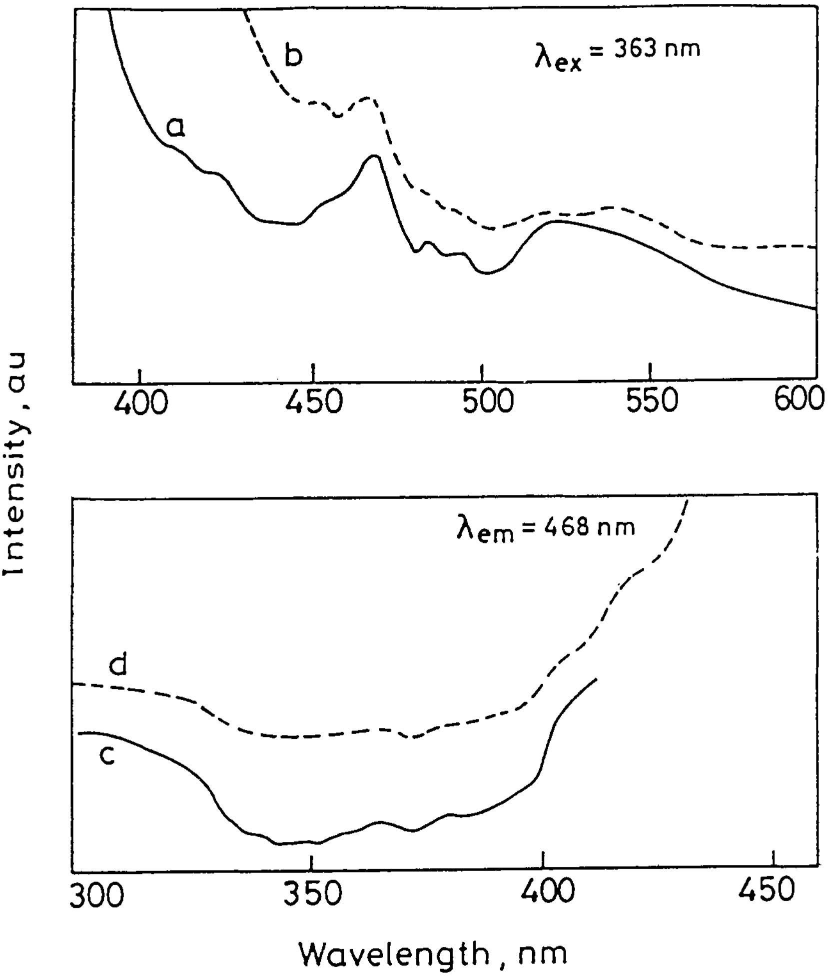


Fig. 3: Fluorescence spectra of film formed on surface of carbon steel after immersion in various solutions.
(a) and (c) Cl^- 60 ppm + PVP 100 ppm
(b) and (d) Cl^- 60 ppm + PVP 100 ppm + Zn^{2+} 5 ppm

appear at 365 and 404 nm.

The emission spectrum (λ_{ex} = 363 nm) of the film formed on the surface of the metal immersed in the solution containing 100 ppm PVP and 5 ppm Zn^{2+} is shown in Fig. 3b. Peaks appear at 467, 483, 539 and 576 nm. This spectrum is due to Fe^{2+}-PVP complex in the presence of $Zn(OH)_2$. The corresponding excitation spectrum (λ_{em} = 468 nm) is shown in Fig. 3d. The peaks appear at 364, 380, 405 and 418 nm.

CONCLUSIONS

The present study leads to the following conclusions.

- Polyvinyl pyrrolidone (PVP) has good inhibition efficiency (IE) in controlling corrosion of carbon steel in an aqueous environment containing 60 ppm of Cl^-, at pH 7.
- The protective film consists of Fe^{2+} - PVP complex; and it is found to be uv-fluorescent.
- At pH 3, the inhibition efficiency decreases.
- At pH 10 the IE is not altered very much.
- Addition of 5 ppm of Zn^{2+} to various concentrations of PVP lowers the IE of PVP, at pH 7, and also at pH 3. But at pH 10, the IE is not altered very much.
- In the presence of Zn^{2+} and PVP, the protective film consists of Fe^{2+}-PVP complex and $Zn(OH)_2$. The protective film is found to be uv-fluorescent.
- Addition of CTAB to PVP system lowers the IE of PVP, after a particular concentration of CTAB. Similar is the case with SDS.
- As the immersion period increases, the IE of the PVP system decreases.

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REFERENCES

1. S. Rajendran, B.V. Apparao and N. Palaniswamy, *Anti-Corrosion Methods and Materials*, **44**, 308 (1997).
2. S. Rajendran, B.V. Apparao and N. Palaniswamy, *Electrochimica Acta*, **44**, 533 (1998)
3. S. Rajendran, B.V. Apparao and N. Palaniswamy, *Anti-Corrosion Methods and Materials*, **46**, 111 (1999).
4. T. Grchev, M. Cvetkovska, T. Stafilov and J.W. Schultze, *Electrochimica. Acta*, **36**, 1315 (1991).
5. G.H. Sedahmed, B.A. Abd-El-Naby, and A.Abdel-Khalik, *Proc 5th Europ. Symp. Corrosion Inhibitors*, Uni. Ferrara, Italy, **1**, 15 (1980).
6. S. Rajendran, R.M. Joany, B.V. Apparao and N. Palaniswamy, *Bulletin of Electrochemistry*, **18**, 25 (2002).
7. P. Dezerville, M. Lenglet, E. Bencher, S. Weber and S. Scherrer, *Proc. 7th Europ. Symp. Cossosion Inhibitors*, Ferrara, Italy, **2**, 861 (1990).
8. P. Falewicz, S. Kuczkowska, and I. Ciepacz, *Pr. Nauk. Inst. Technol. Nieorg. Nawozow Miner. Politech. Wroclaw.*, **33**, 68 (1987).
9. A. John Amalraj, M. Sundaravadivelu, A. Peter Pascal Regis and S. Rajendran , *Proc. of 9th Europ. Symp. Corrosion Inhibitors*, Uni. Ferrara, Italy, 2000.
10. G Wranglen, *Introduction to Corrosion and Protection of Metals*, Chapman and Hall, London, 1985; 236.
11. V.R. Gowariker, N.V. Viswanathan and Jayadev Sreedhar, *Polymer Science*, Wiley Eastern Limited, New Delhi, 1993; 293.
12. R.M. Silverstein, G.C. Bassler and T.C. Morrill, in: *Spectrometric Identification of Organic Compounds*, John Wiley Sons, New York, 1981; 166.