

Research Article

Corrosion and Inhibition Effects of Mild Steel in Hydrochloric Acid Solutions Containing Organophosphonic Acid

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A study has been made on the mechanism of corrosion of mild steel and the effect of nitrilo trimethylene phosphonic (NTMP) acid as a corrosion inhibitor in acidic medium, that is, 10% HCl using the weight loss method and electrochemical techniques, that is, potentiodynamic and galvanostatic polarization measurements. Although corrosion is a long-time process, but it takes place at a faster rate in the beginning which goes on decreasing with due course of time. The above-mentioned methods of corrosion rate determination furnish an average value for a long-time interval. Looking at the versatility and minimum detection limit of the voltammetric method, the authors have developed a new voltammetric method for the determination of corrosion rate at short-time intervals. The results of corrosion of mild steel in 10% HCl solution with and without NTMP inhibitor at short-time intervals have been reported. The corrosion inhibition efficiency of NTMP is 93% after 24 h.

1. Introduction

Mild steel is a major material of construction. It is extensively used in chemical and allied industries for handling alkalis, acids, and salt solutions [1]. Hydrochloric (HCl) acid is the solvent most often employed for chemical cleaning. It attacks a wide range of scales [2]. Nitrogen compounds constitute the largest class of inhibitors for hydrochloric acid [3] solution. During the past decade a number of polymers and phosphonates have been used in different inhibitor compositions in aqueous and acid solutions [4]. They form stable complexes and some times act as detergent also. The role of inhibitor is the prevention of the adsorption of aggressive anions and reduction of the dissolution rate of the passivating oxide. In the present paper we have studied the action and effectiveness of nitrilo trimethylene phosphonic acid (NTMP) as inhibitor for corrosion of carbon steel in (10% HCl) acid solution.

Most of the methods are proposed in the field of corrosion rate determination, but they furnish an average value for a long-time interval [5]. Looking at the sensitivity and minimum detection limits [6, 7] of polarographic techniques, that is, direct current polarography (DCP), differential pulse polarography (DPP), and voltammetric, that is, differential

pulse anodic stripping voltammetric (DPASV) method has been used to determine the corrosion rates and inhibition efficiency of NTMP of mild steel in 10% HCl solution at short time intervals. Significantly it has also been possible to determine the corrosion rates simultaneously with respect to Fe(II) and Fe(III) which is not possible using other methods prevalent in the field. Their results have been discussed in the paper.

2. Experimental

2.1. Chemicals and Reagents. All the chemicals used were of anal R/BDH grade. The inhibitor (NTMP, 99.9% pure) was synthesized at the Central Research Institute For Chemistry, Budapest, Hungary. Experiments were carried out in 10% HCl solution. Mild Steel specimens 50 * 20 * 4 mm size having composition (C-0.23%, P-0.05%, S-0.055%) were used in experiments. These specimen were polished following the usual procedure [8]. All the measurements were carried out at room temperature 30°C.

2.2. Gravimetric Measurements. After abrasion with 600 grit papers all samples were degreased with acetone, pickled

TABLE 1: Results of planned interval test (PIT) on mild steel in 10% HCl solution.

S. no.	Period	Without inhibitor		With inhibitor		% inhibition
		Concentration (milligram $\times 10^2$)	Corrosion rate (milligram centimeter ⁻² hour ⁻¹ $\times 10^2$)	Concentration (milligram $\times 10^2$)	Corrosion rate (milligram centimeter ⁻² hour ⁻¹ $\times 10^2$)	
1	A_1 (3 h)	18.96	21.2	5.21	5.82	72
2	A_t (22 h)	31.05	4.70	6.32	0.96	79
3	A_{t+1} (22 + 3 h)	34.58	4.64	6.40	0.85	82
4	B (3 h)	3.33	3.72	0.50	0.50	96
5	A_c (3 h)	3.53	3.94	0.08	0.08	97

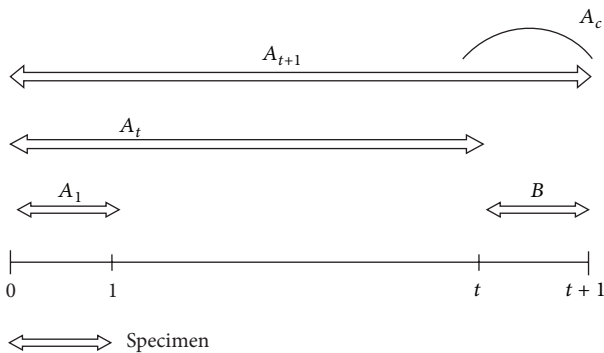


FIGURE 1: Procedure of “planned interval test” technique identical specimen all placed in the some corrosive fluid imposed conditions of the test kept constant for entire time A_{t+1} . The terms A_1 , A_t , A_{t+1} , and B represent corrosive damage experienced by each specimen, A_c is calculated by subtracting A_t from A_{t+1} .

in 15% HCl solution, washed under running tap water, rinsed in distilled water, dried with acetone, and weighed. The variation of solution corrosiveness and corrosion rate as a function of time was investigated using the planned interval test technique [8]. Three weighed specimens were introduced into the solution. These were removed after various exposure times, giving damage factors referred to as A_1 for 22 h, A_t for 3 h, and A_{t+1} for 25 h. A fourth specimen (B) was introduced into the cell for the last period for 3 h. The values of A_1 , B (measured values) and A_c (calculated from A_1 , and A_{t+1}) relate to the same testing period, but under different conditions. This technique is schematically illustrated in Figure 1.

After each experiment, the specimens were cleaned by washing in water and acetone then weighed; from these measurements the corrosion rates were calculated. The methods of evaluating the results and combinations of situations are summarized in Table 1.

2.3. Potentiodynamic Polarization Measurement. The specimen was molded into epoxy resin in order to cover the sides of the rod, while the circular cross section area of the cylinder was exposed to the solution. The specimen was polished and washed with distilled water before the experiment. The potential scan path was 50 mV/5 min. The observed current was plotted against applied potential.

2.4. Galvanostatic Polarization Measurement. The galvanostatic polarization measurements were also made in 10% HCl solution on 10 cm² cylindrical surface of the working electrode. Saturated calomel electrode (SCE) was used as a reference electrode. An AJCO Electronics (model VT S5016) attached to a multiplex galvanometer was used for the galvanostatic studies. The polarization currents were measured by using a cycle of 10 s and changing potential by 10 mV. Both anodic and cathodic cycles were used alternately. The corrosion current density was plotted against the applied potential.

2.5. Voltammetric and Polarographic Measurements. An Elico Pulse Polarograph (model CL-90) was used for these studies. A cell consisting of three electrodes, namely, saturated calomel electrode as a reference, a coiled platinum wire as an auxiliary, and a dropping mercury electrode (for DCP and DPP)/glassy carbon fiber electrode (for DPASV) as a working electrode, was used. The test specimens were polished as discussed earlier, and one such specimen was suspended in 10% HCl solution at room temperature (25°C). Nitrogen gas was bubbled throughout the solution through the experiment to avoid the oxidation of dissolved Fe(II) to Fe(III). A definite aliquot of the solution was withdrawn from the test solution at different intervals (5, 10, 20 min, 1, 2, and 24 h), and polarograms and voltammograms were recorded in deaerated 0.1 M ammonium tartrate + 0.001% gelatin at pH 9.0 \pm 0.1. The pH of the test solution was adjusted using ammonia solution. A similar experiment was performed using 170 mg/L NTMP in 10% HCl solution.

3. Results and Discussion

3.1. Gravimetric Measurement. The results of weight loss determination by gravimetric are shown as corrosion rates in the presence and absence of NTMP inhibitor in Table 1. The data obtained for the periods A_1 and B suggest that solution corrosiveness increases in the base solution (10% HCl) while in the presence of NTMP it decreases ($B < A_1$). The higher corrosivity of the solution can be attributed to the increase in concentration of iron ions in the solution. This suggests that NTMP molecules reduce the stimulating effect of iron ions. By comparison with the data relating to B and A_c it can be concluded that metal corrodibility decreases ($A_c < B$) as a function of time in the presence of the NTMP.

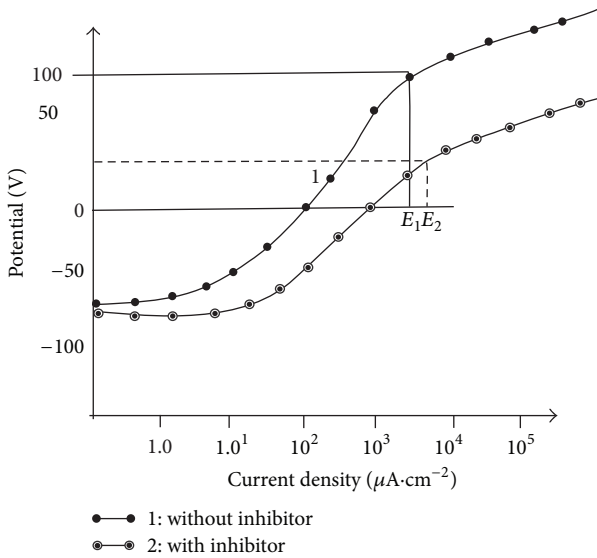


FIGURE 2: Potentiodynamic polarization curves of carbon steel in 10% HCl with, and without inhibitor.

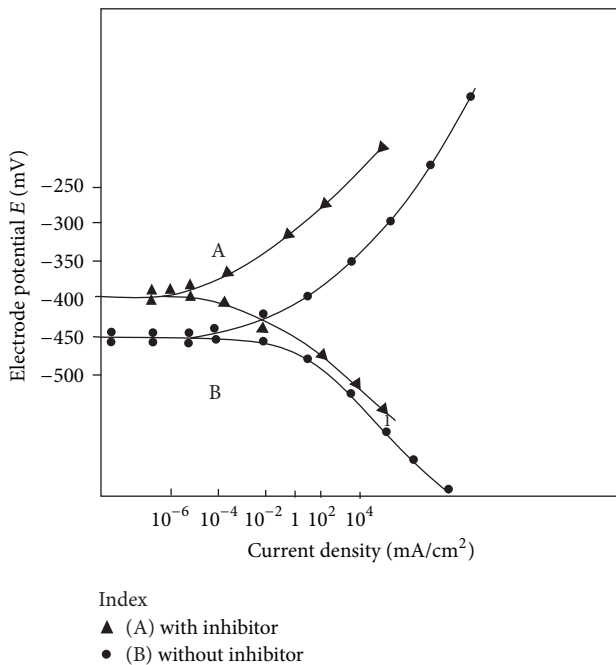


FIGURE 3: Galvanostatic polarization curves of carbon steel in 10% HCl with and without inhibitor.

This indicates that the formation of an inhibitor film requires some time; that is, the inhibition process has an induction period. The increased inhibition effect of NTMP may be explained on the argument that nitrogen of NTMP facilitates complex formation between metal ions coming out in the solution with NTMP and also the formation of complexed film at the metal surface.

3.2. Potentiodynamic Polarization Measurements. Figure 2 shows the results of potentiodynamic polarization measurements in the presence and absence of NTMP inhibitor in

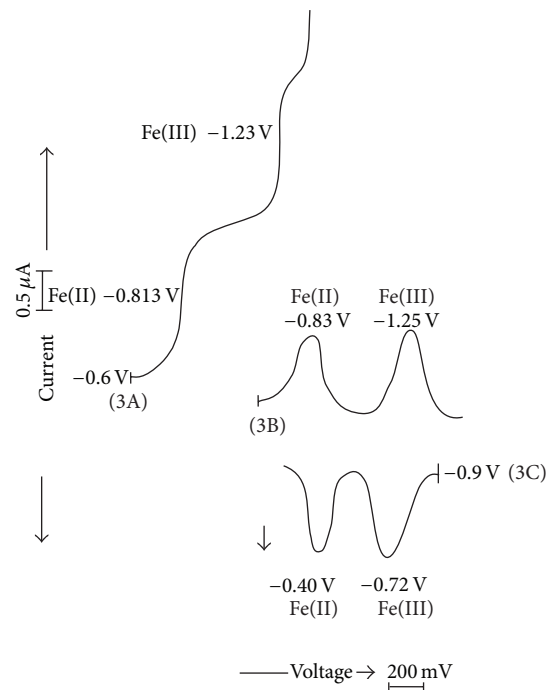


FIGURE 4: (a) Direct current polarogram, (b) Differential pulse polarogram, (c) Differential pulse anodic stripping voltammogram of corrosion solution (10 mL) in 0.1 M ammonium tartrate + 0.001% gelatin at pH 9.0 ± 0.1 after 5 min. of exposure.

10% HCl solution. The curve clearly shows the cathodic and anodic inhibition properties of inhibitor. It is quite clear from the curves that the corrosion potentials are more positive (anodic) than the rest of potentials. The inhibitor shows a remarked effect in lowering the current. However, in the cathodic region the effect is not significant. Thus it could be concluded that NTMP affects the anodic part of the corrosion process. Thus they work as anodic protector.

3.3. Galvanostatic Polarization Measurement. Figure 3 depicts the galvanostatic polarization curves for the corrosion of mild steel in 10% HCl solution with and without NTMP inhibitor. It is clear from the figure that both anodic and cathodic currents decrease in the presence of inhibitor. However, the corrosion potentials are shifted to more electropositive values with NTMP inhibitor, but the Tafel slopes of the curves remain almost the same. The shift in corrosion potential with NTMP is +50 mV. Thus, it could be concluded that the film formed by the inhibitor acts through the blocking effect, mainly on the anodic reaction.

3.4. Voltammetric and Polarographic Measurements. Figures 4(a), 4(b), and 4(c) are the direct current polarogram (DCP), differential pulse polarogram (DPP), and differential pulse anodic stripping voltammogram (DPASV) for corrosion sample after 5 min in 0.1 M ammonium tartrate and 0.001% gelatin at pH 9.0 ± 0.1. The half-wave potential ($E_{1/2}$)/peak potential (E_p) values for Fe(II) and Fe(III) are -0.81 V/-0.83 V and -1.23 V/-1.25 V, respectively, in DCP/DPP

TABLE 2: Corrosion rates with respect to concentration of Fe(II), Fe(III), and total Fe(II + III) for mild steel in 10% HCl without inhibitor using voltammetric and polarographic methods.

(a) DPP mode							
Time	Fe(II)		Fe(III)		Total Fe(II + III)		
	Conc*	CR**	Conc*	CR**	Conc*	CR**	
(1) 5 min	5.91	2.37	8.23	3.31	14.14	5.69	
(2) 10 min	6.13	1.23	9.89	1.99	16.02	3.22	
(3) 20 min	7.93	0.79	11.21	1.12	19.14	1.92	
(4) 1 h	12.16	0.40	12.55	0.42	24.17	0.83	
(5) 2 h	15.98	0.26	16.81	0.28	32.78	0.55	
(6) 24 h	50.57	0.07	56.17	0.07	107.28	0.15	

(b) DPASV mode							
Time	Fe(II)		Fe(III)		Total Fe(II + III)		
	Conc*	CR**	Conc*	CR**	Conc*	CR**	
(1) 5 min	5.92	2.38	8.24	3.31	14.16	5.70	
(2) 10 min	6.15	1.23	9.87	1.98	16.02	3.22	
(3) 20 min	7.93	0.79	11.21	1.12	19.11	1.92	
(4) 1 h	12.16	0.40	12.50	0.42	24.57	0.82	
(5) 2 h	15.98	0.26	16.80	0.28	32.78	0.55	
(6) 24 h	50.57	0.07	56.17	0.07	107.28	0.15	

*Corrosion concentration $\times 10^2$ milligram.**Corrosion rate $\times 10^2$ milligram centimeter⁻² hour⁻¹.

TABLE 3: Corrosion rates with respect to Fe(II) + Fe(III) for mild steel in 10% HCl solution with NTMP inhibitor (170 mg/L).

Time	DPASV mode			DPP mode		
	Conc*	CR**	% inhibition	Conc*	CR**	% inhibition
(1) 5 min	6.28	2.530	55.6	6.26	2.52	55.7
(2) 10 min	6.41	1.290	59.9	6.41	1.290	59.9
(3) 20 min	6.99	0.693	63.9	6.99	0.693	63.9
(4) 1 h	7.18	0.235	71.6	7.02	0.235	71.6
(5) 2 h	7.21	0.119	80.0	7.12	0.119	80.6
(6) 24 h	7.91	0.010	93.3	7.81	0.010	93.3

*Corrosion concentration $\times 10^2$ milligram.**Corrosion rate $\times 10^2$ milligram centimeter⁻² hour⁻¹.

Conflict of Interests

The authors, that is, Manish Gupta, Jyotsna Mishra, and K. S. Pitre declare that they do not have any conflict of interests regarding this paper.

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References

- [1] A. Singh, E. E. Ebenso, M. A. Quraishi et al., "Corrosion inhibition of carbon steel in HCl solution by some plant extracts," *International Journal of Corrosion*, vol. 2012, Article ID 897430, 20 pages, 2012.
- [2] T. Horvath, E. Kalman, G. Kutsan, and A. Rauscher, "Corrosion of mild steel in hydrochloric acid solutions containing organophosphonic acids," *British Corrosion Journal*, vol. 29, no. 3, pp. 215–218, 1994.
- [3] P. Mohan, R. Usha, G. P. Kalaighan, and V. S. Murlidharan, "Inhibition effect of benzohydrazide derivatives on corrosion behaviour of mild steel in 1 M HCl," *Journal of Chemistry*, vol. 2013, Article ID 541691, 7 pages, 2013.
- [4] H. Ryu, N. Sheng, T. Outsuka, S. Fugita, and H. Kajtyama, "Polypyrrole film on 55% al-zn-coated steel for corrosion prevention," *Corrosion Science*, vol. 56, pp. 67–77, 2012.
- [5] A. J. Freelman, *Materials Performance*, vol. 23, pp. 9–11, 1984.
- [6] T. E. Edmonds and J. I. Guoliang, "Carbon fibre micro-electrodes in the differential pulse voltammetry of copper ions," *Analytica Chimica Acta*, vol. 151, pp. 99–108, 1983.
- [7] A. Wachter and R. S. Treseder, "Corrosion testing evaluation of metals for process equipment," *Chemical Engineering Progress*, vol. 43, pp. 315–326, 1947.
- [8] E. Kálmán, F. H. Kármán, J. Telegdi, B. Várhegyi, J. Balla, and T. Kiss, "Inhibition efficiency of n-containing carboxylic and carboxy-phosphonic acids," *Corrosion Science*, vol. 35, pp. 1477–1481, 1993.
- [9] V. K. Chitale and K. S. Pitre, *Reviews in Analytical Chemistry*, vol. 6, pp. 177–184, 1982.
- [10] V. Rai and K. S. Pitre, "Corrosion behaviour of carbon steel in DTPMP inhibited neutral medium," *Indian Journal of Chemistry A*, vol. 42, no. 1, pp. 106–108, 2003.
- [11] J. Shukla and K. S. Pitre, "Corrosion and inhibition kinetics of PVA polymer on carbon steel in sulfuric acid solution," *Indian Journal of Chemistry A*, vol. 44, no. 11, pp. 2270–2273, 2005.
- [12] J. Shukla, P. Jain, and K. S. Pitre, "Inhibitive action of thiourea plus Ca towards corrosion of brass in acidic solution," *Corrosion Reviews*, vol. 22, pp. 145–156, 2004.



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