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A new voltammetric method for corrosion rate determination

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A new voltammetric method has been proposed to determine the corrosion rates of mild steel in 2*N* HCl with and without diethylenetriamine pentamethylene phosphonic acid (DTPMP) inhibitor at short time intervals. Significantly, it has also been possible to determine simultaneously the corrosion rates with respect to Fe(II) and Fe(III). These results have been compared with the average corrosion rates obtained using gravimetric (planned interval test method).

Various organophosphonic acid derivatives are widely used as corrosion inhibitors in neutral and acidic aqueous solutions[1-6]. They not only form stable complexes but also act as detergents. The metal complexes of aminophosphonic acids have been studied extensively in the solid state[7-10], although solution studies have been perhaps more limited[11-13]. In the present paper we have studied the action and effectiveness of diethylenetriamine pentamethylene phosphonic acid (DTPMP) as inhibitor for the corrosion of carbon steel in (2*N* HCl) acid solution. The corrosion and inhibition processes were examined at 30° and 60°C by gravimetric planned interval test (PIT) method.

Most of the methods prevalent in the field of corrosion rate determination furnish an average value for a long time interval. However, looking at sensitivity and minimum detection limits of voltammetric procedure, we have developed a voltammetric differential pulse polarographic (DPP) and differential pulse anodic stripping voltammetric (DPASV)) procedure for the determination of corrosion rates at short time intervals, the results of which have also been discussed.

Materials and Methods

All the chemicals used were of BDH/AR grade. The inhibitor (DTPMP, 99.9% pure) was synthesised at the Central Research Institute for Chemistry, Budapest, Hungary.

The experiments were carried out in 2*N* HCl solution at 30° and 60°C separately.

Steel specimen 50*20*4 mm (Carbon, Steel, C 0.23%, P 0.05%, S 0.055%) were used in the weight loss measurements. These specimen were polished following the usual procedure[2]. The variation of metal corrodibility, solution corrosiveness and corrosion rate as a function of time were investigated with the planned interval test technique[14]. The procedure has been depicted in Fig. 1. After the experiments, the specimen were cleaned with water and acetone, weighed and from the weight loss measurements, the corrosion rates were calculated. Similar experiment was done in the presence of DTPMP inhibitor. The evaluation of results and combination of solutions resulted in the following data.

At 30°C Exposure time		A_1	A_t	A_{t+1}	B	C
		3 h	15 h	18 h	3 h	
Corrosion rate without DTPMP	g.m^{-2}day^{-1}	84.9	148.1	174.1	134.9	253.5
Corrosion rate with DTPMP	g.m^{-2}day^{-1}	13.2	12.1	11.5	10.6	9.9
At 60°—						
Corrosion rate without DTPMP	g.m^{-2}day^{-1}	921.9	1116.1	1163.1	1060.7	1295.0
Corrosion rate with DTPMP	g.m^{-2}day^{-1}	194.4	195.8	192.4	145.5	193.5

An Elico (India), pulse polarograph model CL-90 was used for voltammetric studies. A cell consisting of three electrodes viz. saturated calomel as reference electrode, a coiled platinum electrode as auxillary and a dropping mercury electrode (for DPP) and glassy carbon fibre electrode (for DPASV) as working electrode, were used, respectively. The pulse amplitude used for DPP DPASV

Table 1—Corrosion rates with respect to Fe(II) and Fe(III) for carbon steel in 2*N* HCl without inhibitor using voltammetric methods

Sl. no.	Time	DPASV mode				DPP mode			
		For Fe(II)		For Fe(III)		For Fe(II)		For Fe(III)	
		1	2	1	2	1	2	1	2
1	5 min	7.15	28.00	5.77	23.30	6.20	25.90	6.40	25.90
2	10 min	6.10	13.51	7.55	16.80	10.30	20.80	8.20	16.59
3	20 min	13.00	13.14	8.90	8.99	15.50	15.60	6.20	6.26
4	1h	3.43	1.15	20.00	6.71	15.50	5.20	15.50	5.20
5	2h	5.00	0.83	34.30	5.75	17.60	2.95	25.66	4.29
6	24h	19.25	0.26	673.00	0.94	49.80	0.69	43.90	0.61

(1) Concentration in mg × 10^2; (2) corrosion rate × 10^3 in mg $cm^{-2}h^{-1}$.

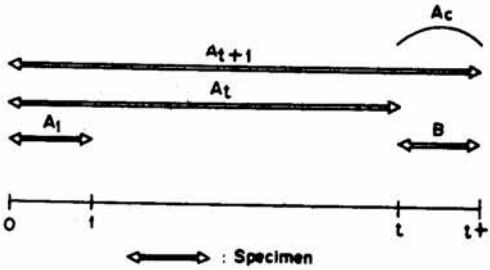

Fig. 1—Procedure of "planned interval test" technique. Identical specimen all placed in the same corrosive fluid imposed conditions of the test kept constant for entire time A_{t+1}. The terms, A_1,. A_t, A_{t+1}, B, represent corrosion damage experienced by each specimen. A_c is calculated by substracting A_t from A_{t+1}

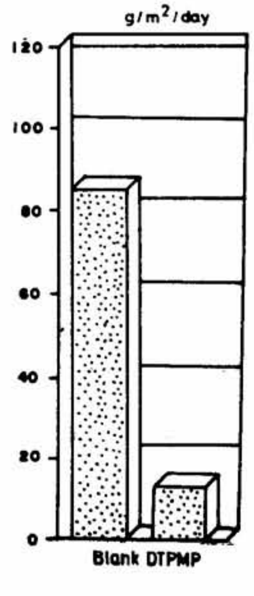

Fig. 2—Corrosion rates (A_1) of carbon steel in 2*N* HCl containing 200 ppm of DTPM phosphonic acid at 30°C

Table 2—Total corrosion rates in 2*N* HCl without inhibitor using voltammetric method

Sl no.	Time	DPASV mode		DPP mode	
		1	2	1	2
1	5 min	12.9	52.22	12.6	51.00
2	10 min	13.6	27.53	18.5	37.44
3	20 min	21.9	22.14	21.5	21.80
4	1 h	23.4	7.85	31.0	10.40
5	2 h	39.3	6.59	43.2	7.24
6	24 h	86.5	1.20	93.7	1.31

(1) Concentration in mg × 10^2; (2) Corrosion Rate × 10^3 in mg $cm^{-2}h^{-1}$.

measurement was 25 mV. The test specimen were polished as discussed earlier and one such specimen was suspended in 350 ml 2*N* HCl solution at room temperature 30°C ± 1°C. Nitrogen gas was bubbled through the solution throughout the experiment to avoid oxidation of dissolved Fe(II) to Fe(III). A definite aliquot of the solution was withdrawn from the test solution at short time intervals (5 min, 10 min, 20 min, 1 h, 2 h, 3 h and 25 h). Polarograms and voltammograms of the test solutions were recorded in deaerated 0.1*M* ammonium tartarate + 0.001% gelatin, *p*H = 9.00 ± 0.02. The *p*H of the analyte was adjusted using ammonia solution. A similar experiment was performed using 10 ml of diethylenetriamine pentamethylene phosphonic acid solution containing 70 mg of the inhibitor in 2*N* HCl.

Results and Discussion

The results of weight loss determinations (at

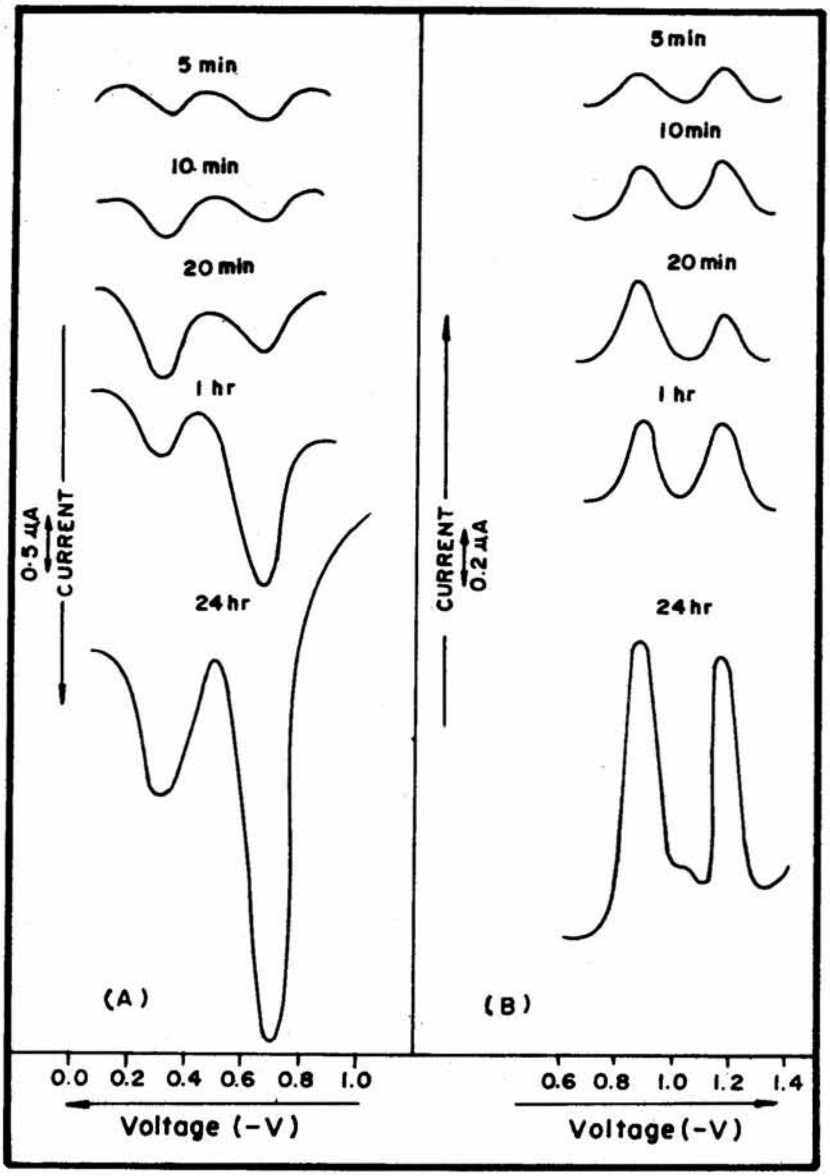

Fig. 3—(A) DPASV and (B) DPP signals of the corrosion solution (10 ml) in $0.1M$ ammonium tartarate $+0.001\%$ gelatin, pH (9.00 ± 0.02) at different time intervals.

30°C) are shown as corrosion rates (A_1) in the presence and absence of DTPMP in Fig. 2. It clearly shows that DTPMP decreases the corrosion rate. Similar results are observed at 60°C. The corrosion rates at different exposure periods, showed that although the increase in temperature from 30° to 60°C resulted in an increase in the corrosion rate, but to a lesser degree with DTPMP. The data obtained for the periods A_1 and B suggest that solution corrosiveness increase in the base solution ($2N$ HCl), while in the presence of DTPMP, 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 DTPMP molecules reduce the stimulating effect of iron ions. By comparison of the data relating to B and A_c it can be concluded that metal coorodibility decreases ($A_c < B$) as a function of time in the presence of the DTPMP, at 30°C. This indicates that the formation of an inhibitor film requires sometime, i.e. the inhibition process has an induction period. The increase in metal corrodibility at 60°C can be attributed to the increase in the real surface of the specimen against time. The increased inhibition effect of DTPMP may be explained on the argument

Table 3—Corrosion rates with respect to (Fe(II) + Fe(III)) for carbon steel in 2*N* HCl with DTPMP inhibitor (200 ppm)

Sl. no.	Time	DPASV mode			DPP mode		
		1	2	3	1	2	3
1	5 min	4.39	17.80	65%	4.44	17.81	65%
2	10 min	4.44	8.90	67%	5.40	10.93	70%
3	20 min	5.55	5.56	74%	5.50	5.56	75%
4	1h	5.56	1.89	75%	6.60	2.21	78%
5	2h	6.55	1.10	83%	7.00	1.17	84%
6	24h	6.66	0.09	92%	7.14	0.09	92%

(1) Concentration in mg × 10^2; (2) corrosion rate in mg $cm^{-2}h^{-1} \times 10^3$; (3) percentage inhibition.

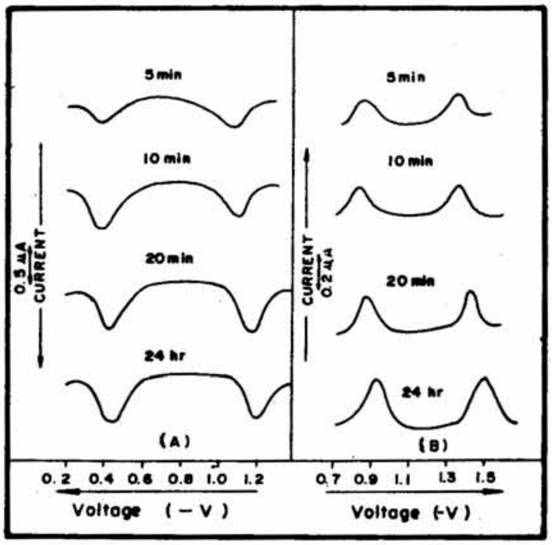

Fig. 4—(A) DPASV and (B) DPP signals for the corrosion of carbon steel in 2*N* HCl with DTPMP (200 ppm) inhibitor at different time intervals, in 0.1*M* ammonium tartarate +0.001% gelatin *p*H (9 ± 0.02)

that algthough there is slight deprotonation of the central nitrogen but the protonation of the two terminal nitrogens are increased, which facilitates complex formation between metal ions coming out in the solution with DTPMP and also the formation of complexed film at the metal surface.

Figures 3A and 3B are the voltammograms and pulse polarograms of the corrosion mixture in 0.1 *M* ammonium tartarate ($pH = 9 \pm 0.02$) at varying time intervals. These curves show that using voltammetric/polarographic procedure it is possible to analyse the presence of Fe(II) and Fe(III) in the solution. Fe(II) and Fe(III) produce two separate well-defined peaks in each case. The peak potentials (E_p) of Fe(II) and Fe(III) are −0.32 V and −0.68 V versus SCE in DPASV mode and −0.83 V and −1.20 V as SCE in DPP mode. The difference in peak potential for Fe(II) and Fe(III) in DPP and DPASV modes may be explained on the basis of increasing ease of reduction on carbon fibre electrode for the Fe(II)/Fe(III) couple, which in turn shifts the peak potentials to more positive values[15,16]. The peak height (i_p) for each of two metal ions over the whole of working experimental range in DPP mode is proportional to its concentration, but, using DPASV mode, i_p is found to be proportional to Fe(II)/Fe(III) concentrations up to Fe(II) (13 mg/l) and Fe(III) (8.9 mg/l), at higher Fe(II)/Fe(III) concentration, the peak due to Fe(II) is suppressed and that of Fe(III) gets an additional height. However, the sum of Fe(II) and Fe(III) concentrations as observed using DPASV mode is found to be nearly equal to that observed using DPP mode. The corrosion rates at different time intervals with respect to Fe(II) and Fe(III) and the sums of Fe(II) and Fe(III) have been calculated and listed in Tables 1 and 2 respectively. Figures 4A and 4B show that DPASV and DPP curves for the corrosion mixture to which 200 ppm DTPMP has been added. A shift in the E_p value for each of the Fe(II) and Fe(III) indicates the M:DTPMP complex formation in the solution. Since the shift in peak potential of Fe(III) is more than that of Fe(II), in the complexed system, it could be concluded that Fe(III) is more reactive in complex formation with DTPMP than Fe(II)[17]. The corrosion rates in the presence of DTPMP have been tabulated in Table 3. A perual of the data in Tables 1, 2, and 3 clearly show that the rate of corrosion is very fast in the beginning of the experiment, which goes on decreasing with due course of time. The corrosion inhibition efficiency of DTPMP is 92% after 24h. A comparison of the corrosion rate data as calculated by voltammetric and weight loss method clearly shows the utility of DTPMP as an inhibitor for the corrosion of carbon steel in acidic medium.

From the above figures and tables, it could be concluded that DPP furnishes dependable data for corrosion rates with respect to Fe(II) and Fe(III) for the corrosion of carbon steel in acidic medium. Although gravimetric, galvanostatic, potentiodynamic and other methods are also in use for corrosion rate determination[1-6], but they furnish an average value of corrosion rate for a long span of time. However, the proposed voltammetric procedure is found to be highly useful for the determination of corrosion rates at short time intervals and that too with respect to different speceis present in the solution e.g. Fe(II) and Fe(III) in the present case, which is otherwise not possible using methods prevalent in the field of corrosion rate determination and also in the field of trace analysis e.g. atomic absorption spectrometry.

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