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Inhibition Effects of Phenols on Corrosion of Mild Steel in Three Mineral Acids

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Inhibition by phenols on the corrosion of mild steel in nitric acid, sulfuric acid and hydrochloric acid media has been studied. A trend observed among the phenols in corrosion inhibition efficiency is *p*-cresol > *m*-cresol > phenol > 2-naphthol > 1-naphthol > 2-nitrophenol. Amongst naphthols, 2-naphthol was stronger inhibitor than 1-naphthol which appears to be relative to their structures. In general 2-naphthol and *p*-cresol are found to be stronger inhibitor over the range of concentrations of acids used. While phenol *m*-cresol and 1-naphthol shown greater inhibition efficiency when they are applied at higher concentrations. 2-Nitrophenol shows oxidizing nature in all the acids over the range of concentrations used.

Key Words: Phenol, Inhibitor, Oxidation, Mild steel, Acidic media.

INTRODUCTION

Iron is one of the most vital metals extensively used in acid media under aerobic and anaerobic conditions where it is easily susceptible to corrosion. Corrosion of iron deprives it of its mechanical strength and sheds scales of rust making metal bars, sheets, pipes, bridges and ship hulls thinner and weaker. Hence there is a need of preservation of metallic properties of iron. Prevention of corrosion and preservation of metallic properties of iron in working media is a thrust area of industrial interest[1].

Various aromatic amines[2], chloro-substitueted anilines[3] and thiocompounds[4] in nitric acid media and amino phenols, nitro-phenols and cresols in alkali media[5,6] are also reported to be used as corrosion inhibitors. Some organic phosphonic acids are well known anticorrosive agents and scale deposit inhibitors and have wide spread use in industrial cooling water systeams[7]. The role of inhibitor is the prevention of the adsorption of aggressive anions and reduction of dissolution rate of the passivating oxide[8].

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On the basis of Chin and Nobe[9], mechanism of anion adsorption and dissolution of metal in aqueous acid media may be presented as below.

$$Fe + H_2O + X^- \rightarrow [FeXOH]_{ads} + H^+ + e^-$$
$$[FeXOH]_{ads} \rightarrow [FeXOH]^+ e^- \text{ (r.d.s.)}$$
$$[FeXOH] + H^+ \rightarrow Fe^{2+} + X^- + H_2O,$$

where $X = Cl^-$ or NO_3^-

Most organic inhibitors act by adsorption on the metal surface and inhibitor adsorption is considered from thermodynamic point of view *i.e.* as adsorption isotherms, energies of adsorption, *etc*[10]. Considering this point of view, in the present work comparative study of the effect of phenols on corrosion of mild steel in nitric acid, hydrochloric acid and sulphuric acid (0.5 M) media are investigated on the basis of weight loss measurements.

EXPERIMENTAL

To access the effect of phenols on corrosion of mild steel in acids, phenol, *p*-cresol, *m*-cresol, 2-naphthol, 1-naphthol and 2-nitrophenol were used. To the 50 mL of standard (0.5 N) acid solutions phenols were added in increasing concentrations (0.5, 1 and 2 %) and cleaned specimen wires of 4" length and 0.108 cm in diameter were dipped at room temperature for 1, 2 and 3 h with one specimen as control for each concentration. All chemical used were of AR grade.

At the end of the experiment, the specimen wires were removed from solutions, cleaned with distilled water and weight losses were recorded. From weight loss, per cent loss in weight (PL), inhibitor efficiency (IE) and free energy (ΔGa) were computed[11].

RESULTS AND DISCUSSION

The results of per cent loss in weight, inhibitor efficiency and free energy values of the phenols in corresponding acids are given in Tables 1-3.

Inhibitor efficiency was calculated as follows:

$$IE(\%) = \frac{Wu - Wi}{Wu} \times 100$$

where IE = inhibitor efficiency, Wu = weight loss of metal in uninhibited acid and Wi = weight loss of metal in inhibited acid.

The values of free energy of adsorption (ΔGa) were calculated with the following equation[12].

$$\log\left[\frac{\theta}{(1-\theta)}\right] - \log B$$

where log B = -1.74 × (ΔGa/2.303 RT) and C is phenol concentration, θ = (Wu–Wi/Wi) is the fraction of metal surface covered by the inhibitor.

TABLE-1
EFFECT OF PHENOLS ON CORROSION OF MILD STEEL IN 0.5 N HNO_3 MEDIA

System		0.5 % conc. phenols			1 % conc. phenols			2 % conc. phenols		
		1 h	2 h	3 h	1 h	2 h	3 h	1 h	2 h	3 h
Control	PL	6.28	9.25	16.33	6.28	9.25	16.33	6.28	9.25	16.33
Phenol	PL	5.81	9.07	14.14	5.75	8.48	15.60	5.17	6.12	10.73
	ΔGa	6776	-4901	12585	5368	3263	13771	-3668	2562	1729
	IE	7.48	1.94	13.41	8.43	8.32	4.47	17.67	33.83	34.29
m-Cresol	PL	3.52	8.18	12.64	3.72	6.17	14.93	2.98	5.96	8.32
	ΔGa	-3371	6021	13028	3231	7159	10472	3125	1379	7886
	IE	43.94	11.56	22.59	40.76	33.29	8.57	52.54	35.56	64.23
p-Cresol	PL	3.43	8.13	10.83	2.75	4.18	13.31	2.95	4.13	5.84
	ΔGa	-7561	-9374	3540	4916	-9009	-9523	-5745	-2048	5796
	IE	45.38	12.10	33.68	56.21	54.81	18.49	53.02	53.35	64.23
2-Nitro phenol	PL	7.23	10.33	16.35	6.97	10.12	18.31	6.52	9.58	13.64
	ΔGa	-2351	-7400	10904	7330	-7159	11618	11441	-2269	14777
	IE	-15.12	-11.67	-0.12	-10.98	-9.40	-12.12	-3.82	-3.56	16.47
1-Naphthol	PL	6.17	9.10	14.83	6.25	9.23	15.4	6.02	6.66	12.21
	ΔGa	-5241	-5406	1343	5370	-4556	1121	-3047	-580	12850
	IE	1.75	1.62	9.18	0.47	0.22	4.40	4.14	28.0	25.22
2-Naphthol	PL	3.95	8.23	14.08	5.19	8.08	14.98	5.10	6.03	10.21
	ΔGa	-5745	-4418	3540	971	7573	8676	3668	-5429	13028
	IE	37.10	11.02	13.77	17.35	12.5	8.26	18.78	24.81	37.4

PL = per cent loss in weight; ΔGa = Free energy; IE = Inhibitor efficiency.

TABLE-2
EFFECT OF PHENOLS ON CORROSION OF MILD STEEL IN 0.5 N SULFURIC ACID MEDIA

System		0.5 % conc. phenols			1 % conc. phenols			2 % conc. phenols		
		1 h	2 h	3 h	1 h	2 h	3 h	1 h	2 h	3 h
Control	PL	2.12	3.97	4.65	2.12	3.97	4.65	2.12	3.97	4.65
Phenol	PL	1.88	3.29	4.26	1.93	3.64	3.93	2.02	2.13	2.72
	ΔGa	3125	1147	-7713	-7479	8408	3459	8652	-5311	-555
	IE	11.32	17.12	8.38	8.96	8.31	21.72	4.72	46.34	41.5
m-Cresol	PL	1.35	3.06	3.97	1.83	2.46	3.0	0.92	1.18	1.48
	ΔGa	-9209	1147	-5741	1730	-2383	1172	-266	384	3176
	IE	36.32	22.92	14.62	13.67	38.0	35.48	56.6	70.27	68.17
p-Cresol	PL	1.04	2.86	3.40	1.30	2.05	2.83	0.92	1.16	1.26
	ΔGa	-1729	6679	-556	-3459	-6457	-1395	-5740	-5329	2940
	IE	50.94	27.95	26.88	38.69	48.36	39.13	56.60	70.78	72.90
2-Nitro Phenol	PL	2.50	5.96	9.70	3.40	5.94	9.97	3.06	6.41	11.08
	ΔGa	-9209	-5231	-4369	-3222	-3346	-2676	-2570	-1380	4230
	IE	-17.92	-50.12	-108.6	-60.37	-49.62	-114.4	-44.33	-61.46	-138.2
1-Naphthol	PL	1.69	3.12	4.17	1.83	3.37	3.40	1.05	1.49	1.58
	ΔGa	5193	2636	7079	-7479	5292	-237	-1729	-262	0000
	IE	20.28	21.4	10.32	13.67	15.11	26.8	50.47	62.46	66.02
2-Naphthol	PL	2.18	3.8	4.54	2.02	3.69	4.22	2.05	2.68	3.73
	ΔGa	0000	1747	40	7922		6575	6585	1229	4585
	IE	1.88	4.28	2.36	4.72	7.05	9.24	3.30	32.49	19.78

PL = per cent loss in weight; ΔGa = Free energy; IE = Inhibitor efficiency.

TABLE-3
EFFECT OF PHENOLS ON CORROSION OF MILD STEEL IN 0.5 N HYDROCHLORIC ACID MEDIA

System		0.5 % conc. phenols			1 % conc. phenols			2 % conc. phenols		
		1 h	2 h	3 h	1 h	2 h	3 h	1 h	2 h	3 h
Control	PL	1.37	2.57	3.80	1.37	2.57	3.80	1.37	2.57	3.80
Phenol	PL	1.23	2.26	3.2	1.27	2.14	3.60	1.28	2.44	2.07
	ΔGa	1729	-5868	1601	5791	1468	-6994	-2729	3197	2925
	IE	7.2	12.06	15.78	7.29	16.73	5.26	6.57	5.1	45.5
m-Cresol	PL	1.09	1.82	2.88	1.08	2.02	3.32	1.12	2.22	1.68
	ΔGa	2729	3667	3335	1780	803	5084	7525	3667	-1928
	IE	20.43	29.18	24.21	21.16	21.40	12.63	18.24	13.61	55.78
p-Cresol	PL	1.08	1.58	2.20	1.05	1.58	2.20	1.09	1.39	1.68
	ΔGa	4066	-4372	1601	1780	-836	-262	534	-3753	-4853
	IE	21.16	38.57	42.10	23.35	38.52	42.10	20.43	45.91	55.78
2-Nitro phenol	PL	2.42	3.88	6.74	2.83	6.08	8.69	3.39	7.17	8.69
	ΔGa	-5407	-10217	4575	-100	-2396	-2485	4349	-572	-4312
	IE	-76.64	-50.97	-77.36	-106.56	-10.11	-128.68	-147.4	-178.9	-128.68
1-Naphthol	PL	1.27	2.35	3.61	1.30	2.32	3.63	1.32	2.48	3.12
	ΔGa	4066	-6507	1601	00	7096	3330	-3561	8825	5060
	IE	7.29	8.56	5.0	5.10	9.72	4.47	3.65	3.5	17.89
2-Naphthol	PL	1.17	2.25	3.16	1.13	2.03	3.53	1.16	2.35	1.91
	ΔGa	-5407	5366	4575	2766	7096	-8407	4349	8825	-4853
	IE	14.59	12.45	16.84	17.52	21.0	7.10	15.32	8.56	49.73

PL = per cent loss in weight; ΔGa = Free energy; IE = Inhibitor efficiency.

Effect of acid media: A comparative study of the effect of phenols on corrosion of mild steel wire in 0.5 molar acids reveals that the wire is more susceptible to corrosion in nitric acid (6.28, 9.25 and 16.33 Pl) followed by sulphuric acid (2.12, 3.97 and 4.65 Pl) and hydrochloric acid (1.37, 2.57 and 3.80 Pl) as seen from controlled treatments. In nitric acid, most of the phenols used show increased efficiency at higher concentrations in nitric acid media (IE values are lower in diluted and higher in concentrated solutions) while they are better inhibitors over the range of concentrations (comparatively high IE values) except for 2-nitro phenols (which shows negative IE values) in hydrochloric acid and sulphuric acid media.

Effect of phenol concentration: Increase in concentration of phenols resulted in decrease of per cent loss in weight indicating enhanced inhibitor efficiency at given acid concentration[13]. Among the phenols used, *p*-cresol and *m*-cresol (positive IE values) show better inhibitor efficiency, while 2-nitro phenol (negative IE values) appears to increase the oxidizing action of acids thus increasing the per cent loss in weight. The trend observed in Pl values and IE values of phenols (in HNO_3, H_2SO_4 and HCl) in decreasing order as *p*-cresol (IE = 45.38, 50.94, 21.16) > *m*-cresol (IE = 43.94, 36.32, 20.43) > phenol (IE = 7.48, 1.94, 13.41) > 2-nitrophenol (IE = -15.12, -11.67, -0.12). This trend seems to be closely related to their structures and substituents present. Introduction of electron donating methyl group shows positive effect and electron withdrawing nitro group negative effect on inhibitor efficiency of phenols. However, IE values are lowered when methyl group is shifted from *meta* to *para* position.

In naphthols, phenolic OH group at 2-position might easily bound to metal surface, thus preventing loss of metal more efficiently than at 1-position. Among naphthols used, 2-naphthol (IE = 37.10, 1.88, 14.59) seems to be more effective over 1-naphthol (IE = 1.75, 20.28, 7.29) in all three acids.

Effect of time period: Per cent loss in weight increases with time in presence as well as in absence of phenols, but this increase in per cent loss in weight when treated with phenol is much less as compared with control. Difference in per cent loss of weight in uninhibited as well as inhibited solutions increased with increased phenol concentration and increase in time, in all the acids. Decrease in per cent loss in weight at increased concentration of phenols and at higher time period may be due to more adsorption of phenols on the surface of metals which prevents corrosion reaction[14]. This is also evident from higher IE values at increased concentration.

Inhibitor efficiency: Negative inhibitor efficiency values at lower concentration of phenols and positive values at higher concentration in nitric acid reveals that they are more effective when applied in higher concentration (Figs. 1-3).

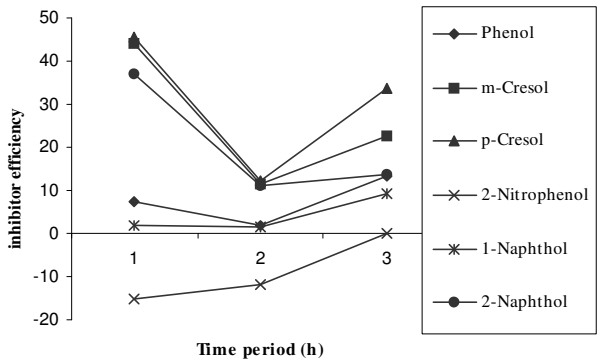

Fig. 1. Inhibitor efficiency at 0.5 % concentration of phenol in 0.5 N nitric acid

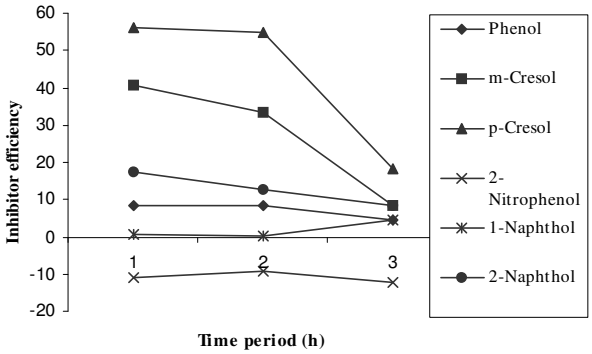

Fig. 2. Inhibitor efficiency at 1 % concentration of phenol in 0.5 N nitric acid

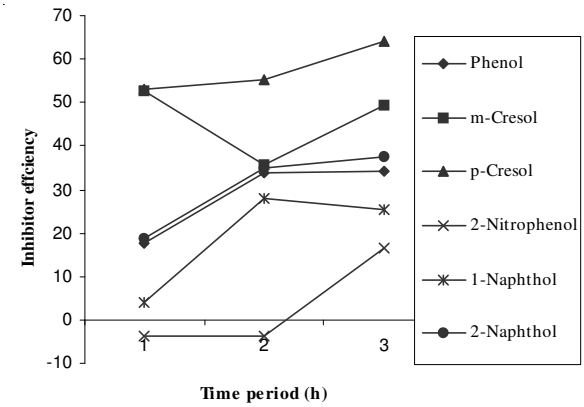

Fig. 3. Inhibitor efficiency at 2 % phenol concentration in 0.5 N nitric acid

In hydrochloric acid (IE values -17.12 to -108.6 at 2 % concentration) (Figs. 4-6) and in sulphuric acid (IE values -76.64, to -77.36 at 2 % concentration) (Figs. 7-9), media 2-nitrophenol shows decreasing efficiency values with increased concentration indicating it is not an appropriate

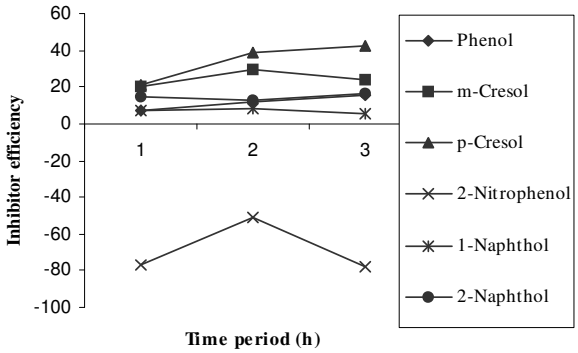

Fig. 4. Inhibitor efficiency at 0.5 % phenol concentration in 0.5 N hydrochloric acid

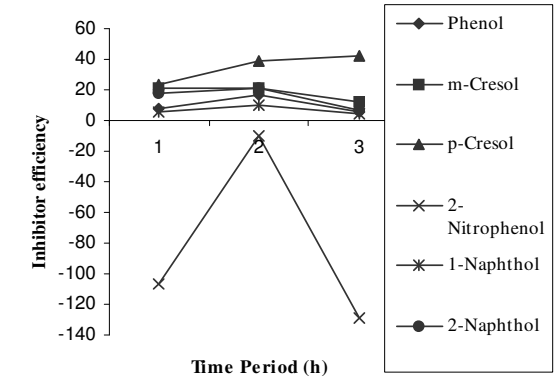

Fig. 5. Inhibitor efficiency at 1 % phenol concentration in 0.5 N hydrochloric acid

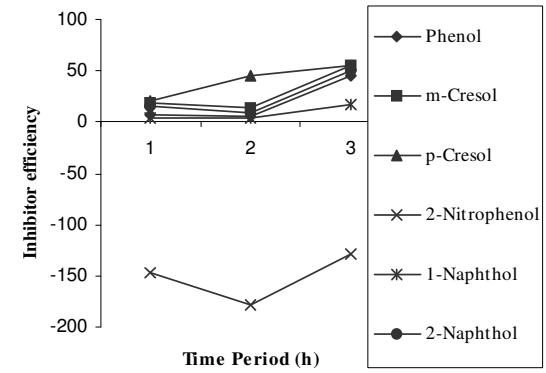

Fig. 6. Inhibitor efficiency at 2 % phenol concentration in 0.5 N hydrochloric acid

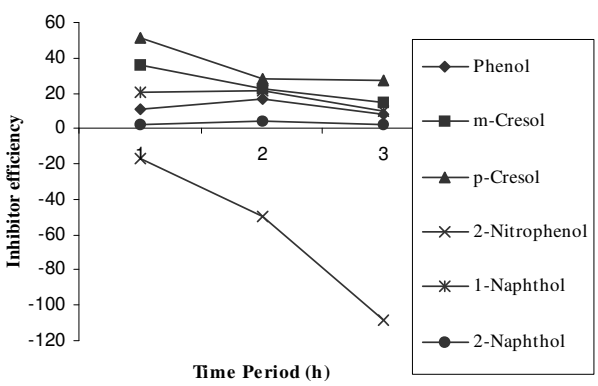

Fig. 7. Inhibitor efficiency at 0.5 % phenol concentration in 0.5 N sulfuric acid

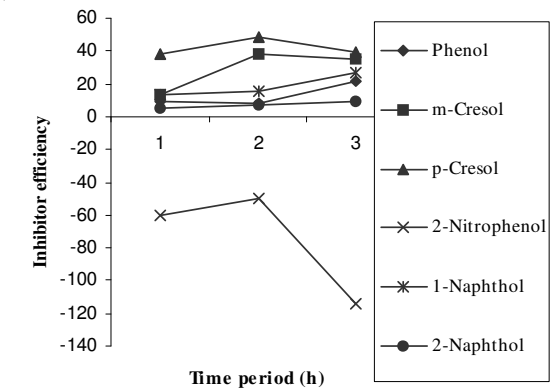

Fig. 8. Inhibitor efficiency at 1 % phenol concentration in 0.5 N sulfuric acid

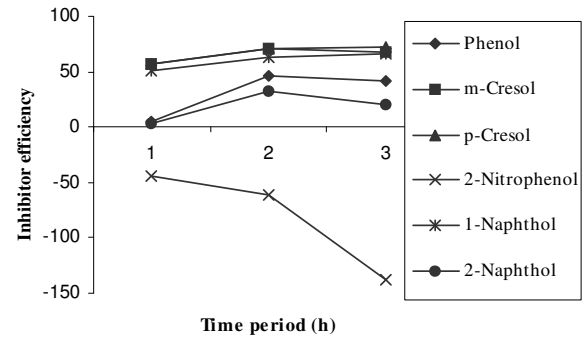

Fig. 9. Inhibitor efficiency at 2 % phenol concentration in 0.5 N sulfuric acid

corrosion inhibitor. While other phenols showing increased positive IE values indicating increased efficiency with increase in concentration and time period are better corrosion inhibitors.

Free energy: Negative free energy values of *p*-cresol shows that it is best effective inhibitor in all the three acids used[15]. These values tend to become negative (ΔGa = 4066 to -4853) with time when used in hydrochloric acid. However in nitric acid (ΔGa = -7561 to 5796) and in sulfuric acid (ΔGa = -1729 to 2940) media efficiency decreases with time as they show negative ΔGa values changing into positive.

2-Nitro phenol having negative free energy values (ΔGa = -2351 to 14777 in HNO_3) (ΔGa= -540 to -4312 in HCl) (ΔGa = -1729 to 2940) initially, shows positive free energy values as time passes. Among naphthols, 2-naphthol having comparatively lower negative free energy values over 1-naphthol is better corrosion inhibitor, while other phenols do not reveal significant trend in the free energy values.

Conclusions

Addition of some phenols to the acid media decreases the rate of corrosion. The extent of inhibition depends on both the concentration of phenol and time period. Among the three acids, mild steel is more susceptible to corrosion in nitric acid. 2-Nitro phenol showing more negative IE values is not an appropriate inhibitor. Efficiency of inhibitor increases with concentration of phenols and time period except for 2-nitro phenol. All the phenols, excluding 2-nitro phenol are good inhibitors in hydrochloric acid followed by sulphuric acid and nitric acid media.

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