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Inhibition Effects of Phenols on Corrosion of Mild Steel in Nitric Acid

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Effects of phenols on the corrosion of mild steel in various concentrations of nitric acid have been evaluated. Per cent loss in weight was found increase linearly with increase in acid concentration. Among the phenols used, *p*-cresol appears to be good inhibitor followed by *m*-cresol and phenol. 2-Nitro phenol reveals its oxidizing nature as indicated by increased loss in weight when compared with control. In case of naphthols; 2-naphthol seems to be more effective inhibitor as compared to 1-naphthol. An e.m.f. measurements in nitric acid media indicated that they are inversely related to corresponding weight losses. The trend observed in I.E. values is in the order as *p*-cresol > *m*-cresol > 2-naphthol > phenol > 1-naphthol > 2-nitro phenol.

Key Words: Phenols as inhibitors, Inhibitor efficiency, Nitric acid media.

INTRODUCTION

All metallic corrosion processes occur by the transfer electronic charge in aqueous solutions and are considered to be electrochemical in nature. Corrosion of steel in nitric acid media is rapid electrochemical reaction taking place at the anodic area and may be represented as follows

$$Fe \rightarrow Fe^{3+}_{interface} + 3e \text{ (charge transfer step)}$$

$$Fe^{3+}_{interface} \rightarrow Fe^{3+}_{bulk} \text{ (mass transfer step)}$$

This rapid or active dissolution of iron during corrosion seriously affects the adsorption process[1]. Corrosion inhibition of mild steel in aqueous acidic media solutions by different organic compounds has been widely studied[2-8]. Organic inhibitors are also used in several industrial processes to control the metal dissolution. Compounds containing phenolic OH group act as corrosion inhibitors by adsorption on metal surface when exposed to metal/solution interface[9-13]. Inhibiting action of organic compounds is normally related to interaction by adsorption between the metal surface and inhibitor known as the interface inhibition[14].

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It is reported that the adsorption of inhibitor results in an increase of over potential of the proton discharge process or an increase of ohmic resistance as result of formation of inhibitor film, at meal electrolyte interface[15,16].

In present work, inhibition efficiency of phenols over wide concentration range of nitric acid media is evaluated and an attempt is made to correlate weight losses with corresponding changes in e.m.f. values.

EXPERIMENTAL

Mild steel wire from local manufacturer with 4″ length and 0.108 cm in diameter were used for corrosion study. The specimen wires received were cleaned and exposed to constant 0.5 % amount (0.250 g in 50 of acid solution) of phenols in nitric acid media for 1, 2 and 3 h within the concentration range of 0.0625, 0.125, 0.25, 0.5 N taking one specimen as control for each concentration. At the regular intervals (1, 2 and 3 h) specimen wires were removed, cleaned with distilled water and weight losses were recorded, from the weight loss, inhibitor efficiency and free energy were computed[17].

In another set of experiment, e.m.f. measurements were carried out with increased amount (0.5, 1 and 2 %) of phenols in 0.5 n nitric acid media, changes in e.m.f. values were recorded before and at the intervals of 0.5, 1, 2 and 3 h after the introduction of wires in the system. they are correlated with corresponding weight losses.

RESULTS AND DISCUSSION

Results of percent loss in weight, inhibitor efficiency and e.m.f. values are given in Tables 1 and 2.

Inhibitor efficiency of phenols was computed from the following formula

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

IE = inhibitor efficiency, Wi = weight loss of metal in inhibitor solution, Wu = weight loss of metal in unhibited solution.

The values of free energy of adsorption (ΔGa) were calculated with the following equation[19].

$$\log C = \log\left(\frac{\theta}{1-\theta}\right) - \log B$$

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

Effect of acid concentration: It is observed that percent loss in weight, inhibitor efficiency increase with increase in acid concentration (Fig. 1). In group first *p*-cresol (IE = 70.20) appears to be stronger inhibitor followed by *m*-cresol (IE = 52.26), phenol (IE = 30.0) and 2-nitro phenol

TABLE-1
EFFECT OF PHENOLS ON THE CORROSION OF MILD STEEL IN VARIOUS CONCENTRATIONS OF NITRIC ACID

System		0.5 N HNO_3			0.25 N HNO_3			0.125 N HNO_3			0.0625 N HNO_3		
		1 h	2 h	3 h	1 h	2 h	3 h	1 h	2 h	3 h	1 h	2 h	3 h
Control	PL	5.00	6.31	8.38	2.67	3.71	5.00	1.19	1.98	2.56	0.97	1.07	1.50
Phenol	PL	3.50	4.38	6.37	2.42	2.85	4.40	0.99	1.14	2.19	0.68	1.03	1.23
	IE	30.00	30.58	23.98	9.36	23.18	12.00	16.40	17.17	14.45	30.92	3.73	18.00
m-Cresol	PL	2.37	3.63	5.77	2.22	2.61	3.93	0.97	1.50	1.66	0.52	1.00	99.00
	IE	52.26	42.47	31.14	16.85	29.67	21.40	18.48	24.29	35.15	46.39	6.54	34.00
p-Cresol	PL	1.49	3.41	5.69	2.15	2.32	2.72	0.95	1.30	1.42	0.44	0.79	0.86
	IE	70.20	45.95	32.10	19.47	37.46	45.60	20.16	34.34	44.53	54.63	26.16	42.66
2-Nitro phenol	PL	5.61	6.85	8.44	2.68	3.81	5.88	1.53	2.06	2.66	0.65	1.08	1.88
	IE	-12.20	-8.55	-0.71	-0.37	-2.69	-17.60	-28.50	-4.04	-3.90	-1.03	-0.93	25.33
1-Naphthol	PL	4.03	6.00	8.38	2.45	3.05	4.88	1.11	1.84	2.37	0.71	1.04	1.43
	IE	19.40	4.90	11.93	8.23	17.78	2.40	6.72	7.07	7.42	36.80	2.80	3.33
2-Naphthol	PL	2.61	3.90	6.13	2.35	2.78	4.48	0.98	1.39	2.17	0.86	1.00	0.97
	IE	47.88	38.19	24.84	11.98	25.06	10.40	17.64	20.79	15.23	32.98	6.54	35.33

PL = Per cent loss in weight; IE = Inhibitor efficiency.

TABLE-2
EFFECT OF PHENOL CONCENTRATION ON CORROSION ON MILD STEEL IN NITRIC ACID MEDIA

System		0.5 % conc. phenol					1 % conc. phenol					2 % conc. phenol				
		0 h	0.5 h	1 h	2 h	3 h	0 h	0.5 h	1 h	2 h	3 h	0 h	0.5 h	1 h	2 h	3 h
Control	E	370	509	560	575	565	370	509	560	575	565	370	509	560	575	565
	ΔE		139	190	205	195		139	190	205	195		139	190	205	195
	PL					63.73					63.73					63.73
Phenol	E	353	325	340	290	361	344	346	355	314	348	352	373	385	384	395
	ΔE		-28	-13	-63	8		2	11	-30	4		139	33	32	43
	PL					45.80					41.62					4047
	ΔGa					-330					3011					-2996
	IE					28.13					34.69					36.49

System		0.5 % conc. phenol					1 % conc. phenol					2 % conc. phenol				
		0 h	0.5 h	1 h	2 h	3 h	0 h	0.5 h	1 h	2 h	3 h	0 h	0.5 h	1 h	2 h	3 h
m-Cresol	E	690	550	443	408	407	682	533	555	559	585	537	410	425	380	398
	ΔE		-140	-247	-282	-283		-149	-127	-123	-97		21	-112	-137	-139
	PL					40.62					31.32					31.14
	ΔGa					-3664					3933					-527
	IE					36.26					50.85					51.13
p-Cresol	E	705	429	570	625	635	695	455	585	605	636	678	650	605	625	633
	ΔE		-276	-135	-80	-70		-240	-110	-90	-59		-127	-73	-53	-45
	PL					27.67					22.08					20.32
	ΔGa					575					1530					-16.08
	IE					56.58					65.35					68.12
2-Nitro Phenol	E	406	555	452	425	409	395	480	431	419	394	393	446	427	399	414
	ΔE		149	46	19	3		85	36	24	-1		53	34	6	22
	PL					68.06					64.92					63.89
	ΔGa					-3304					2042					-5475
	IE					-6.79					-1.86					-0.25
1-Naphthol	E	472	365	375	373	380	410	392	362	363	369	410	382	355	360	285
	ΔE		-107	-97	-99	-92		-18	-48	-47	-50		-28	-55	-50	-125
	PL					48.34					47.30					42.78
	ΔGa					-1930					-156					-720
	IE					24.14					25.78					32.87
2-Naphthol	E	434	450	423	407	402	460	345	360	360	245	462	322	354	355	253
	ΔE		16	-11	-27	-32		115	-100	-100	-215		-140	-108	-107	-209
	PL					42.73					39.21					38.02
	ΔGa					-1546					14.46					-2978
	IE					32.95					38.47					40.34

PL = percent loss in weight, ΔGa = Free energy, IE = Inhibitor efficiency, E = e.m.f., ΔE = Difference in e.m.f.

(IE = -12.20) (Table-1). This may be due to change in methyl group from *para* to *meta* position in cresols. Introduction of methyl group appears to lower the oxidizing character of phenol as seen from higher efficiency of cresols in corrosion inhibition of steel, while in 2-nitro phenols, acidic character and oxidizing power of the media is increased due to nitro group, thus increasing the percent loss in weight. It is also found that per cent loss in weight is higher in solutions treated with phenols at low acid concentrations as compared to control.

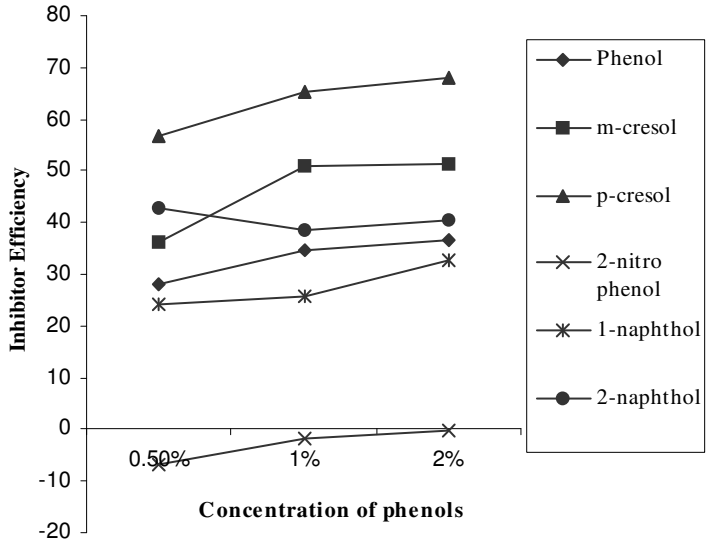

Fig. 1. Effect of phenol concentration on inhibitor efficiency

In group second, 2-naphthol (IE = 47.8) seems to be good inhibitor over the 1-naphthol (IE = 19.4). This may be due to shifting of phenolic OH group to second position. Phenols are reported to function as inhibitor in the following ways:

1. By decreasing the oxidizing power of acid to some extent.
2. Being adsorbed on the metal surface.
3. By exerting common ion effect.

Adsorption of phenols can takes place through negatively charged oxygen atom of phenolate ion due to electrostatic attraction of the phenol molecule. Because of lone pair of unshared electron on the oxygen atom may be attached to the anodic points on metal surface.

E.M.F. Study: Effect of phenols on the e.m.f. of 0.5 N nitric acid-metal media shows linear relationship with time and weight loss. However this trend is reversed when system is treated with phenols resulting in gradual decrease of e.m.f. values of cresol where loss in weight is lowest (PI =

27.67 %), resulted in maximum increase of e.m.f. (ΔE = -276) (IE = 56.58), (Table-2). This is followed in almost all systems over the range of acid concentrations used. This may be due to hindrance of complex formed between metal ion and the phenols to the movement of electrons in cell and on the tendency of phenols to form complex with metal ions. Almost similar trend as observed in per cent loss in weight and inhibitor efficiency values is revealed in e.m.f. values, the trend in the decreasing order is *p*- cresol (ΔE = -276) > *m*-cresol (ΔE = -140) > 1-naphthol(ΔE = -107) > phenol (ΔE = -28) > 2-naphthol (ΔE = 16) > 2-nitro phenol (ΔE = 149) (Figs. 2-4).

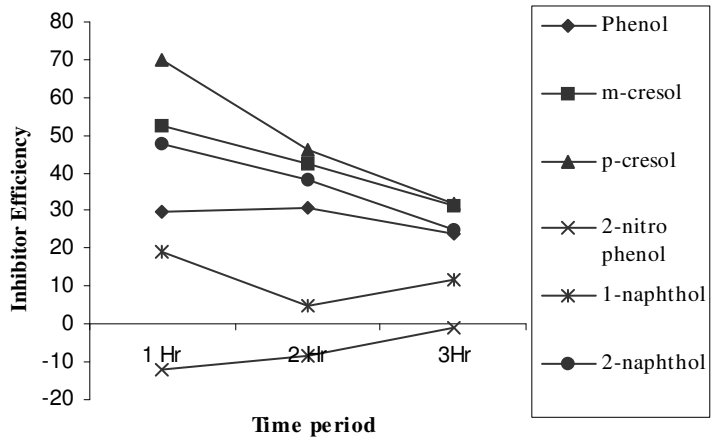

Fig. 2. Effect of time period on inhibitor efficiency of phenons in 0.5 N nitric acid

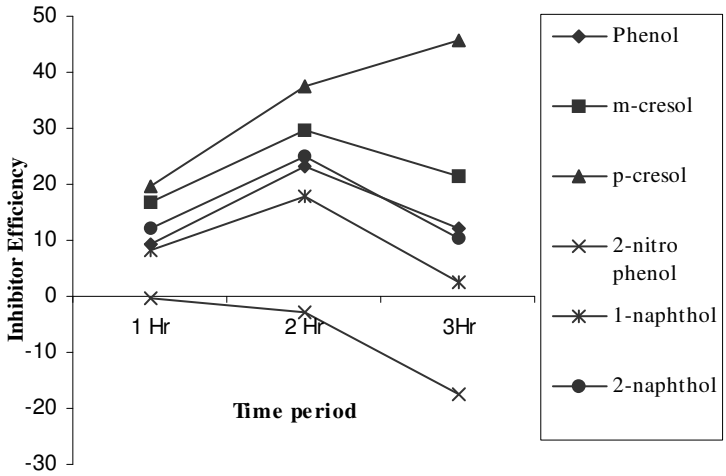

Fig. 3. Effect of time period on inhibitor efficiency of phenols in 0.25 N nitric acid

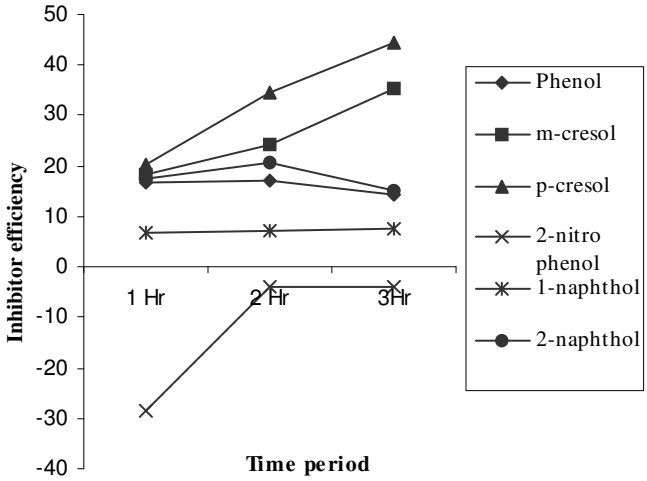

Fig. 4. Effect of time period on inhibitor efficiency of phenols in 0.125 N nitric acid

Effect of phenol concentration: Increase in concentration of phenols resulted in decrease of per cent loss in weight indicating enhanced efficiency at a given acid concentration. At lower level of acid and phenol concentration, most of the phenols used are not efficiently inhibiting the corrosion of mild steel in the acid media, which implies that they must be applied at optimum concentration.

Free energy: Values of free energy decrease with increase in concentration of phenols (increased IE values). Almost all the phenols used show negative free energy values, in naphthols, 2-naphthol showing lower free energy values (ΔG = -2798.66) seems to be better inhibitor over the 1-naphthol. (ΔG = -720.53) as seen from Table-2.

Conclusions

Addition of some phenols in nitric acid decreases the corrosion rate. Inhibitor efficiency increases with concentration of acid and phenol. 2-Nitro phenol does not show inhibition property under the used conditions. Inhibitor efficiency and e.m.f. values indicate inhibition occurs by the adsorption of phenols on the surface of metal, thus decreasing the per cent loss in weight. Per cent loss in weight is found to be more in nitric acid at lowest concentration. Among the phenols used, *p*-cresol shows better inhibiting property.

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