Polyamines As Inhibitors of Corrosion of Mild Steel In Hydrochloric Acid Solutions

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POLYAMINES have previously been investigated as inhibitors for the corrosion of aluminum-3S (1), aluminium-51S (2), aluminum aluminium-56S (3), aluminium-57S (4) and zinc (5) in hydrochloric acid solutions. It is however well known that the results obtained with a particular metal or alloy cannot be easily applied to another metal. The present article reports results obtained during investigations on the use of four polyamines namely ethylenediamine, diethylenetriamine, triethylenetetraamine and tetrathylenepentamine as inhibitors for the corrosion of mild steel in hydrochloric acid solutions.

THE influence of parameters like inhibitor concentration time, hydrochloric acid concentration has been investigated. The mechanism of inhibitor action has been studied by the galvanostatic method. The preparation of specimens and corrosion tests were carried out as described in our earlier publication[6]. The influence of time and hydrochloric acid concentration on the efficiency of inhibitors is given in table 1. The influence of current density on the cathode and anode potentials of mild steel in 1.0 N HCl, 6.0 N HCl is given in figures 1 and 2 respectively.

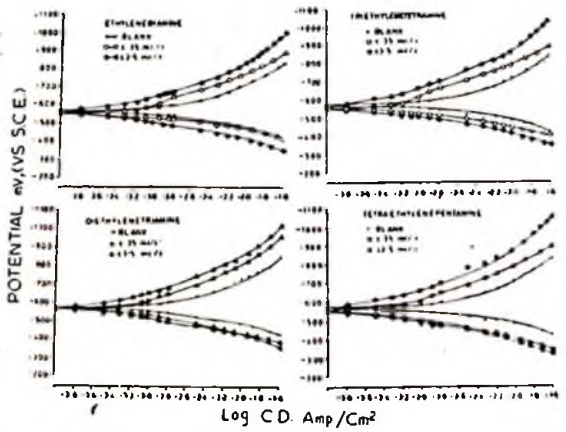


Fig. 1. Influence of current density on cathode and anode potentials of Mild Steel in 1.0 N hydrochloric acid solution in presence and absence of inhibitors.

Observations : The corrosion of mild steel in hydrochloric acid solutions increases with time as well as with hydrochloric acid concentration. Polarisation measurements in 1.0 N HCl indicate that the corrosion process is cathodically controlled.

Ethylenediamine : Even at 4.35 ml/l concentration, ethylenediamine affords 59-82% protection to mild steel in 1.0-4.0 N solutions of hydrochloric acid, and at 43.5 ml/l concentration, it gives 81-91% protection. In general, its efficiency falls with an increase in hydrochloric acid concentration.

In 1.0 N and 2.0 N solutions of hydrochloric acid the efficiency of ethylenediamine improves with time. In 3.0 N and 4.0 N solutions of hydrochloric acid it is initially low (>50%) but thereafter it is constant for the durations of study. At smaller durations, its efficiency increases with an increase in HCl concentration but at higher durations, its efficiency falls with an increase in HCl concentration (Table 1).

Diethylenetriamine : In 1.0 N HCl, diethylenetriamine is a satisfactory inhibitor even at 4.35 ml/l concentration. At 43.5 ml/l concentration, it affords 82-91% protection to mild steel in 1.0-4.0 N solutions of hydrochloric acid, In general, its efficiency decreases with an increase in hydrochloric acid concentration.

In 1.0 N 2.0 N and 3.0 N solutions of HCl, the efficiency of diethylenetriamine increases with the passage of time (Table 1). In 4.0 N HCl, initially, it is low but thereafter it is nearly constant for the durations of study (Table 1). Upto 6 hours, the efficiency of diethylenetriamine increases with an increase in HCl concentration but for 12 and 24 hrs. durations its efficiency decreases with an increase in HCl concentration (Table 1).

Triethylenetetramine : Even at 4.35 ml/l concentration triethylenetetramine affords 82-87% protection to mild steel in 1.0-4.0 N solutions of hydrochloric acid and with a tenfold increase in its concentration, the protection afforded is 92%. At effective concentration, the efficiency of triethylenetetramine is nearly constant in 1-4.0 N hydrochloric acid.

In 1.0 N to 4.0 N solutions of hydrochloric acid, the efficiency of triethylenetetramine improves with

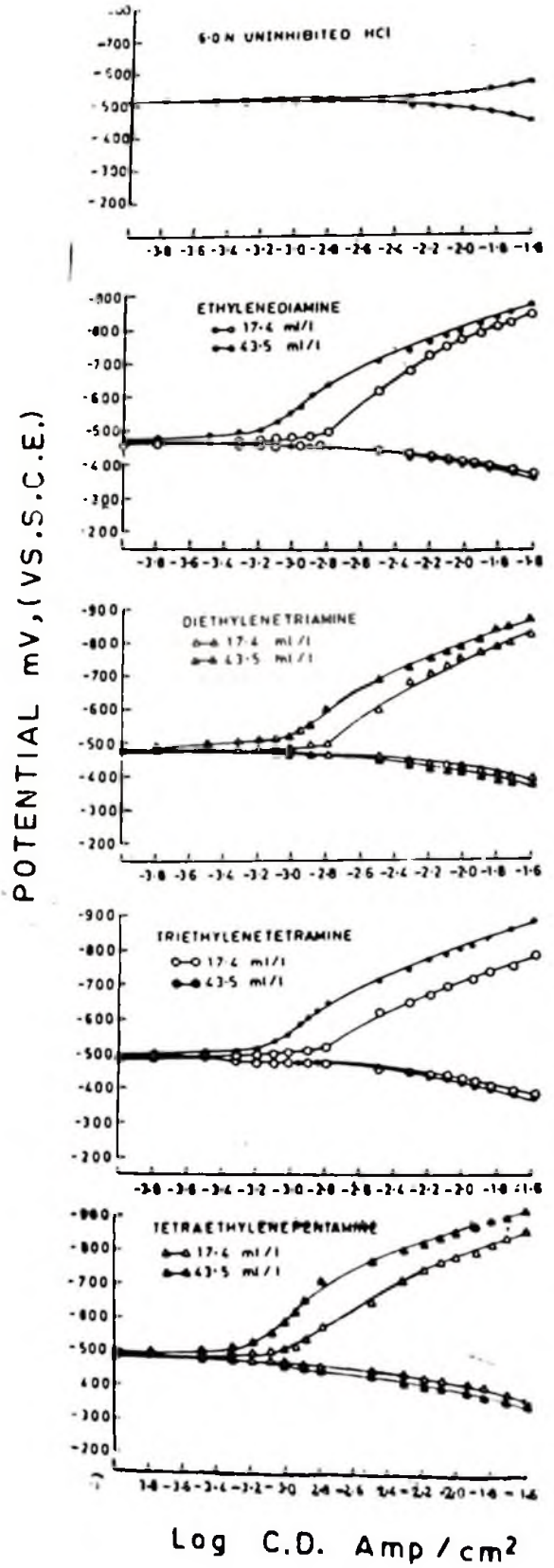


Fig. 2. Influence of current density on cathode and anode potentials of Mild Steel in 6.0 N hydrochloric acid solution in presence and absence of inhibitors.

the passage of time (Table 1). The efficiency of triethylenetetramine in general improves with an increase in HCl concentration for 3 5, 9 hours duration but it is constant in 1.0 N HCl-4.0 N HCl range for 12-24 hours duration (Table 1).

Tetraethylenepentamine : At 4.35 ml/l concentration, it protects mild steel to an extent of 84-87% and at 43.5 ml/l concentration the protection afforded is 92-95%. The efficiency of tetraethylenepentamine is improved with an increase in hydrochloric acid concentration (Table 1).

In 1.0 N to 4.0 N solutions of hydrochloric acid, the efficiency of tetraethylenepentamine improves with the passage of time (Table 1).

Addition of these substances to 1.0 N HCl or 6.0 N HCl shifts the corrosion potential in the positive direction as can be seen from the following data :

	1.0 N HCl	6.0 N HCl
Ethylene diamine	+ 10 mv	+ 30 mv
Diethylenetriamine	+ 10 mv	+ 20 mv
Triethylenetetramine	+ 20 mv	+ 10 mv
Tetraethylenepentamine	+ 20 mv	+ 10 mv

At both the concentrations of hydrochloric acid, the polyamines are mixed inhibitors with predominant effect on cathodic reaction.

Adsorption : Plots of log surface coverage against log inhibitor concentration show that Freundlich adsorption isotherm is obeyed in the effective concentration range.

Polarisation data : The tafel slopes and inhibitor efficiencies calculated from polarisation curves in 1.0 N HCl and 6.0 N HCl are given in the table 2. In general there is a good correlation between the percentage efficiencies calculated from polarisation data and loss in weight data. At lower inhibitor concentration, the protectivity is generally lesser than that at higher inhibitor concentration. This tallies well with lower values of tafel slopes obtained at lower inhibitor concentrations.

Influence of temperature: Activation energies of mild steel in inhibited 1.0 N HCl were calculated from Arrhenius plots, It was observed that in uninhibited hydrochloric acids, the activation energy of mild steel is 18.0 K Cal. per mole. In the

TABLE 1

Effect of time and hydrochloric acid concentration on the corrosion loss (mg/dm²) of mild steel (Values in the brackets show % efficiency)

Temperature : 35°±0.5°C

Inhibitor concentration (ml/l)	Normality of HCl	1 hour	3 hours	6 hours	9 hours	12 hours	24 hours
Nil	1.0	32	72	171	328	592	1229
	2.0	64	134	250	701	1160	1668
	3.0	90	425	900	1439	2222	4729
	4.0	124	1029	2642	3658	4806	7066
Ethylenediamine 43.5 ml/1	1.0	17 (47)	32 (56)	40 (77)	52 (84)	66 (89)	115 (91)
	2.0	27 (58)	55 (59)	96 (62)	144 (79)	177 (85)	207 (88)
	3.0	42 (53)	91 (79)	166 (82)	256 (82)	433 (81)	876 (81)
	4.0	57 (54)	142 (86)	462 (83)	594 (84)	933 (81)	1060 (85)
Diethylenetriamine 43.5 ml/l	1.0	16 (50)	30 (58)	37 (78)	50 (85)	65 (89)	110 (91)
	2.0	30 (53)	55 (59)	93 (63)	144 (84)	148 (87)	191 (89)
	3.0	40 (56)	94 (78)	164 (82)	240 (83)	302 (86)	854 (82)
	4.0	61 (51)	149 (86)	368 (81)	559 (85)	913 (81)	1036 (85)
Triethylenetetramine 43.5 ml/l	1.0	16 (50)	29 (60)	35 (80)	50 (85)	64 (89)	102 (92)
	2.0	34 (47)	60 (55)	87 (65)	97 (86)	114 (90)	140 (92)
	3.0	41 (54)	96 (77)	174 (81)	193 (87)	254 (89)	381 (92)
	4.0	66 (47)	146 (86)	264 (90)	317 (91)	432 (91)	548 (92)
Tetraethylenepentamine 43.5 ml/l	1.0	16 (50)	27 (63)	34 (80)	47 (86)	63 (89)	99 (92)
	2.0	28 (56)	45 (66)	81 (68)	83 (88)	95 (92)	130 (92)
	3.0	35 (61)	73 (83)	122 (86)	140 (90)	169 (92)	260 (95)
	4.0	51 (59)	100 (90)	175 (93)	212 (94)	260 (95)	332 (95)

TABLE 2

Tafel parameters and efficiency of inhibitors in 1.0 N and 6.0 N HCl

Inhibitor and Inhibitor concentration ml/l	TAFEL SLOPE b		Energy transfer coefficient Cathodic	CORROSION CURRENT Amp/cm² ×10⁻⁴		Inhibitor efficiency (%) from (6)	Inhibitor efficiency (%) from (6)	Inhibitor efficiency from loss in weight method
	Anodic (Volts)	Cathodic (Volts)		From extrapolation of cathodic trafel line	From intersection of of cathodic and anodic lines at open circuit potential			
1	2	3	4	5	6	7	8	9
Uninhibited 1.0 N HCl	0.06	0.125	0.48	2.27	2.08	—	—	—
Ethylenediamine 43.5 ml/l	0.09	0.17	0.35	0.39	0.28	85	87	41-90
Diethylenetriamine 43.5 ml/l	0.1	0.23	0.26	0.28	0.21	88	90	50-91
Triethylenetetramine 45.5 ml/l	0.09	0.22	0.27	0.24	0.16	89	92	50-92
Tetraethylenepentamine 43.5 ml/l	0.12	0.23	0.26	0.16	0.16	93	92	51-92
Unihibited 6.0 N HCl	0.06	0.11	0.55	4.87	3.6	—	—	—
Ethylenediamine 43.5 ml/l	0.08	0.19	0.32	0.13	0.32	97	91	94
Diethylenetriamine 43.5 ml/l	0.09	0.20	0.30	0.25	0.56	95	84	62
Triethylenetetramine 43.5 ml/l	0.10	0.20	0.30	0.22	0.32	95	91	97
Tetraethylenepentamine 43.5 ml/l	0.06	0.17	0.35	0.06	0.13	99	96	97

presence of the inhibitors, the activation energy of mild steel was found to be activation energy k cal/mole.

ethylenediamine	43.5 ml/l	19.7
diethylenetriamine	43.5 ml/l	16.8
triethylenetetramine	43.5 ml/l	9.6
tetraethylenepentamine	43.5 ml/l	14.4

Thus the protectivity of the last three compounds, improves with an increase in temperature.

Cathodic protection : Studies in cathodic protection of mild steel in 6.0 N HCl show that cathodic protection by impressed current is possible Results are given in table 3. In uninhibited 6.0 N HCl 1.30 am/dm² current is required to give complete protection to mild steel.

Aliphatic polyamines are very good inhibitors for the corrosion of mild steel in hydrochloric acid. This fact is also reflected in the results of cathodic protection. At effective inhibitor concentrations the polyamines considerably reduce the protective current. It is interesting to note that the efficiency of polyamines does not show significant variation with increasee in chain length but in the presence of external cathodic current, there is a significant improvement in inhibitor efficiency with an increase in chain length which is evident from the following data :

TABLE 3

Weight loss in the absence and presence of protection current. Electrode potentials and efficiencies in 6.0 N HCl

Inhibitor concentration ml/l or %	Without external cathodic current			With external cathodic current			
	Weight loss mg/dm²	Inhibitor efficiency (%)	Open circuit potential in mv. with ref. to S.C.E.	Current for complete protection amp/dm²	Protective potential in mV with ref. to S.C.E.	Theoretical current needed for complete protection amp/dm²	Ratio of theoretical current to observed current
Nil	14.58	—	-500	1.300	-660	0.453	0.35
Ethylenediamine							
17.4 ml/l	134.4	91	-460	0 398	-650	0.0417	0.11
43.5 ml/l	82.6	94	-470	0.194	-640	0.0256	0.13
Diethylenetriamine							
17.4 ml/l	117.8	92	-470	0.453	-660	0.0366	0.01
43.5 ml/l	61.5	96	-490	0.184	-640	0.019	0.098
Triethylenetetramine							
17.4 ml/l	97.5	93	-480	0.243	-670	0.03	0.12
43.5 ml/l	48.6	97	-490	0.162	-650	0.015	0.092
Tetraethylenepentamine							
17.4 ml/l	61 6	96	-480	0.130	-670	0.019	0.15
43.5 ml/l	43 5	97	-490	0.0972	-655	0.014	0.14

Inhibitor	Protective current (Amp/dm²)
Diethylenetriamine	0.194
Triethylenetetramine	0.162
Tetraethylenepentamine	0 0972

It has been shown by Rajagopalan[7] that with quinoline, (β-naphthol thiourea and gelatine in the case of mild steel in 5% sulphuric acid) the potential corresponding to the protection current is not a constant value and varies with each system. (This is in agreement with the present work). They further state that the protective potential remains the same for the same system at all concentrations of the inhibitor though the protection current varies. The present study however reveals that the protective potentials change with inhibitor concentration.

In the case of ethylenediamine, diethylenetriamine, triethylenetetramine tetraethylenepentamine the protective potentials become more positive with an increase in the inhibitor concentration. This may indicate that the preferential effect of these inhibition is on the local cathodes and as the concentration of the inhibitor is increased. The local anodes are also affected. The difference effect is positive in the presence and absence of inhibitors.

From the above description, it can be seen that the efficiency of polyamines improves with an increase in chain length e.g. with an increase in hydrochloric acid concentration, from 1.0 N to 4.0 N, the efficiency of ethylenediamine and diethylenetriamine decreases, that of triethylenetetramine remains constant but there is an actual improvement in the efficiency of tetraethylenepentamine.

It can be seen from table 1 that with an increase in chain length, there is an improvement in the efficiency of polyamines with the passage of time.

Conclusions : All the polyamines are highly effective inhibitors for the corrosion of aluminium

alloys in hydrochloric acid solutions but they are not as effective for steel acd zinc in hydrochloric acid. For all the a'umininm alloys aliphatic polyamines completely arrest the corrosion in 0.5 N hydrochloric acid upto one week and in 1.0 N hydrochloric acid upto 72 hours. Moreover, the aliphatic polyamines give complete protection to aluminium alloys 3S, 51S, 57S, 65S for 30 minutes in the temperature range 35-55°C. For mild steel, the efficiency of polyamines improves with an increasing chain length and hydrochloric acid concentration. In the present work polyamines have been found to be cathodic inhibitors for the corrosion of mild steel in hydrochloric acid solutions, however, Hoar and Khera[8] found that polyamines are predominantly anodic inhibitors for mild steel in sulfuric acid. Hugel[9] studied polyamines as inhibitors for the corrosion of mild steel in 6.0 N hydrochloric acid. His studies indicated that ethylenediamine (38%) and diethylenetriamine (45%) are not very satisfactory inhibitors, but triethylenetetramine (84%) is a satisfactory inhibitor. The present study, however, indicates that, all the four polyamines are quite satisfactory inhibitors at effective inhibitor concentration, however, their efficiency improves with the passage of time and increase in hydrochloric acid concentration. Hackerman[10] studied the adsorption of corrosion inhibitors for iron in hydrochloric acid. He investigated α, ω – aliphatic diamines as corrosion inhibitors in the series $NH_2(CH_2)_nNH_2$ where n = 2 to 12. Maximum efficiency is given by the molecule having n = 3 but further increase in the number of carbon atoms upto 8 does not improve the efficiency. we have also observed that the efficiency of polyamines with an increase in chain length.

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