

Inhibiting Properties of Some Amines on Corrosion Behaviour of Mild Steel in Phosphoric Acid Solution at Various Temperatures

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The inhibition effect of triethanolamine, triethylamine and diethylamine on corrosion of mild steel in phosphoric acid solutions has been studied. The mass loss and polarization techniques have been employed at 302–333 K. Results obtained reveal that all compounds are good inhibitors. The inhibition efficiency of the inhibitors increases with increase in inhibitor concentration. The effect of temperature on corrosion behaviour of mild steel indicates that inhibition of inhibitors decreases with increasing temperature. The inhibition efficiency decreases with increasing concentration of phosphoric acid. At all the inhibitor concentration in 1 and 5 N phosphoric acid solution at 302–333 K for 5 h immersion period, the inhibition efficiency of inhibitors decreases in the order diethylamine > triethylamine > triethanolamine. These inhibitors are fitted to Tempkin's adsorption isotherm. The values of activation energy and free energy of adsorption have also been calculated. The plots of W_f against time (days) at 302 K give straight line, which suggests that it obeys first order kinetics. The rate constant k and half life time $t_{1/2}$ have also been calculated.

Key Words: Mild steel, Phosphoric acid, Corrosion inhibition, Tempkin's adsorption isotherm, Potentiodynamic polarization.

INTRODUCTION

Phosphoric acid (H_3PO_4) is a major chemical product, which has many important uses especially in the production of fertilizers. Most of the acid is produced from phosphate rock by wet process. General nickel-base alloys and stainless steel are frequently used in many parts of the wet process and a considerable quantity of data has been published about the resistance of these materials to corrosion by phosphoric acid solution^{1–5}. Most of the previous studies were focused on the inhibition of stainless steel or chromium-nickel steel in HCl or H_2SO_4 solutions using organic compounds containing nitrogen, sulfur and oxygen atoms as corrosion inhibitors^{6,7}. Mild steel is extensively used in industries especially for structural applications. But its susceptibility to rusting in humid air and its very high dissolution rate in acidic media are the major obstacles in its use on a large scale. Hence, the study of corrosion inhibition of mild steel in aqueous aggressive media is very important. Different nitrogen containing organic compounds have been studied as corrosion inhibitors for mild steel^{8–10}. Aliphatic, heterocyclic and aromatic amines have been extensively investigated as corrosion inhibitors^{11–13}. According to Hackerman *et al.*^{14,15} the inhibitive properties of a series of secondary aliphatic and cyclic amines

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in acid media are controlled by the percentage of π -orbitals of free electrons on the nitrogen atoms of these compounds.

In this paper, the results of a study on the inhibition properties of three amines on mild steel in 1 and 5 N phosphoric acid solutions are reported. The comparative studies on corrosion inhibition properties of triethanolamine (TEA), triethylamine (TriEA), diethylamine (DEA) for comparing their corrosion inhibition effects in phosphoric acid media by mass loss and potentiodynamic polarization at 302–333 K have been reported.

EXPERIMENTAL

Mass loss measurement: Mild steel specimens were cut to the size of 5×1 cm from the mild steel sheets having the following percentage composition: Fe = 9.686, Ni = 0.013, Mo = 0.015, Cr = 0.043, S = 0.014, P = 0.009, Si = 0.007, Mn = 0.196, C = 0.017. Mass loss measurements were performed as per ASTM method described previously^{16–18}. Mass loss measurements were carried out in 1 and 5 N concentration of phosphoric acid with inhibitors like triethanolamine (TEA), triethylamine (TriEA) and diethylamine (DEA) in the concentration range of 0.5 to 2.5% at 302–333 K for an immersion period of 5 h with and without inhibitors. At 302 K, the immersion period of 24, 48, 72 and 96 h were also studied. All the solutions were prepared using AR grade chemicals with double distilled water.

Potentiodynamic polarization measurement: Polarization measurements were carried out in a conventional three-electrode cell assembly. Mild steel strips of same composition coated with lacquer with an exposed area of 1 cm^2 were used as working electrodes. The saturated calomel electrode and the platinum foil were used as reference and counter electrode, respectively. The potentiodynamic polarization was carried out using BAS-100A model instrument and the experiments were carried out at 302–333 K.

RESULTS AND DISCUSSION

Mass loss studies: The mass loss of the mild steel coupons in 1 and 5 N phosphoric acid in the absence and presence of different concentrations of inhibitors (0.5–2.5%) at 302–333 K was determined. From the mass loss values determined, the inhibition efficiencies (IE%) and surface coverage (θ) were calculated using the following equations^{19, 20}:

$$\text{IE \%} = \frac{W_u - W_i}{W_u} \times 100 \quad (1)$$

$$\theta = \frac{W_u - W_i}{W_u} \quad (2)$$

were W_u and W_i are the corrosion rates for mild steel in the absence and presence of inhibitor respectively in the phosphoric acid solution at the same temperature. The values are given in Tables 1 (a–c).

It clearly indicates that addition of inhibitors to the acid has reduced the corrosion rate. The inhibition efficiency and surface coverage increased with increase in concentration of inhibitors and decreased with rise in temperature from 302 to 333 K and in acid concentration from 1 to 5 N. The values of rate of corrosion

and inhibition efficiencies of all inhibitor compounds were found to depend on their molecular structure. The inhibition efficiencies of these compounds have been found to be in the following order:



TABLE-Ia
CALCULATED RATE OF CORROSION, INHIBITION EFFICIENCY (IE%)
AND SURFACE COVERAGE (θ) VALUES FOR TRIETHANOLAMINE
FROM MASS LOSS DATA IN 1 N AND 5 N H_3PO_4

Temp. (K)	Conc. of TEA (%)	1 N			5 N		
		Rate of corrosion (mmpy)	Surface coverage (θ)	Inhibition efficiency (IE%)	Rate of corrosion (mmpy)	Surface coverage (θ)	Inhibition efficiency (IE%)
302	Blank	6.80	—	—	26.22	—	—
	0.5	2.53	0.6290	62.90	14.11	0.4620	46.20
	1.0	1.98	0.7090	70.90	10.64	0.5942	59.42
	1.5	1.76	0.7410	74.10	7.81	0.7020	70.20
	2.0	1.03	0.8490	84.90	5.22	0.8014	80.14
	2.5	0.38	0.9444	94.44	3.22	0.8820	88.20
313	Blank	11.93	—	—	70.21	—	—
	0.5	5.00	0.5812	58.12	39.17	0.4422	44.22
	1.0	3.99	0.6659	66.59	30.75	0.5620	56.20
	1.5	3.32	0.7220	72.20	25.64	0.6349	63.49
	2.0	2.29	0.8081	80.81	16.21	0.7692	76.92
	2.5	1.02	91.4400	91.44	10.40	0.8519	85.19
333	Blank	19.82	—	—	157.39	—	—
	0.5	8.97	0.5476	54.76	94.20	0.4015	40.15
	1.0	7.31	0.6310	63.10	74.12	0.5291	52.91
	1.5	5.66	0.7145	71.45	61.92	0.6066	60.66
	2.0	4.53	0.7716	77.16	43.38	0.7244	72.44
	2.5	2.73	0.8623	86.23	27.56	0.8249	82.49

Table-2 shows the calculated values of activation energy E_a (kJ/mol), free energy of adsorption ΔG_{ads} (kJ/mol), rate constant k (sec^{-1}) and half-life $t_{1/2}$ (sec) for mild steel corrosion in 1 N and 5 N phosphoric acid with and without inhibitors. Energy of activation (E_a) has been calculated from the slopes of plots of $\log p$ vs. $1/T$ in Figs. 1 and 2 for TEA (similar plots were also obtained for TriEA and DEA) and also with the help of the Arrhenius equation²¹⁻²³:

$$\log \frac{p_2}{p_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad (3)$$

where p_1 and p_2 are the corrosion rates at temperatures T_1 and T_2 respectively. E_a values given in Table-2 show that the E_a values for the corrosion of mild steel in 1 and 5 N phosphoric acid are 28.86 and 48.34 kJ/mol respectively. In acid containing inhibitors, the E_a values are found to be higher than of the uninhibited system. The higher values of E_a indicate physical adsorption of the inhibitors on metal surface²⁴. The values of E_a calculated from the slopes of Arrhenius plot and by using eqn. (1) are approximately almost similar

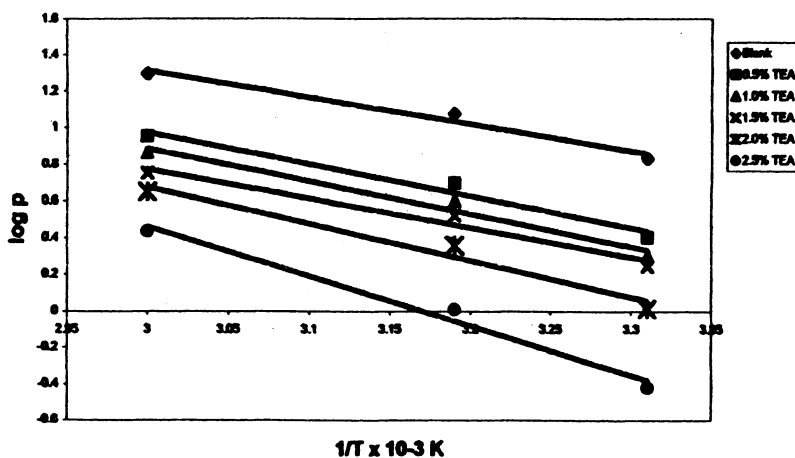
Fig. 1. Arrhenius plot for 1 N H₃PO₄ with TEA

TABLE-Ib
CALCULATED RATE OF CORROSION, INHIBITION EFFICIENCY (IE%) AND
SURFACE COVERAGE (θ) VALUES FOR TRIETHYLAMINE
FROM MASS LOSS DATA IN 1 N AND 5 N H₃PO₄

Temp. (K)	Conc. of TriEA (%)	1 N			5 N		
		Rate of corrosion (mmpy)	Surface coverage (θ)	Inhibition efficiency (IE%)	Rate of corrosion (mmpy)	Surface coverage (θ)	Inhibition efficiency (IE%)
302	Blank	6.80	—	—	26.22	—	—
	0.5	2.39	0.6490	64.90	11.75	0.5520	55.20
	1.0	1.72	0.7480	74.80	10.11	0.6143	61.43
	1.5	1.10	0.8388	83.88	6.58	0.7490	74.90
	2.0	0.92	0.8648	86.48	3.62	0.8620	86.20
	2.5	0.21	0.9692	96.92	2.52	0.9039	90.39
313	Blank	11.93	—	—	70.22	—	—
	0.5	4.65	0.6101	61.01	34.97	0.5020	50.20
	1.0	3.53	0.7040	70.40	27.79	0.6043	60.43
	1.5	2.43	0.7967	79.67	20.78	0.7041	70.41
	2.0	1.71	0.8567	85.67	14.07	0.7996	79.96
	2.5	0.91	0.9241	92.41	9.56	0.8639	86.39
333	Blank	19.82	—	—	157.39	—	—
	0.5	7.73	0.6098	60.98	84.25	0.4647	46.47
	1.0	6.36	0.6791	67.91	70.06	0.5549	55.49
	1.5	4.42	0.7769	77.69	52.13	0.6688	66.88
	2.0	3.39	0.8290	82.90	28.31	0.7566	75.66
	2.5	2.35	0.8814	88.14	23.79	0.8489	84.89

The free energy of adsorption (ΔG_{ads}) at different temperatures was calculated from the following equation²⁵.

$$\Delta G_{\text{ads}} = -RT \ln (55.5 K) \quad (4)$$

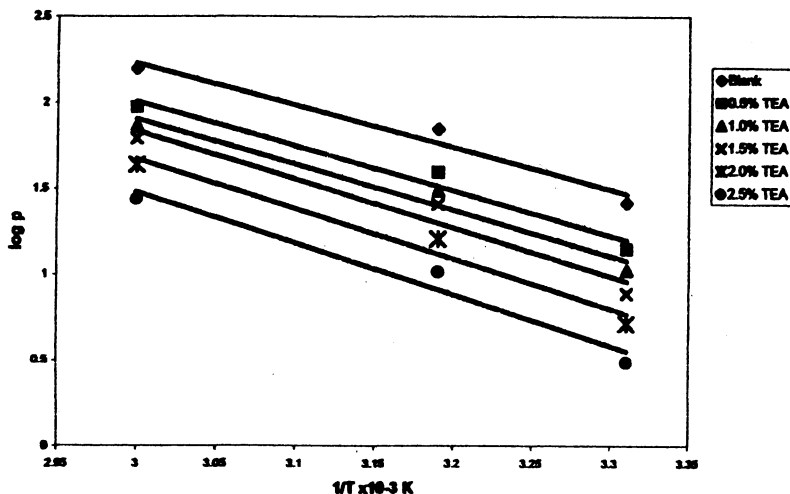


Fig. 2. Arrhenius plot for 5 N H₃PO₄ with TEA

and K is given by
$$K = \frac{\theta}{C(1 - \theta)} \tag{5}$$

where θ is surface coverage on the metal surface, C is concentration of inhibitor in mol/L and K is equilibrium constant.

From Table-2, the values of ΔG_{ads} obtained indicate the spontaneous adsorption of the inhibitor and are usually characteristic of strong interaction with the metal surface. It is found that the ΔG_{ads} values are less than -40 kJ/mol (less -ve values) indicating that inhibitors are physically adsorbed on the metal surface^{26, 27}.

The values of rate constant k were evaluated from the plots of log W_f vs. time (days) in Figs. 3 and 4 for TEA (similar plots were also obtained for TriEA and DEA). Linear plots were obtained which revealed first order kinetics. The values of half-life t_{1/2} were calculated using the equation below²².

$$t_{1/2} = \frac{0.693}{k} \tag{6}$$

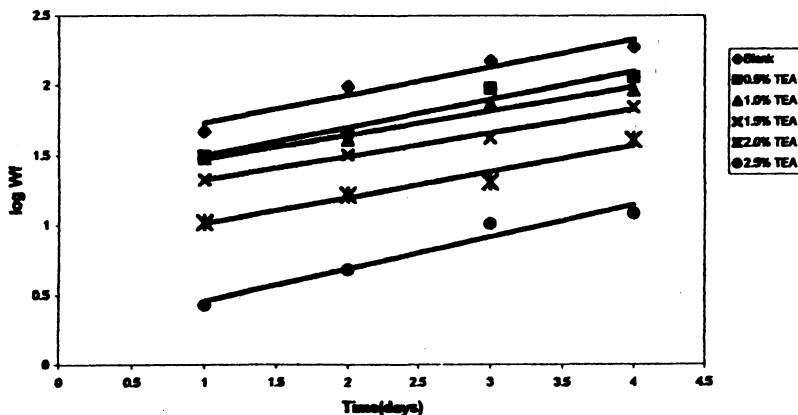


Fig. 3. Plot of log w_f vs. time (days) for 1 N H₃PO₄ with TEA

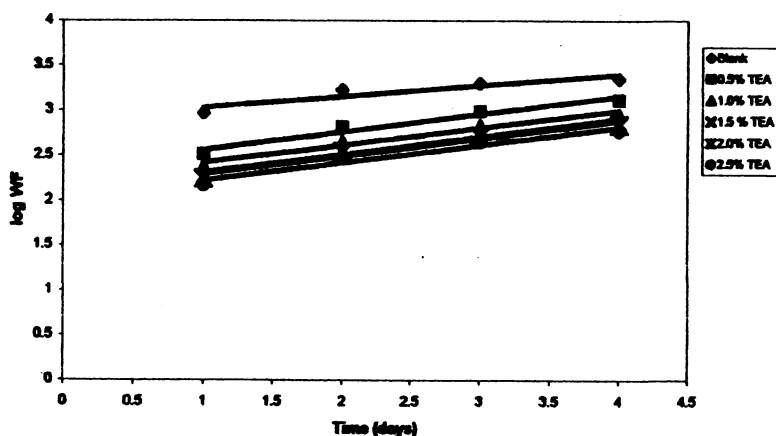
Fig. 4. Plot of $\log w_f$ vs. time (days) for 5 N H_3PO_4 with TEA

TABLE-Ic
CALCULATED RATE OF CORROSION, INHIBITION EFFICIENCY (IE%) AND SURFACE COVERAGE (θ) VALUES FOR DIETHYLAMINE FROM MASS LOSS DATA IN 1 N AND 5 N H_3PO_4

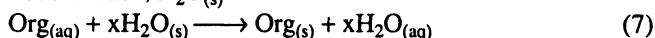
Temp. (K)	Conc. of DEA (%)	1 N			5 N		
		Rate of corrosion (mmpy)	Surface coverage (θ)	Inhibition efficiency (IE%)	Rate of corrosion (mmpy)	Surface coverage (θ)	Inhibition efficiency (IE%)
302	Blank	6.80	—	—	26.22	—	—
	0.5	2.01	0.7041	70.41	10.44	0.6020	60.20
	1.0	1.44	0.7890	78.90	8.21	0.6870	68.70
	1.5	0.95	0.8610	86.10	6.22	0.7627	76.27
	2.0	0.65	0.9048	90.48	3.10	0.8820	88.20
	2.5	0.18	0.9734	97.34	1.90	0.9277	92.77
313	Blank	11.93	—	—	70.22	—	—
	0.5	3.76	0.6848	68.42	29.64	0.5779	57.79
	1.0	3.08	0.7420	74.20	24.54	0.6506	65.06
	1.5	1.79	0.8497	84.97	18.79	0.7323	73.23
	2.0	1.21	0.8990	89.90	9.19	0.8691	86.91
	2.5	0.83	0.9310	93.10	8.53	0.8786	87.86
333	Blank	19.82	—	—	157.39	—	—
	0.5	7.17	0.6381	63.81	71.71	0.5444	54.44
	1.0	6.25	0.6849	68.49	58.77	0.6266	62.66
	1.5	4.08	0.7944	79.44	52.89	0.6640	66.40
	2.0	2.79	0.8593	85.93	28.38	0.8197	81.97
	2.5	2.21	0.8888	88.88	24.95	0.8415	84.15

TABLE-2
CALCULATED VALUES OF ACTIVATION ENERGY E_a (kJ/mol), FREE ENERGY OF ADSORPTION ΔG_{ads} (kJ/mol), RATE CONSTANT k (s^{-1}) AND HALF-LIFE $t_{1/2}$ (s) FOR MILD STEEL CORROSION IN 1 N AND 5 N PHOSPHORIC ACID WITH INHIBITORS

Inhibitors	Conc. of inhibitors (%)	E_a from eqn. (1) (kJ/mol)	E_a from Arrhenius plot (kJ/mol)	$-\Delta G_{ads}$ (kJ/mol)			Rate constant $k \times 10^{-6}$ (s^{-1})	Half-life $t_{1/2}$ (s^{-1})
				302 K	313 K	333 K		
TEA + 1 N H_3PO_4	Blank	28.86	28.72	—	—	—	5.73	120934
	0.5	34.14	34.00	19.65	19.84	20.73	5.14	134706
	1.0	35.23	35.46	18.82	18.98	19.77	4.88	142085
	1.5	31.51	31.12	18.20	18.61	19.70	4.81	144452
	2.0	39.95	40.17	19.18	19.12	19.73	4.61	150293
	2.5	53.19	52.99	21.39	20.96	20.82	4.27	162484
TriEA + 1 N H_3PO_4	Blank	28.86	28.72	—	—	—	5.73	120934
	0.5	31.66	32.07	19.98	20.28	21.51	5.06	136823
	1.0	35.28	35.10	19.43	19.56	20.49	4.72	146897
	1.5	37.52	37.49	19.82	19.80	20.75	4.53	152937
	2.0	35.52	35.60	19.62	20.16	20.87	4.42	156617
	2.5	65.15	65.12	23.06	21.43	21.43	4.11	168808
DEA + 1 N H_3PO_4	Blank	28.86	28.72	—	—	—	5.73	120934
	0.5	34.31	34.71	19.87	20.36	21.08	4.80	144452
	1.0	39.60	40.02	19.28	19.30	19.75	4.32	160479
	1.5	39.32	40.74	19.53	20.01	20.23	4.05	171020
	2.0	39.30	40.15	19.88	20.43	20.69	3.81	181829
	2.5	67.65	67.00	22.70	20.93	20.82	3.65	189778
TEA + 5 N H_3PO_4	Blank	48.34	48.74	—	—	—	22.82	30370
	0.5	51.21	51.67	17.94	18.38	19.10	20.95	33074
	1.0	52.36	52.55	17.53	17.83	18.60	20.47	33852
	1.5	55.85	55.45	17.71	17.57	18.35	20.25	34206
	2.0	57.12	57.60	18.34	18.51	19.04	19.16	36158
	2.5	58.94	57.99	19.33	19.35	20.03	18.39	37679
TriEA + 5 N H_3PO_4	Blank	48.34	48.74	—	—	—	22.82	30370
	0.5	53.14	54.12	18.96	19.13	19.94	20.69	33506
	1.0	52.22	53.00	17.87	18.41	19.02	20.18	34344
	1.5	55.83	55.70	18.43	18.51	19.23	20.15	34569
	2.0	55.48	55.50	19.56	19.11	19.63	18.92	36616
	2.5	60.56	60.89	20.03	19.73	20.66	18.15	38180
DEA + 5 N H_3PO_4	Blank	48.34	48.74	—	—	—	22.82	30370
	0.5	51.98	51.50	18.73	19.16	20.00	20.26	34206
	1.0	53.10	53.00	17.94	18.16	19.04	19.96	34716
	1.5	57.74	57.60	17.89	18.12	18.37	19.51	35519
	2.0	59.73	59.20	19.28	19.67	19.88	19.22	36055
	2.5	69.46	68.99	20.07	19.32	19.68	18.71	37040

The rate constant k decreases with increase in concentration of inhibitors whereas the half-life increases with concentration of inhibitors²². The adsorption of the organic molecules can affect in several ways the behaviour of the electrochemical reactions involved in the corrosion process. The action of organic inhibitors also depends on the type of interaction between the substance and the metallic surface. This interaction causes a change either in the electrochemical process mechanism or in the surface available to the process²⁸⁻³⁰.

Adsorption isotherms: The electrochemical process on the metal surface is likely to be closely related to the adsorption of the inhibitor³¹ and the adsorption is known to depend on the chemical structure of the inhibitor³²⁻³⁴. The adsorption of the inhibitor molecules from aqueous solution can be regarded as quasi-substitution process³² between the organic compound in the aqueous phase, $\text{Org}_{(\text{aq})}$ and water molecules at the electrode surface, $\text{H}_2\text{O}_{(\text{s})}$.



where x , the size ratio, is the number of water molecules displaced by one molecule of organic inhibitor.

Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions. The most frequently used isotherms are those of Langmuir, Frumkin, Parsons, Temkin, Flory-huggins and Bockris-Sinkles³⁵⁻³⁸. All these isotherms are of the general form:

$$f(\theta, x) \exp(-2a\theta) = KC \quad (8)$$

where $f(\theta, x)$ is the configuration factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm³⁹.

The plot of surface coverage (θ) obtained by mass loss method *vs.* $\log C$ for different concentrations of the compound show a straight line indicating that the adsorption of the compounds from acid on mild steel surface follows Temkin's adsorption isotherm²⁵. This also points to corrosion inhibition by these compounds being a result of their adsorption on the metal surface. Figs. 5 and 6 show the Temkin's adsorption isotherm for TEA. Similar plots were also obtained for TriEA and DEA.

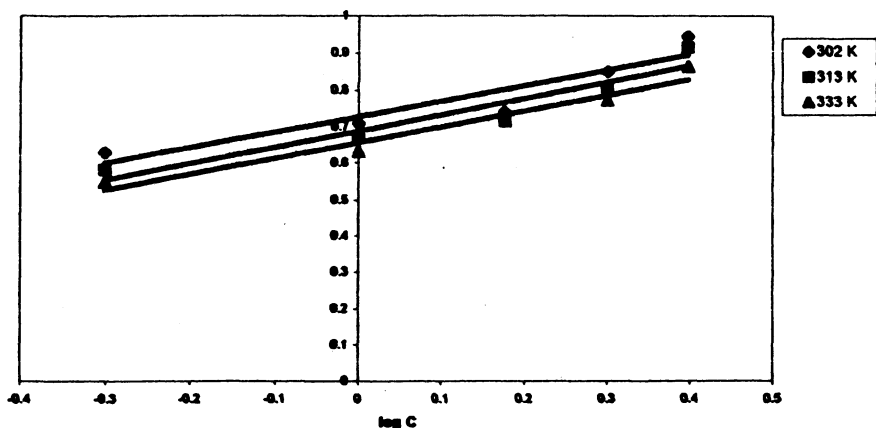


Fig. 5. Temkin's adsorption isotherm plot for 1 N H_3PO_4 with TEA

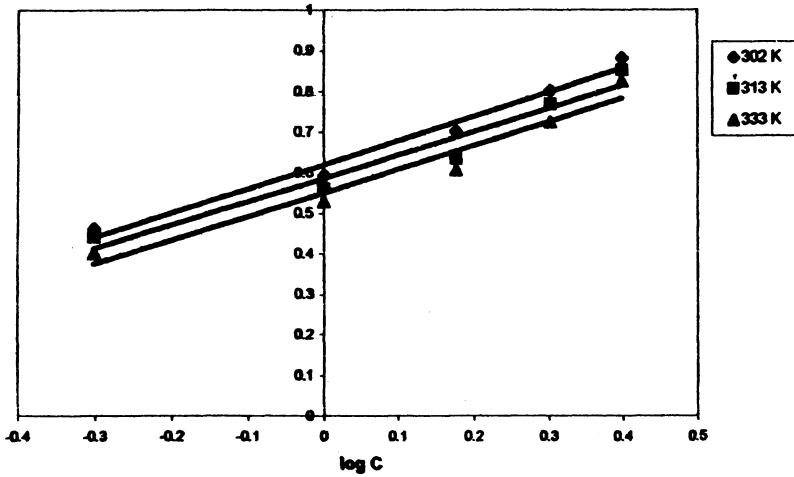


Fig. 6. Tempkin's adsorption isotherm plot for 5 N H_3PO_4 with TEA

Potentiodynamic polarization studies: The polarization behaviour of mild steel functioning as cathode as well as anode in the test solutions is shown in Fig. 7 for 1 N H_3PO_4 at 302 K for TEA. (similar curves were also obtained for

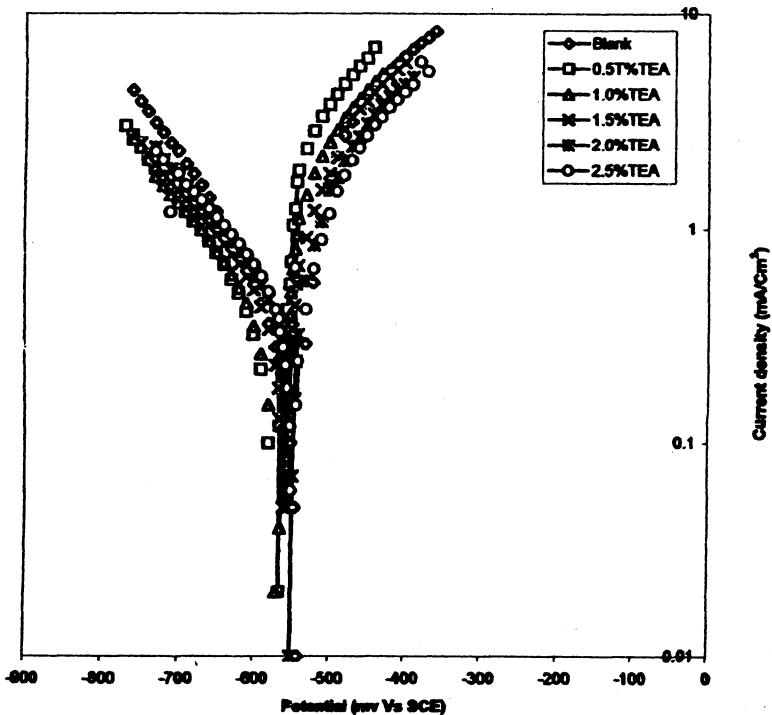


Fig. 7. Typical potentiodynamic curves for mild steel in 1 N H_3PO_4 with TEA at 203 K

TriEA and DEA in 1 N and 5 N phosphoric acid at 302–333 K) and the electrochemical data obtained from the studies are shown in Table-3. It is evident that amines bring about considerable polarization of the cathode as well as anode. It was, therefore, inferred that the inhibitive action is of mixed type. The cathodic and anodic Tafel slopes increased with increasing inhibitor concentrations and the increase was predominant in the case of the former indicating that the cathodic inhibition dominating through the inhibitive activity is of mixed nature. The non-constancy of Tafel slopes for different inhibitor concentration reveals that the inhibitor act through their interference in the mechanism of the corrosion processes at the cathode as well as the anode.

The corrosion parameters deduced from Tafel polarization such as corrosion current i_{corr} , corrosion potential E_{corr} , Tafel constants B_a and $-B_c$ and inhibition efficiency are given in Table-3. The i_{corr} values decrease with the increasing concentration of inhibitors. The inhibition efficiencies were determined from the values of corrosion current and the inhibition efficiency values were found to show good agreement with those obtained from mass loss measurements.

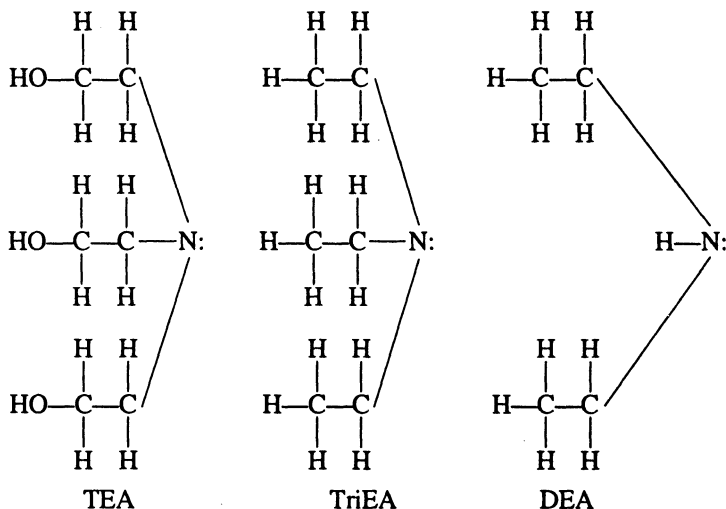
TABLE-3
ELECTROCHEMICAL POLARIZATION PARAMETERS FOR THE CORROSION
BEHAVIOUR OF MILD STEEL IN 1 N AND 5 N PHOSPHORIC ACID
IN ABSENCE AND PRESENCE OF INHIBITORS AT 302–333 K

Conc. of inhibitors (%)	1 N					5 N				
	E_{corr} vs. SCE (mv)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	Tafel constants (mv/decade)		IE %	E_{corr} vs. SCE (mv)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	Tafel constants (mv/decade)		IE (%)
			B_a	$-B_c$				B_a	$-B_c$	
Blank	-543	210	50	130	—	-510	700	50	150	—
0.5 TEA	-570	80	50	127	61.90	-549	384	49	147	45.14
1.0 TEA	-566	64	47	120	69.52	-540	292	49	143	58.28
1.5 TEA	-557	53	46	122	74.76	-538	205	47	145	70.71
2.0 TEA	-551	42	50	116	80.00	-534	139	44	140	80.14
2.5 TEA	-548	14	44	110	93.33	-530	86	43	139	87.71
Blank	-543	210	50	130	—	-510	700	50	150	—
0.5 TriEA	-578	75	45	126	64.29	-580	308	50	145	56.00
1.0 TriEA	-567	55	44	121	73.81	-570	276	48	140	60.57
1.5 TriEA	-563	35	46	117	83.33	-567	184	44	138	73.71
2.0 TriEA	-560	27	45	114	87.14	-560	97	43	135	86.14
2.5 TriEA	-559	11	42	105	94.76	-555	63	40	133	91.00
Blank	-543	210	50	130	—	-510	700	50	150	—
0.5 DEA	-592	64	40	124	69.52	-588	273	47	145	61.00
1.0 DEA	-580	47	40	120	77.62	-570	228	44	143	67.43
1.5 DEA	-569	28	38	116	86.67	-563	160	40	137	77.14
2.0 DEA	-553	21	37	114	90.00	-552	88	37	135	87.43
2.5 DEA	-553	6	34	110	97.14	-540	60	35	130	91.43

Conc. of inhibitors (%)	1 N					5 N				
	E_{corr} vs. SCE (mv)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	Tafel constants (mv/decade)		IE %	E_{corr} vs. SCE (mv)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	Tafel constants (mv/decade)		IE (%)
			Ba	-Bc				Ba	-Bc	
313K										
Blank	-535	680	100	150	—	-505	1000	30	175	—
0.5 TEA	-550	280	95	145	58.82	-530	568	28	170	43.20
1.0 TEA	-546	231	93	140	66.03	-527	441	28	165	55.90
1.5 TEA	-540	184	90	136	72.94	-520	380	27	160	62.00
2.0 TEA	-538	128	85	130	81.18	-518	239	26	157	76.10
2.5 TEA	-536	64	80	125	90.59	-510	150	23	155	85.00
Blank	-535	680	100	150	—	-505	1000	30	175	—
0.5 TriEA	-555	267	93	148	60.74	-560	489	27	169	51.10
1.0 TriEA	-550	196	90	145	71.18	-555	391	28	165	60.90
1.5 TriEA	-546	133	86	138	80.44	-552	302	26	163	69.80
2.0 TriEA	-542	91	84	133	86.62	-547	213	25	160	78.70
2.5 TriEA	-540	48	79	126	92.94	-542	140	24	159	86.00
Blank	-535	680	100	150	—	-505	1000	30	175	—
0.5 DEA	-575	221	92	144	67.43	-572	435	30	166	56.50
1.0 DEA	-566	175	90	140	74.21	-560	359	28	163	64.10
1.5 DEA	-560	112	86	138	83.50	-553	279	27	160	72.10
2.0 DEA	-554	85	83	136	87.21	-549	144	25	158	85.56
2.5 DEA	-547	58	80	133	91.50	-540	125	24	155	87.50
333K										
Blank	-523	1400	150	150	—	-483	3000	75	190	—
0.5 TEA	-545	650	140	145	53.57	-520	1823	75	185	39.23
1.0 TEA	-542	509	135	140	63.64	-512	1403	72	182	53.23
1.5 TEA	-533	412	130	137	70.57	-507	1214	72	180	59.53
2.0 TEA	-530	333	125	132	76.21	-502	806	70	174	73.13
2.5 TEA	-526	203	120	130	85.50	-496	493	68	170	83.57
Blank	-523	1400	150	150	—	-483	3000	75	190	—
0.5 TriEA	-540	564	138	148	59.71	-537	1632	73	187	45.56
1.0 TriEA	-537	464	135	134	66.86	-520	1347	71	184	55.10
1.5 TriEA	-532	321	130	128	77.07	-517	1027	70	181	65.58
2.0 TriEA	-530	235	129	124	83.21	-510	758	68	178	74.73
2.5 TriEA	-528	173	130	120	87.64	-506	480	66	173	84.00
Blank	-523	1400	150	150	—	-483	3000	75	190	—
0.5 DEA	-560	519	150	142	62.94	-540	1365	70	186	54.50
1.0 DEA	-552	455	147	138	67.50	-543	1149	70	183	61.70
1.5 DEA	-547	294	147	135	78.97	-530	1029	68	180	65.70
2.0 DEA	-540	198	145	130	85.88	-523	579	66	174	80.70
2.5 DEA	-535	179	140	132	87.21	-510	489	65	170	83.20

Mechanism of inhibition

Structure of triethanolamine (TEA), triethylamine (TriEA) and diethylamine (DEA) are given below:



+I effect is medium in diethylamine (DEA), high in triethylamine (TriEA) and very high in triethanolamine (TEA). As the +I effect increases the inhibition efficiency decreases due to the electron releasing power increasing; so the corrosion increases.

Triethanolamine shows the lowest inhibition. This is due to the structure, as the degree of chain branching appears to have the opposite effect with respect to charge density. The number of the functional groups is assumed⁴⁰⁻⁴² to reduce the protective properties owing to steric hindrance but the protection could be improved by functional groups acting as adsorption centres. So, triethanolamine shows lower inhibition than triethylamine and diethylamine. Same way, in case of triethylamine also, which shows less inhibition than diethylamine⁴³.

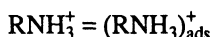
The steric effect of branching chains on the adsorption of free amines increased with increasing degree of branching in the alkyl group, which results in the lowering of the inhibition efficiency⁴⁴. This is related to the presence of three sites available to form coordinated bonds with iron atom through the two lone pairs of electrons on to N-atoms and the electron cloud on aromatic ring. Better inhibiting characteristic of diethylamine than triethylamine can be explained by steric hindrance in tertiary amine which may have influence on the electron density and on the base strength⁴⁵.

The result so obtained may be clarified on the basis of inductive effect of diethylammonium ion and lone pair of electrons present on N-atom. Two ethyl groups in diethylamine increase electrodensity on N-atom because of the inductive effect. Hence, lone pair of electrons of nitrogen atom is readily available for interaction with the metallic surface. In water, diethylamine forms diethylammonium ion carrying positive charge on nitrogen atom. This ion is associated with water molecules through H-bonding. During polarization diethylammonium ion adheres to the anodic sites of the electrode *via* oxygen atom containing lone pair of electrons (in anodic polarization) and *via* nitrogen atom carrying positive charge (in cathodic polariza-

tion) and covers a large surface area. Consequently, a film is formed on the metal surface and therefore the resistance increases. As a result, current density decreases⁴⁶.

As the number of alkyl group increases, the lone pair of electrons will become more available due to +I effect of alkyl group and the basicity of the amine will increase on alkylation. When a proton is added to N-atom, it increases crowding around the N-atom. This crowding results in strain, which becomes maximum in tertiary amines. Due to this, the stability of the molecule is reduced, *i.e.*, its basicity is reduced. This is borne out by the fact that the size of the alkyl group increases, thereby increasing the steric repulsion⁴⁷. The results are in agreement with the results obtained by Talati *et al.*⁴⁸

In acid solutions, amine molecule will take part in the following reaction:



The formed onium ion is adsorbed on the cathodic regions of the metal surface due to electrostatic attraction. The adsorbed onium ion can orient itself freely. The positive charges of the adsorbed onium ion make the potential of the layer of the electrical double layer more positive. Also, the carbon-hydrogen-chain in the onium ion obstructs the passage of positive ions to cathodic surface. As a result, the rate of the local cathodic reaction decreases considerably⁴⁹.

Finally discussed, the solubility of the inhibitor decreases and its adsorptive ability increases correspondingly but the reactivity of the molecules could also decrease⁴⁷. The solubility of the inhibitors decreases in the order of TEA > TriEA > DEA.

So the inhibition efficiency has been in the following order:

Diethylamine > Triethylamine > Triethanolamine.

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