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Corrosion inhibition effect of tetramines for mild steel in 1M HCl

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Abstract

In this investigation, attempts have been made to study the inhibitive effect of triethylene tetramine (TETA) and hexamethylene tetramine (HMTA) for mild steel in 1 M hydrochloric acid in the concentration range of 10^{-6} to 10^{-2} M by weight loss, DC polarization methods and AC impedance spectroscopy. Results indicate that the addition of tetramines to the acid reduce the rate of metal attack. For both the amines, inhibition efficiency increases with the concentration of amine. The inhibition efficiency of the hexamethylene tetramine is less when compared to that of triethylene tetramine.

Keywords: Corrosion inhibition; Mild steel; Acid

1. Introduction

The investigation of the inhibition of corrosion of iron is a matter of high theoretical as well as practical interest [1]. It is a well known fact that acids are used in many operations such as pickling, cleaning, descaling, etc. For the said purpose, hydrochloric acid is always superior and more economical than sulphuric acid because—ferrous chloride formed on the surface is highly soluble in water and hence no smut formation on the surface; and—the cementite phase (Fe_3C) normally present in the steel is more readily soluble in HCl. Because of their aggressiveness, inhibitors are used to reduce the rate of dissolution of metals. Compounds containing nitrogen, sulphur and oxygen are being used for this purpose [2]. The most effective and efficient inhibitors are organic compounds having π bonds in their structures. The efficacy of an organic compound as a successful inhibitor is mainly dependent on its ability to get adsorbed on the metal surface which consists of the replacement of water molecule at a corroding interface as

$$\mathrm{Org}_{(\mathrm{Sol})} + n\mathrm{H_2O} \rightarrow \mathrm{Org}_{(\mathrm{ads})} + n\mathrm{H_2O}_{(\mathrm{Sol})}$$

The adsorption of these compounds is influenced by the electronic structure of the inhibiting molecules [3,4] and also by the steric factors, aromaticity, electron density at the donor atoms and also by the presence of functional groups such as =NH, –N=N–, –CHO, R–OH, R=R, etc. in the inhibitor molecule

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[5,6]. The role of molecular area [7] and molecular weight [8] of the organic molecule on its inhibition efficiency was also reported. Aniline and alkylamine [9] *p*-substituted anilines [10] are reported for its inhibition which is mainly due to the π electron interaction and the formation of co-ordination bond between Fe–N substituted anilines. More recently polymer amines [11,12] were evaluated for their inhibition properties on the corrosion of iron and steel in acid solutions. The *ortho* substituted anilines [13] and polyanilines [14,15] were also studied more recently. Amines are a class of well known inhibitors for acid solution and are known to exert a high degree of protection for ferrous materials. Search of literature reveals that the inhibitive effect of cyclic and aliphatic primary, secondary and tertiary amines are well documented [16–29] and till date very few literature is available for the corrosion inhibitive effect of tetramines. Hence in the present investigation inhibitive effect of triethylene tetramine (TETA) and hexa methylene tetramine (HMTA) have been studied for mild steel in 1 M hydrochloric acid containing tetramine in the concentration range of 10^{-6} to 10^{-2} M.

2. Experimental

Mild steel specimens of percentage composition C 0.18, N 0.18, P 0.012, Si 0.0247, S 0.01 and Fe rest were used. The specimens were cut to the size of 10 mm × 50 mm for immersion studies and were lacquered so as to expose an area of 1 cm^2 for all electrochemical studies. The specimens for electrochemical studies were polished with 1/0, 2/0, 3/0 and 4/0 emery papers washed with flowing water and degreased with trichloroethylene. Solutions were prepared using Analar grade chemicals (supplied by BDH, India) with triple distilled water. For weight loss method, weighed triplicate specimens were immersed in test solution for a period of 1 h and after that washed with flowing water, dried and reweighed. Since industrial descaling and pickling processes where acid inhibitors find immense application are done with acid solutions for a time duration of less than 1 h, 1 h immersion in weight loss method has been chosen in this study. The inhibition efficiency of the added inhibitor is obtained from the weight loss measurements using the relationship:

$$\text{IE\%} = \frac{\text{WL} - \text{WL}_\text{i}}{\text{WL}} \times 100$$

where WL and WL_i are the weight losses without and with the addition of the inhibitors, respectively.

Electrochemical studies were carried out using conventional three electrode cell with larger area platinum foil as counter electrode and saturated calomel electrode (SCE) as reference electrode. Solatron electrochemical analyser (model 1280 B) interfaced with an IBM computer was used for measurements. The polarization studies were made after the specimen attained a steady state potential. The polarization was carried out using a Corware software from a cathodic potential of −0.2 V to an anodic potential of +0.2 V with respect to the corrosion potential at a sweep rate of 0.5 mV/s. E versus log *I* curves were plotted. The linear TAFEL segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities. The corrosion inhibition efficiency was evaluated from the measured i_corr values using the relationship:

$$\text{IE\%} = \frac{i_\text{corr} - i'_\text{corr}}{i_\text{corr}} \times 100$$

where i_corr and i'_corr are the corrosion current densities without and with the addition of various concentrations of the inhibitor, respectively.

For linear polarization measurements a sweep from −0.02 to +0.02 V versus open circuit potential at a sweep rate of 0.5 mV/s was used. The polarization resistance, R_p, is obtained as the slope of the "η versus i" curve at the vicinity of corrosion potential E_corr. This DC method of perturbation yields R_p which includes the solution resistance R_s. The inhibition efficiencies were evaluated from the polarization resistance, R_p values as

$$\text{IE\%} = \frac{R'_\text{p} - R_\text{p}}{R'_\text{p}} \times 100$$

where R_p and R'_p are the polarization resistances without and with the addition of inhibitors, respectively.

Z plot software was used for data acquisition and analysis of interfacial impedance. AC signals of 10 mV amplitude and a frequency spectrum from

100 KHz to 0.01 Hz was impressed and the Nyquist representations of the impedance data were analysed with Zview software. The charge transfer resistance R_{ct} is obtained as the diameter of the semi circle of Nyquist curve. By doing so, in this AC method of perturbation, the contributions from the solution resistance is eliminated. The inhibition efficiency was evaluated from the measured charge transfer resistance R_{ct} values as

$$\mathrm{IE\%} = \frac{R'_{ct} - R_{ct}}{R'_{ct}} \times 100$$

where R_{ct} and R'_{ct} are the charge transfer resistance values in the absence and presence of inhibitors, respectively. The interfacial double layer capacitance C_{dl} is obtained from the frequency of the point having maximum imaginary component (i.e. the point corresponding to the top of the semi circle) as

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}}$$

where "f_{max}" corresponds to the frequency having maximum imaginary component.

3. Results and discussions

The weight loss for the immersion of the coupons for 1 h is given in Table 1 along with the inhibition efficiencies for TETA and HMTA in the concentration range 10^{-6} to 10^{-2} M. From the table, it is evident that the addition of TETA and HMTA both decrease the metal dissolution rate but the former is more effective at lower concentration than the latter. Moreover, increase of concentration of the added inhibitor increases the inhibition efficiency irrespective of the molecular structure of the amine.

Table 1
Inhibition efficiencies of tetramines evaluated by weight loss method

Concentration (M)	HMTA		TETA	
	Corrosion rate (mpy)	IE (%)	Corrosion rate (mpy)	IE (%)
Blank	12.31	–	12.31	–
10^{-6}	10.03	18.5	3.08	75.0
10^{-5}	9.06	26.4	2.56	79.2
10^{-4}	8.60	30.1	2.26	81.6
10^{-3}	3.91	68.2	1.97	84.0
10^{-2}	2.50	79.7	1.40	88.6

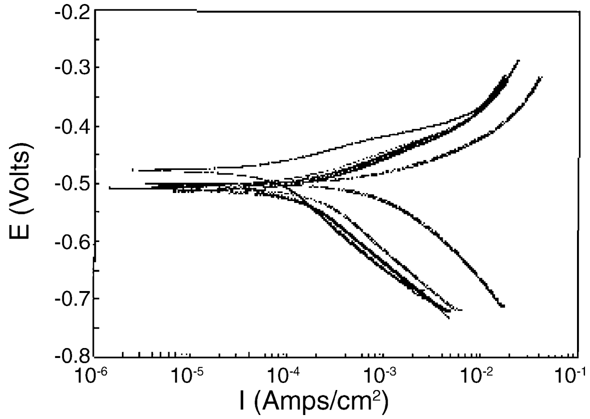

Fig. 1. Polarisation behaviour of MS in 1 M HCl—effect of TETA. (□) Blank; (■) 10^{-6} M; (○) 10^{-5} M; (●) 10^{-4} M; (◇) 10^{-3} M; (◆) 10^{-2} M.

The potentiodynamic polarization curves of mild steel in 1 M HCl with the addition of various concentrations of TETA and HMTA is shown in Figs. 1 and 2, respectively. The corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic Tafel slope (b_a) and cathodic Tafel slope (b_c) deduced from the curves are given in Table 2. The corrosion current density values decreases from 1.25 μA/cm^2 of the blank acid to 0.2 and 0.12 μA/cm^2, respectively, for the addition of 10^{-2} M of HMTA and TETA resulting in 84 and

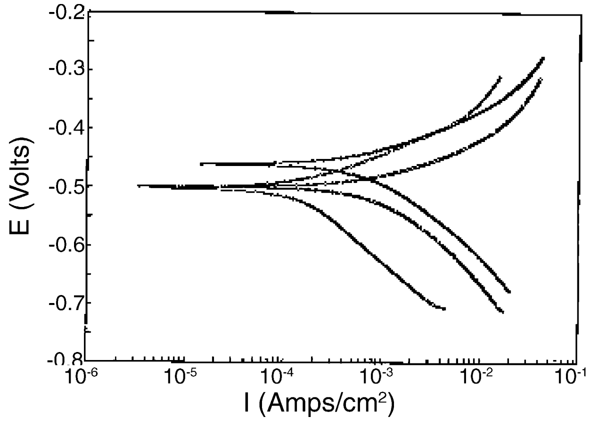

Fig. 2. Polarisation behaviour of MS in 1 M HCl—effect of HMTA. (□) Blank; (■) 1 × 10^{-6} M; (○) 1 × 10^{-2}.

Table 2
Electrochemical parameters for the corrosion of MS in 1 M HCl—effect of tetramines

Concentration of amine (M)	E_{corr} (mV /SCE)	b_a (mV/dec)	b_c (mV/dec)	I_{corr} (μA/cm^2)	IE (%)
Blank	−499	110	135	1.25	–
Hexamethylene tetramine					
10^{-6}	−475	102	122	0.97	20.4
10^{-5}	−477	110	123	0.87	30.4
10^{-4}	−499	100	130	0.80	36.0
10^{-3}	−501	95	133	0.33	73.6
10^{-2}	−503	105	130	0.20	84.0
Triethylene tetramine					
10^{-6}	−506	90	138	0.28	77.6
10^{-5}	−509	84	136	0.20	83.2
10^{-4}	−515	90	138	0.18	85.6
10^{-3}	−505	85	138	0.16	87.2
10^{-2}	−485	80	137	0.12	90.4

90.4% of inhibition efficiencies. As in the case of weight loss method, the increase in concentration of the inhibitor decreases the I_{corr} values. E_{corr}, b_a and b_c values do not change appreciably with the addition of the inhibitor indicating that the inhibitor is not interfering the anodic dissolution or cathodic hydrogen evolution reactions independently but acts as mixed type of inhibitor.

Polarization resistance values (R_p) obtained from the LPR method (Table 3) showed a steep increase in value from 17.7 Ω cm^2 for that of blank to 199.8 and 234 Ω cm^2 for the addition of the highest concentrations of HMTA and TETA, respectively. In accordance with weight loss and Tafel polarization methods, TETA performs better than HMTA for a particular concentration added.

The Nyquist representation of electrochemical impedance spectroscopic values for mild steel in 1 M HCl containing different concentrations of TETA and HMTA are presented in Figs. 3 and 4, respectively.

These plots having the shape of semi circle indicated the activation controlled nature of the reactions with single charge transfer process. The existence of depressed nature of the semi circle with its center of the semicircle below the x axis is the characteristics of solid electrodes and is attributed to the increased micro-roughness of surface and other inhomogenetics of solid electrode during corrosion

Table 3
Corrosion parameters for MS in 1 M HCl—effect of tetramines

Concentration (M)	Impedance method				LPR	
	R_{ct} (Ω cm^2)	C_{dl} (μF cm^2)	Surface coverage, θ	IE (%)	R_p (Ω cm^2)	IE (%)
Bl	14.8	49.8	–	–	17.7	–
Hexamethylene tetramine						
10^{-6}	21.1	25.3	0.4920	30	26.5	33
10^{-5}	31.6	20.0	0.5984	53	38.1	54
10^{-4}	34.7	19.3	0.6124	55	40.5	56
10^{-3}	75.7	12.9	0.7410	80	70.9	75
10^{-2}	113.7	10.5	0.7892	87	119.8	85
Tetraethylene tetramine						
10^{-6}	63.9	18.2	0.6345	77	78.0	77
10^{-5}	107.9	13.2	0.7349	86	114	85
10^{-4}	116.7	12.2	0.7550	87	128.1	86
10^{-3}	142.2	12.7	0.7450	89	137	87
10^{-2}	193.8	12.5	0.7490	92	234	93

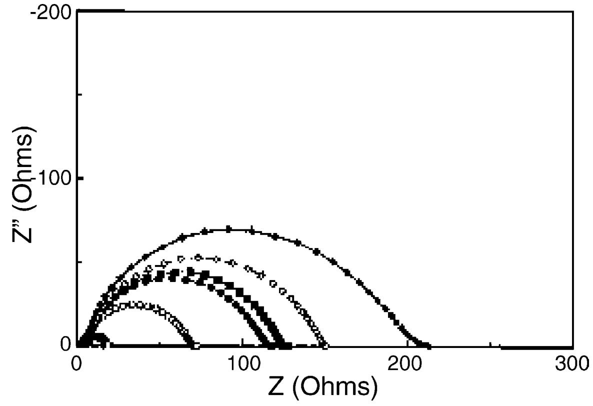

Fig. 3. Impedance behaviour of MS in 1 M HCl—effect of TETA. (□) Blank; (■) 10^{-6} M; (○) 10^{-5} M; (●) 10^{-4} M; (◇) 10^{-3} M; (◆) 10^{-2} M.

[30,31]. The diameter of the semicircle gives the charge transfer resistance "R_{ct}" equivalent to the polarization resistance R_p which is inversely proportional to corrosion rate. With the increase in concentration of tetramines the charge transfer resistance increases. The charge transfer resistance R_{ct} and the interfacial double layer capacitance C_{dl} derived from these curves are given in Table 3. R_{ct} increase from the value of 14.8 Ω cm^2 for the blank acid to 113.7 and 193.8 Ω cm^2 for the highest concentration of HMTA and TETA, respectively. The solution resistances observed in Fig. 3 is almost same while there is a slight difference in Fig. 4 but the numerical values are in the narrow range of 3–9 Ω cm^2. Conversion of excess HMTA in to ammonia in presence of HCl might be a reason for this small increase in solution resistance.

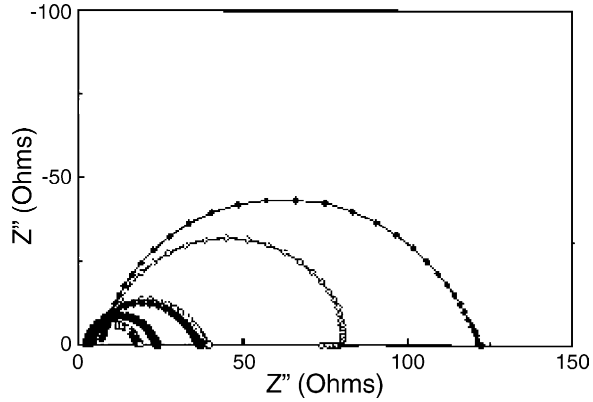

Fig. 4. Impedance behaviour of MS in 1 M HCl—effect of HMTA. (□) Blank; (■) 10^{-6} M; (○) 10^{-5} M; (●) 10^{-4} M; (◇) 10^{-3} M; (◆) 10^{-2} M.

The interfacial double layer capacitance C_{dl} decreases from 49.8 μF cm^{-2} for the blank to 10.5 and 12.5 μF cm^{-2} for HMTA and TETA, respectively. The surface coverage θ was estimated from the measured double layer capacitance C_{dl} values using the relationship:

$$\theta = \frac{C_{dl} - C'_{dl}}{C_{dl}}$$

where C_{dl} and C'_{dl} are the double layer capacitances in the absence and presence of inhibitors, respectively.

Corrosion of iron in acidic chloride solutions was found to occur as follows [32,33]:

$$Fe + H_2O \leftrightarrow Fe.H_2O_{ads}$$

$$Fe.H_2O_{ads} + Cl^- \leftrightarrow FeCl^-_{ads} + H_2O$$

$$FeCl^-_{ads} + OH^- \leftrightarrow FeOH^+ + Cl^- + 2e$$

$$FeOH^+ + H^+ \rightarrow Fe^{2+} + H_2O$$

or

$$Fe + Cl^- \leftrightarrow FeCl^-_{ads}$$

$$FeCl^-_{ads} + H_2O \leftrightarrow FeOH^-_{ads} + H^+ + Cl^-$$

$$FeOH^-_{ads} \leftrightarrow FeOH_{ads} + e$$

$$FeOH_{ads} \leftrightarrow FeOH^+_{ads} + e$$

$$FeOH^+_{ads} \leftrightarrow Fe^{2+} + OH^-$$

In the present study the observed anodic Tafel slope of 100 ± 10 mV/decade suggests that the first electron transfer step is slow:

$$Fe + Cl^- \leftrightarrow FeCl^-_{ads}$$

$$FeCl^-_{ads} + H_2O \leftrightarrow FeOH^-_{ads} + H^+ + Cl^-$$

$$FeOH^-_{ads} \leftrightarrow FeOH_{ads} + e$$

$$FeOH_{ads} \leftrightarrow FeOH^+_{ads} + e$$

$$FeOH^+_{ads} \leftrightarrow Fe^{2+} + OH^-$$

Anodic Tafel slopes were not very much influenced by the presence of inhibitors. This suggests that the inhibitors did not change the mechanism of metal dissolution. By adsorption on the surface, prevented the dissolution of iron. At first the metal atom leaves the crystal lattice to form surface adsorptive complexes, then those complexes are discharged to form hydrated ions which will diffuse further into the bulk solution. Weight loss method give the average integrated value of corrosion rate over the immersion period of 1 h whereas the electrochemical methods yield instantaneous corrosion rate values. Moreover, the surface state of the anode is always changing as it dissolves. As a result, I_{corr} obtained from electrochemical methods differ considerably from that obtained from weight loss method.

The observed corrosion data in presence of amine suggests that inhibition of dissolution of steel occurs, through the adsorption of amine at the local anodic as well as cathodic sties.

On the anodic site, the effect of amine on the anodic partial reaction is mainly attributed to the chemisorption of the amine on the metal surface through co-ordination bond formation between the metal and to the electron pair on the nitrogen atom. The inhibition efficiencies therefore depend on the adsorptive power of the amine and the coverage area (spatial effect) of the adsorbed molecule.

The cathodic partial reaction is the hydrogen evolution reaction. Presence of amine does not much affect the shape of the curve but shift the corrosion current towards a lower value, implies that the inhibition of corrosion is also through the adsorption on cathodic sites. In acid solutions, amine molecules will form 'onium ion' and this will in turn gets adsorbed on the cathodic regions of the metal surface due to electrostatic attraction [34]. Also the onium ion obstructs the passage of ions to the cathodic surface. As a result, the rate of the local cathodic reaction decreases considerably. This inhibition depends greatly on the stability and adsorptive power of the onium ion.

But the nature of the interaction of the inhibitor on the metal surface during the corrosion inhibition can be deduced more correctly by studying the adsorption characteristics. For getting adsorbed on the metal surface from the aqueous solution, each organic molecule has to displace 'n' molecules of water. Thermodynamics of the exchange of adsorbate between the bulk and the interface therefore depends on the relative size of the adsorbate. Such competitive adsorption of amine molecule from solution is similar to a quasi-chemical substitution process [35]:

$$\text{Amine}_{(s)} + n\text{H}_2\text{O}_{\text{ads}} \rightarrow \text{amine}_{\text{ads}} + n\text{H}_2\text{O}_{(s)}$$

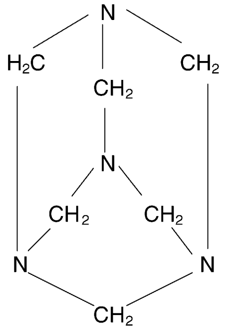

Fig. 5. Cage structure of HMTA.

The thermodynamics of this reaction depends upon the number of water molecules 'n', replaced by the amine.

Results of the study indicate that the inhibition efficiency of TETA is maximum even at lower concentration and for HMTA the critical concentration necessary for better protection is higher. The observed inhibition efficiency of TETA can be explained by the adsorption of amine molecule parallel to the steel surface. The lone pair of electrons in the nitrogen atom can form co-ordination bond with the iron by sharing the electrons with the unfilled levels. Thus each molecule of TETA can form bond with two iron atoms and effectively covers the surface even at lower concentration (10^{-2} M). On the other hand, in the case of HMTA, due to the cage structure (Fig. 5), it cannot cover the electrode surface effectively at lower concentration and needs a high optimum concentration for effective inhibition of steel corrosion. The adsorption of TETA molecule on steel surface can be visualized as given in Fig. 6. Adsorption isotherms gives the relationship between the coverage of corroding interface by the adsorbed species and the concentration of the inhibitor molecules in the solution. Interpretation of inhibitor performance can be done by fitting the data to one of the adsorption isotherms. In the present case, various adsorption

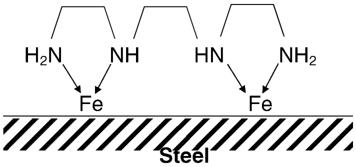

Fig. 6. Adsorption of TETA over iron surface.

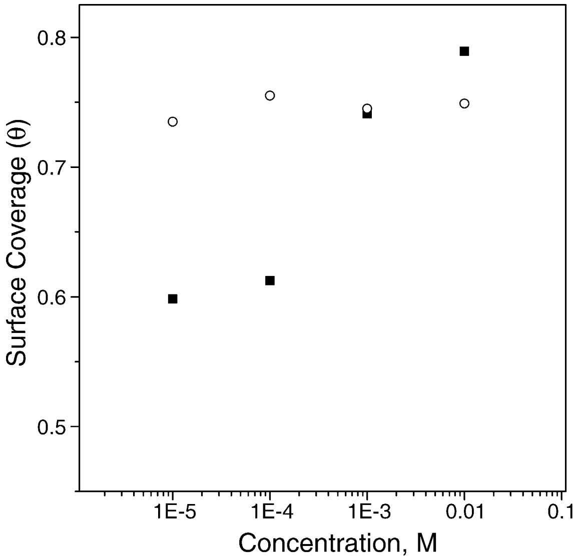

Fig. 7. Temkin adsorption isotherm for tetramines. (■) HMTA; (○) TETA.

isotherms have been tried and it was found that the Temkin adsorption isotherm wherein the surface coverage θ versus logarithmic concentration of the inhibitor will be a linear one is best fitting (Fig. 7). It is seen from Fig. 7 that the slope of the TETA line is very small and the θ values around 0.75 ± 0.1 at all concentrations and the slope of the HMTA line is very high with values increase from 0.6 to 0.78 for the concentration range studied again confirms the trend of inhibition efficiency values estimated by all other methods. Calculation of free energy of adsorption from the isotherm plots and obtaining other thermodynamical data by conducting experiments at various temperatures is the plan of our future study.

4. Conclusions

Both TETA and HMTA are found to inhibit the corrosion of iron in 1N HCl. Of these, the inhibition efficiency of TETA is maximum even at lower concentration (10^{-2} M) and for HMTA the critical concentration necessary for better protection is higher. The inhibition efficiency of TETA can be explained by the adsorption of amine molecule parallel to the steel surface. The inhibition efficiencies also depend on the adsorptive power of the amine and the coverage area (spatial effect) of the adsorbed molecule.

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