Ethanolamines as Corrosion Inhibitors for
Zinc in Sulfamic Acid

V.A. Champaneri and R.T. Vashi*

Department of Chemistry, Navyug Science College, Surat-395 009, India
E-mail: vashirajendra@yahoo.co.in

The corrosion of zinc in sulfamic acid containing ethanolamines has been studied. In plain acid, corrosion increases with concentration of acid and with the temperature. At constant acid concentration, the inhibition effeciency of ethanolamines increases with inhibitor concentration. Similarly, at constant inhibitor concentration, the inhibition efficiency increases with the increase in concentration of acid. Ethanolamines show excellent inhibitor in all acid concentration as well as at all inhibitor concentration at 301 K. The efficiency of the inhibitors decreases in the order: ethanolamine > diethanolamine > triethanolamine. As temperature increases, percentage of inhibition decreases. The mode of inhibition action appears to be chemisorption since the anodic and cathodic regions through general adsorption following the Langmuir isotherm. Anodic and cathodic galvanostatic polarization curves show little anodic but significant cathodic polarization.

Key Words: Corrosion, Zinc, Sulfamic acid, Ethanolamines.

INTRODUCTION

Sulfamic acid (NH_3O_3S) is a strong acid and is used as a cleaner for rust, algae and scale from condensors and cooling tower[1]. Zinc is one of the most vital non-ferrous metal, having extensive use metallic coating and in construction material. Zinc sheet immersed in 3 % sulfamic acid solution for 48-95 h at 20 to 25 ºC shows corrosion rate of 2200 mil/y for 4 h immersion period at 66 ºC. Zinc sheet immersed in various concentration of sulfamic acid indicates a various corrosion rate, *viz.*, 2200 mil/y for 3 %, 7800 mil/y for 12 % and 730 mil/y for 20 % sulfamic acid solution for 48-95 h at 20 to 25 ºC[2]. Vashi and Champaneri studied the effect of nitro amines[3], toluidines[4], chloroanilines[5] as corrosion inhibitors for zinc in sulfamic acid. Vashi *et al.*[6] studied ethanolamines as corrosion inhibitors for zinc in phosphoric acid and found that ethanolamine gave better inhibition than diethanolamine and triethanolamine. Vashi *et al.*[7] studied ethanolamines as corrosion inhibitors for zinc in nitric acid and found percentage inhibition in the order: ethanol amine > diethanolamine > triethanol amine. Aliphatic amines, heterocyclic amines and aromatic amines have been extensively investigated as corrosion inhibitors[8-10]. Bhajiwala[11] have studied the effect of ethanolamines on corrosion of zinc in binary

acid mixture (HNO_3 + H_3PO_4) in various concentration and reported that the inhibition efficiency (I.E.) of various amines increases with the increase in inhibitor concentration. The present study was undertaken to evaluate various ethanolamines as corrosion inhibitors and to understand corrosion behaviour of zinc in sulfamic acid.

EXPERIMENTAL

Rectangular specimens (5.5 cm × 2.5 cm × 0.2 cm) of zinc having an area of 0.3074 dm^2 were used for the determination of the corrosion rate. The chemical composition of test specimen was found to be 98.5 % Zn, 0.03 % Pb, 0.02 % Cd and 0.01 % Fe. All the specimens were cleaned by buffing to obtain a mirror like finish. A specimen, suspended by a glass hook, was immersed in 230 mL of the test solution at 301 K and left exposed to air for 24 h period. After the test, the specimens were cleaned by using 10 % chromic acid solution[12] having 0.2 % $BaCO_3$. After cleaning, the specimens were washed with distilled water followed by acetone and dried with air dryer. Triplicate experiments were performed in each case and the mean value of the weight losses are reported.

To study the effect of temperature on corrosion of zinc in 0.1 M sulfamic acid, the specimens were immersed in 230 mL. of the corrosive solution and weight loss was determined at solution temperature of 313, 323 and 333 K for an immersion period of 3 h without and with ethanolamines at 5,10 and 15 mM concentration. Attention is paid to compensate the evaporational loss of corrosive media. Clarke[13] and ASTM[14] pointed out that thermostatic control to within ±1 ℃ usually be considered satisfactory.

The variation of the open circuit potential of the zinc electrode (having an area of 0.0675 dm^2) immersed in 0.1 M sulfamic acid without as well as with the various ethanolamines at 5 mM concentration, potential was measured immediately after the immersion using Ag/AgCl reference electrode with the help of primary circuit, as a function of time. The potential values were carefully and continuously recorded after each intervals of 5 min till the potential attained a steady value ($E_{const.}$).

For polarization study, metal specimens having an area of 0.0771 dm^2 were immersed to 230 mL corrosive medium. Zinc metal (working electrode) was polished with a fine emery paper, cleaned with distilled water and acetone. The test cell includes the metal specimen and the solution in which the specimen is to be tested. The Ag/AgCl electrode used as a reference electrode and placed in saturated KCl solution and it contacts the solution *via* the salt-bridge tube. The external current was supplied from a regulated power supply using an auxiliary Pt-electrode. The polarization studies were made using potentiostat/galvanostat (EG and G PARC model-273). Glavanostatic polarization has been taken with and without inhibitors in sulfamic acid, which indicates anodic and cathodic polarization.

RESULTS AND DISCUSSION

Inhibition efficiency: To assess the effect of corrosion of zinc in sulfamic acid ethanolamines were added and their inhibition efficiency (I.E.) has been calculated as follows:

$$I.E. (\%) = \frac{Wu - Wi}{Wu} \times 100 \tag{1}$$

where, Wu = Weight loss of metal in uninhibited solution, Wi = Weight loss of metal in inhibited solution.

TABLE-1
CORROSION LOSS (CL) AND INHIBITION EFFICIENCY (I.E.) OF ZINC IN
SULFAMIC ACID CONTAINING ETHANOLAMINES AS INHIBITORS
Effective area of specimen: 0.3074 dm^2, Immersion period: 24 h, Temp.: 301 ± 1 K

Inhibitor	Inhibitor concentration mM	Acid concentration					
		0.1 M		0.5 M		1.0 M	
		CL mg/dm^2	I.E. %	CL mg/dm^2	I.E. %	CL mg/dm^2	I.E. %
A	–	152.5	–	210.9	–	223.0	–
	5	100.8	33.9	133.2	36.8	134.3	39.8
B	10	40.0	73.8	51.3	75.7	36.7	83.5
	15	22.2	85.5	26.1	87.6	17.0	92.4
	5	113.0	25.9	147.8	29.9	141.0	36.8
C	10	63.1	58.7	66.0	68.7	54.4	75.6
	15	28.0	81.6	28.2	86.6	18.9	91.5
	5	116.0	23.9	154.1	26.9	147.6	33.8
D	10	107.2	29.7	143.7	31.9	125.4	43.8
	15	88.6	41.9	95.4	54.8	63.3	71.6

A = Sulfamic acid, B = Sulfamic acid + Ethanolamine, C = Sulfamic acid + Diethanolamine, D = Sulfamic acid + Triethanolamine, CL = Corrosion loss.

Corrosion in pure sulfamic acid: The corrosion loss increases with an increase in sulfamic acid concentration. The corrosion loss was 152.5, 210.9 and 223.0 mg/dm^2 in 0.1, 0.5 and 1.0 M acid concentration, respectively for a period of 24 h at the room temperature (301 ± 1 K) (Table-1). A plot of log (θ/1−θ) *versus* log C (acid concentration) also indicates the same trend (Fig. 1).

Corrosion in presence of inhibitors: To assess their protective value, aliphatic amines like ethanolamine, diethanolamine and triethanolamine were added in 5, 10 and 15 mM concentration to 0.1, 0.5 and 1.0 M sulfamic acid.

At constant acid concentration, the inhibition efficiency (I.E.) of the ethanolamines increases with the inhibitor concentration, *e.g.*, 1.0 M acid in the case of ethanolamine, the inhibition efficiency was found to be 39.8, 83.5 and 92.4 % with respect to 5, 10 and 15 mM inhibitor concentration respectively (Table-1).
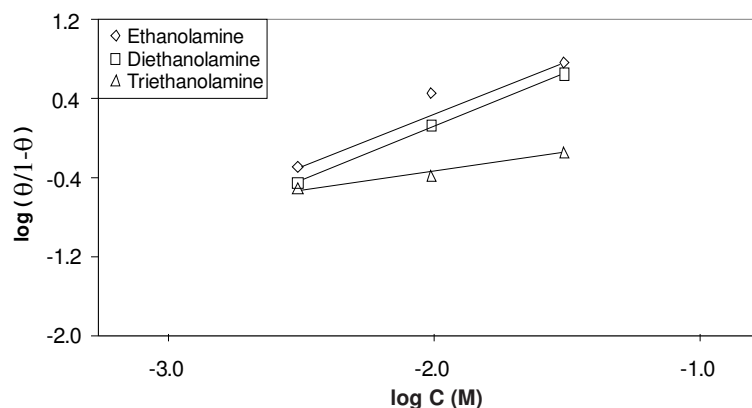
Fig. 1.   Plot of log (θ/1–θ) *versus* log C for aliphatic amine in 0.1 M sulfamic acid
           concentration

At constant inhibitor concentration, the I.E. increases with the increase in sulfamic acid concentration. At 15 mM inhibitor concentration, the I.E. of ethanolamine is 85.5, 87.6 and 92.4 % with respect to 0.1, 0.5 and 1.0 M sulfamic acid concentration, respectively (Table-1). At 15 mm inhibitor concentration and in 1.0 m acid, the efficiency of inhibitors decreases in the order: ethanolamine (92.4 %) > diethanolamine (91.5 %) > triethanolamine (71.6 %). The results indicates that ethanolamine act as a better inhibitor.

Effect of temperature: To determine the effect of temperature on corrosion, corrosion rate was measured in 0.1 M sulfamic acid containing 5, 10 and 15 mM inhibitor concentration at solution temperature of 313, 323 and 333 K for an immersion period of 3 h. The results in Table-2 shows that corrosion increases with a rise in temperature. In 0.1 M sulfamic acid at 15 mM inhibitor concentration, the I.E. values for ethanolamine were 90.0, 88.2 and 84.1 % which indicates that as temperature increases I.E. decreases.

Energy of activation (Ea): The values of the energy of activation (Ea) was calculated from the equation,[15]

$$\log\left(\frac{P_2}{P_1}\right) = \frac{Ea}{2.303\,R\left[\left(\frac{1}{T_1}\right) - \left(\frac{1}{T_2}\right)\right]} \qquad (2)$$

$$Ea \text{ from the graph} = 2.303 \times R \times Slope \qquad (3)$$

where, P_1 and P_2 are the corrosion rates.

A comparison of the values of the Ea for the corrosion process in inhibited as well as uninhibited sulfamic acid reveals that the 'Ea' values are higher in inhibited than in uninhibited acid (Table-2).

The mean value of Ea for uninhibited acid was 58.7 kJ mol^{-1} where as for inhibited acid the Ea values lies in the range of 64.2 to 82.9 kJ mol^{-1}. The mean

TABLE-2
EFFECT OF TEMPERATURE ON CORROSION LOSS (CL), ENERGY OF
ACTIVATION (Ea) FOR CORROSION OF ZINC IN 0.1 M SULFAMIC
ACID AT VARIOUS INHIBITOR CONCENTRATION
Effective area of specimen: 0.3074 dm^2 Immersion period: 3 h

Inhibitor	Inhibitor conc. mM	Temperature (K)						Energy of activation (Ea) kJ mol^{-1}		
		313		323		333		313-323 K	323-333 K	Mean Ea
		CL mg/ dm^2	I.E. (%)	CL mg/ dm^2	I.E. (%)	CL mg/ dm^2	I.E. (%)			
A	-	195.2	-	335.7	-	749.5	-	45.6	71.8	58.7
B	5	54.4	72.1	110.2	67.2	291.9	61.1	59.2	87.1	73.2
	10	32.8	83.2	66.5	80.2	171.6	77.1	59.3	84.7	72.0
	15	19.6	90.0	39.8	88.2	119.4	84.1	59.5	98.3	78.9
C	5	70.0	64.1	142.7	57.5	374.3	50.1	59.8	86.2	73.0
	10	42.7	78.1	86.7	74.2	231.8	69.1	59.5	88.0	73.7
	15	27.1	86.1	59.6	82.2	164.5	78.1	66.3	90.7	78.5
D	5	96.7	50.5	181.1	46.1	421.8	43.7	52.7	75.6	64.2
	10	50.5	74.1	99.8	70.3	269.3	64.1	57.2	88.8	73.0
	15	33.0	83.1	76.5	77.2	221.6	70.3	70.7	95.1	82.9

Inhibitor	Ea from Arrhenius plot	Heat of adsorption, Q$_{ads}$ kJ mol^{-1}		Free energy of adsorption (ΔG^0a) kJ mol^{-1}			
		313-323 K	323-333 K	313 K	323 K	333 K	Mean
A	57.4	-	-	-	-	-	-
B	69.8	-19.7	-23.9	-18.9	-18.9	-18.7	-18.8
	68.8	-16.9	-16.4	-20.6	-20.7	-20.8	-20.7
	75.2	-15.7	-30.8	-22.1	-22.4	-22.0	-22.2
C	69.7	-23.5	-26.8	-17.9	-17.8	-17.5	-17.7
	70.3	-18.3	-22.5	-19.7	-19.8	-19.7	-19.7
	75.0	-24.7	-23.6	-21.2	-21.1	-21.0	-21.1
D	61.2	-14.9	-8.43	-16.5	-16.5	-16.8	-16.6
	69.6	-16.2	-25.2	-19.2	-19.3	-19.1	-19.2
	79.2	-31.4	-31.6	-20.6	-20.2	-19.9	-20.2

A = Sulfamic acid, B = Sulfamic acid + Ethanolamine, C = Sulfamic acid + Diethanolamine,
D = Sulfamic acid + Triethanolamine, CL = Corrosion loss.

values of Ea as calculated from the Arrhenius equation were almost the same (± 5.0 kJ mol^{-1}) in most of the cases. For ethanolamines the mean value of Ea in decreasing order was found as follows: ethanolamine 82.9 kJmol^{-1} > diethanolamine > triethanol-amine (64.2 kJ mol^{-1}). The value of the Ea were calculated from the slope of the Arrhenius plots of log δ (corrosion loss) *vs.* (1/T) × 10^3 (Fig. 2).

Heat of adsorption (Q$_{ads}$): The values of the Heat of adsorption (Q$_{ads}$) was calculated from the equation,[15]

$$Q_{ads} = 2.303 \, R \left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right) \right] \times \left[\frac{T_1.T_2}{T_2 - T_1} \right] \qquad (4)$$
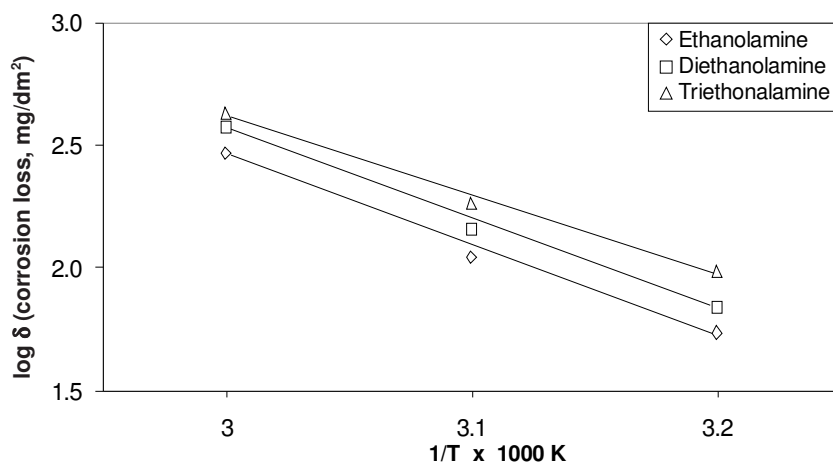
Fig. 2.   Arrhenius plots for corrosion of zinc in 0.1 M sulfamic acid in absence and presence of 5 mM inhibitor concentration

where, θ_1 and θ_2 are the fractions of the metal surface covered by the inhibitors at temperature T_1 and T_2 in Kelvin, respectively and R is a gas constant (R = 0.008314 kJ.mol^{-1}).

It was evident that in all ethanolamines Q_{ads} values were negative and varies from -8.43 to -31.6 kJ mol^{-1} (triethahanolamine) concentration at 15 mM (Table- 2).

Free energy of adsorption (G^0a): The value of G^0a from aqueous solution were calculated with the help of the equation,[16]

$$\log C = \log\left(\frac{\theta}{1-\theta}\right) - \log B \qquad (5)$$

where, log B = $-1.74 - (\Delta G^0 a/2.303\ RT)$ and C is the inhibitor concentration in mole and log B is formation constant.

The value of G^0a was calculated at different temperatures and different inhibitor concentrations in 0.1 M sulfamic acid for the period of 3 h, which show that as the temperature increases the value of G^0a increases (becomes less negative), while percentage of I.E. decreases (Table-2). The mean $\Delta G^0 a$ values are vary from -16.6 to 22.2 kJ mol^{-1}.

Effect of polarization: Electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), the value of Tafel parameters (βa, βc and B) and percentage I.E. calculated from polarization method and weight loss method in 0.1 M sulfamic acid having 5 mM inhibitor concentration given in Table-3. Anodic and cathodic galvanostatic polarization curves for zinc in 0.1 M sulfamic acid containing 5 mM concentration of ethanolamines show polarisation of both the anodes as well as the cathodes. The I.E. were calculated from corrosion currents obtained by the extrapolation of cathodic and anodic Tafel lines are given in Table-3 agree well with those obtained from weight loss data (within ± 2 %).

TABLE-3

POLARIZATION DATA AND INHIBITION EFFICIENCY (IE %) OF
ETHANOLAMINES FOR ZINC IN 0.1 M SULFAMIC ACID

Effective area of specimen: 0.077 dm^2; Inhibitor concentration: 5 mM

System	E_{corr} (mV)	I_{corr} (μA /cm^2)	Tafel slope (mV/decade)		B (mV)	Rp (Ohm/cm^2)	I.E. (%) from methods	
			βa	$-\beta c$			Weight loss	By polarization
A	−920	1.20	14	−10	2.88	2.40	−	−
B	−890	0.82	13	−14	2.93	3.57	34.0	31.7
C	−870	0.91	17	−10	2.74	3.01	26.0	24.2
D	−895	0.94	15	−12	2.89	3.07	24.0	21.7

A = Sulfamic acid, B = Sulfamic acid + Ethanolamine , C = Sulfamic acid + Diethanolamine, D = Sulfamic acid + Triethanolamine, βa = Anodic Tafel constant, βc = Cathodic Tafel constant B = ($\beta a \times \beta c$/[2.3($\beta a + \beta c$)]Rp = B/I_{corr}

Mechanism of corrosion: Sulfamic acid acts as strong acid. The probable chemical reaction taking place in sulfamic acid is as under. It undergoes hydrolysis in aqueous solution.

$$NH_2SO_3H + H.OH \rightarrow NH_4^+ + HSO_4^- \qquad (6)$$
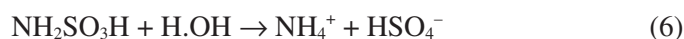
Generally, zinc dissolves in sulfamic acid solution due to somewhat hydrogen type of attack, the reaction taking place at the microelectrodes of the corrosion cell being represented as,

$$Zn \rightarrow Zn^{2+} + 2e^- \text{ (anodic reaction)} \qquad (7)$$

NH_4^+ (inorganic base) may on hydrolysis gives H^+ ions or H_3O^+ ions in solution by the following reactions:

$$NH_4^+ + H.OH \rightleftharpoons NH_4OH + H^+ \qquad (8)$$
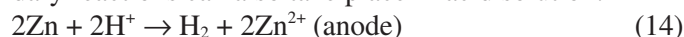
$$NH_4^+ + H.OH \rightleftharpoons NH_3 + H_3O^+ \qquad (9)$$

Reduction reaction is indicated by a decrease in valence or the consumption of electrons as shown in equation (10):

$$2H^+ + 2e^- \rightarrow 2H_{(ads)} \text{ (cathodic reaction)} \qquad (10)$$

H_2 gas is liberated by any of the two following reactions:

$$H + H = H_2 \uparrow \qquad (11)$$

or $$H + H^+ + e^- = H_2 \uparrow \qquad (12)$$

or $$H + H_3O^+ + e^- = H_2 \uparrow + H_2O \qquad (13)$$
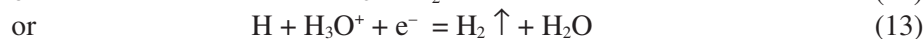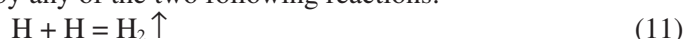
The following secondary reactions can also take place in acid solution:

$$2Zn + 2H^+ \rightarrow H_2 + 2Zn^{2+} \text{ (anode)} \qquad (14)$$

Corrosive attack of sulfamic acid on zinc which may be mainly due to the formation of HSO_4^- during the ionization of acid. However, inhibitors prevent the auto-catalytic cycle of the formation of HSO_4^- which results into inhibition of the corrosion of zinc in sulfamic acid. The mechanism of inhibition of corrosion is generally belived to be due to the formation and maintainnes of protective film on the metal surface. The I.E. of ethanolamines in decreasing order are as follows: ethanolamine > diethanolamine > triethanolamine.

Among ethanolamines the pKa value decreases in the following order : 9.5 (ethanolamine) > 8.9 (diethanolamine) > 7.8 (triethanolamine). The result shows that higher the pKa value higher and higher the I.E.

Ethanolamine
pKa = 9.5, l.p. = 3

Diethanolamine
pKa = 8.9, l p.   = 5

Triethanolamine
pKa = 7.8, l.p. = 7
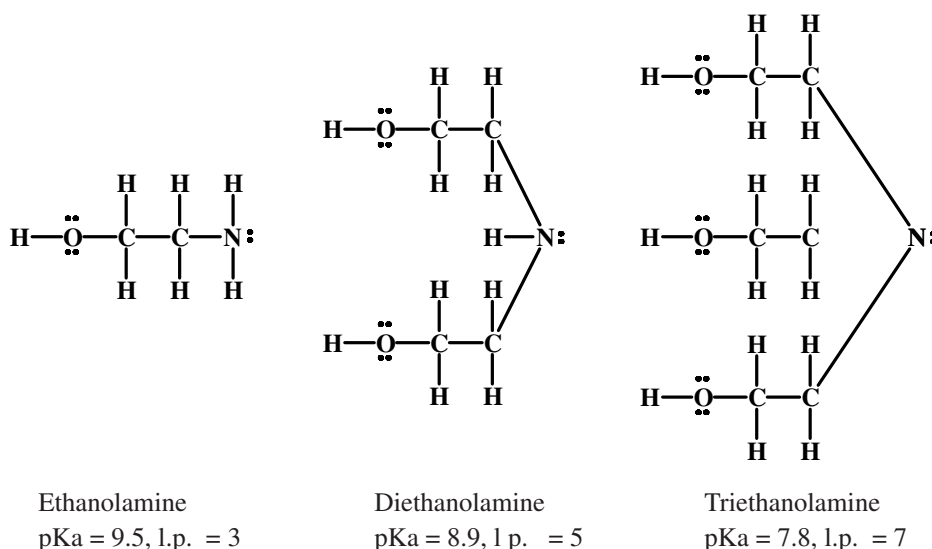
Lone pair are increases in the following order: 3 (ethanolamine) < 5 (diethanolamine) < 7 (triethanolamine), which indicates that as the lone pair of electrons increases corrosion rate increases and I.E. decreases.

As the number of ethanol groups increase on N-atom, it increases crowding around N-atom. This crowding result in strain which is less in ethanolamine and maximum in triethanolamine. Due to this, the stability of molecule is high in ethanol-amine than triethanolamine and so basicity is also reduce. Because of this effect ethanolamine gave higher inhibition than diethanolamine and triethanolamine in this acid.

The results are in agreement with the work of Vashi *et al.*[6,17] and Stupnisek *et al.*[18]. The better inhibiting characteristic of secondary amine than tertiary amine can be explained by steric hindrance in tertiary amines which may have influence as the electron density and on the base strength. The order can be explained on the basis of the influence of electron withdrawing ability of OH group in alkanol group and the overcrowding on the nitrogen atom[19].

Conclusion

(i) The corrosion loss of zinc increases with the increase of acid concentration. (ii) The I.E. of ethanolamines increases with the increase of inhibitor concentrations at all concentration acid studied. (iii) Mean 'Ea' increase with the increase in inhibitor concentration suggesting chemisorption of the inhibitor molecule. (iv) The negative G^0a value indicates spontaneous nature of adsorption process. (v) Ethanolamines

have shifted the electrode potential (OCP) in noble direction in most of the cases suggest the inhibition property of amines in acid. (vi) In a comparative study of I.E. of ethanolamines the I.E. was found in the decreasing order as follows: ethanol-amine > diethanolamine > triethanolamine. (vii) There is a good agreement in the value of I.E. calculated by weight loss data and polarization technique. (viii) It was observed that the mode of corrosion was pitting type to a lesser extent, where as uniform to a greater extent.

REFERENCES

1. N.I. Sax and R.J. Lewis, Harvey's Condensed Chemical Dictionary, CBS Publication, Delhi, India, edn. 11, p. 1104 (1990).
2. International Nickel Company.
3. R.T. Vashi and V.A. Champaneri, *Bull. Electrochem.*, **13**, 353 (1997).
4. R.T. Vashi and V.A. Champaneri, *Ind. J. Chem. Technol.*, **4**, 184 (1997).
5. R.T. Vashi and V.A.Champaneri, *Trans. SAEST*, **32**, 5 (1997).
6. R.T. Vashi, D. Naik and H.M. Bhajiwala, *Bull. Electrochem.*, **21**, 415 (2005).
7. R.T. Vashi, S.A. Desai, V.A. Champaneri and R.N.Patel, *Bull. Electrochem.*, **20,** 187 (2004).
8. M. Hackerman and J.D. Sudbery, *J. Electrochem. Soc*., **97**, 109 (1950).
9. V.K.V. Unni and J.C. Ramachar, *J. Electrochem. Soc. (Japan)*, **33**, 157 (1965).
10. N.K. Patel, S.S. Sampat, J.C. Vora and R.M. Trivedi, *Workst. Korros*., **10**, 809 (1990).
11. H.M. Bhajiwala and R.T.Vashi, *Bull. Electrochem.*, **17**, 441 (2001).
12. E.J. Stroud, *J. Appl. Chem.*, **1**, 93 (1951).
13. W.C. Clarke, Corrosion, International Nickel Company, 51 (1956)
14. Am. Soc. Testing Materials, Spec. Tech. Publ., p. 93 (1950).
15. N. Subramanian and K. Ramkrishna., *Ind. J. Tech*., **8**, 369 (1970).
16. A.M.S. Abdel and A.E.L. Saied, *Trans. SAEST*, **16**, 197 (1981).
17. R.T. Vashi, S.A. Desai, V.A. Champaneri and R.N. Patel, *Bull. Electrochem.*, **20**, 187 (2004).
18. E.L. Stupnisek, D. Kopper and A.D. Mance, *Bull. Electrochem*., **14**, 10 (1998).
19. R.M. Ramnathan, A. Subramanian, S. Alwarappan, T. Vasudeven and S.V. Iyer, *Bull. Electrochem.*, **17**, 1 (2001).