

ETHANOLAMINES AS CORROSION INHIBITORS FOR PURE NICKEL IN SULPHURIC ACID SOLUTIONS

VS MURALIDHARAN, M VEERASHANMUGAMANI and G PARUTHIMAL KALAI GNAN

Central Electrochemical Research Institute, Karaikudi - 623 006

ABSTRACT

Mono-, di- and tri-ethanolamines have been studied as inhibitors for pure nickel in sulphuric acid solutions. Potentiostatic polarisation studies have been carried out to follow the corrosion rate in presence and in absence of these amines. A temperature dependence study on the corrosion rates revealed that these inhibitors enhance the activation energy. The anodic and cathodic Tafel slopes were not found to be affected; this suggests that these inhibitors do not alter the rate-determining step of either anodic or cathodic reactions. The adsorption of these amines, offering inhibition, has been discussed in terms of Langmuir isotherm. A detailed investigation on this is presented in this paper.

Key words: Ethanolamines, corrosion inhibitor, nickel

INTRODUCTION

A large number of aliphatic organic compounds, mainly those containing nitrogen, oxygen and sulphur atoms, cause a distinct decrease in corrosion rate of metals in acid media. Aniline, pyridine, n-butylamine and cyclo-hexylamine were found to be effective inhibitors for nickel in sulphuric acid solutions [1]. The effectiveness of inhibition varies with the nature of the amine molecule. Mixtures of octylamine and propionic acid, or of N:N' dimethyl octylamine and butanol have been studied as inhibitors in sulphuric acid by linear sweep voltammetry. The inhibitors were adsorbed in two ways, either by electron donation or by protonation [2].

Ethanolamines have been known as vapour phase inhibitors for steel exposed to marine and industrial atmospheres. The use of substituted ethanolamines as inhibitors for nickel in 1N sulphuric acid is investigated here.

EXPERIMENTAL

The electrodes were prepared from high purity (6N) nickel and made into cylindrical rods having an area of cross section of 0.196 cm^2 . The rod was embedded in teflon gaskets with suitable electrical connections. For removing corrosion products, if any, formed on the surface, a dip in 1N H_2SO_4 for 5 minutes was made before polishing it in 1/0, 2/0, 3/0 and 4/0 emery papers. The specimens were degreased in trichloroethylene and immersed in the solution under study.

A three-electrode cell assembly was used. Saturated calomel electrode was used as the reference electrode. The test electrode potential was followed in a printing voltmeter - IEC make. The temperature of the solution was kept constant. The potential of the test electrode with reference to the saturated calomel electrode was maintained constant by means of a potentiostat and the steady current flowing between the test and the auxiliary electrode was measured in the meter.

The solution under study was deoxygenated by passing purified hydrogen for at least one hour, and mono-, di- and tri-ethanolamines were used as inhibitors.

RESULTS AND DISCUSSION

Potentiostatic polarisation experiments were carried out after immersing the electrode in the solution under study and the open circuit potential reached a steady value. Corrosion currents were obtained by extrapolation of anodic and cathodic Tafel lines to the corrosion potential. In all experiments, the anodic Tafel line extrapolation gave a higher corrosion current compared with the cathodic Tafel line extrapolation method. The corrosion currents obtained by anodic Tafel line extrapolation were used for analysis. The anodic Tafel slope of $50 \pm 10 \text{ mV/decade}$ and a cathodic Tafel slope of $110 \pm 10 \text{ mV/decade}$ at 30°C for nickel in 1N H_2SO_4 were not altered in the presence of inhibitors in the concentration range studies.

The inhibitor efficiency has been calculated for mono ethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) from the corrosion currents.

The percentage inhibition efficiency = $\frac{I_{\text{corr}} - I'_{\text{corr}}}{I_{\text{corr}}} \times 100$

where I_{corr} and I'_{corr} are the corrosion rates in absence and in presence of the inhibitors respectively.

Table I: Energy of activation for corrosion of nickel in 1.0 N sulphuric acid

Solution	% inhibition at 30°C	E, K cal/mole
1.0 N H ₂ SO ₄	—	5.5
1.0 N H ₂ SO ₄ + 0.05 M MEA	73	9.1
1.0 N H ₂ SO ₄ + 0.05 M DEA	40	6.9
1.0 N H ₂ SO ₄ + 0.05 M TEA	33	7.1

Table I compares the values obtained for percentage inhibition and energy of activation for corrosion. If it is assumed that the step prior to inhibition is adsorption, by forming a monolayer, covering at any instant a fraction of the metal surface in an uniform or random manner, and the free fraction of the surface is $1 - \theta$, MEA exhibits more inhibition than DEA and TEA at 30°C and above.

All the three inhibitors raise the energy of activation and MEA is found to raise it more when compared with DEA and TEA. This marked change in energy of activation suggests that these amines may either participate in the electrode process or may change the potential difference of the metal/solution interface by adsorption. Since there is no change in the anodic and cathodic Tafel slopes in presence of these inhibitors, inhibition may be due to adsorption, which changes the interfacial potential difference.

Adsorption may be electrostatic, chemisorption, or simply blocking the active sites. An adsorption isotherm gives the relationship between the coverage of an interface with the adsorbed species (the amount adsorbed) and the concentration of the species in solution. Interpretation of performance of adsorbent type of organic inhibitors can be enhanced by fitting the data to one of the known adsorption isotherms. Inhibitors which obey Langmuir adsorption isotherm can be deduced from the plot of $\log \theta / 1 - \theta$ vs $\log C$. Under these circumstances,

$$\frac{\theta}{1 - \theta} = AC \exp [-\Delta G_{\text{ads}} / RT]$$

where A is a constant independent of temperature and dependent on the characteristics of the system of adsorption, C is the inhibitor concentration, and ΔG_{ads} is the heat of adsorption. Fig. 1 gives the typical plot of $\log \theta / (1 - \theta)$ vs $\log C$ for all these amines in 1 N H₂SO₄ at 30°C. It may be

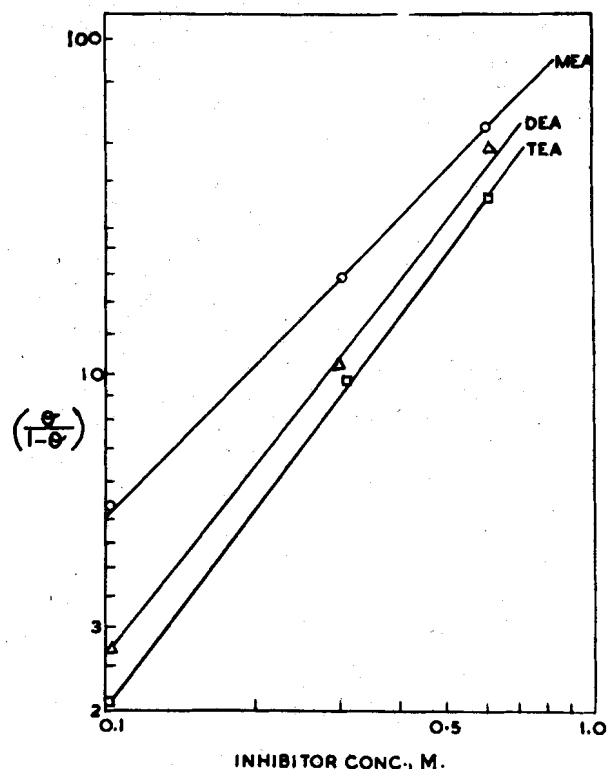


Fig. 1: $\theta / (1 - \theta)$ vs C plot for pure nickel in 1.0N H₂SO₄ containing inhibitors at 30°C

concluded that adsorption of these inhibitors follow Langmuir isotherm. Increase of temperature increases the rate of corrosion, but there is no definite correlation between inhibition and increase in concentration of inhibitors above 30°C.

HO-CH₂-CH₂-NH₂ Mono-ethanol amine (MEA)

HO-CH₂-CH₂ } NH
HO-CH₂-CH₂ } Di-ethanol amine (DEA)

HO-CH₂-CH₂ } N
HO-CH₂-CH₂ } Tri-ethanol amine (TEA)
HO-CH₂-CH₂ }

Adsorption depends upon molecular size, shape, charge distribution, deformability of the surface active groups as well as the charge on the metal undergoing corrosion [3]. Owing to the acidity of the medium, the amines may exist in the

protonated form. The stability of the protonated form increases with the electron density on the nitrogen atom. MEA exhibits higher inhibition as it enhances the formation of the protonated species. In DEA and TEA, due to the inductive effect, the electron density on the nitrogen atom has been decreased, and the formation of the protonated species has been slowed down. Since ethanolamines have got more than one centre, viz. nitrogen and oxygen for electron donation, the participation of the lone pair of oxygen is also possible. But all the lone pairs of electrons on oxygen atoms may not come closer to the metal, as the size of the molecule hinders adsorption. Though DEA and TEA have more oxygen atoms, their participation is restricted due to steric hindrance.

CONCLUSION

Mono-, di- and tri-ethanolamines offer inhibition for the

corrosion and dissolution of pure nickel in 1N H₂SO₄ by Langmuir adsorption at the metal/solution interface. The increase in energy of activation on addition of ethanolamines suggests that these inhibitors reduce the corrosion rate by changing the potential at metal/solution interface by adsorption.

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