



EFFECT OF DIAZEPINES ON CORROSION OF BRASS

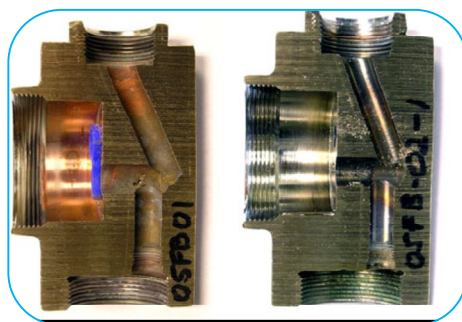
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ABSTRACT:

The role of diazepines on the corrosion of 60/40 brass in 0.1M nitric acid has been studied with respect to effect of concentration, immersion time and temperature on the dissolution rates of brass. The thermodynamic parameters determined from the knowledge of surface coverage and adsorption isotherms. The corrosion rates and inhibitor efficiencies obtained from weight loss and polarization are compared found to be in good agreement. The mechanism of inhibitor action is proposed.



KEY WORDS: Diazepines, corrosion of brass, inhibitors

INTRODUCTION: -

The corrosion of brass in Nitric acid is a well-known process. The literature survey reveals the fact that variety of organic inhibitors containing nitrogen and sulphur are found to be efficient inhibitors to minimise the damage. The role of diazepines with nitrogen bearing donors for copper & zinc is well known. In this report an attempt has been made to test the efficacy of these compounds as corrosion inhibitors .

EXPERIMENTAL

The weight loss measurements are carried out in three necked flask under thermostat control under stirred and unstirred conditions by using magnetic stirrer. Dissolution rates with and without inhibitor are determined. Specially designed 60/40 brass crystal triple distilled water & analytical grade Nitric acid used. Polarization measurements were carried out in galvanostatic conditions in a anodic dissolution cell and over potentials were recorded by using high accuracy digital Multimeter. Analysis of solutions are obtained by atomic absorption spectroscopy or by using Spectrophotometer.

RESULTS

Corrosion Rates

The corrosion rates of brass in 0.1M nitric acid slightly decreased in Presence of diazepines. Corrosion rate for brass in 0.1M nitric acid decreased from $9.96\text{mg cm}^{-2}\text{ hr}^{-1}$ to $8.00\text{mg cm}^{-2}\text{ hr}^{-1}$ and $6.05\text{ mg cm}^{-2}\text{hr}^{-1}$ in presence of DMBDA and

7-Me DMBDA respectively at a concentration 10^{-4} M. In case of 10^{-4} M 7-CI-DMBDA the corrosion rate was found to be almost equal to the of corrosion rate of brass in 0.1M nitric acid. To study the influence of these diazepines on corrosion rate of brass in presence of varied concentration of diazepines .At higher concentration, DMBDA and 7 -Me DMBDA moderately decreased the corrosion rate of brass. The corrosion rates of brass in 0.1M nitric acid in presence of different concentrations of diazepines are recorded.

Percentage Protection

The inhibitor efficiency of diazepines for corrosion of brass was evaluated from the knowledge of weight loss measurements using the equation.

$$\%P = (W_0 - W) / W_0 \times 100$$

W_0 and W represent weight loss without and with inhibitor respectively.

The inhibitor efficiencies of diazepines at different concentration are shown in Table-1. From the table, it is clear that, DMBDA and 7-Me DMBDA, at higher concentrations provide some protection against corrosion of brass in 0.1M nitric acid. However, 7-CI-DMBDA does not act as a corrosion inhibitor even at higher concentration. At a given concentration, the values of %P are found to be in the order:

$$7\text{-Me DMBDA} > \text{DMBDA} > 7\text{-CI-DMBDA}$$

Table 1
Effect of temperature inhibitor efficiency in stirred 0.1M HNO_3

Temperature	Inhibitor efficiency (%P)		
	DMBDA	7-Me-DMBDA	7-CI-DMBDA
293	58	72	23
303	50	65	19
313	40	45	5

Table 2
Thermodynamic parameters in presence of 10^{-2} M diazepines at 303K

Thermodynamic Parameter	DMBDA	7-Me-DMBDA	7-CI-DMBDA
E_a (KJ mole $^{-1}$)	31.9	41.8	25.7
$-\Delta G^0$ (KJ mole $^{-1}$)	29.8	39.2	17.3
ΔH^0 (KJ mole $^{-1}$)	82.9	118.2	49.4
ΔS^0 (JK $^{-1}$)	390	520	296

E_a - Energy of activation

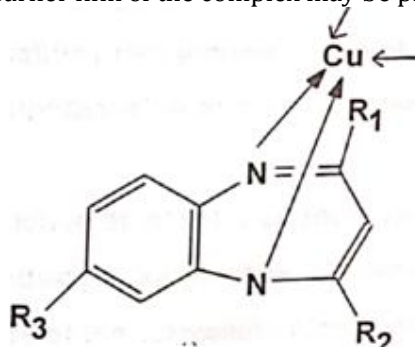
DISCUSSION

It is established that the corrosion behaviour of brass in nitric acid is comparable to that of copper and the same arguments valid for copper in nitric acid be extended for brass also

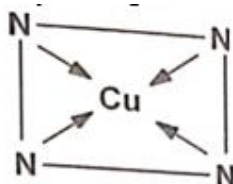
The details of the processes involved and the type of complex formation under different on going conditions in presence of organic ligands is established.

In presence of diazepines as inhibitors, formation is observed to take place. However, the investigations contain two N atoms as donor weak bases and the corrosive medium nitric acid, oxidising agent, the moderate inhibitive properties formation of an adherent protective film on the

In the first stage of corrosion of brass, quasi-type of compound with diazepines through to complex formation. Based on the earlier film of the complex may be proposed to have the structure:



In general, the complex may be represented as •



Such a film formed acts as passive barrier for the corrosion of brass in nitric acid. Zinc may also form similar type of complex. These observations are supported by the works on complexes of diazepines with copper and zinc by Kulkarni et.al.

The formation of such a film brings about change in dissolution characteristics of brass and corrosion rates as well.

During anodic polarization, the changes in etch figures in presence of inhibitors is attributed to the complex formation on the surface of brass.

Further, anodic polarization studies adequately support the above observations. Due to the presence of complex film on the surface, the removal of atoms from reactive sites becomes more difficult and requires high energy. The increase in anodic polarization potential and shift in Tafel slope in presence of diazepines justifies this argument, which is further supported by the linear variation of overpotential with surface coverage (Fig. 2).

The interaction of inhibitor on the brass surface during inhibition process has been deduced by means of adsorption characteristics. The thermo-dynamics of the corrosion process depends on the number (n) of water dipoles replaced by inhibitor molecule during adsorption. The value of the configurational function "n" for a given inhibitor depends on the mode of adsorption. The standard free energy of adsorption (ΔG°) was evaluated [20].

The entropy of adsorption was evaluated from the relation between $\ln \theta / (1 - \theta)$ and T. The thermodynamic parameters are presented in Table - 2. The thermodynamic parameters are found to be in the same order as that of %P values



A plot of conc. of inhibitor Vs

$$\left[\frac{\{\theta + n(1 - \theta)\}^{n-1}}{n^n} \right]$$

was made to obtain the most probable values of "n". The "n" values are found to be 9, 8 and 12 for DMBDA, 7-Me-DMBDA and 7-Cl-DMBDA respectively. This indicates the different modes of adsorption of the specified diazepines.

The negative values of G^0 favour the interaction of diazepines with brass surface during corrosion process. The %P depends on the adsorbing capacity and concentration of inhibitor. The %P values at higher concentration observed for diazepines indicate they are moderately good inhibitors at high concentrations.

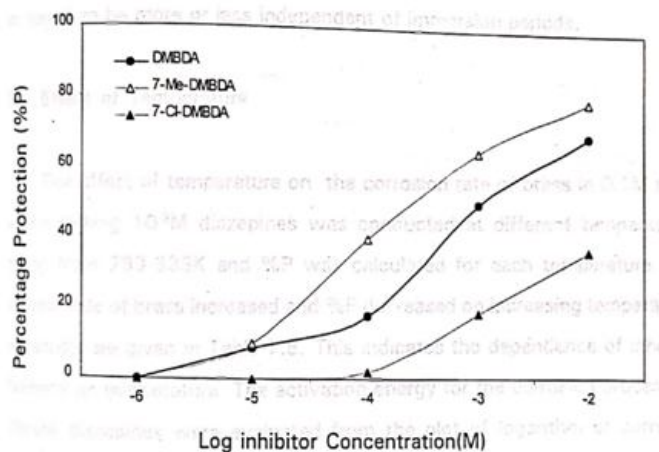


Fig. 1

Variation of percentage protection (%P) with concentration of diazepines at 303K

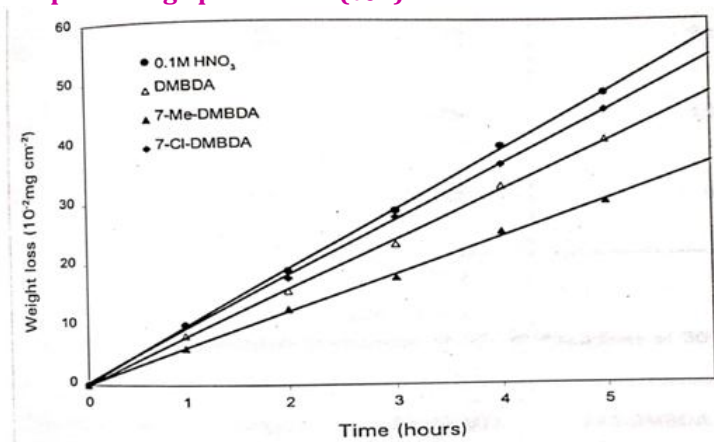


Fig. 2

Variation of weight loss of brass with immersion time in stirred 0.1 M HNO₃ with 10⁻⁴ diazepines at 303K

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