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Protection Effect of N-acetyloxindolylidene-p-Chlorophenyl Butenolide on Corrosion of Zinc in Acid Solution

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Abstract:

The effect of N-acetyloxindolylidene -p- chlorophenyl butenolide[1] on the corrosion of zinc in 2M HNO_3 was studied by different methods including thermometry, weight loss and galvanostatic polarization. The results showed that this substance retards the dissolution of zinc in nitric acid solution. It was also shown that there is an apparent agreement between the inhibiting efficiencies concluded from the different employed methods. The inhibiting effect of this substance, most probably, functions through physical adsorption in accordance with the Langmiur isotherm.

Introduction:

The importance of the inhibition of zinc corrosion in acid media was reported previously by Desai, et al.[2] Several other reports discussed the inhibition in electrochemical energy generators having a reactive zinc anode, galvanized steel used in industry[3-8] and zinc metal itself in the case of atmospheric pollution.[3-8]

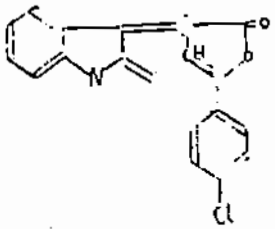
Organic compounds are widely used as corrosion inhibitors[3-15]. Most of these organic inhibitors are

compounds containing at least one polar functional group, having atoms of N, O, and/or S. In general, the polar function is regarded as the reaction center for establishment of chemisorption process. These organic inhibitors were used in aqueous corrosion of metals such as Fe, Al, Cu, Ni and Zn.[9-15] Thiourea and its derivatives were used to protect zinc in IN H_2SO_4[16,17] . Also, other workers used different ammonium derivatives to inhibit corrosion of zinc in IN HCl and IN H_2SO_4.[2-8, 16-18] and also the use of benzotriazole, benzothiazole derivatives and phosphonium salts in protection of zinc from corrosion in acid solutions.[19]

We thought that it is important and interesting to study the inhibiting effect of N-acetyloxindolylidene-p-chlorophenyl butenolide[1] on the corrosion of zinc in nitric acid solution, since this compound contains functional corrosion inhibiting polar groups, carbonyl and chloride, and was not tried before as corrosion inhibitor.

Experimental and Methods of Calculations:

The expected to be inhibitor used[1], N-acetyloxindoly-ledene-p-chorophenyl butenolide,



is a reddish black solid, very stable at high temperatures, checked for purity by elemental analysis and I.R. spectra.

The zinc used was spectroscopically pure (99.7%). All chemicals used were of A.R. grade. The solutions were prepared from bidistilled water. Zinc-test pieces measuring 2x5 cm^2 were used as electrodes in the weight loss method and in the thermometric method. The surface was mechanically polished on different grades of emery paper, degreased with acetone and then washed thoroughly with water, dried and then weighed. Corrosion tests were carried out in 50 ml beakers in which the specimen was suspended for 30 minutes in the test solution. The specimen was then removed, rinsed with conductivity water and finally dried and weighed. All corrosion tests were carried out in aerated unstirred solutions. Each experiment was carried out twice and the mean of the results was computed.

Temperature changes of the system involving zinc electrode in 2M HNO_3 solution were followed as a function of time in absence and presence of different concentrations of the inhibitor used. Each experiment was carried out with a newly polished electrode and with a fresh portion of the solution.

Galvanostatic anodic polarisation experiments were carried out under unstirred conditions with a fine luggen

capillary to avoid ohmic polarisation. Galvanostatic condition was maintained using a constant current. Zinc electrode was used in the form of a rod 5mm in diameter. A saturated calomel electrode and a platinum electrode were used as a reference and auxiliary electrodes, respectively.

Inhibition effeciencies were calculated as follows:

a) The calculation for the thermometric measurements were carried out by the Mylius method[20]

$$\% \text{ Inhibition} = \frac{(RN)\text{ free} - (RN)\text{in}}{(RN)\text{free}} \times 100 \quad \ldots\ldots\ldots \quad (1)$$

$$\text{where RN} = \frac{Tm - Ti}{t} \ ^{\circ}C \text{ min.}^{-1} \quad \ldots\ldots\ldots \quad (2)$$

where Tm and Ti are the maximum and initial temperatures, respectively, and t is the time in minutes taken to attain Tm.

b) Weight loss measurements

$$\% \text{ Inhibition} = \left(1 - \frac{W_2}{W_1}\right) \times 100 \quad \ldots\ldots\ldots \quad (3)$$

where W_1 and W_2 are the corrosion rate in absence and presence of a certain concentration of the inhibitor.

c) Galvanostatic polarisation measurements

$$\% \text{ Inhibition} = \frac{I - I^{-}}{I} \times 100 \quad \ldots\ldots\ldots \quad (4)$$

where I and I^{-} are the corrosion currents in absence and presence of the inhibitor respectively.

Results and Discussion:

The curves showing the change of temperature with time for zinc in 2M HNO_3 were followed in the absence and presence of the inhibitor[1]. The effect of gradually increasing the concentration of the added inhibitor on the thermometric curves is shown in Fig. (1).

These curves are characterised by a sharp rise and finally a decrease, after attaining a maximum value. The slope of the rising parts of the curves decreases in presence of the inhibitor. This indicates that the additives act as general inhibitors and adsorb on both anodic and cathodic sites[21]. The rising parts of the curve indicate direct attack of the corrosive medium, i.e. anodic dissolution of zinc. If these parts were exactly parallel and with constant slope, the process would be mainly anodically controlled.

A plot of % reduction in RN vs. log C is in fact similar to an adsorption isotherm, (Fig. 2). The curve obtained is invariably sigmoid in nature, and this behaviour is explainable on the basis of a single step adsorption process[22]. This curve consists of an initial ascending portion which passes to a region of constancy indicating the completion of a monolayer of the adsorbate.

Fig. (3) shows the variation of the protection efficiency, P of zinc metal as a function of the concentration of the inhibitor in 2M HNO_3 solution at different temperatures. The protection efficiency P of the inhibitor was calculated by the following equation:-

$$P = 100 \left(1 - \frac{W_2}{W_1} \right) \qquad (3)$$

where W_1 and W_2 are the corrosion rates in absence and presence of a certain concentration in the medium, approaching complete protection (84%) at 0.01M of the inhibitor.

Fig. (3) also shows the effect of the concentration of the inhibitor at various temperatures on the protection efficiency of zinc. It is clear that the percentage inhibition increases with increasing inhibitor concentration. In general, also, it can be seen from Fig. (3) that the protection efficiency increases with decreasing the temperature. Fig. (4) shows the variation of the corrosion rate of zinc in 2M HNO_3 as a function of the concentration of the used inhibitor at different temperatures. It can also be observed from Fig. (4) that, at constant temperature, the corrosion rate decreases as the concentration of the tested substance increases.

It can be seen that if the inhibitor functions via adsorption mechanism, i.e. the degree of coverage is directly

proportional to the protection efficiency, in accordance with the Langmiur isotherm relationship:-

$$\text{Log } \frac{P}{1-P} = \text{Log } [I] + \text{constant.} \qquad (5)$$

(where [I] is the inhibitor concentration), then this relation should result in a straight line with a slope of unity. Fig. (5) shows that such plots are in agreement with the Langmiur adsorption isotherm. Interaction of adsorbed species by mutual repulsion or attraction would cause the slope of the plot to deviate from unity.

It was pointed out[23] that the logarithm of the corrosion rate is a linear function of $\frac{1}{T}$ (Arrhenius equation), where T is the absolute temperature.

$$\text{Log corrosion rate} = - \frac{Ea}{(RT)} + B \qquad (6)$$

where Ea is the apparent activation energy, R is the universal gas contant (1.98 Cal/mole. degree) and B is a constant. In Fig. (6) the logarithm of the corrosion rates of zinc are plotted as function of ($\frac{1}{T}$) in absence and presence of the studied inhibitor, respectively. From Fig. (6) the calculated value of the apparent activation energy is 9.21 Kcal/mole, a value that agrees with that reported previously[10]. This value is also of the order of the activation energies encountered for the hydrogen evolution reaction[24]. This is in accordance with the fact that

the hydrogen evolution reaction in the absence of an inhibitor is the rate determining step for the overall corrosion reaction. For 10^{-4} to 10^{-2}M inhibitor solutions, the calculated value of the activation energies are 9.67 and 11.98 Kcal/mole, respectively (Fig. 6). These differences are not considered to be significant. Therefore, the presence of the studied inhibitor does not affect the activation energy of the corrosion process. These results indicate that the tested substance does not change the mechanism of the rate-determining step of the corrosion process, although it, significantly, reduces the rate of corrosion itself.

Pig. (7) shows the anodic polarisation curves of zinc in 2M HNO_3 at different concentrations of the studied substance at 30°C. The anodic polarisation curves shifted to more positive values as the inhibitor concentration increases. These results confirm the assumption that the substance used acts as a powerful type of inhibitor, and so affects hydrogen evolution and anodic metal dissolution.

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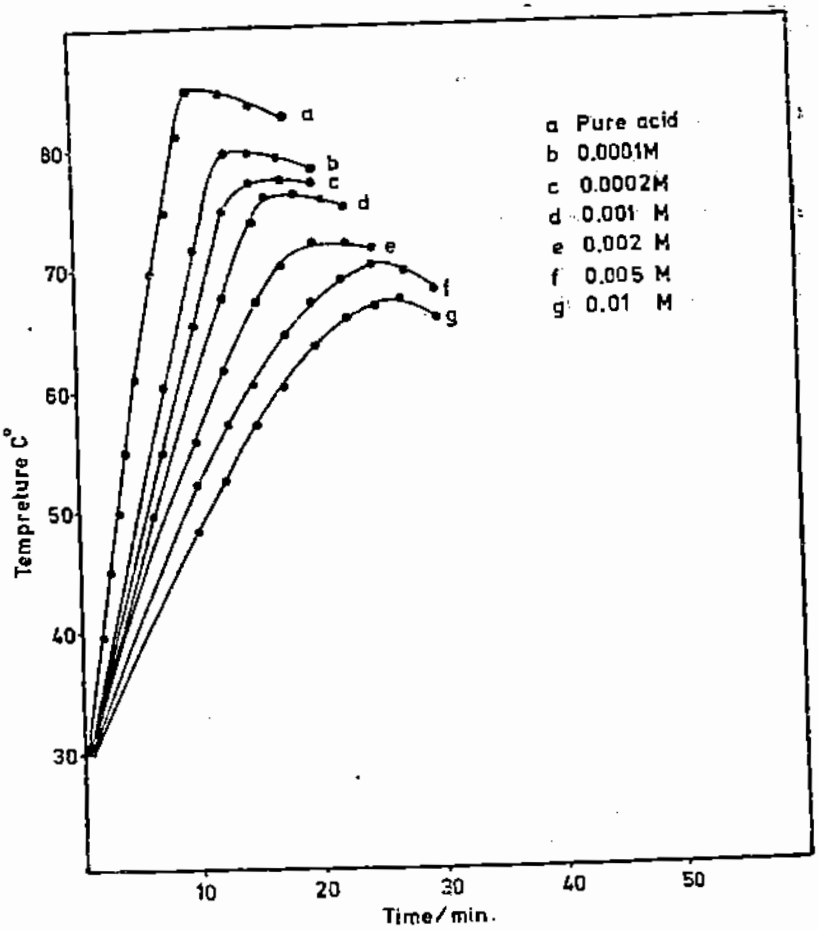

Fig.(1) : Effect of addition of the used substance on the thermometric behaviour of Zn in 2M HNO_3

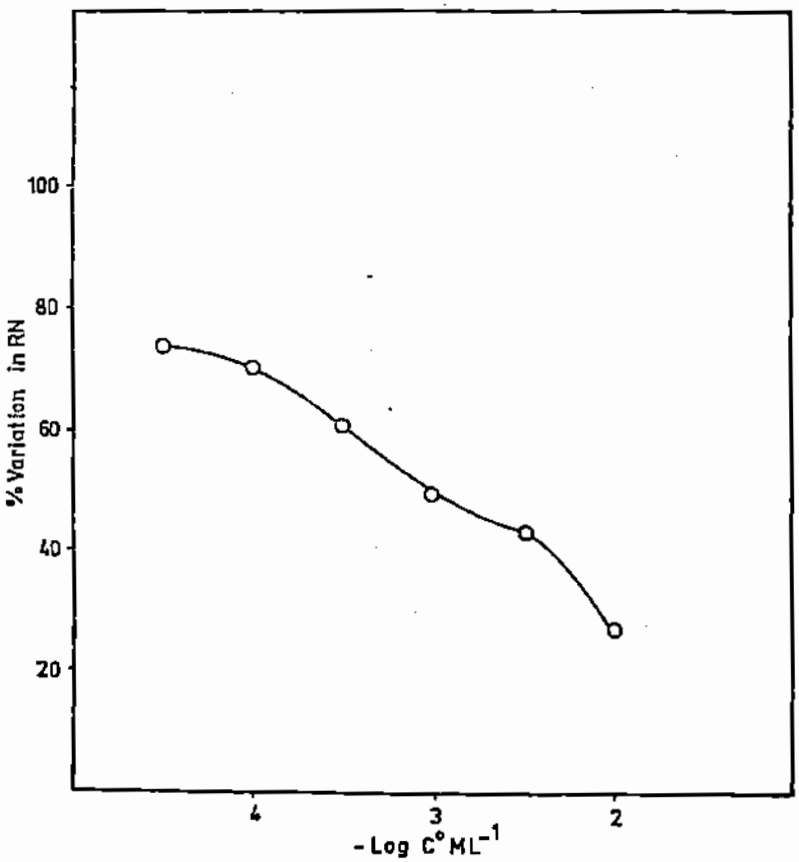

Fig.(2): Percent variation of RN with concentration of the used substance .

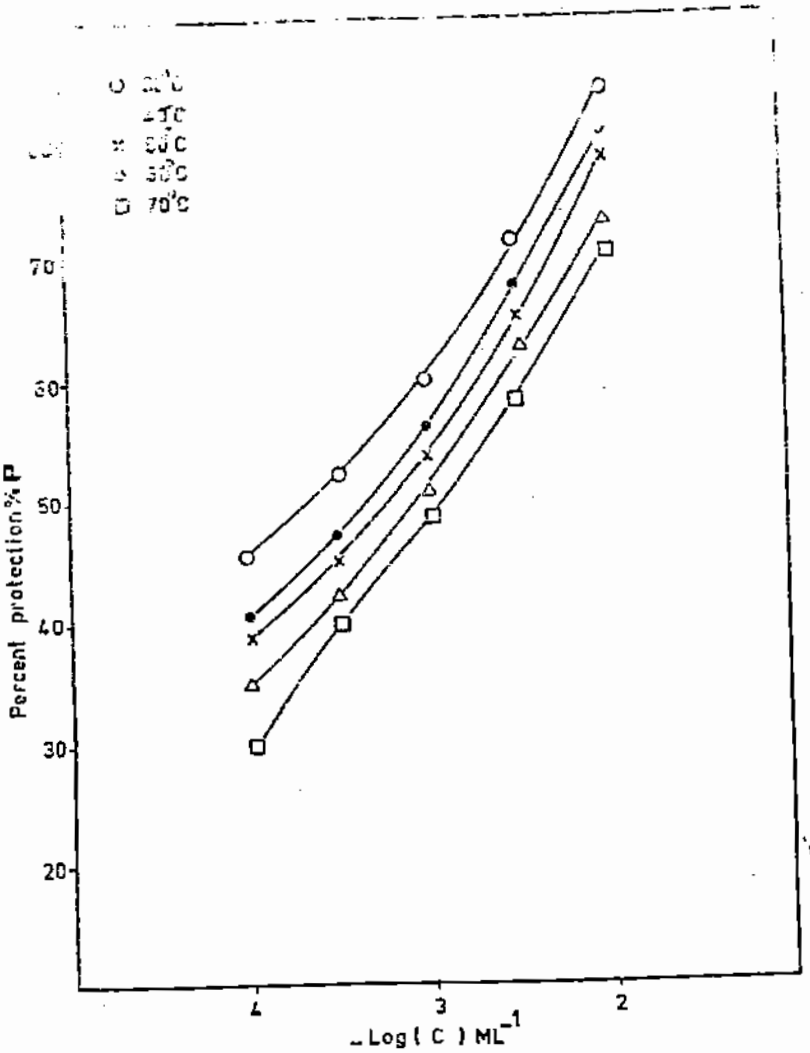

Fig.(3): Effect of concentration of inhibitor on the protection efficiency of Zn in 2M HNO_3 at various tenperatures.

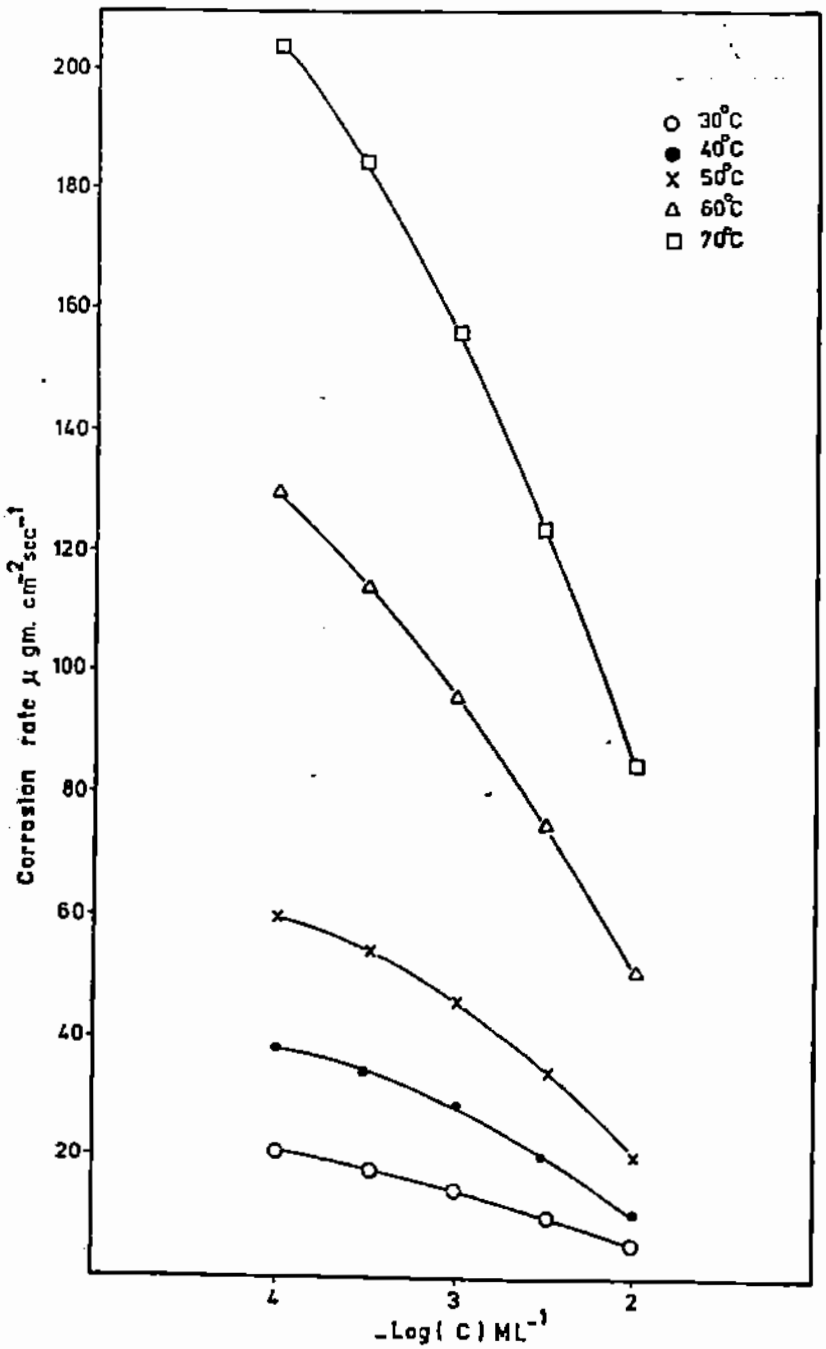

Fig.(4): Effect of the concentration of inhibitor on the corrosion rate of Zn in 2M HNO_3 at different temperatures.

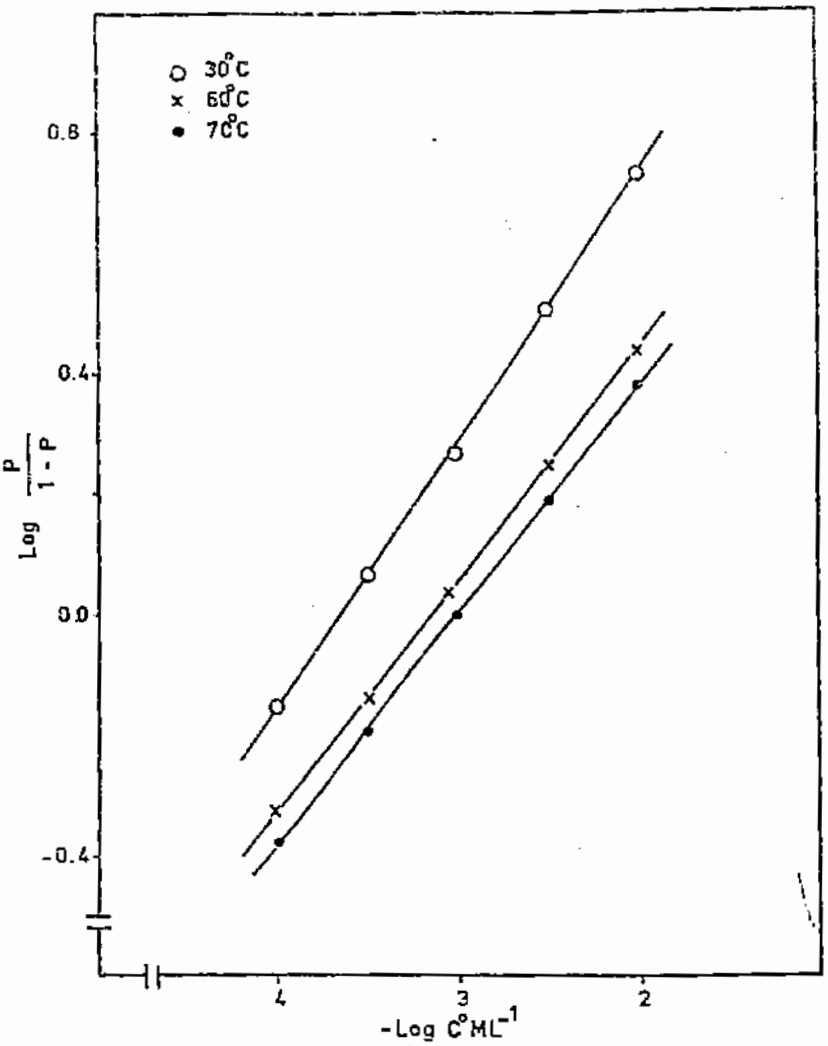

Fig.(5): Plot of $\text{Log}\frac{P}{1-P}$ vs. log concentration of inhibitor for Zn in 2M HNO_3 at different temperatres.

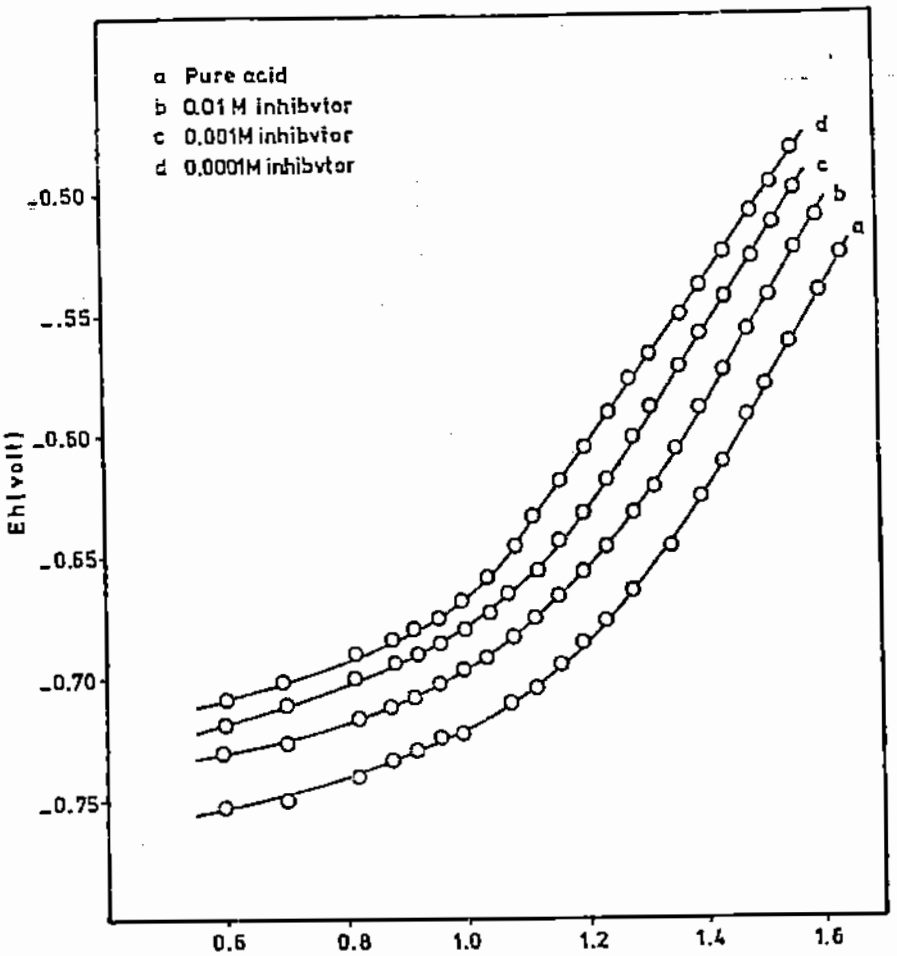

Fig. (7): Anodie Tafel plots for Zn in 2M HNO_3 at different concentrations of substance[1]

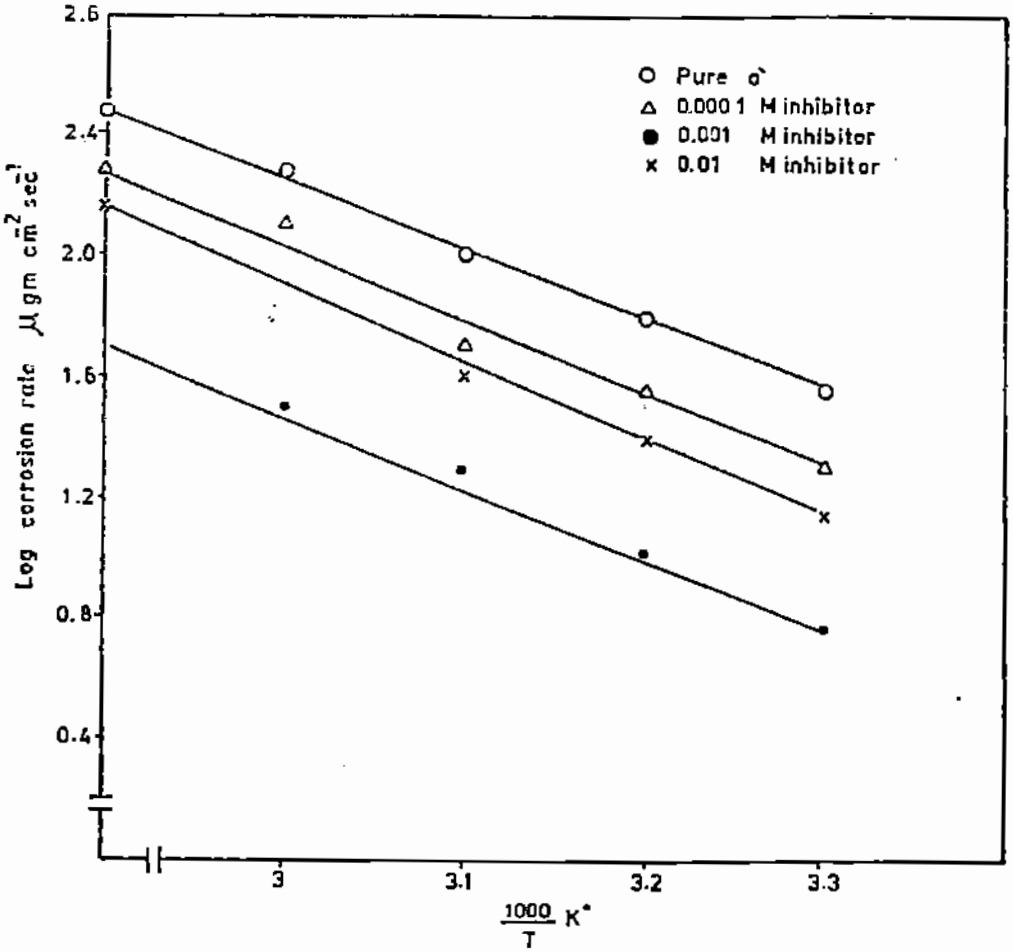

Fig.(6):Arrhenius plot of the corrosion rate of Zn in 2 M HNO_3 in absence and presence of inhibitor.