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Inhibition of Corrosion of Nickel in Nitric Acid by N-Acetyloxindolylidene *p*-Chlorophenyl Butenolide

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The use of N-acetyloxindolylidene-*p*-chlorophenyl butenolide as inhibitor of the corrosion of nickel in 2M HNO_3 solution has been studied at different temperatures. The protection efficiency increases with decreasing temperatures and reaches 76% at 30°C. The results of the apparent activation energies in the absence and presence of the inhibitor suggest that the inhibitor does not change the mechanism of the rate determining step of the corrosion process. The mechanism of inhibition was proposed on the basis of the formation of a protective film by the inhibitor molecules on the metal surface. Cathodic polarisation curves were measured galvanostatically in 2M HNO_3 solution in the absence and presence of different concentrations of the substance at 30°C, which confirmed the protection efficiency of the substance under investigation.

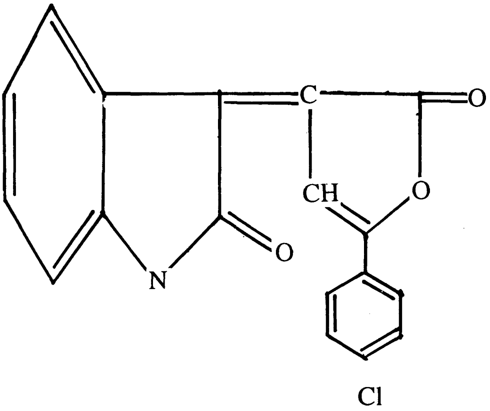
INTRODUCTION

The anodic dissolution of nickel in different acid solutions in the presence of organic and inorganic inhibitors has recently been studied[1–13]. Polarisation measurements offer information about the influence of inhibitors on the cathodic and anodic processes, in addition to usual data they provide about corrosion rates. Nitrogen containing organic corrosion inhibitors, which are adsorbed at the metal/solution interface, thus reducing the metal activity, have been investigated by many authors[14–16] using mild steel, zinc and aluminium. Studies have also been made on nickel in acid solutions[17, 18]. Since N-acetyloxindolylidene-*p*-chlorophenyl butenolide showed high efficiency in protecting copper[19] and zinc[20] in acid solutions, so in the present study we investigated the efficiency of this substance as an inhibitor for the acid corrosion of nickel.

EXPERIMENTAL

The nickel used was spectroscopically pure (99.98%). Weight loss was measured for 9 cm^2 apparent surface area. These sheets were cleaned by degreasing in methanol, dipping in concentrated HNO_3 and washing. The procedure was repeated several times before weighing and immersing in the corrosive medium. The corrosion rate was calculated from weight loss on the basis of the apparent surface area. The immersion time at different temperatures and concentrations was 30 minutes in all experiments. The average of four specimens was taken at each concentration using a fresh electrode surface and batch of electrolytes each time. The results were quite reproducible.

N-Acetyloxindolylidene *p*-chlorophenyl butenolide was of the highest purity available[1]. Various concentrations of the substance ranging from 10^{-2}–10^{-4} were used in 2M HNO_3 solutions. The solutions were prepared using bidistilled water, and the temperature was adjusted to within ±0.1°C.



The effect of the substance on the anodic polarisation of Ni was carried out under unstirred conditions, with a fine luggen capillary to avoid ohmic polarisation. Galvanostatic conditions were maintained using a constant current. Nickel was used in the form of rods, 5 mm in diameter each. A saturated calomel electrode and a platinum electrode were used as reference and auxiliary electrodes, respectively.

RESULTS AND DISCUSSION

The protection efficiency, *P*, of the inhibitor was calculated using equation (1)

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

where W_1 and W_2 are the corrosion rates in the absence and presence of a certain concentration of inhibitor. Fig. 1 shows the variation of the protection efficiency P, of Ni metal as a function of the concentration of the inhibitor in 2M HNO_3 solution at different temperatures. As can be seen, the per cent protection inhibition increases with increase of the inhibitor concentration in the medium, approaching (77.5%) at 0.01 M. It is also clear that the protection efficiency increases with decreasing temperature.

This conclusion was substantiated by showing the variation of corrosion rate of Ni in 2M HNO_3 as a function of the concentration of inhibitor at different temperatures (Fig. 2). It is observed that, at constant temperature, the corrosion rate decreases as the concentration of the substance increases.

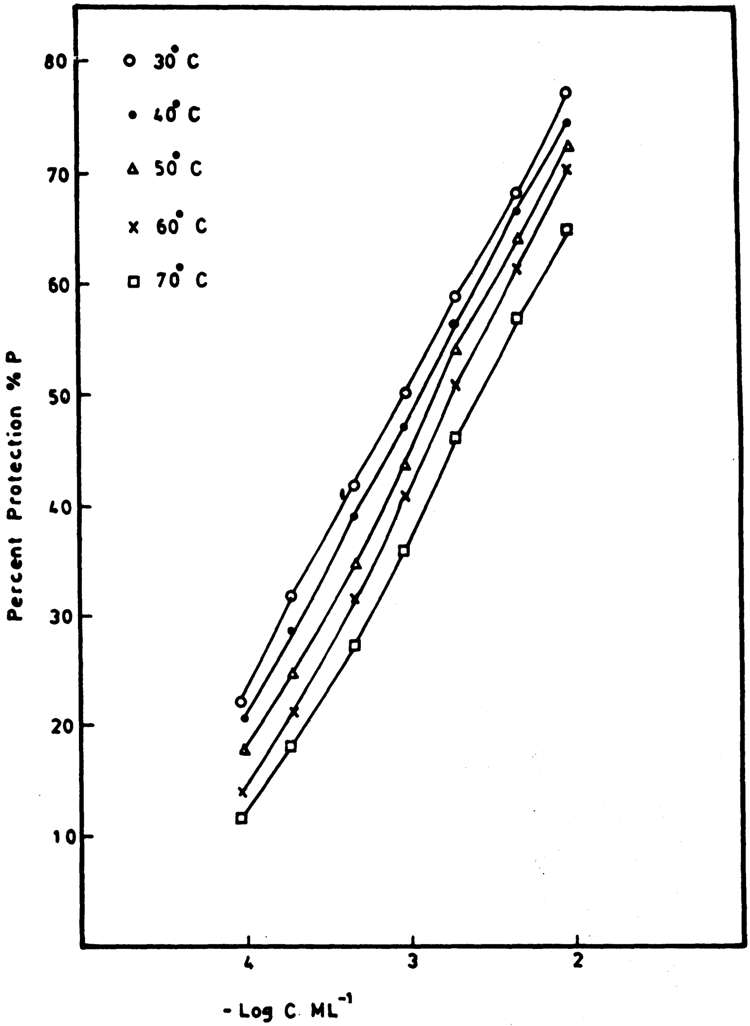


Fig. 1 Effect of concentration of the inhibitor on the protection effeciency of Ni in 2M HNO_3 at various temperatures.

As is known, if the inhibitor functions *via* an adsorption mechanism, *i.e.* the degree of coverage equals the protection efficiency, the Langmuir isotherm relationship

$$\log \frac{P}{1-P} = \log I \text{ (constant)} \tag{2}$$

should yield a straight line with a slope of unity (where I is the inhibitor concentration). Fig. 3 shows such plots, in which equation (2) is not confirmed. Consequently it can be concluded that the protection imported by the substance agrees with the *film* theory of the protective activity proposed by Balezin

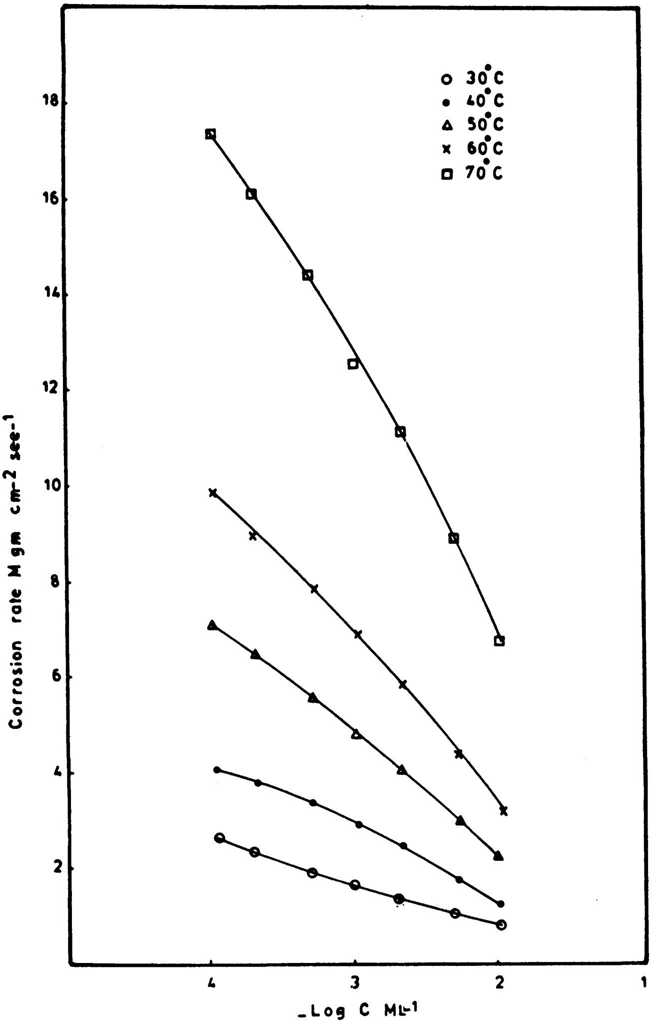


Fig. 2 Effect of the concentration of the inhibitor on the corrosion rate of Ni in 2M HNO_3 at various temperatures.

et al.[21] in which inhibition is due to the formation of a protective film on the metal surface. The diffusion of metal ions through this film becomes the rate determining step.

It was pointed out[21] that the logarithm of the corrosion rate is a linear function of $\frac{1}{T}$ (Arrhenius equation), where T is the absolute temperature.

$$\text{log corrosion rate} = -\frac{E_a}{RT} + B \qquad (3)$$

E_a is the apparent activation energy, R is the universal gas contant (1.987 cal/mole degree) and B is a constant.

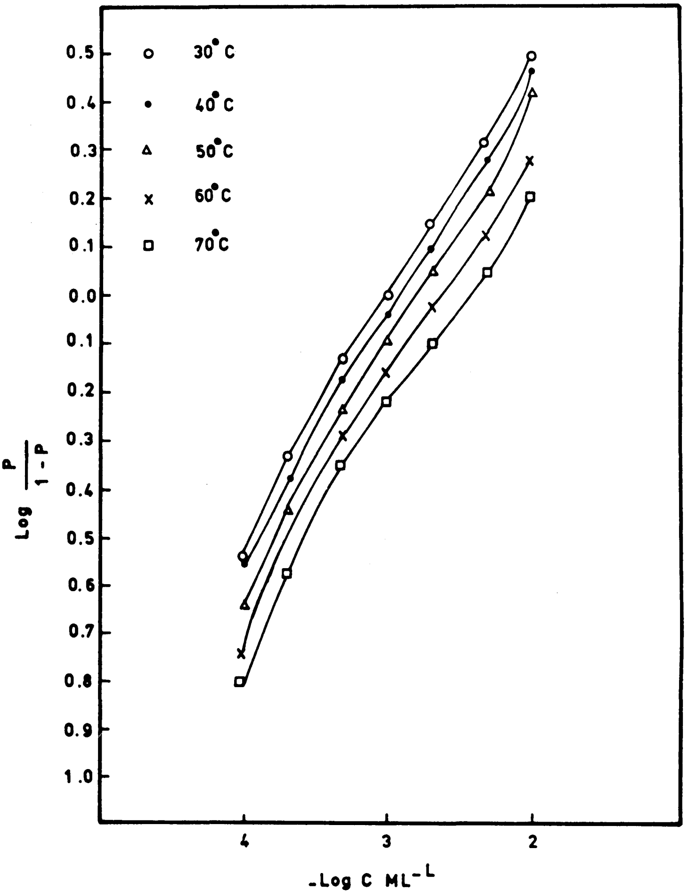


Fig. 3 Plot of P/1-p vs log concentration of the inhibitor for Ni in 2M HNO_3 at various temperatures.

The logarithms of the corrosion rates of nickel are plotted as a function of $\frac{1}{T}$ in the absence and presence of the tested substance. The relationship for all the curves is linear and the activation energy E_a for the pure acid is computed to be 9.21 kcal/mole. This value is comparable with some values reported by Desai *et al.*[22]. It is also of the order of the activation energies encountered for the hydrogen evolution reaction.[23] The calculated values of the apparent activation energies in the presence of 10^{-3} and 10^{-2} M inhibitor concentration are 10.13 and 11.05 kcal/mole, respectively. These differences are not considered to be significant.

Therefore, the presence of the inhibitor does not affect the activation energy of the corrosion process. These results indicate that the inhibitor does not change the mechanism of the rate determining step of the corrosion process, although it significantly reduces its rate.

Fig. 4 shows the effect of the inhibitor on E–I curves of the cathodic polarisation (hydrogen evolution reaction), where E_h is the potential of nickel electrode and I is the current applied for cathodic polarisation. The strong inhibiting effect of the substance can be seen in these curves. It is found that the corrosion potential (E_{corr}) is shifted to more noble direction for the higher concentration of the tested inhibitor and to the active direction for the blank solution. These results are in good agreement with those obtained from corrosion rate measurements. From all the previous results, it is clear that N-acetyloxindolylidene-*p*-chlorophenyl butenolide acts as a good inhibitor for nickel in acid solution.

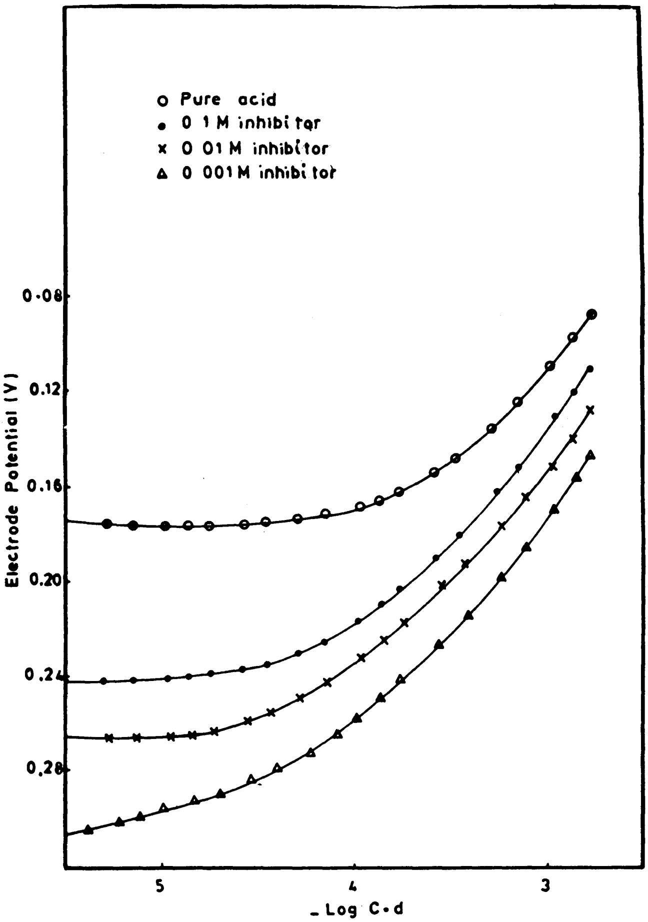


Fig. 4 Effect of the concentration of substance on the cathodic current potential curves for nickel in 2M HNO_3.

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