Asian Journal of Chemistry Vol. 5, No. 4 (1993), 1108–1118

Effect of N-Acetyloxindolylidene-*p*-chlorophenyl Butenolide on the Corrosion of Copper in Nitric acid Under Annealing Temperatures

O.R. KHALIFA*, E.A. EL-AHMAD and A.A. MISBAH
Chemistry Department, University College for Women
Ain Shams Univeristy Cairo, Egypt.

The effect of N-acetyloxindolylidene-*p*-chlorophenyl butenolide as inhibitor on the corrosion behaviour of copper in 2M HNO_3 solution has been studied. The weight-loss technique showed that the use of N-acetyloxidolylidene-*p*-chlorophenyl betenolide affected the corrosion rate of the copper metal. The protection efficiency increases with increasing the substance concentration approaching 82% at 0.01M. In general, the protection efficiency increases with decreasing temperature. Thermometric measurements were carried out in 2M HNO_3 in presence and absence of the tested substance. Potential measurements of copper electrode showed that it was shifted to the noble direction with increasing tested substance. Cathodic polarisation was studied on free 2M HNO_3 and in presence of different concentrations of the tested substance.

INTRODUCTION

Copper is extensively used in various industrial operations and the study of its corrosion inhibition is of great importance.

Some amino compounds are known to be excellent corrosion inhibitors[1]. The inhibition was attributed to the destruction of HNO_2 by the inhibitor and thus stop autocatalytic propagation of reduction[3,4]. Some substituted phenols also reduce the rate of dissolution of copper in nitric acid[5]. Here is reported the corrosion inhibition property by N-acetyloxinolylidene-*p*-chlorophenyl butenolide[6].

EXPERIMENTAL

The copper used was spectroscopically pure (99.7%). Weight loss was measured on sheets of apparent surface area of 10 cm^2. These sheets were pre-cleaned by degreasing in methanol, dipping in concentrated HNO_3 and washing. The procedure was repeated several times before weighing and immersion in the corrosive medium. The corrosion rate was calculated on the basis of the apparent surface area. The immersion time at different temperatures and concentrations was 30 min. in all experiments, the averages from four specimens were taken at each concentration, each with a fresh electrode surface and batch of electrolyte.

The thermometric measurements were carried out by the Mylius method[7]. The rate of the reaction is characterized by the reaction number, (RN), which is defined as[7].

$$RN = \frac{T_{max} - T_i}{t} \text{ °C/min}$$

where T_{max} and T_i are the maximum and initial temperatures respectively and t is the time in minutes taken to attain T_{max}.

Cathodic polarisation measurements were carried out in a polarization cell[8]. A platinum electrode (2 cm^2 platinum sheet welded to a platinum wire sealed to glass) was also used. The electrode as before was prepared from analaR copper rode, of 1 cm^2 area. Cathodic polarization was studied on free HNO_3 and in presence of different concentration of the inhibitor. Potential measurements of copper was also studied in presence and absence of the inhibitor.

RESULTS AND DISCUSSION

Fig.-1 shows the variation of the protection efficiency (P) of copper metal as a function of the concentration of the inhibitor in HNO_3 solution at different temperatures. The protection effeciency (P) of the inhibitor was calculated by the following equation (1).

$$P = 100(1 - W_2/W_1) \qquad (1)$$

where $W_1$and W_2 are the corrosion rates in absence and presence of a certain concentration of inhibitor. As shown the percentage inhibition increases with increasing the inhibitor concentration in the medium, approaching complete protection (82%) at 0.01 M.

Fig. 1 also shows the effect of the concentration of the inhibitor at various temperatures of the protection effeciency of Cu. Clearly the percentage inhibition increases with increasing inhibitor concentration. In general, the protection effeciency increases with decreasing temperature.

Fig. 2 shows the variation of the corrosion rate of Cu in 2M HNO_3 as a function of the concentration of the tested substance[6] at different temperatures. It was observed that at a constant temperature, the corrosion rate decreases at the concentration of the tested substance[6] increases.

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

$$\log \frac{P}{1 - P} = \log [I] + \text{constant} \qquad (2)$$

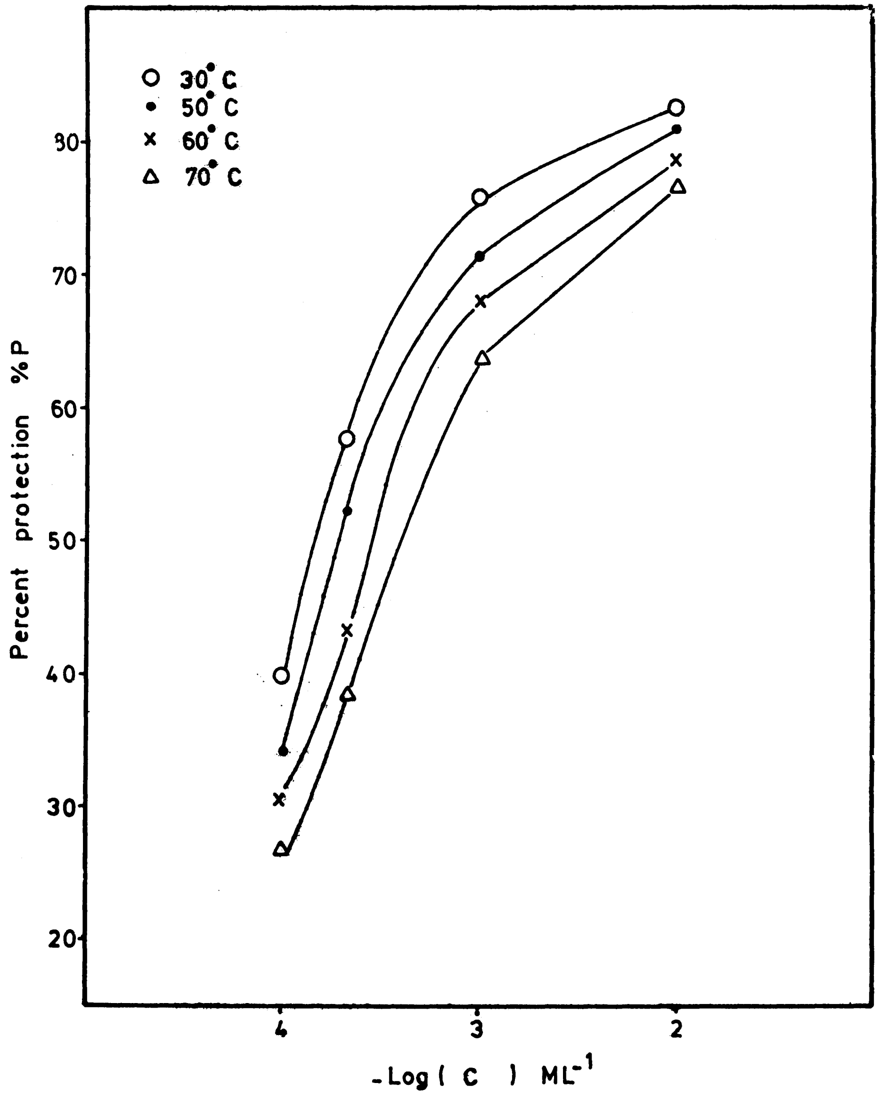

Fig. 1 Effect of concentration of substance on the protection efficiency of Cu in 2M HNO_3 at various temperatures.[6]

Where [I] is the inhibitor concentration. This relation gives a straight line with a slope of unity. Fig. 3 shows such plots, where equation (2) is not confirmed. Consequently, it can be concluded that the protection imparted by substance[6] agrees with the film theory of protective activity proposed by Balezin *et. al*[9], in

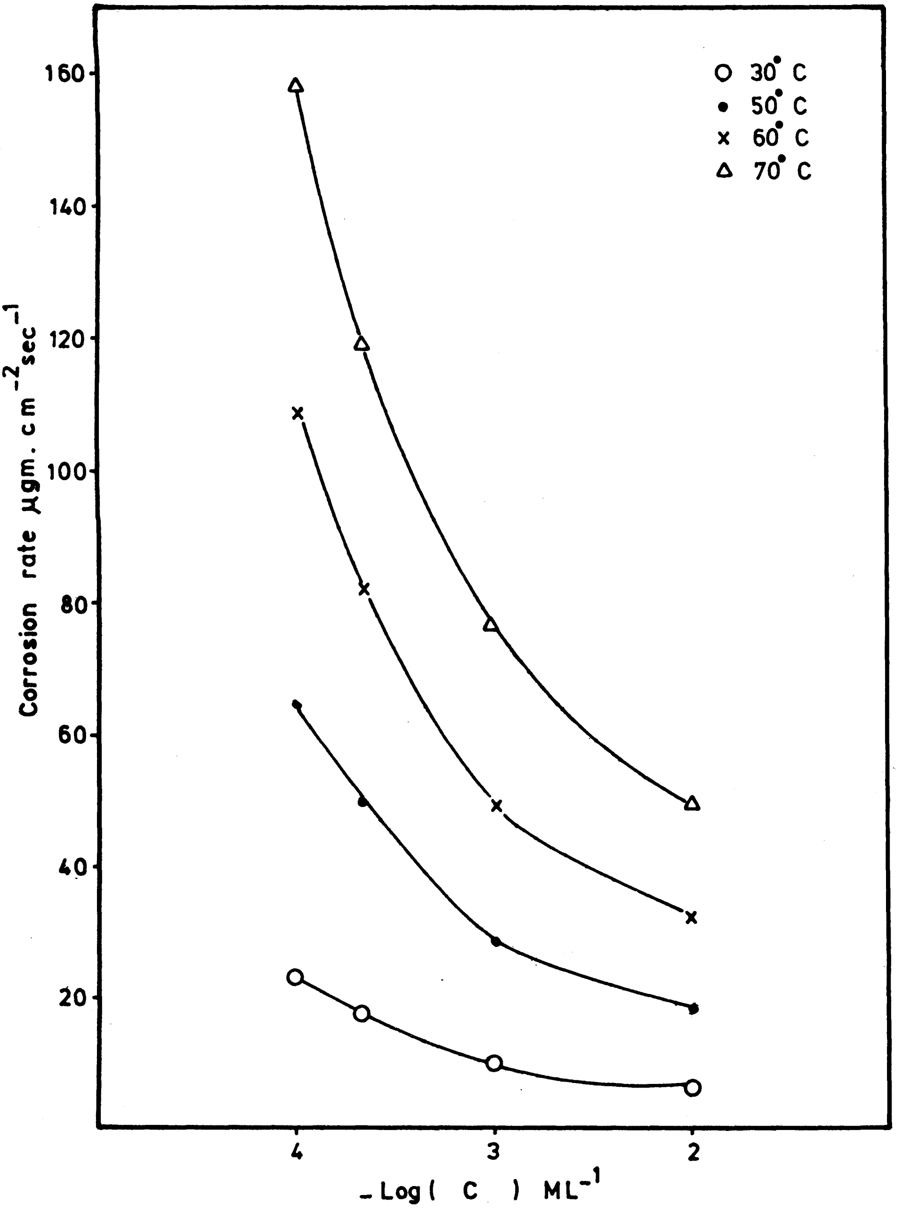

Fig. 2 Effect of the concentration of substance on the corrosion rate of Cu in 2M HNO_3 at various temperatures.[6]

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.

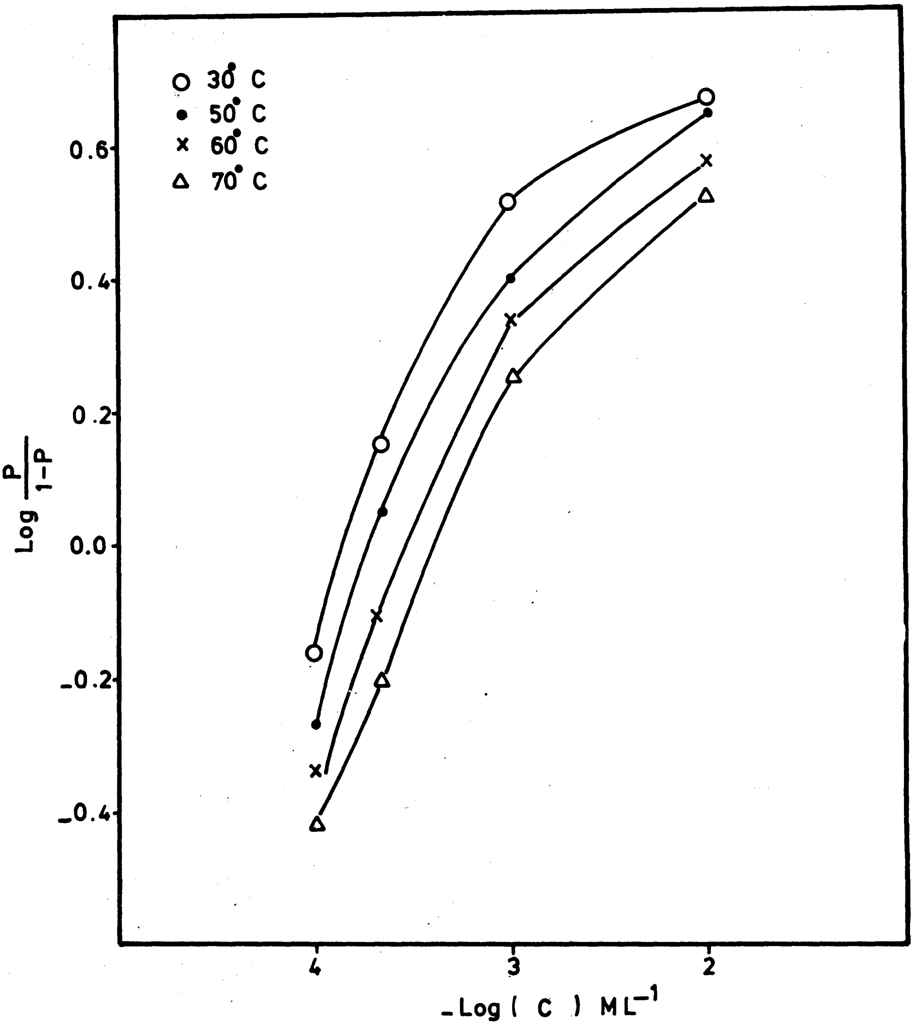

Fig. 3 Plot of log $\frac{P}{1-P}$ vs. log concentration of substance[1] for Cu in 2M HNO3 at various temperatures.

It is pointed[9] out that the logarithm of the corrosion rate is a linear function of 1/T (Arrhenius equation), where T is the temperature in Kelvin:

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

Where Ea is the apparent activation energy, R is the universal gas constant (1.987 cal/mole. degree) and B is a constant. In Fig. 4 the logarithms of the corrosion

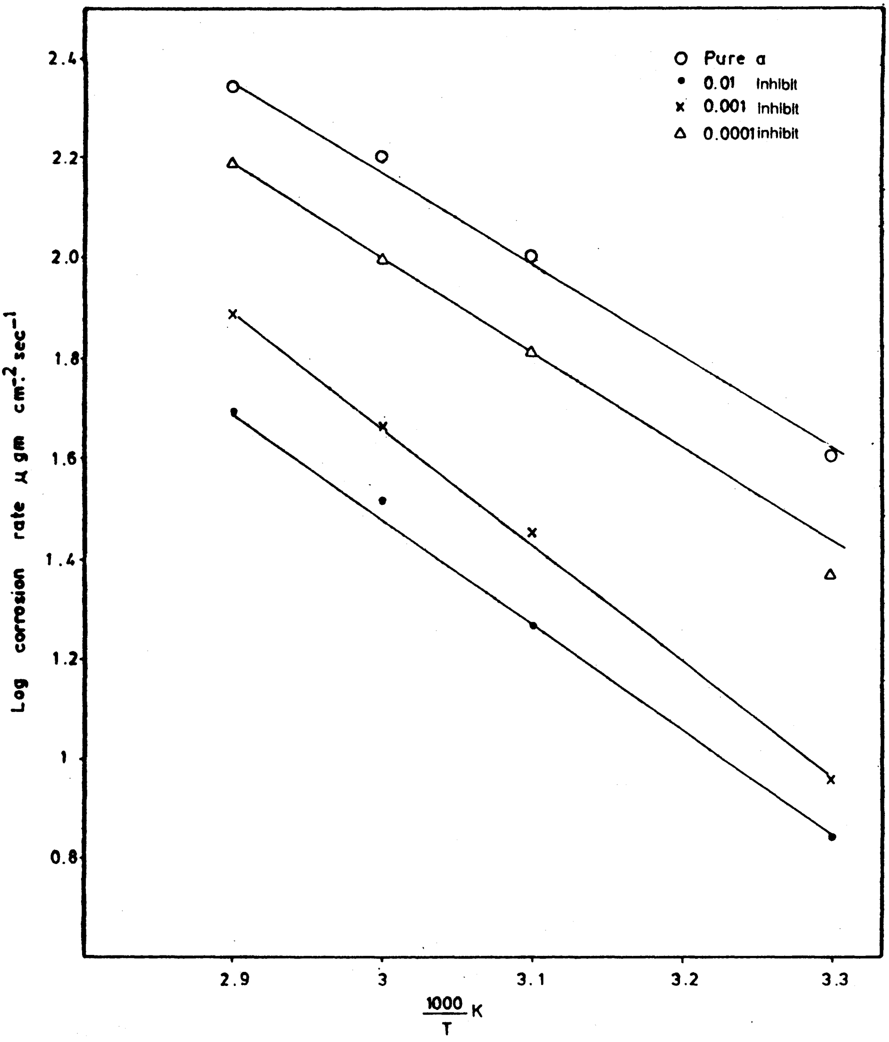

Fig. 4 Arrhenius plot of the corrosion rate of Cu in 2M HNO_3 in absence and presence of substance[6].

rate of Cu are plotted as a function of $(\frac{1}{T})$ in absence and presence of inhibitor[6] respectively. From Fig. 4 the calculated value of the apparent activation energy is 8.75 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[11]. 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} and 10^{-2} M inhibitor solutions, the calculated value of the apparent activation energies are 9.212 and 8.75 Kcal/mole, respectively (Fig. 4). These differences are not considered to be significant. Therefore, the presence of the substance does not affect the activation energy of the corrosion process. These results indicate that the tested substance[6] does not change the mechanism of the rate determining step of the corrosion process, although it significantly reduces its rate.

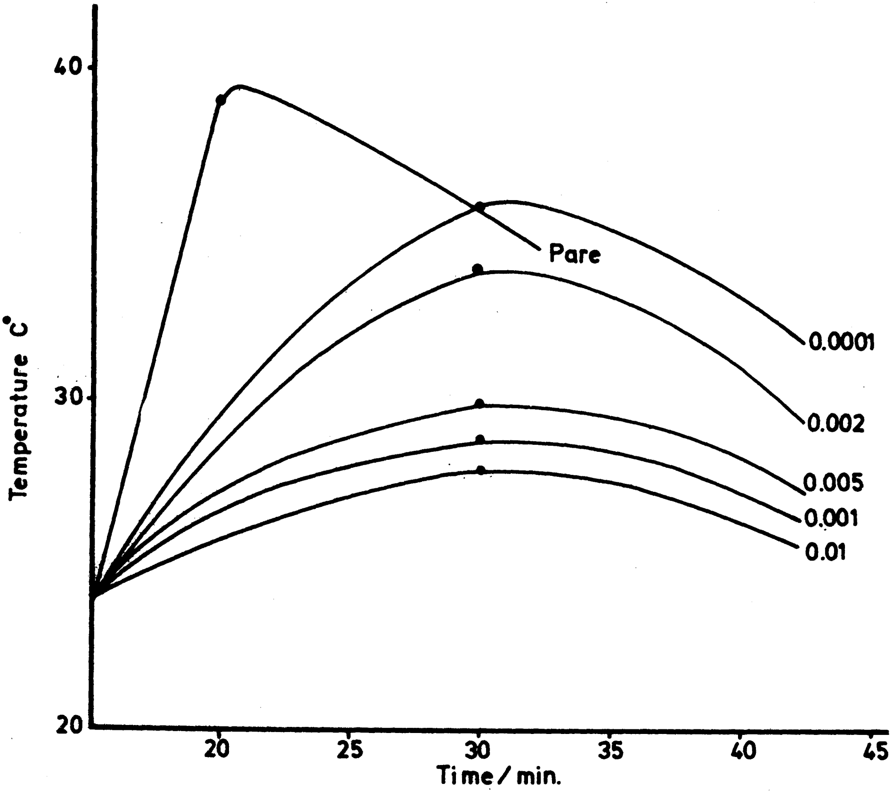

Fig. 5 Effect of addition of the substance on the thermometric behaviour of Cu in 2M HNO$_3$[6]

Fig. 5 shows the effect of the addition of the increasing concentration of the substance[6] on the thermometric behaviour of Cu in 2M HNO$_3$. The percentage variation in (RN) induced by the added substance[6] is defined as:

$$\text{Percentage variation} = \frac{\text{RN add.} - \text{RN free}}{\text{RN add.}} \times 100 \qquad (3)$$

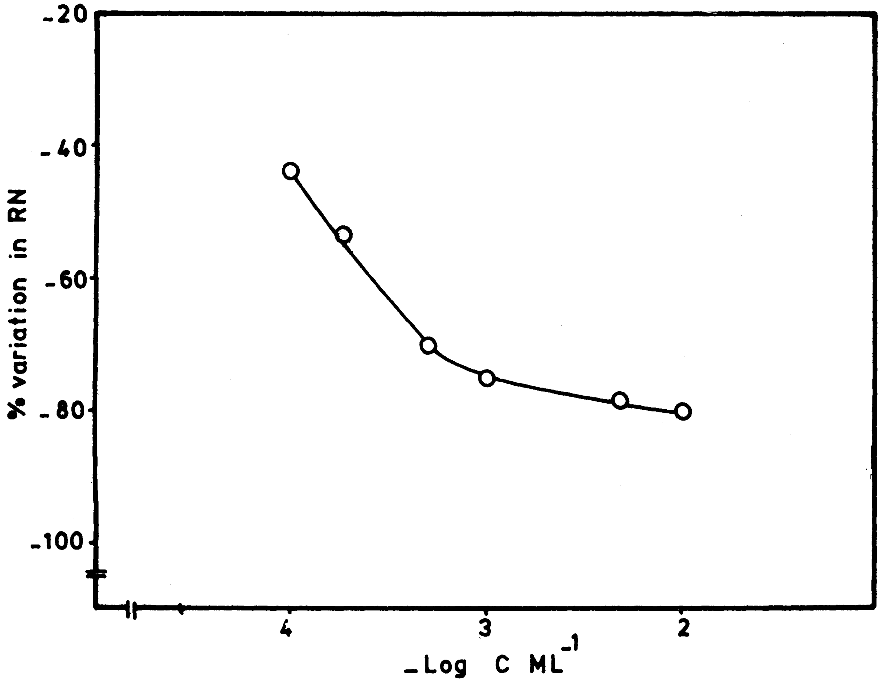

Fig. 6 Percentage variation of RN with tested substance^6 additive.

The variation is represented as function of molar concentration in Fig. 6. Inspection of Fig. 5 and 6 reveals that added inhibitor affects the dissolution of Cu in two different ways, depending on their concentration. Low concentrations cause the RN to decrease through both the decrease in T_{max} as well as through the prolongation of the time required to attain the maximum.

The 2M HNO_3 potential of Cu electrode immersed in solutions of free 2M HNO_3 and containing substance^6 of different concentrations (0.0001, 0.001, 0.005 and 0.01 M) was measured as a function of time within a period of 140 min.

The steady state potential obtained is plotted as a function of the logrithm of the molar concentrations and the curve is shown in Fig. 7. As evident from the curve the potential increases with the substance^6 concentration *i.e.* the potential is shifted to noble direction with increasing the substance^6 concentration.

Fig. 8, shows the effect of the substance on E-I curves of the cathodic polarisation (hydrogen evolution reaction). The strong inhibiting effect of the substance^6 can be seen in these curves. It is found that the corrosion potential

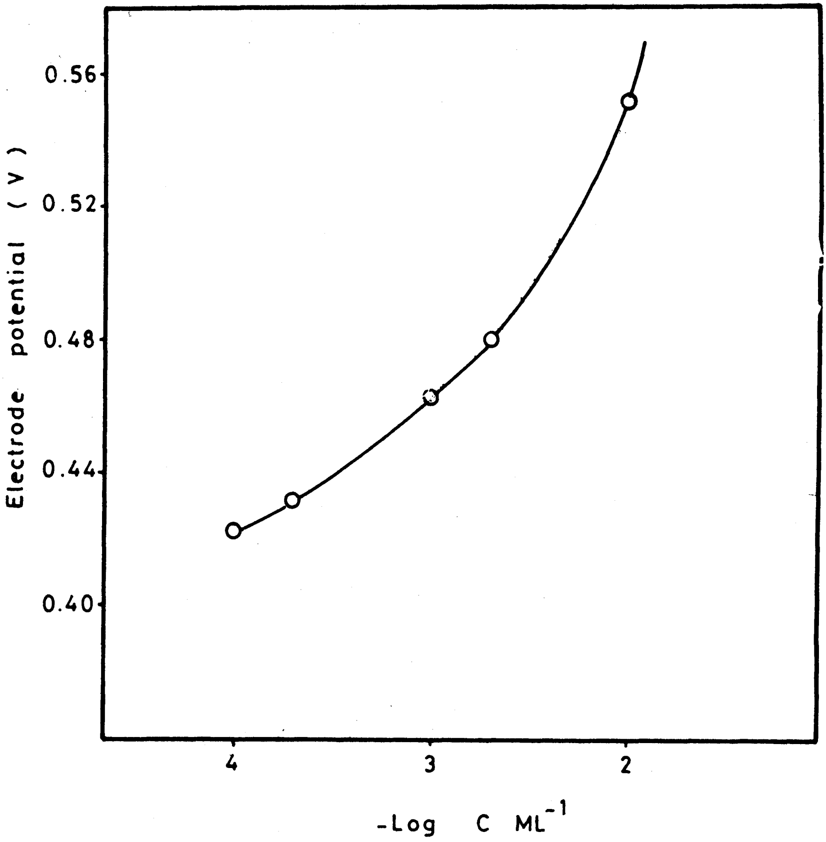

Fig. 7 Effect of concentration of substance on the potential of Cu.[6]

(E_{corr}) is shifted to more noble direction for the higher concentration of the tested substance[6] and to active direction for the blank solution. These results are in good agreement with those obtained from corrosion rate measurements and thermometric measurements.

From all the previous data, it is clear that N-acetyloxindolydene-*p*-chlorophenyl butenolide acts as an inhibitor.

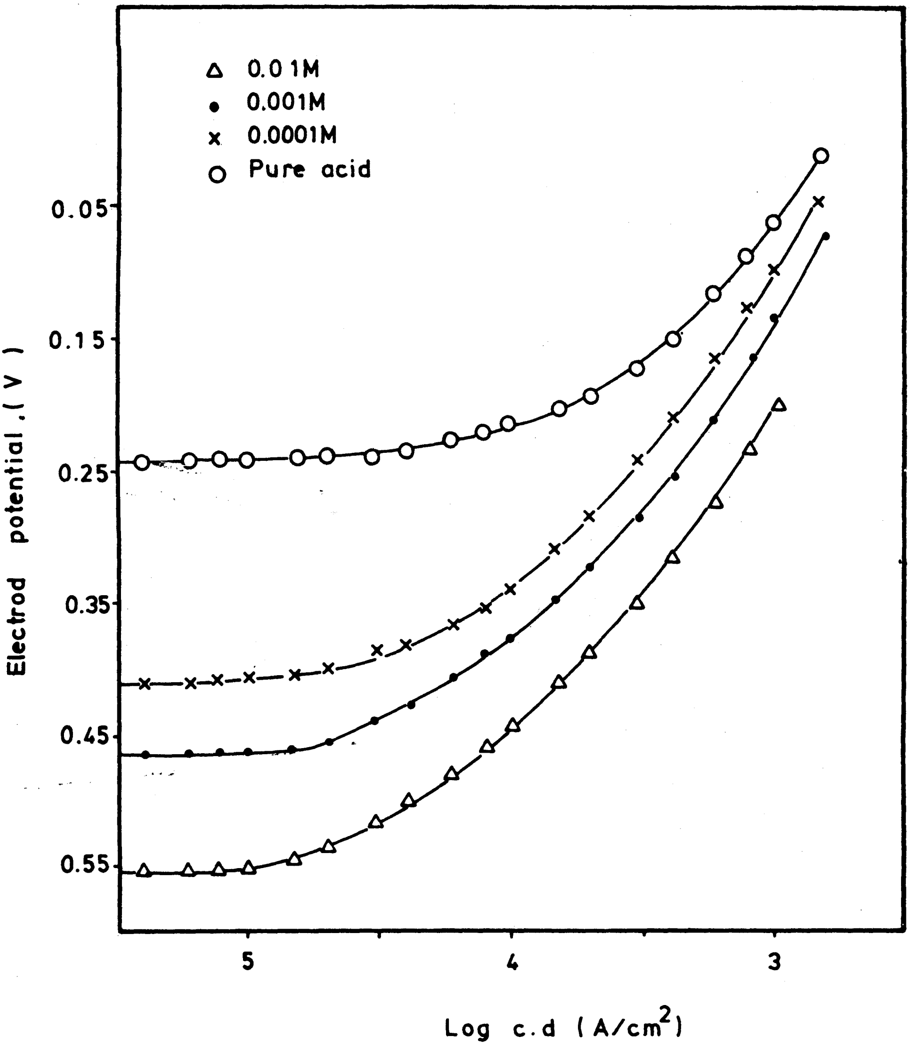

Fig. 8 Effect of concentration of substance on the cathodic current potential curves for Cu in 2-0 M $HNO_3{}^6$

REFERENCES

1. M.N. Desai, Y.C. Shah and B.K. Punjami, *Br. Corros. J.*, **4**, 309 (1969).
2. S.S. Rana and M.N. Desai, *Indian J. Technol.*, **5**, 393 (1967).
3. B. Sanyal and K. Srivastava, *Br. Corros. J.*, **8**, 28 (1973).
4. A.M. Shams El-Din and M.Y. Fakhr, *Corros. Sic.*, **14**, 635 (1974).
5. A.S. Fouda and A.K. Mohamed, *Werk. U. Korros.*, **39**, 23 (1988).

6. A.M. El-Abbady, M.A. Omara and N.G. Kandite, *Rev. Roumaine Chim.*, **19**, 79 (1974).
7. F. Mylius, *Z. Metabk*, **14**, 233 (1972).
8. S.A. Awad, *Electrochim. Acta.*, **7**, 677 (1962).
9. I.N. Putilova, S.A. balezin and V.P. Brannik, Metallic Corrosion Inhibitors, Pergamon Press, Oxford (1960).
10. M.N. Desai, B.C. Thakar, P.M. Chhaya and M.H. Gandhi, *Corros. Sci.*, **19**, 9 (1979).
11. B.E. Conway, Electrochemical Data, Elsevier, NY., p. 347 (1952).

(*Recieved*: 21 December 1992; *Accepted*: 27 February 1993) AJC–579