Asian Journal of Chemistry Vol. 5 No. 3 (1993), 749–754

Inhibiting Effect of Poly-4-Vinylpyridine on the Acid Corrosion of Copper

O.R. KHALIFA*, I.A. ABDUL HAMID, S.M. MOKHTAR and A.A. KASSAB
Chemistry Department, University College for Women
Ain Shams University, Cairo, Egypt

The efficiency of poly-4-vinylpyridine (poly-4-VP) as an inhibitor for acid corrosion of Cu was investigated. The effect of poly-4-VP on the corrosion rate was measured in 3 M HNO_3 at various temperatures and concentrations. It was observed that poly-4-VP has a significant inhibiting effect on the corrosion of the metal; protection efficiencies approaching 80% were measured. The results of the apparent activation energies in absence and in presence of the inhibitor suggest that poly-4-VP 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 poly-4-VP molecules on the metal surface.

INTRODUCTION

Many data now exist on the use of various types of organic compounds as inhibitors for the aqueous corrosion of metals such as Al, Fe, Cu and Nl[1–6]. The inhibitive power of such organic inhibitors has been interpreted in terms of many different factors, such as their molecular structures, molecular area and molecular weights. As an example the inhibitive action of benzotriazole (BTA) on Cu in acidic solutions is due to the formation of a polymeric Cu-BTA complex, which is more than a monolayer on the surface[4].

In this work we study the effect of poly-4-vinylpyridine (poly-4-VP) as an inhibitor for the acid corrosion of copper. The effects of poly-4-VP on the corrosion rate, corrosion potential and activation energy of Cu in 3 M HNO_3 were investigated.

The results were analysed with the purpose of determining the inhibitive power of poly-4-VP at various temperatures and concentrations and to elucidate the mechanism of its inhibitive action.

EXPERIMENTAL

The copper used was spectroscopically pure (99.7%). Weight loss was measured on sheets of 20 cm^2 apparent surface area. These sheets were precleaned by degreasing in methanol, dipping in conc. 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 15 minutes in all experiments, and averages from four specimens were taken at each concentration, each with a fresh electrode surface and batch of electrolyte. The results were quite reproducible.

The poly-4-vinylpyridine polymer was of the highest purity available. Various concentrations of poly-4-VP ranging from 10^{-4} to 5×10^{-2} were used in 3 M HNO_3 solution. The solutions were prepared from bidistilled water, and the temperature was adjusted to ± 1°C.

The effect of poly-4-VP on the potential of Cu electrode in 3M HNO_3 was investigated at room temperature.

RESULTS AND DISCUSSION

The protection efficiency, P, of the inhibitor was calculated by equation (1):

$$P = 100(1 - W_2/W_1) \tag{1}$$

where W_1 and W_2 are the corrosion rates in absence and in presence of a certain concentration of inhibitor. Fig. 1 shows the variation of the protection efficiency P, of copper metal as a function of the concentration of poly-4-vinylpyridine in 3 M HNO_3 solution at different temperatures. As seen, the percentage inhibition increase with the increase of poly-4-VP concentration in the medium, approaching complete protection (80%) at 0.05 M. It is also clear that the protection efficiency increases with decreasing temperature.

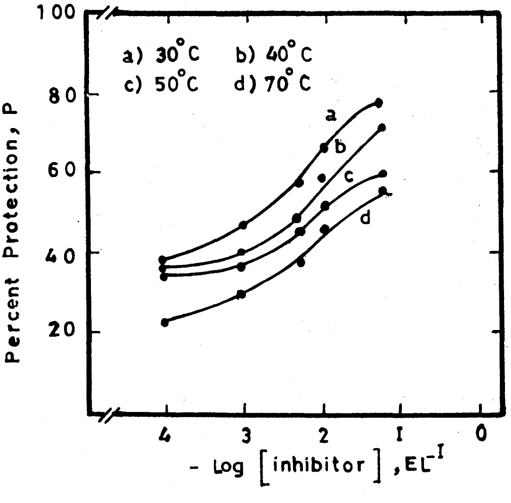

Fig. 1. Effect of the concentration of poly-4-VP on the protection efficiency of copper in 3.0 M HNO3 at various temperatures

The variation of the corrosion rate of Cu in 3 M HNO_3 as a function of the concentration of inhibitor at different temperatures is shown in Fig. 2. It was observed that, at constant temperature, the corrosion rate decreases as the concentration of poly-4-VP increases.

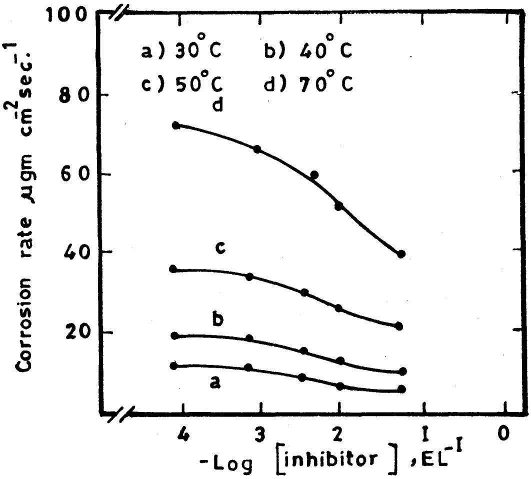

Fig. 2. Effect of the concentration of poly-4-VP on the corrosion rate of copper in 3.0 M HNO_3 at various temperatures

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

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

where [I] is the inhibitor concentration, should be a straight line with a slope of unity. This relation is seen in Fig. 3, in which equation (2) is not confirmed. Thus,

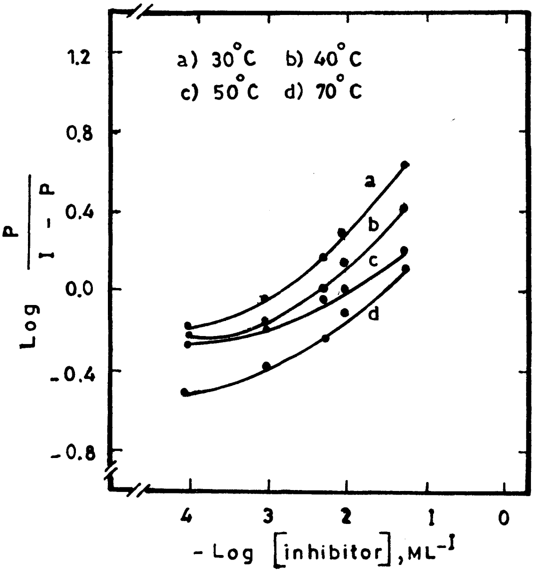

Fig. 3. Plot of log P/(I – P)vs. log concentration of poly-4-VP for the corrosion rate of copper in 3.0 M HNO_3 at various temperatures

it can be suggested that the protection imparted by poly-4-VP agrees with the film theory of protective activity proposed by Balezin *et al.*[7], in which inhibition is due to the formation of a protective film on the metal surface. The diffusion of the metal ions through this film becomes the rate-determining step. These results are in agreement with the previous results reported for the inhibition of Cu corrosion by triazole[5] and benzotriazole[8], where inhibition is attributed to the formation of an insoluble copper triazole film on the metal surface.

It is pointed out[7] that the logarithm of the corrosion rate is a linear function of 1/T (Arrhenius equation), where T is the temperature in degrees Kelvin:

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

where, E_a 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 rates of Cu are plotted as a function of 1/T in absence and in presence of poly-4-VP inhibitor.

The calculated value of the apparent activation energy in absence of inhibitor

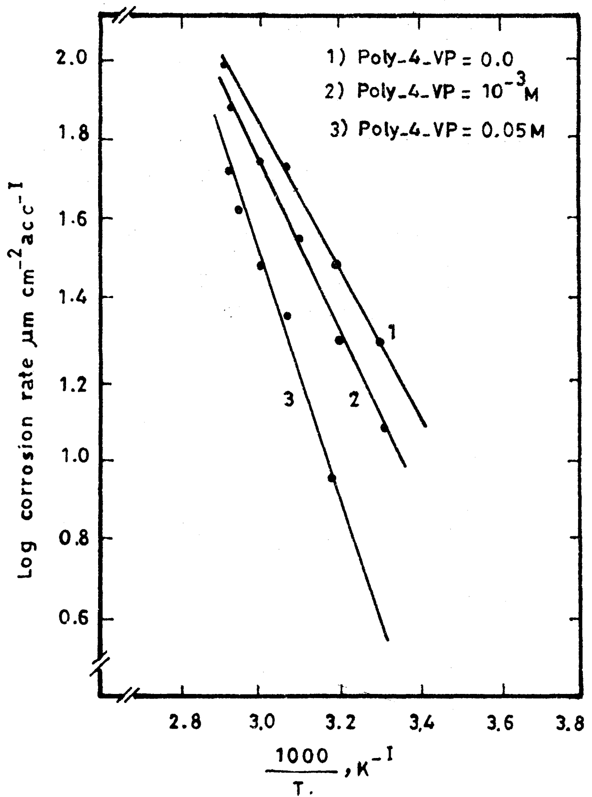

Fig. 4. Arrhenius plot of the corrosion rate of copper in 3.0 M HNO_3 in absence and in presence of poly-4-VP

is 8.3 kcal/mole, a value which is similar to that reported previously[9]. This value is also of the order of the activation energies encountered for the hydrogen evolution reaction[10]. This is in accordance with the fact that the hydrogen evolution reaction in absence of an inhibitor is the rate-determining step for the overall corrosion reaction. For 10^{-3} and 5×10^{-2} M poly-4-VP solutions, the calculated values of the apparent activation energies are 9.17 and 12.52 kcal/mole, respectively.

These differences are not considered to be significant. Therefore, the presence of poly-4-VP does not affect the activation energy of the corrosion process. These results also indicate that poly-4-VP does not change the mechanism of the rate-determining step of the corrosion process.

Fig. 5 represents the relation between potential and the logarithm of poly-4-VP concentration at room temperature. It is obvious from that diagram that the potential is shifted to noble direction with the increase of inhibitor concentration. It is concluded that the inhibitive effect of the poly-4-VP is due to the formation of a protective film on the surface of copper metal. The diffusion of metal ions through film becomes the rate-determining step.

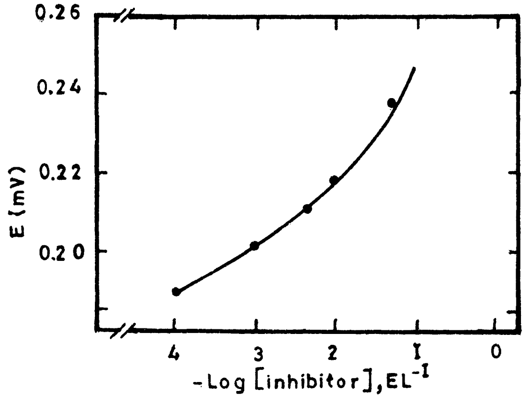

Fig. 5. Effect of the concentration of poly-4-VP on the potential curve for copper in 3.0 M HNO_3 at room temperature

REFERENCES

1. G. Trabenelli and V. Carossitti, in: Advances in Corrosion Science and Technology, (Eds.) M.G. Fontana and R.W. Staehle, Vol. 1, p. 147, Plenum Press, New York (1970).
2. M.N. Desai, U.C. Thaber, P.M. Chhaya and M.H. Gandhi, *Corrosion Sci.*, **19**, 9 (1979).
3. R.R. Anand, R.M. Hurd and N. Hackerman, *J. Electrochem. Soc.*, **112**, 138, 144 (1965).
4. G.W. Poling, *Corrosion Sci.*, **10**, 359 (1970).
5. P.G. Fox and P.A. Bradely, *Corrosion Sci.*, **20**, 643 (1980).

6. R.M. Abd El Gulil and A.A. Abd El-Fattah, *Corrosion Prevention and Control*, **34**, 149 (1987).
7. F.N. Putilova, S.A. Balezin and V.P. Brannik, Metallic Corrosion Inhibitors, Pergamon Press, Oxford (1960).
8. P.G. Fox, G. Lewis and P.J. Boden, *Corrosion Sci.*, 19, 457 (1979).
9. B.M. Abo El-Khar, O.R. Khalifa, I.A. Abdel-Hamid and A.M. Azzam, *Corrosion Prevention and Control*, **34**, 152 (1987).
10. B.F. Conway, Electrochemical data, Elsevier, New York, p. 347 (1952).

(*Received*: 1 November 1992; *Accepted*: 15 November 1992) AJC–520