

Protection of Nickel Metal by Vinyl Polymer
In Nitric Acid

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ABSTRACT

The effect of polyvinylpyrrolidone as a protective substance on the corrosion on nickel metal in 4M HNO₃ solution has been studied at different temperatures ranging from 30°C to 80°C. The weight-loss technique showed that polyvinylpyrrolidone impart a significant protecting effect on the corrosion rate of nickel metal. The protection efficiency in the presence of this polymer reached about 82% at 0.1M inhibitor concentration. The results of the apparent activation energies in absence and in presence of the inhibitor suggest that polyvinylpyrrolidone does not change the mechanism of the rate determining step of the corrosion process. The results are analyzed in terms of the formation of a protective film on the metal surface.

INTRODUCTION

There now exists a large volume of literature on the use of organic compounds containing nitrogen, oxygen and/or sulphur functional groups, acting as inhibitors Helmutley, Walter and Stenger (1952) for the aqueous corrosion of metals such as Fe, Al, Cu and Ni Annand, Hurd and Hackerman (1965) Trabonelli and Carossitti (1970) Poling (1970) Desai, Thaber, Chhaya and Gandhi (1979), Fox and Bradley (1980), Abo El-Khair (1983) and Abdel Gulil and El Fattah (1987). The inhibitive power of these organic corrosion inhibitors has been interpreted in terms of many different factors, including their molecular structures, molecular area and molecular weights, It was observed that the inhibition effectiveness of poly-

amines and ethanolamine for the corrosion of Al functions mainly by adsorption and their neutralizing effect has a secondary role in inhibition Desai, Tnabir, Chhaya and Gandhi(1979). The acid corrosion inhibition of steel in presence of polyvinylpyridine polymer is due to multicentre adsorption of the polymer at several points on the molecule Annand, Hurd and Gaskerman (1965). The inhibitor action of benzotriazole (BTA) on Cu in acidic solution is due to the formation of polymeric Cu BTA complex, which is more than a monolayer, on the surface plating (1970) . This film inhibits the cathodic hydrogen evolution reaction much more effectively than the oxygen reduction .

In this work, the application of polyvinylpyrrolidone of average molecular weight of 40,000 (PVP 40) as an inhibitor for the acid corrosion of Ni was investigated . The effect of (PVP 40) on the inhibiting efficiency, corrosion rate and apparent activation energy of Ni corrosion in 4M HNO_3 was studied, The results were analyzed with a view to determine the inhibiting power of PVP at various temperatures and concentrations and to elucidate the mechanism of its inhibitive action .

EXPERIMENTAL :

The Nickel used was spectroscopically pure (99.98%). Weight loss was measured on sheets of 9 cm^2 apparent surface area, These sheets were precleand 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 averages from four specimens were taken at each concentration each with a fresh elect-

rode surface and batch of electrolyte. The results were quite reproducible.

The polyvinylpyrrolidone (PVP) of molecular weight 40,000 was of the highest purity available. Various concentration of polyvinylpyrrolidone (PVP) ranging from 10^{-4} to 10^{-1} M were used in 4M HNO_3 solution. The solutions were prepared from bidistilled water, and the temperature was adjusted to $\pm 0.1^\circ\text{C}$.

The effect of polyvinylpyrrolidone on the potential of Ni electrode in 4M HNO_3 was investigated at room temperature.

RESULTS AND DISCUSSION :

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

$$P = 100 \left(1 - \frac{w_2}{w_1} \right) \dots\dots\dots(1)$$

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 Ni metal as a function of the concentration of polyvinylpyrrolidone in 4M HNO_3 solution at different temperatures. As seen the percent inhibition increases with the increase of polyvinylpyrrolidone concentration in the medium, approaching complete protection (82%) at 0.1M. It is also clear that the protection efficiency increases with decreasing temperature.

The variation of corrosion rate of Ni in 4M 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 polyvinylpyrrolidone increases.

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

$$\text{Log } P/(1-p) = \text{log } (1) + \text{constant} \dots\dots\dots(2)$$

where (1) 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 it can be suggested that the protection imparted by polyvinylpyrrolidone agrees with the film formation Putilova, Balezia and Brannik (1960) where 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. These results are in agreement with the previous results reported for the inhibition of Ni corrosion by triphenyltetrazolium chloride (TTC) Abd El-Gulil and Abd-El-Fattah (1987). Fig(4) shows an Arrhenius plot of the corrosion process of Ni in 4M HNO₃ (using Arrhenius) equation (3) .

$$\text{log corrosion rate} = -E_a/R + B \dots\dots\dots(3)$$

where, E_a is the apparent activation energy, R is the universal gas constant and B is a constant .

The results fit a satisfactory straight line with an activation energy of 11.9 K cal/mole. This value is comparable with some values reported previously Abd El-Khair, Khalifa, Abdel-Hamid and Azzam(1987). It is also of the order of the activation energies encountered for the hydrogen evolution reaction Conway (1952). The calculated values of the apparent activation energies in the presence of 10⁻⁴ and 10⁻¹M inhibitor concentration are 11.054 K cal/mole and 11.97.K cal /mole respectively see Fig. (4) Thus, the presence of polyvinylpyr-

olidone does not affect the activation energy of the corrosion process. The above evidence indicates that the presence of polyvinylpyrrolidone does not change the mechanism of the nature of the rate-determining step of the corrosion process, although it significantly reduces its rate .

The open-circuit potential of Ni electrode immersed in 4M HNO_3 acid in absence and in presence of PVP of concentration ranging between 10^{-3}M to 10^{-1}M was followed as a function of time till steady state values were established. The results of these measurements are shown in Fig(5). The potential shows drift: within the first two hours from immersion the change of potential within this period does not appear to follow a common course . The potential values remain then almost constant within the next hour.

Fig(6) represents the relation between the steady state potential and the logarithm of polyvinylpyrrolidone at room temperature . It is obvious from this diagram that the potential is shifted to noble direction with the increase of inhibitor concentration .

It is concluded that the inhibitive effect of the polyvinylpyrrolidone is due to the formation of a protective film on the surface of nickel metal. The diffusion of metal ions through the film becomes the rate - determining step .

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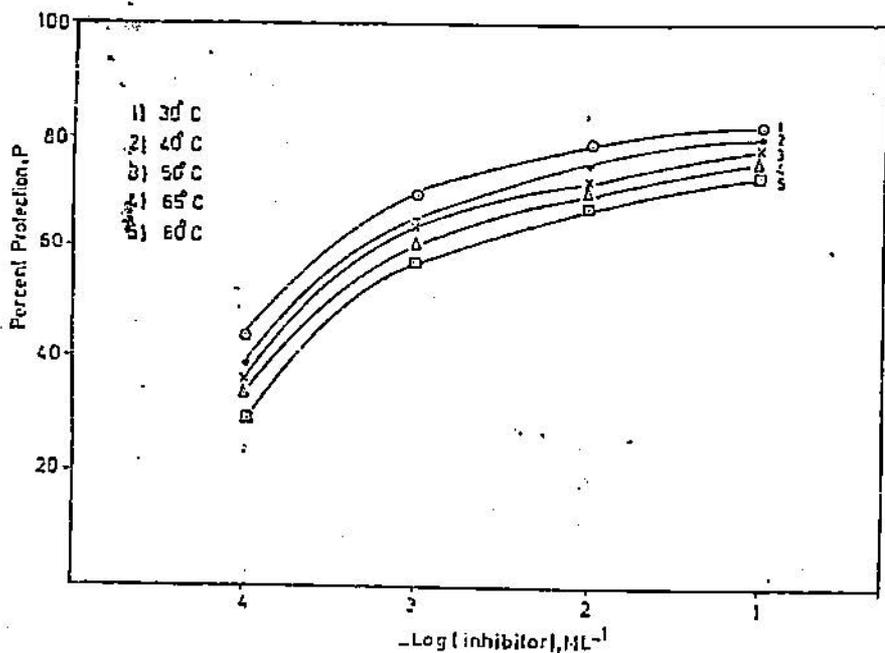


Fig. 1. : Effect of the concentration of polyvinylpyrrolidone on the protection efficiency of Ni in 4.0M HNO_3 at various temperatures.

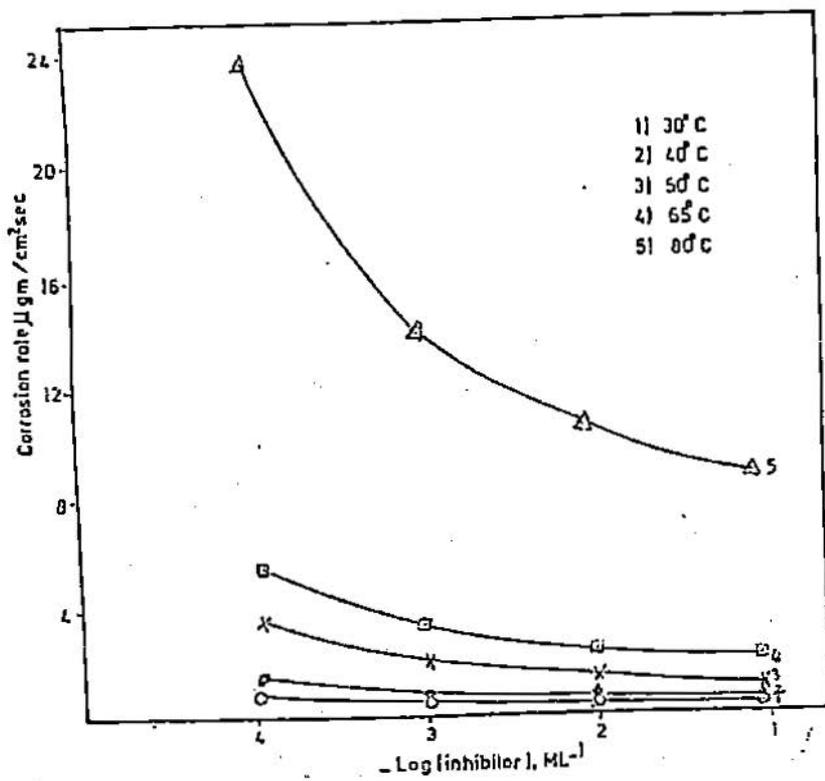


Fig. 2 : Effect of the concentration of polyvinylpyrrolidone on the corrosion rate of Ni in 4.0M HNO_3 at various temperatures.

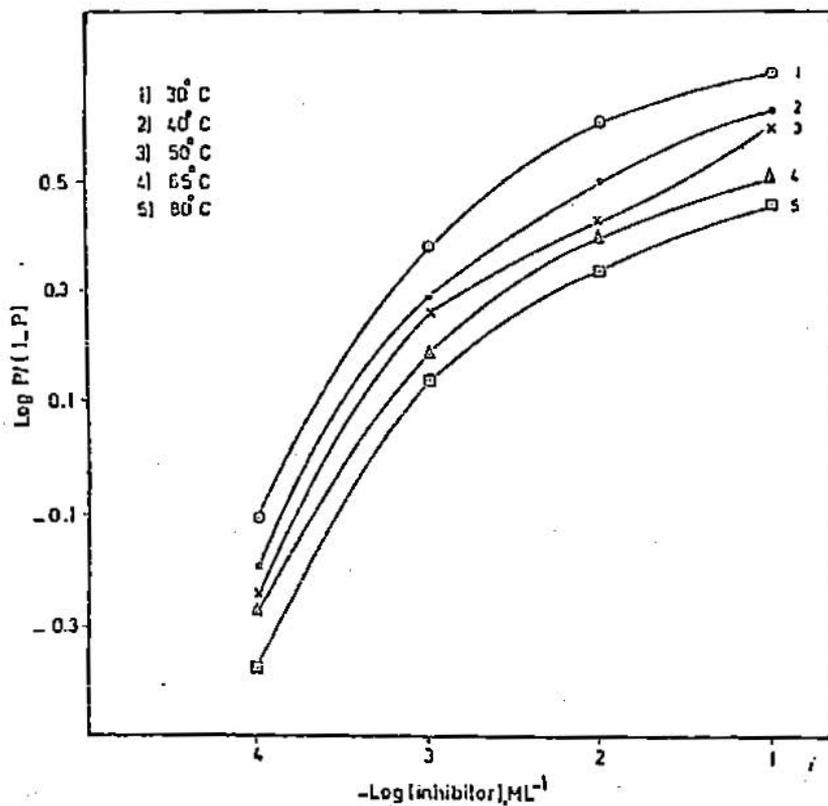


Fig. 3 : Plot of $\log P/(1-p)$ vs. \log concentration of polyvinylpyrrolidone on the corrosion rate of Ni in 4.0M HNO_3 at various temperatures.

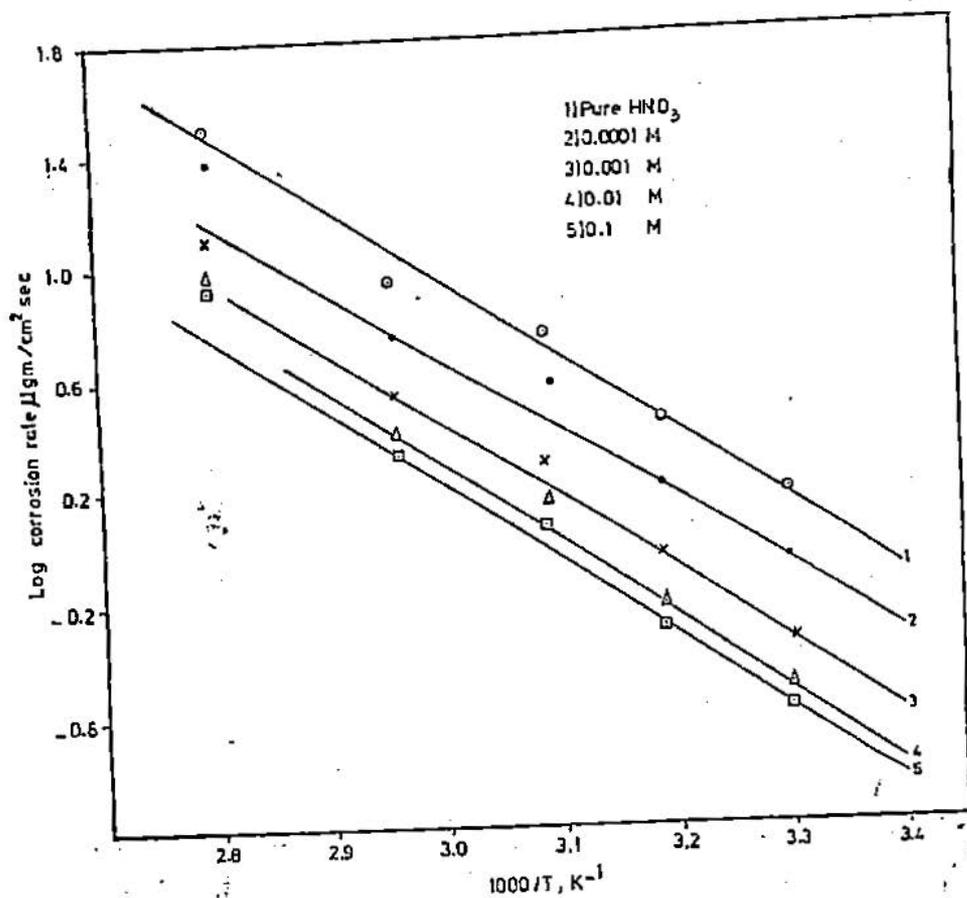


Fig. 4 : Arrhenius plot of the corrosion rate of Nickel in 4.0M HNO_3 in absence and in presence of polyvinylpyrrolidone.

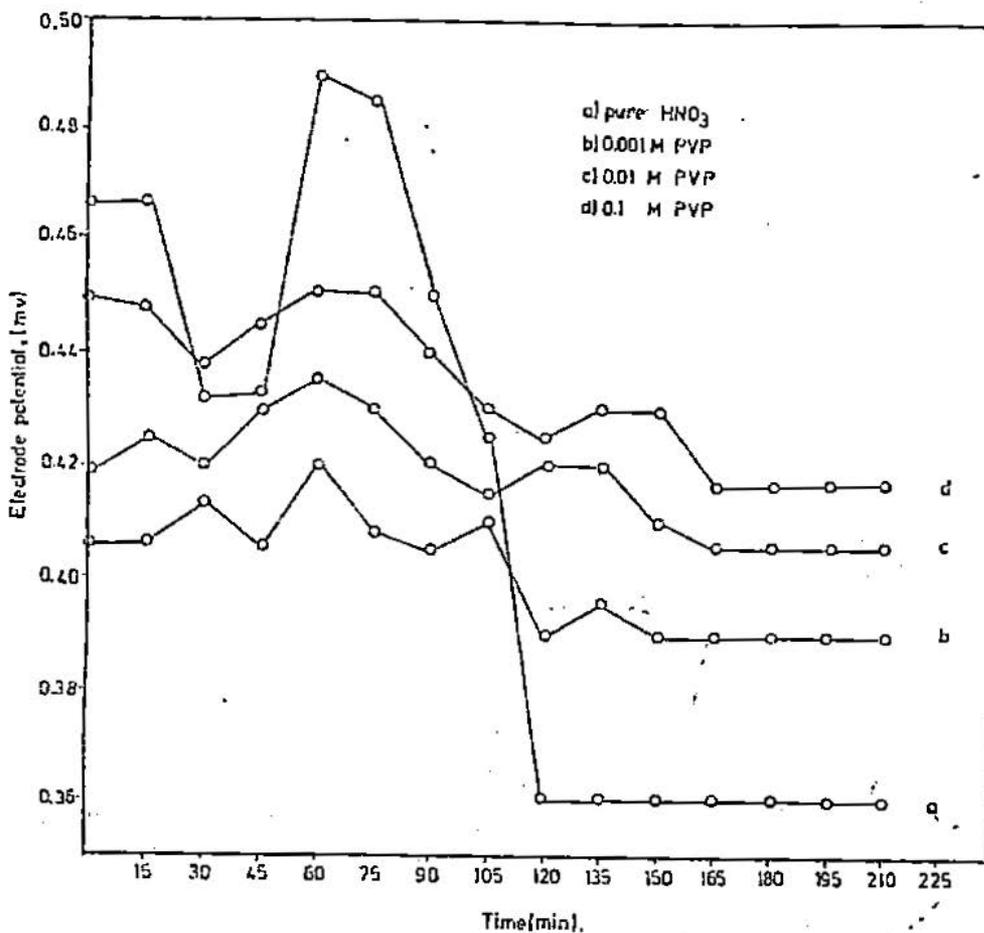


Fig. 5 : Variation of electrode potential of Nickel with time in absence and in presence of polyvinylpyrrolidone.

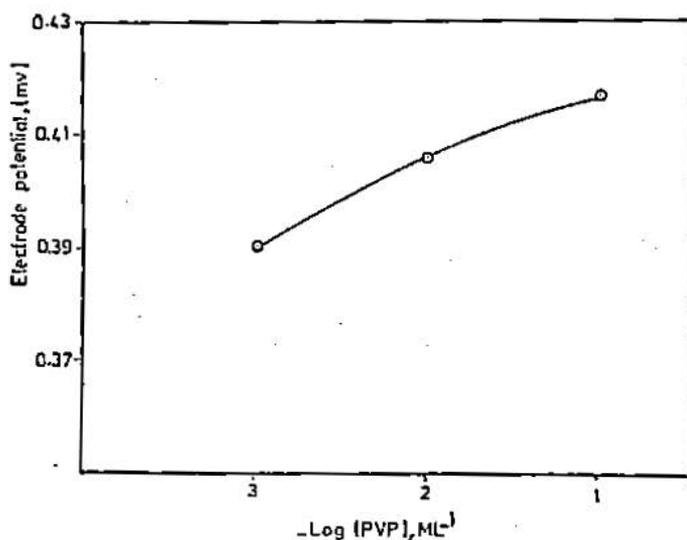


Fig. 6 : Effect of the concentration of polyvinylpyrrolidone on the potential curve for Nickle in 4.0M HNO_3 at room temperature.

حماية تآكل فلز النيكل في محلول حمض
النيتريك عن طريق فينيل بوليمر

تم دراسة تأثير فينيل بوليمر كمثبط لتآكل فلز النيكل في حمض النيتريك ذو تركيز 4 جزئ، جرامي وتركيزات مختلفة من فينيل بوليمر وقد وجد أن نسبة الحماية تزداد بزيادة تركيز فينيل البوليمر الى ان تصل الى 85% عند تركيز 0.1 م. جزئ، جرامي من فينيل البوليمر عند درجة 30°م كما ان نسبة الحماية تقل بزيادة درجة الحرارة .

وهذه النتائج تتفق مع تكوين طبقة حامية على سطح الفلز كما ان قيمة طاقة التنشيط المحسوبة تتفق مع تفاعلات تصاعد الهيدروجين وبحساب طاقات التنشيط في وجود العامل المثبط وجد انه لا يغير من ميكانيكية التفاعل ولكنها تقلل من سرعة التفاعل وبدراسة جهد قطب النيكل في وجود المثبط وجد ان الجهد يتجه الى الاقل سالبة بزيادة تركيز للمثبط .