

INHIBITION OF ACID CORROSION OF CADMIUM BY
SODIUM MOLYBDATE



By:

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ABSTRACT

The effect of sodium molybdate as inhibitor on the corrosion behaviour of Cd in 1.0M HCl solution has been studied at different temperatures. The weight-loss technique showed that the sodium molybdate affect the corrosion rate of the metal.

The protection efficiency increases with decreasing temperature and it rises in the presence of sodium molybdate, the protection efficiency was 95% at 1.0M of MoO_4^{-2} inhibitor concentration.

Potential measurements of Cd electrode showed that it was shifted to the noble direction with increasing molybdate concentration.

INTRODUCTION

In previous studies connected with the corrosion of metals, the corrosion of iron and steel has drawn the attention of many workers due to their importance in every day life.

Studies were done on iron in acid medium containing some inorganic salts as inhibitors Helmutley, stenger and Werner (1952). Now various types of organic compounds were used as inhibitors for the corrosion of metals such as Fe, Al, Cu and Ni. Trabonelli and Carassiti (1970), Desai, Thakar, Chhaya and Gandhi (1979), Annand, Hurd and Hackerman (1965), Poling (1970), Fox and Bradely (1980) and Abo El-Khair (1983). These studies showed that passivity was not limited to monolayers or to very thin films.

In this work we study the effect of sodium molybdate Na_2MoO_4 as an inhibitor for the acid corrosion of Cd. The effects of the Na_2MoO_4 on the corrosion rate, and potential of Cd in 1M HCl were investigated.

The results were analysed to determine the inhibitive power of Na_2MoO_4 and also the mechanism of its inhibitive action was elucidated.

EXPERIMENTAL

The potential of Cd electrode was measured as a function of time within the period of three hours in 1 M HCl containing sodium molybdate of concentration varying from 1M to 10^{-3}M .

The electrode was prepared from analar Cd (B.D.H). Before use the electrode was abraded successively to 00 finish, degreased with acetone and then washed thoroughly with water. Each experiment was carried out with a newly polished electrode and with fresh portion of solution. A saturated calomel electrode was used as a reference electrode. The potential was measured with the aid of a Cambridge potentiometer.

Determination of the corrosion rate was also carried out using the weight-loss technique. Experiments were performed on Cd pieces measuring 25 cm². The test pieces were first degreased with methanol and then etched in concentrated HNO₃ for ¼ minute. They were then washed with conductivity water, dried in alcohol and ether and then weighed. Corrosion tests were carried out in a 100 ml beaker 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. Results were duplicated and the mean was computed.

RESULTS AND DISCUSSION

Fig. 1 shows the variation of the protection efficiency, p of Cd metal as a function of the

concentration of sodium molybdate in 1M HCl solution at different temperatures. The protection efficiency P of the inhibitor was calculated by the following equation (1).

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

Where W_1 and W_2 are the corrosion rates in absence and in presence of a certain concentration of inhibitor. As shown the percentage inhibition increases with increasing the MoO_4^{-2} concentration in the medium, approaching complete protection (95%) at 1M.

Fig. 1 also shows the effect of the concentration of sodium molybdate at various temperatures on the protection efficiency of Cd. Clearly, the percentage inhibition increases with increasing MoO_4^{-2} concentration. In general, the protection efficiency increases with decreasing temperature.

Fig. 2. shows the variation of the corrosion rate of Cd in 1.0M HCl as a function of the concentration of MoO_4^{-2} at different temperatures. It was observed that, at a constant temperature, the corrosion rate decreases as the concentration of MoO_4^{-2} 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 Langmiur isotherm relationship:

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

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 MoO_4^{-2} agrees with the film theory of protective activity proposed by Balezin et al., Pufilova, Balezin and Drannik (1960) 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 is pointed [Pufilova, Balezin and Drannik (1960)] out that the logarithm of the corrosion rate is a linear function of $1/T$ (Arrhenius equation), where T is the temperature in Kelvin:

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

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 Cd are plotted as a function of $(1/T)$ in absence and in presence of MoO_4^{-2} inhibitor,

respectively. From Fig. 4 the calculated value of the apparent activation energy is 10.13 Kcal/mole, a value that agrees with that reported previously as Abo El-Kair (1987). This value is also of the order of the activation energies encountered for the hydrogen evolution reaction as Electrochemical Data (1952). 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. Therefore, the presence of MoO_4^{-2} does not affect the activation energy of the corrosion process. These results indicate that MoO_4^{-2} does not change the mechanism of the rate-determining step of the corrosion process, although it significantly reduces its rate.

The 1M HCl potentials of Cd electrode immersed in solutions of free 1M HCl and ^{base} containing MoO_4^{-2} of different concentrations (0.001, 0.01, 0.1 and 1.0M) were measured as a function of time within a period of 140 min. (Fig.5).

The potential shows drifts within the first hour from immersion. The change of potential with this period does not appear to follow a common course. The potential values remain almost constant within the next hour.

The steady state potential obtained after 140 min. of immersion is plotted as a function of the logarithm of the molar concentrations and the curve is shown in Fig.5. As evident from the curve the potential increases with the MoO_4^{-2} concentration i.e. the potential is shifted to noble direction with increasing MoO_4^{-2} concentration.

From all the previous data, it is indicated that the sodium molybdate acts as an inhibitor.

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تآكل قطب الكاديوم في الوسط الحامض (حمض الهيدروكلوريك)
في وجود أيونات المولبيدات

في هذا البحث تم قياس تأثير مولبيدات الصوديوم كمثبط لتآكل
فلز الكاديوم في تركيز 1 جزيء من محلول حمض الهيدروكلوريك عند درجات
حرارة مختلفة .

وقد أثبتت هذه القياسات أن مولبيدات الصوديوم مثبط جيد لتآكل
الكاديوم .

وقد وجد أن نسبة الحماية تقل بزيادة درجة الحرارة وتزداد بزيادة
تركيز مولبيدات الصوديوم وكانت أعلى نسبة للحماية 95% عند تركيز 1 جزيء
من مولبيدات الصوديوم عند درجة حرارة 30° م .

وعند قياس جهد فلز الكاديوم وجد أنه يزداد بزيادة تركيز
المولبيدات .

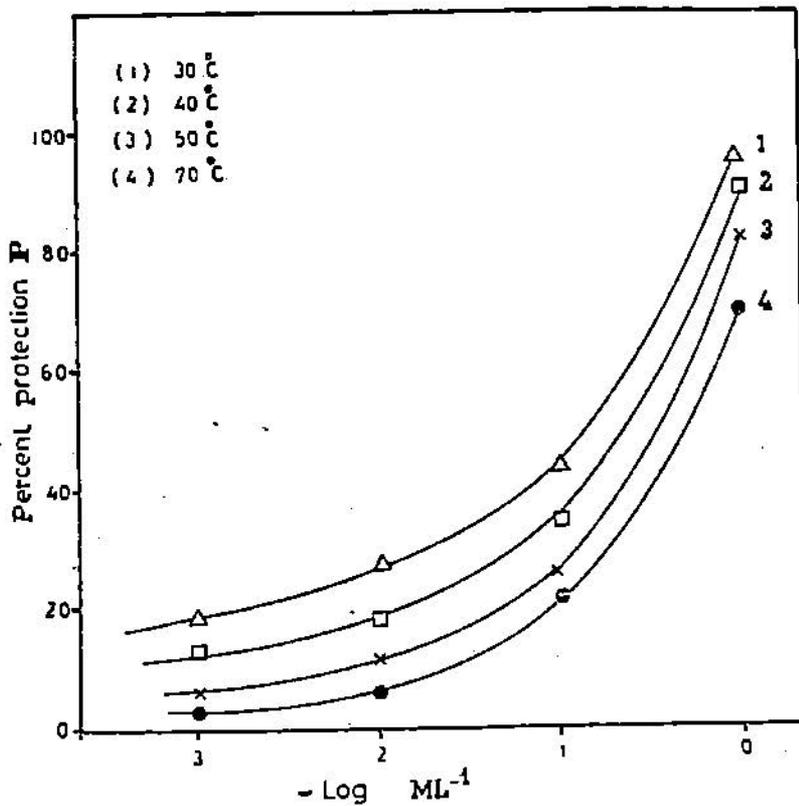


Fig (1): Effect of the concentration of Na_2MoO_4 on the protection efficiency of Cd in 1M HCl at various temperatures.

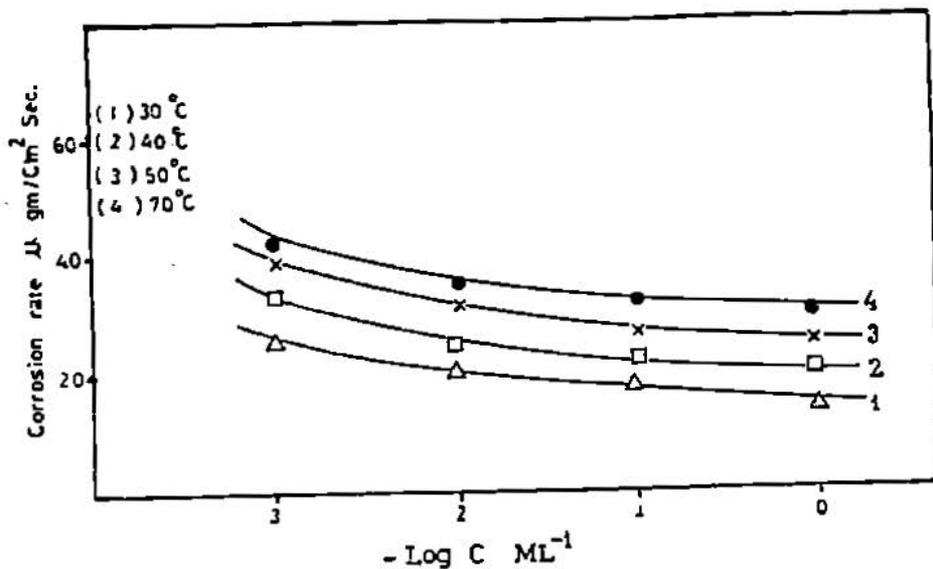
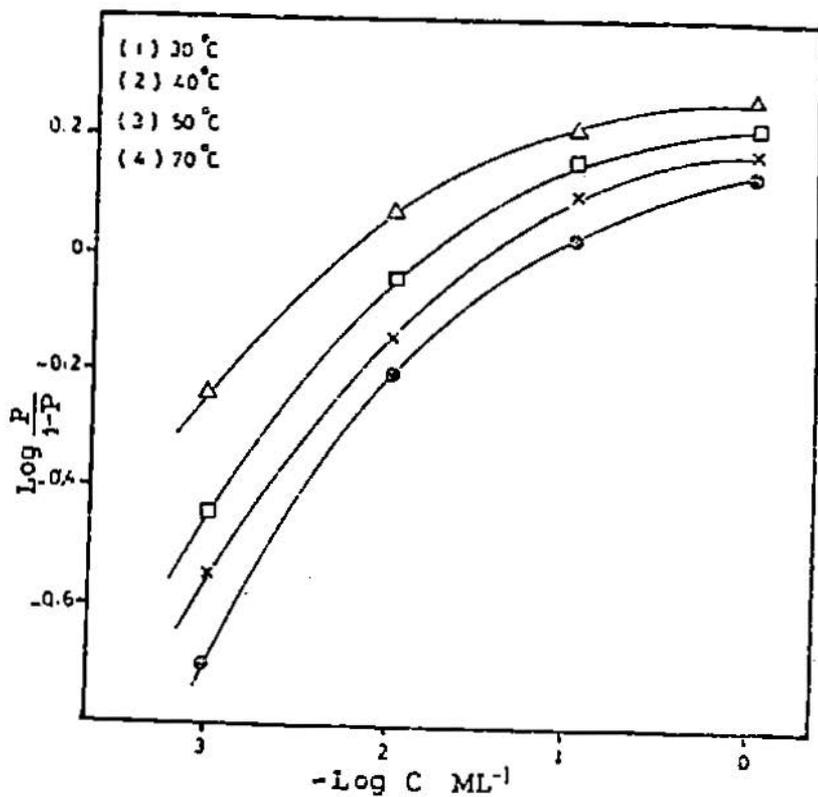


Fig (2): Effect of the concentration of MoO_4^{-2} on the corrosion rate of Cd. in 1M HCl at various temperatures.



Fig(3) Plot of $\log \frac{P}{(1-P)}$ vs. Log concentration of MoO_4^{-2} on the corrosion rate of Cd in 1M HCl at various temperatures.

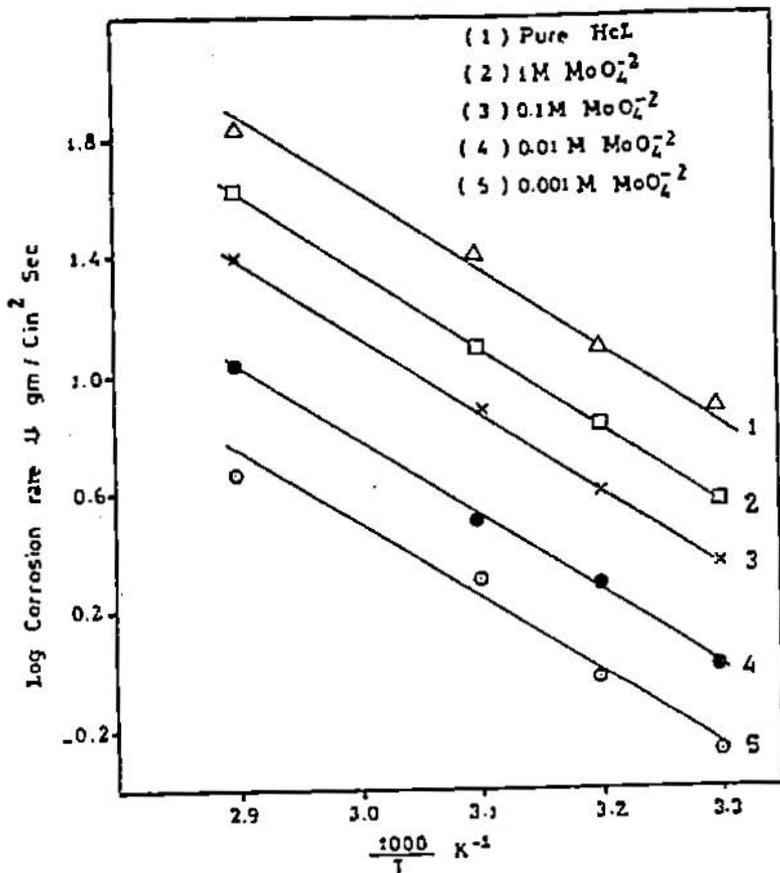
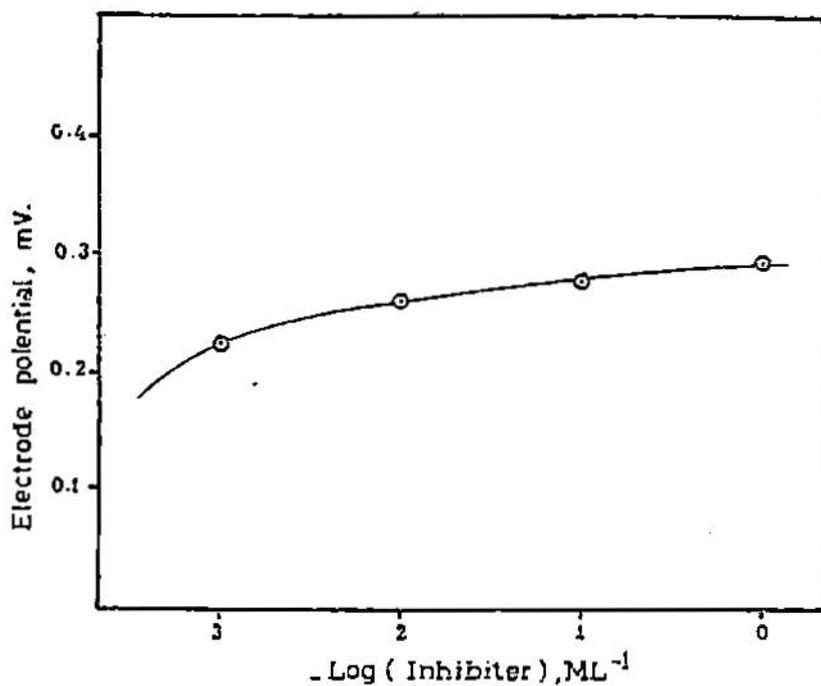


Fig (4) : Arrhenius plot of the corrosion rate of Cd in 1M HCl in absence and presence of MoO_4^{2-} .



Fig(5) : Effect of the concentration of MoO_4^{-2} on the potential curve for Cd in 1M HCl at room temperature.