

“TRIARYL AND TRIALKYL PHOSPHITES AS CORROSION INHIBITORS FOR COPPER IN NITRIC ACID”

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ثلاثي آريل وثلاثي الكيل الفوسفات كمتبطات لتآكل النحاس في حمض النتريك

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تم دراسة تأثير بعض ثلاثي آريل وثلاثي الكيل الفوسفات كموانع لتآكل النحاس في محلول ٣ ع حمض نتريك ، وذلك بالطريقة الجلفانوستاتيكية وطريقة فقد الوزن ، كلتا الطريقتين أعطت نتائج متماثلة . وقد دلت النتائج على أن هذه المواد تعمل خلال الادمصاص الكيميائي تابعة أيزوثرم لانجمير ، وأن هذه المواد تثبط كلاً من التفاعل المهبطي والمصعدي . وقد حسبت ونوقشت بعض الدوال الترموديناميكية مثل طاقة التنشيط ، المحتوى الحراري للتنشيط ، وانتروبية التنشيط والطاقة الحرة للتنشيط ، وقد وجد أن طاقة التنشيط تزداد بوجود الموانع وأيضاً بزيادة تركيزات هذه الموانع . ودلت نتائج التغير في الطاقة الحرة للتنشيط أن عملية التآكل هذه عملية تلقائية .

Key Words: Copper, Inhibitors, Triaryl and Trialkyl phosphites.

ABSTRACT

Some triaryl and trialkyl phosphites were investigated as inhibitors of the corrosion of copper in nitric acid. The values of inhibitor efficiency from weight-loss measurements are in good agreement with those obtained from polarization studies. Potential and polarization data indicate that the action of all compounds used are of a mixed type, they hinder both anodic and cathodic reactions. The inhibitors appear to function through general adsorption following the Langmuir adsorption isotherm.

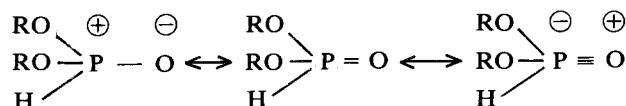
The effect of temperature on the rate of corrosion with and without inhibitors was studied using weight-loss techniques. Some thermodynamic functions were also computed.

INTRODUCTION

Copper is extensively used in various industrial operations and the study of its corrosion inhibition is of great importance. Most investigations on the corrosion of copper have been carried out on etched surfaces which may not give steady corrosion rates. Oxygen-and nitrogen-containing organic compounds have been tried as corrosion inhibitors for metals (Patel *et al*, 1973, Abd El Wahab *et al*, 1985, Desai *et al*, 1973 and Patel *et al*, 1975).

Dus 1967, reported that phosphorous compounds usually used as filming inhibitors, they adsorbed on metal surfaces through their polar group or head and the non polar tail of the compound may be vertically oriented to the metal surface.

Most of phosphorous compounds (Vogel, 1978) change into diphosphite ($\begin{matrix} H \\ \diagdown \\ O \end{matrix} P \begin{matrix} OR' \\ \diagup \\ OR' \end{matrix}$) in an acid medium and can be represented as resonance hybride (Cotton, *et al*, 1962) as follows:

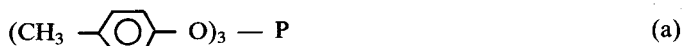


This representation shows that the polar group or head is $\gg P = O$ and the tail is the aryl or alkyl groups.

EXPERIMENTAL

The corrosion inhibitors used were:

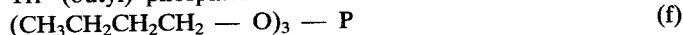
Tri- (4-tolyl) phosphite



Tri- (phenyl) phosphite



Tri- (butyl) phosphite



Tri- (propyl) phosphite
 $(\text{CH}_3\text{CH}_2\text{CH}_2 - \text{O})_3 - \text{P}$ (d)

Tri- (isopropyl) phosphite
 $(\text{CH}_3)_2\text{CH} - \text{O})_3 - \text{P}$ (e)

Tri- (ethyl) phosphite
 $(\text{CH}_3\text{CH}_2 - \text{O})_3 - \text{P}$ (c)

Chemicals used were of analytical grade. The solutions were made from freshly prepared twice distilled water. All the experiments were carried out under stirred and aerated conditions at $25 \pm 1^\circ\text{C}$. Copper in the form of wire (99.7%) in the case of polarization measurements, was fixed in glass tubing, such that only a surface area of 0.3 cm^2 was exposed to the corrosive medium. The copper surface was mechanically polished on 4/0 emery paper using ethanol as lubricant. The polished surface was thoroughly washed with triple distilled water and then introduced into the corrosive medium. Copper coupons of $20 \times 20 \times 1 \text{ mm}$ were used in the weight-loss method. The results obtained over experiments in the inhibited and uninhibited acid, gave corrosion rates which were reproducible to within 5%.

For polarization measurements, a saturated calomel electrode and a platinum wire were used as reference and auxiliary electrodes, respectively. Currents from constant current device measured with a multimeter with an accuracy of $\pm 4\%$. Corrosion potentials were recorded using a digital Ionalyzer device (Orion model 701A). The potential at any given current under similar experimental conditions was reproducible within 7%.

The detailed experimental procedure has been given elsewhere (Gatos, 1956).

RESULTS AND DISCUSSION

Anodic and cathodic polarization of copper was carried out under galvanostatic conditions in 3M nitric acid with and without different concentrations of inhibitors at 298°K . At all current densities during polarization of time. Fig. 1 shows the results of

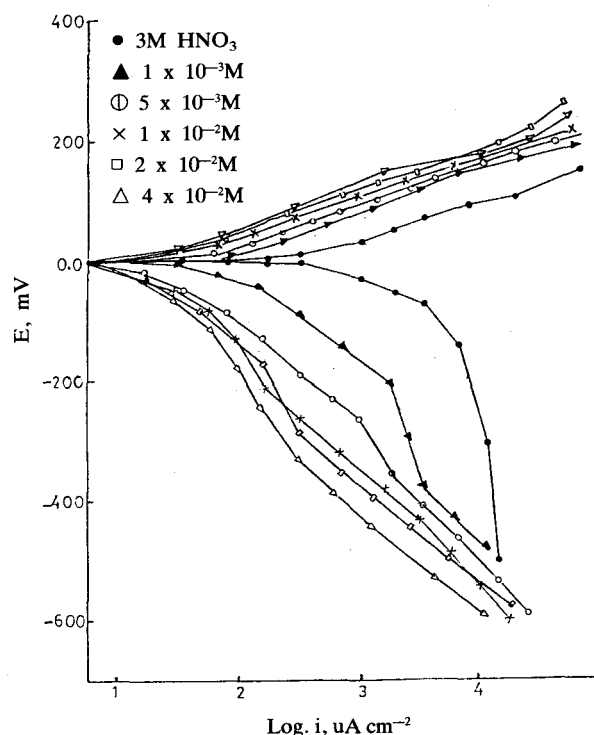


Fig. 1: Galvanostatic polarization curves of copper in 3M HNO_3 alone and containing different concentrations of compound (a).

anodic and cathodic polarization measurements on copper in 3M nitric acid containing different concentrations of inhibitor (a) [Tri- (4-tolyl) phosphite]. The results obtained for the other inhibitors were quite similar.

Table 1 shows the effect of inhibitor (a) concentration on: the free corrosion potential (E_{corr}), Tafel slopes (β_a and β_c), corrosion current (I_{corr}), percent reduction in I_{corr} and the degree of surface coverage (θ).

The corrosion current densities were determined by extrapolating anodic and cathodic Tafel lines to free corrosion potential values.

Table 1

The effect of inhibitor (a) concentration on the free corrosion potential, Tafel slopes, corrosion current density, reduction in I_{corr} and surface coverage for anodic and cathodic polarization of copper in 3M nitric acid at 298°K .

Concentration M/L	$-E_{\text{corr}}$ mV	β_c mV/current decade	β_a mV/current decade	I_{corr} $\mu\text{A}/\text{cm}^2$	% reduction in I_{corr}	θ
0.0	0.00	70	80	375.8	---	---
1×10^{-3}	15.0	65	83	113.5	69.8	0.698
5×10^{-3}	15.0	70	80	29.9	92.0	0.920
1×10^{-2}	20	75	75	21.1	94.4	0.944
2×10^{-2}	25	75	74	15.0	96.0	0.960
4×10^{-2}	25	80	73	6.9	98.2	0.982

The inhibition efficiency (P_I) was calculated from the following relationship:

$$\% P_I = \frac{I_{\text{corr., pure}} - I_{\text{corr., add.}}}{I_{\text{corr., pure}}} \times 100 \quad (1)$$

At an inhibitor concentrations ($4 \times 10^{-2} - 1 \times 10^{-3}M$), the inhibition efficiencies of various inhibitors, increase in the order:

$$a > b > f > d > c > e.$$

Recently, the nature of inhibitor interaction on the corroding surface during corrosion inhibition of metals and alloys has been deduced in terms of adsorption characteristics (Rudresh *et al*, 1977, Dinnappa *et al*, 1982) of the inhibitor. The surface coverage (θ) data are very useful while discussing the adsorption characteristics. The degree of surface coverage (θ) of each inhibitor at a given concentration is evaluated from the following expression:

$$\frac{i}{i_0} = 1 - \theta \quad (2)$$

where i and i_0 are the corrosion current densities (corrosion rates) in the presence and in the absence of the inhibitor, respectively. The plot of $\log \theta/1 - \theta$ vs. $\log C$ (inhibitor concentration) Fig. 2 gives a straight lines which are in good agreement with the following relation:

$$\log C = \log \frac{\theta}{1 - \theta} - \log A \quad (3)$$

The nature of this adsorption process as being either a physical or chemical process may elucidated from the magnitude of the heat of adsorption, Q . The latter was estimated by the relation:

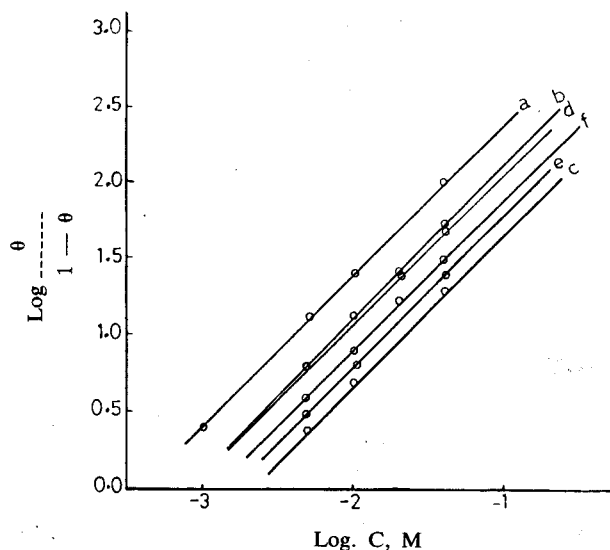


Fig. 2: $\log \frac{\theta}{1 - \theta}$ vs. $\log C$ curves for all the additives.

$$\left[\frac{d \log C}{d (1/T)} \right] = - \frac{Q}{2.303R} \quad (4)$$

which has been found to be 3.4 — 4.2 Kcal/mole. deg. These values of Q lie in the range which characterizing physical adsorption. So, the adsorption of the additives on the surface of copper is likely to be of a physical nature, i.e. the adsorption process occurs along a specific centre of the inhibitor. From the results of Table 2 it may be generalized that the more efficient inhibitor the less value of Q it has and vice versa.

Table 2

Thermodynamic parameters for adsorption of inhibitors on to copper surface in 3M nitric acid containing $4 \times 10^{-2}M$ inhibitors.

Inhibitors	E Kcal/mol	$\Delta G^{\circ}_{\text{ads.}}$ Kcal/mol	$\Delta S^{\circ}_{\text{ads.}}$ Cal/K.mol.	Q Kcal/m	Slope of $d \log C/d (1/T)$
Free acid	4.61	---	---	---	---
e	12.9	5.7	27.5	4.2	0.90
c	14.3	5.8	20.0	3.9	0.85
f	17.1	6.2	15.0	3.7	0.80
d	16.0	5.9	17.5	3.8	0.82
b	18.2	6.3	10.0	3.6	0.78
a	19.1	6.9	5.0	3.4	0.74

Equation 3 shows that the adsorption of these compounds follow the Langmuir adsorption isotherm.

Fig. 3 shows the effect of the period of immersion on the corrosion of copper in presence and in the absence of different concentrations of compound (a). The curves are characterized by an initial slow rise in weight-loss followed by a sharp rise. The curves obtained in presence of additives fu! below that of the free acid. The weight-loss of copper depends upon the type and

the concentration of the additive in the same way as the polarization does.

The inhibition effect of this additive was determined by the relation:

$$P_w = \frac{(\text{Wt. loss})_{\text{pure}} - (\text{Wt. loss})_{\text{add.}}}{(\text{Wt. loss})_{\text{pure}}} \times 100 \quad (5)$$

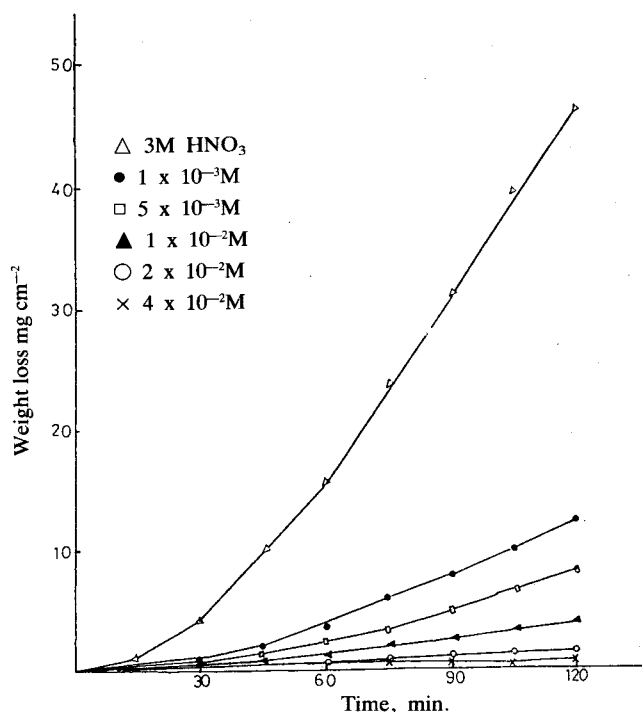


Fig. 3: Weight loss — time curves for compound (a) in 3M HNO₃.

where the change in weight was calculated per cm² per minute.

The effect of temperature on the dissolution of copper in the presence and in the absence of additives by the weight-loss technique has been studied. Fig. 4 shows the Arrhenius plots [log

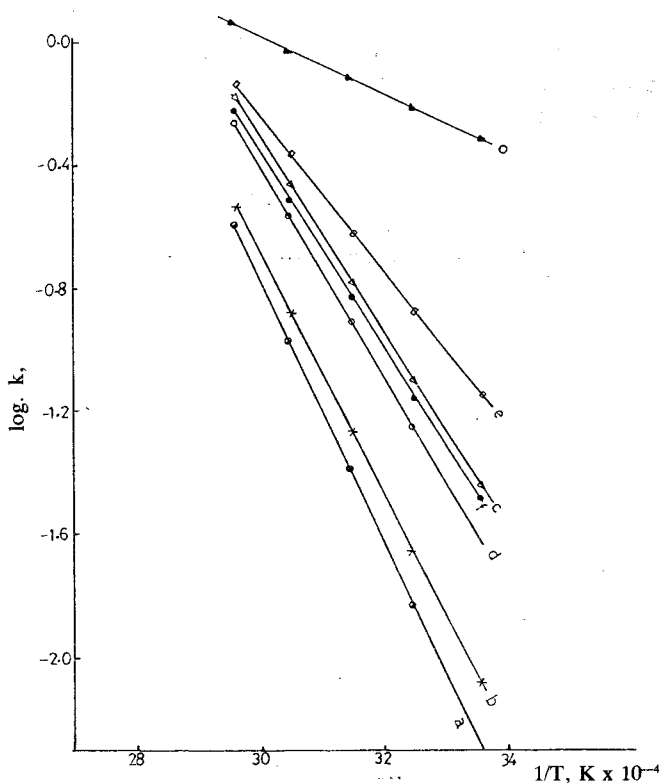


Fig. 4: Log. *k* vs. $1/T$ curves for copper dissolution in 3M HNO₃ in presence and in absence of 4×10^{-2} M additives.

k (corrosion rate) vs. $1/T$ (absolute temperature)] for different additives at 4×10^{-2} M). The plots are rectilinear and the activation energies from the slopes of the curves are calculated. The Arrhenius activation energy values, *E*, obtained from the slopes of log *k* vs. $1/T$ are presented in Table 2. These values increase with increasing inhibition efficiency of the additives and suggest that the process is activation controlled.

The values of free energy of adsorption $\Delta G^{\circ}_{ads.}$, are given in Table 2 at 298 °K. The results show that compound (a) which gives maximum efficiency shows more negative free energy of adsorption including that it is strongly adsorbed on the metal surface. The negative values of $\Delta G^{\circ}_{ads.}$, indicate the spontaneous adsorption of the additives on the copper surface.

The entropy of adsorption, $\Delta S^{\circ}_{ads.}$, was evaluated (Mayanna, 1977) from the relation between $\Delta G^{\circ}_{ads.}$, and *T* Fig. 5 and its values are recorded in Table 2.

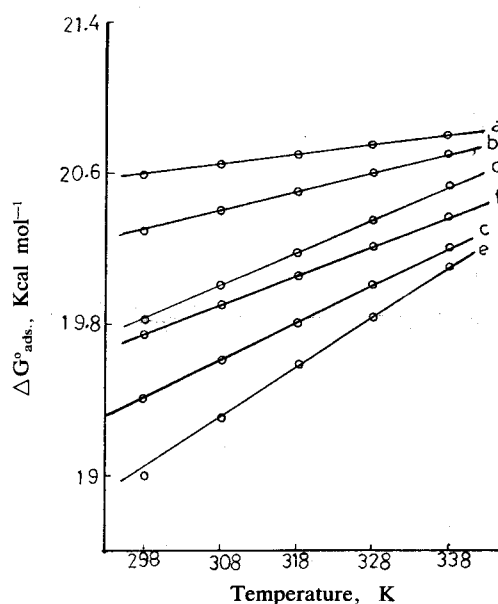


Fig. 5: Relation between $\Delta G^{\circ}_{ads.}$ and temperature for different triaryl and trialkyl phosphites.

One could expect the degree of adsorption by these inhibitors on copper to be in the order:

$$a > b > f > d > c > e.$$

This is also in agreement with the observed order of corrosion inhibition Table 3.

The inhibition efficiency depends on many factors including number of adsorption sites or functional group, basicity and molecular size. In the present case the >P=O group is the probable center of adsorption and this center like the keto group (>C=O) in shape but this type of centers (>P=O) are probably adsorbed on the surface of metal via oxygen and phosphorus atoms according to the type of resonance (Cotton *et al*, 1962). The basicity of >P=O group may be affected by the polar character and the branching of the substituents in the α -position. The order of the effect of electron release is:

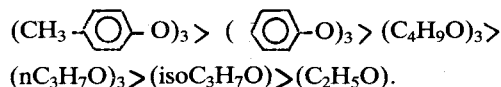


Table 3

Comparison between efficiency of corrosion inhibition as determined by polarization and weight loss at $4 \times 10^{-2}M$ 298 °K.

Inhibitor	% inhibition from:	
	Polarization	Weight loss
a	99.1	99.1
b	98.2	98.2
f	97.5	96.5
d	97.0	92.4
c	96.3	84.8
e	96.0	81.0

This order runs parallel to the order of inhibition efficiency. Inhibitor (b) comes after inhibitor (a) in inhibiting the corrosion of copper. This is due to the presence of CH_3- group in (a) which increases its molecular size and its basicity. Inhibitor (f) comes after inhibitor (b) in the inhibiting efficiency, this due to that phenyl group (tail covers larger area than aliphatic one).

Inhibitors (f), (d), (c) and (e) occupied these places in the order of inhibition efficiency according to the length of the aliphatic chain (tail), since the inhibition efficiency decreases with decrease of aliphatic chain length, one see that inhibitor (c) comes before inhibitor (e) inspite of them having the same number of alkyl groups. This may be due to the steric hindrance in the branched inhibitor (e).

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