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Corrosion inhibition of copper in near neutral aqueous solutions by gamma-pyrodiphenone

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The inhibition effect of gamma-pyrodiphenone (γPD) on copper corrosion in near neutral sulphate solutions was investigated. Weight loss and polarization measurements show a high inhibition efficiency ($>96\%$) of γPD on copper corrosion at extremely low concentrations. γPD suppresses active copper dissolution and oxygen reduction. The potentiodynamic cathodic reduction measurements showed an inhibition of oxide formation and stabilization of the Cu_2O oxide in the presence of γPD. XPS measurements suggested that the high inhibition effect of γPD on copper corrosion is due to the adsorption of γPD molecules, as a first stage, and the formation of a film with a polymer-like structure by coordination of γPD with Cu_2O on prolonged exposure.

Keywords: *copper corrosion inhibition*, *gamma-pyrodiphenone*, *XPS*

1. Introduction

The efficiency of organic azoles (benzotriazole, tolyltriazole, mercaptobenzothiazole) as corrosion inhibitors for copper is well established [1–5]. The inhibiting action of these compounds in neutral solutions has been attributed to the formation of a polymeric film on the metal surface. Recently, some other classes of organic compounds have been tested as potential inhibitors of copper corrosion [6–11] inparticular. Heterocyclic compounds containing N, S, O donor atoms have been found to be useful.

Our previous studies [12] have shown that gamma-pyrodiphenone provides a strong inhibiting effect on copper corrosion in a simulated cooling water. The molecular structures of the γ-pyrodiphenone are presented in Fig. 1. Tautomeric equilibrium exists between the enolic form (A) and the zwiter-ion structure (B). The delocalization of the π-electron system in the molecule has been observed together with rotation of the pyridil ring. The presence of three donor atoms, and the steric conformation of the molecule determine the chemical properties and adsorption of γ-pyrodiphenone on the copper surface [13].

The aim of the present work is to study the mechanism of inhibition of γ-pyrodiphenone on the corrosion of copper in near neutral aqueous solutions. Sodium sulphate solution (pH 5.6) was chosen because of the effect of sulphate-ions on anodic copper dissolution [14, 15]. Electrochemical measurements and XPS analyses were combined to characterize the nature and structure of the inhibitor layer.

2. Experimental details

The inhibitor 6-(γ-pyridil)6,7-dihydro-5H-dibenzo[a,b] cyclo-heptendion-5,7, called γ-pyro-diphenone (γPD), was synthesized and purified using the method described in [16]. The concentration of the inhibitor was varied from 0.5 to 10 mg dm^{-3}. The electrolyte was 0.1 M Na_2SO_4 (pH 5.6) prepared with Fluka grade reagent and redistilled water. All measurements were carried out at 25 °C.

Weight loss measurements were conducted with samples of electrolytic copper (99.9%) 10 day tests as described earlier [12]. The electrochemical experiments were carried out in a conventional three-electrode cell with a platinum counter electrode and a saturated calomel electrode (SCE) as reference. The working electrode of spectrally pure copper with an area of 0.2 cm^2 was fixed to the holder by epoxy resin. The electrode surface was polished mechanically with abrasive paper to N : 1200, degreased with acetone and washed thoroughly with bidistilled water. Anodic and cathodic polarization curves were

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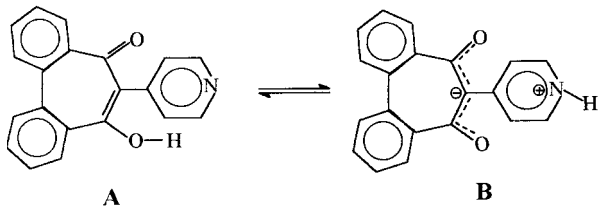

Fig. 1. Molecular structure of γ-pyrodiphenone.

recorded starting from E_{corr} at a sweep rate of $1\,mV\,s^{-1}$.

The surface composition was analysed using Microlab VG Scientific equipment with MgK_α exciting radiation (1253.6 eV) and a hemispherical analyser for secondary electron registration. The binding energy was calibrated with respect to the C1s spectral line at 285.0 eV. The base pressure in the spectrometer chamber was maintained at 10^{-9} torr during the measurements. Peak deconvolution was carried out using a routine peak-fitting technique similar to that described in [17]. Surface elemental stoichiometries were calculated from peak area ratios and experimentally calibrated sensitivity factors. Details concerning the XPS analysis of the copper surface are provided elsewhere [18].

3. Results and discussion

3.1. *Weight loss measurements*

Weight loss measurements were carried out to evaluate the inhibition efficiency of γPD at different concentrations. After the corrosion tests in 0.1 M Na_2SO_4 with addition of γPD the copper surface remained bright. The inhibition efficiency increased with increase in γPD concentration and an excellent inhibiting effect IE_{wl} (protection factor 99.6%) was achieved at a concentration of $5\,mg\,dm^{-3}$.

3.2. *Polarization behaviour*

The effect of γPD on the partial corrosion reactions was determined by polarization measurements. The current-potential curves of copper in aerated sulphate solution with and without inhibitor after 1 h of immersion are presented in Fig. 2. In near neutral, aerated solution the predominant cathodic reaction is oxygen reduction. Rapid copper dissolution is noticed on the anodic side. The obtained anodic Tafel slope of $40\,mV\,decade^{-1}$ corresponds to a dissolution mechanism involving two consecutive one electron charge transfer steps. The same anodic mechanism has been shown to exist in acidic solutions [19]. With the addition of γPD the cathodic, as well as the anodic, processes were effectively inhibited. The corrosion potential shifted slightly in the positive direction as the γPD concentration increases. The anodic Tafel slope does not change at inhibitor concentrations up to $4\,mg\,dm^{-3}$, which indicates that at these concentrations γPD suppresses the dissolution of copper

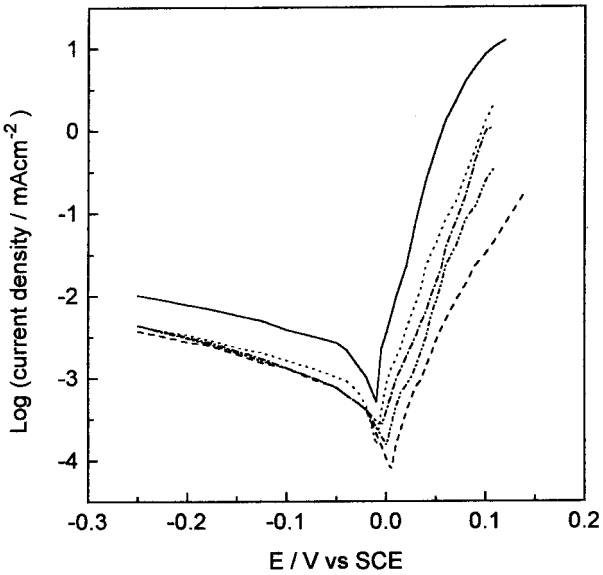

Fig. 2. Current–potential curves of copper in 0.1 M Na_2SO_4 solution after 1 h exposure at E_{corr} (——) and in the presence of different concentrations of γPD: (·····) 1, (–·–·–) 2, (–··–··–) 3, and (– – –) $5\,mg\,dm^{-3}$.

without changing the mechanism of the process. An increase in the anodic Tafel slope to $45\,mV\,decade^{-1}$ is observed at concentration of $5\,mg\,dm^{-3}$. The values of the inhibition efficiency, $IE(\%)$ were determined by $IE_p = (1 - i_o/i_i) \times 100$, where i_o and i_i are the corrosion current densities without and with addition of inhibitor, determined by extrapolation of anodic Tafel lines to the corrosion potential E_{corr}. The obtained values of IE_p were compared with those obtained by the weight loss measurements (Table 1). The $IE(\%)$ values determined by the two methods are in reasonably good agreement. Maximum protection is obtained at $5\,mg\,dm^{-3}$ γPD. The results obtained indicate the predominant effect of the γPD on the anodic dissolution of copper.

After 24 h immersion of the copper electrode in 0.1 M Na_2SO_4 (Fig. 3) the cathodic process is suppressed to some extent, but the rate of active copper dissolution does not change. This indicates that the oxide layer formed on the copper acts as a barrier to oxygen diffusion and does not inhibit the copper dissolution. In the presence of $5\,mg\,dm^{-3}$ γPD a decrease in the cathodic, as well as the anodic, current densities is observed. The anodic Tafel slope increases to $60\,mV\,decade^{-1}$ in the presence of $5\,mg\,dm^{-3}$ γPD. This is most probably due to improvement in the protective properties of the inhibiting film.

Table 1. Inhibition efficiency determined from weight loss measurements (IE_{wl}) and from polarization measurements (IE_p)

γPD concentration / mg dm^{-3}	IE_{wl} / %	IE_p / %
1	24.5	84.9
2	83.2	90.9
3	94.2	95.2
4	96.9	95.4
5	96.9	95.8

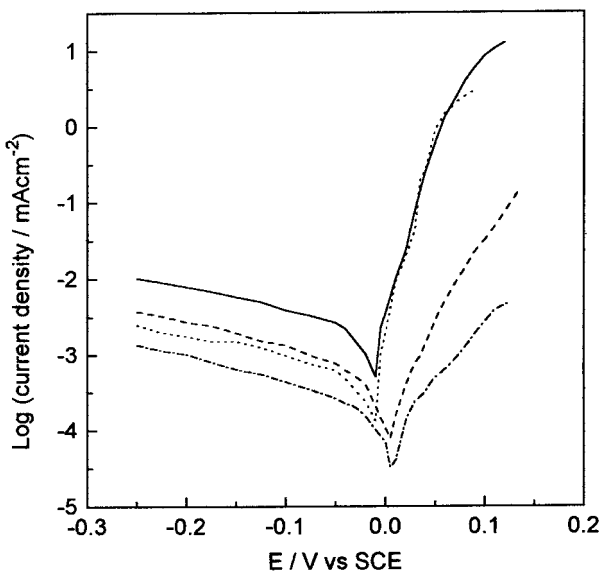

Fig. 3. Current–potential curves of copper in 0.1 M Na_2SO_4 solution (——) and in the presence of 5 mg dm^{-3} γPD (– – –) after 1 h exposure at E_{corr}; after 24 h exposure at E_{corr} in 0.1 M Na_2SO_4 solution (·····) and in the presence of 5 mg dm^{-3} γPD (–·–·–).

From a practical point of view it is important for an inhibitor to suppress the formation of the oxide layer on the copper surface. The formation of the copper(I) oxide in near neutral solution may be due either to precipitation of Cu_2O from solution or direct oxidation of copper [20]. The solid-state formation of Cu_2O is likely as the cathodic reaction of oxygen reduction will result in an increased pH at the copper surface. The effect of γPD on the initial stage of oxide formation was studied by potentiodynamic cathodic reduction (scan rate 10 mV s^{-1}) after different exposure times in solution at open-circuit potential.

The reduction curves of the layers formed on copper at rest potential after 1 h and 24 h exposure in 0.1 M sulphate solution are presented in Fig. 4. The reduction of copper species overlaps with oxygen reduction, which is the dominant cathodic corrosion reaction. After 1 h of exposure in inhibitor-free solution two peaks Ic at −0.710 V and IIc at −0.900 V appear on the reduction curves. The peak Ic is a result of the reduction of the native oxide layer [20] and the electrodeposition of soluble copper(II) species produced at open-circuit potential. The amount of charge passed in the reduction of peak Ic increases slightly with time and the peak potential shifts in the negative direction. The second reduction peak at −0.900 V is characteristic of reduction of Cu_2O. The peak appears after 15 min of immersion. After 1 h of immersion the charge consumed for reduction of the Cu_2O film is 3 mC cm^{-2}, corresponding to an average thickness of 8 nm. The charge associated with this peak increases with time, which indicates oxide layer growth. After 24 h only one main reduction peak is found at −1.000 V with a small hump at −0.700 V. The thickness of the Cu_2O layer is calculated to be 240 nm.

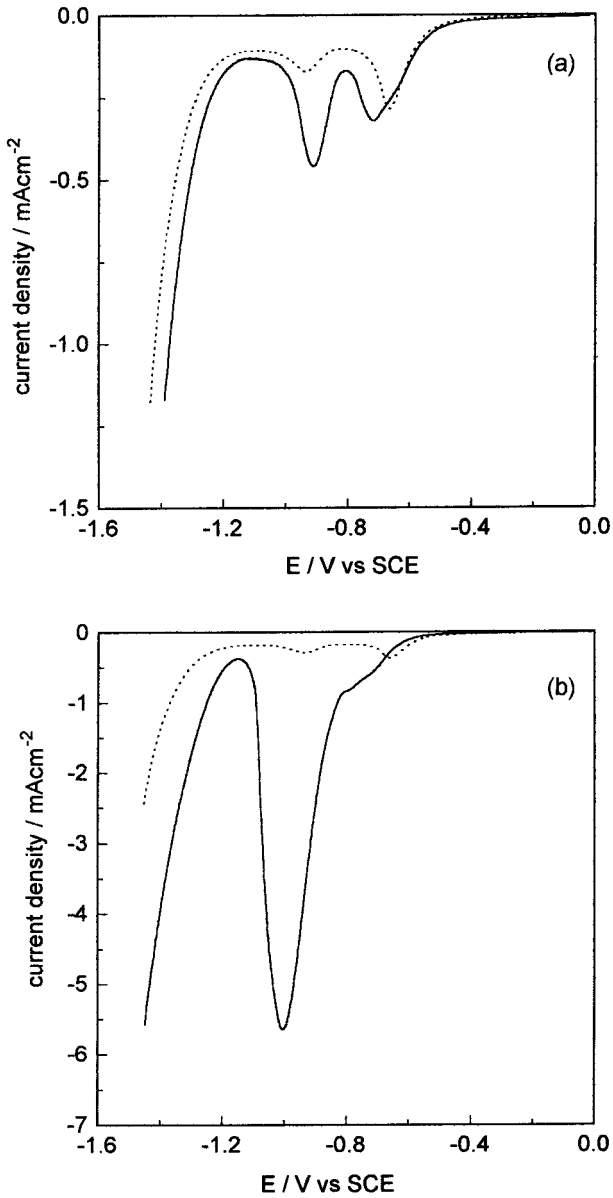

Fig. 4. (a) Potentiodynamic reduction curves of copper after 1 h exposure in 0.1 M Na_2SO_4 solution (—) and in the presence of 5 mg dm^{-3} γPD (·····). (b) after 24 h exposure.

In the presence of 5 mg dm^{-3} γPD after 1 h at rest potential two peaks appear on the reduction curves. The peak Ic at −0.670 V is presumably due only to the reduction of the native oxide layer on copper as γPD inhibits the formation of soluble copper(II) species. The position of peak IIc is shifted in the negative direction and the charge consumed for reduction of Cu_2O decreases markedly. The amount of charge for reduction of peak IIc (0.7 mC cm^{-2}) does not increase after 24 h exposure (Fig. 4(b)). This indicates the inhibition of oxide formation and stabilization of the Cu_2O oxide in the presence of γPD.

3.3. *Characterization of surface by XPS measurements*

The XPS spectrum of pure γPD powder samples was obtained. The C1s line had a broad profile with several components, as expected due to the different electronic surroundings of carbon atoms in the γPD

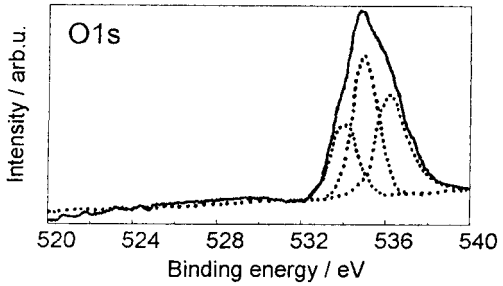

Fig. 5. O1s Photoelectron spectrum of γPD powder sample.

molecule. A narrow N1s peak was observed. Peak deconvolution of the O1s line revealed three types of bonded oxygen (Fig. 5) due to the formation of dimers between γPD molecules.

The XPS spectra of the copper surface were obtained after 1 h exposure of samples to 0.1 M Na_2SO_4 solution with different γPD concentrations. The main interest lies in the detailed C1s, O1s, N1s and $Cu2p_{3/2}$ spectra which indicate adsorption of the inhibitor. The binding energies of the O1s, N1s and C1s lines of the inhibitor film on copper coincide with the binding energies of the γPD powder sample after correction of the charging effects (ΔE_{ch} = 1.6 eV). This is indicative of adsorption of γPD molecules on the copper surface. The N1s signal did not appear at concentration 1 and 2 mg dm^{-3}. Probably, at lower concentration, the γPD molecule is adsorbed on the copper surface through the nitrogen atom and, because of the large size of benzene rings, the N1s line is not registered.

The detailed spectra of the O1s lines obtained at different concentrations of γPD are presented in Fig. 6. The peak deconvolution of the O1s line gives contribution of four oxygen species with binding energies of 530.9, 532.2, 533.1 and 534.4 eV, respectively. According to literature data [16, 19], the oxygen species with binding energy 530.9 eV can be assigned to Cu_2O. The other oxygen species correspond to the three types of oxygen atoms in the γPD molecule. The oxygen at 533.1 eV may be due both to the oxygen atom from the γPD molecule or oxygen from the adsorbed water, the two types of oxygen being indistinguishable because of the small chemical shift. The contribution of the various types of oxygen to the overall O1s peak as a function of inhibitor concentration is given in Table 2. A considerable change in composition of O1s peak is observed at a γPD concentration of 3 mg dm^{-3}. At this concentration the calculated values of the atomic ratios O/Cu and C/Cu have a maximum (Table 3). These results provide evidence for a change in the thickness and structure of the inhibitor film at concentrations above 3 mg dm^{-3} due to the different orientation of the adsorbed molecule on the surface. Indeed, at concentrations above 3 mg dm^{-3}, a two-dimensional condensation in the adsorbed layer has been determined via the capacity measurements [13].

The XPS analysis of a copper surface after 24 h exposure to a solution containing 5 mg dm^{-3} of γPD

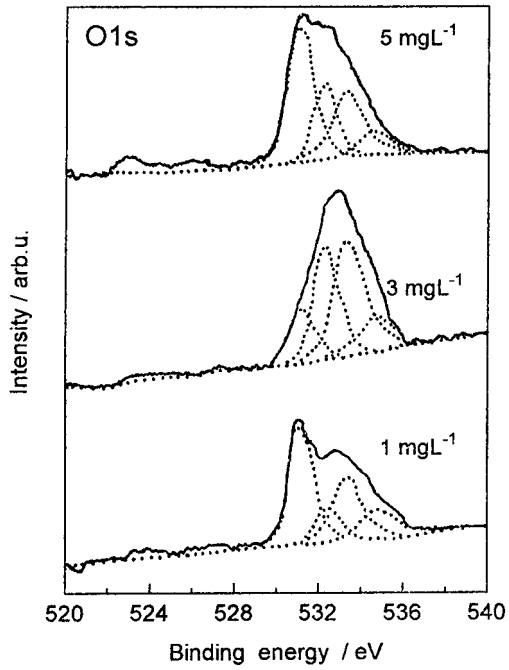

Fig. 6. O1s Photoelectron spectra of copper after 1 h exposure to solutions with different γPD concentrations.

Table 2. Contribution of subpeaks to overall O1s peak at different γPD concentrations

γPD concentration / mg dm^{-3}	$O_{530.9\ eV}$ / %	Subpeak contribution		
		$O_{533.1\ eV}$ / %	$O_{532.2\ eV}$ / %	$O_{534.4\ eV}$ / %
1	44	28	13	15
2	35	25	24	16
3	15	43	29	13
4	42	23	25	10
5	42	25	23	10

Table 3. Calculated O/Cu and C/Cu atom ratios at different γPD concentrations

γPD concentration / mg dm^{-3}	Atom ratios	
	O/Cu	C/Cu
1	1.50	5.71
2	3.22	12.33
3	5.60	31.2
4	2.11	8.73
5	1.57	6.05

shows insignificant changes in the relative amounts of the different oxygen species. However, a small shoulder appears on the $Cu2p_{3/2}$ line at higher binding energies (Fig. 7). Peak deconvolution indicates a contribution of two peaks at BE = 932.6 eV and BE = 934.1 eV, respectively. According to the literature [21] the appearance of a second peak at 934.1 eV arises from a coordination of Cu_2O with organic ligands. The steric conformation and the electron delocalization in the γPD molecule provide

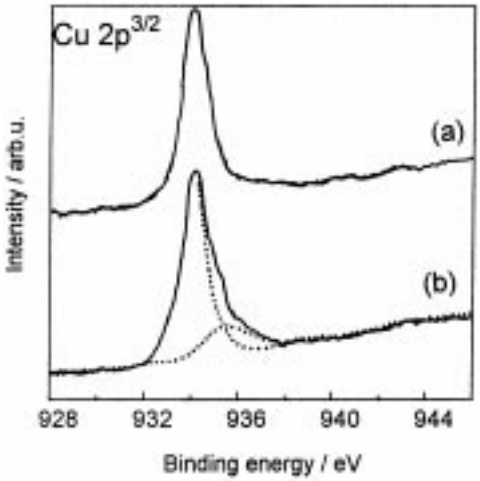

Fig. 7. (a) $Cu2p_{3/2}$ Photoelectron spectra of copper after 1 h exposure to 0.1 M Na_2SO_4 solution with 5 mg dm^{-3} γPD and (b) after 24 h exposure to 0.1 M Na_2SO_4 solution with 5 mg dm^{-3} γPD.

the possibility of coordination with Cu_2O. As a result the cuprous ion is stabilized against further oxidation [22] and the protective properties of the inhibiting film of γPD are improved.

4. Conclusions

The following conclusions can be drawn:

(i) γ-Pyrodiphenone showed a high inhibition efficiency towards copper corrosion in near neutral sulphate solutions at extremely low concentrations.
(ii) In the presence of γPD the cathodic, as well as the anodic, process was effectively inhibited.
(iii) The potentiodynamic cathodic reduction measurements indicated inhibition of oxide formation and stabilization of the Cu_2O oxide in the presence of γPD.
(iv) XPS measurements showed that the high inhibition effect of γPD on copper corrosion is due to the adsorption of γPD molecules, as a first stage, and the formation of a polimer-like film by coordination of γPD with Cu_2O on prolonged exposure.

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