EFFECT OF THE MOLECULAR STRUCTURE OF CYANINE DYE ON THE ELECTROCHEMICAL CORROSION BEHAVIOUR OF METALLIC COPPER IN NITRIC ACID SOLUTION*

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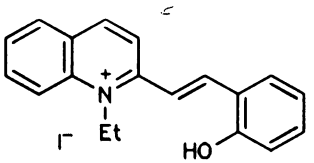
The effect of 2-(2-hydroxystyryl)quinolinium-1-ethyl iodide (*I*) and 4-(2-hydroxystyryl)quinolinium-1-ethyl iodide (*II*) cyanine dyes on the corrosion behaviour of copper metal in nitric acid solution has been studied. Weight loss measurement, galvanostatic polarization curves, open-circuit potential variation of copper electrode with time and the cathodic protective current values indicate that cyanine dye *I* gives a better anticorrosive effect than dye *II*. The inhibition effect in case of the two cyanine dyes is more pronounced in case of the addition of dye to the corrosion medium than that obtained in case of copper metal coated by dye thin film (previously treated in dye solutions) before immersion in corrosive medium.

The electrochemical corrosion behaviour of copper in acidic media was the subject of study by several authors[1 - 4]. Awad et al.[1] studied the corrosion rate and potentials of copper at 30 °C in aqueous solutions containing (0.001 – 1) M $NaNO_3$, NaCl, Na_2SO_4, Na_3PO_4 (as well as $K_2Cr_2O_7$) acidified with the corresponding acids. They found that the increase of acidity led to an increase in the corrosion rate of copper metal. The inhibition effect by heterocyclic compounds on the corrosion of copper metal has also been investigated[2], the electrochemical polarization studies and weight loss results showed that the presence of 3-phenyl-1,2, 4-triazol-5-thione and 2-amino-4,6-dimethylpyrimidine at lower concentrations gave a higher corrosion protection for copper. This behaviour is attributed to the formation of copper complex layer at the metal surface. Substituted anilines were used as a corrosion inhibitors for copper metal in nitric acid solution[3], the inhibition effect depends mainly on the nature of the substituted group and its position to the aromatic ring, as well as its concentration. It was suggested that these compounds act as cathodic inhibitors of the acid corrosion of copper, and the adsorption of amines on the metal surface play a significant role in the inhibition.

* Part II in the series: Cyanine Dyes as Corrosion Inhibitors; Part I: Chem. Tech. Biotechnol. *38*, 89 (1987).

In a previous communication we have shown that cyanine dye molecule namely 2-(2-hydroxystyryl)pyridinium-1-ethyl iodide inhibits the corrosion of copper metal in nitric acid solution[5]. The corrosion inhibition effect is more pronounced in case of copper metal coated by dye thin film than that obtained by its addition to the corrosion medium. In this paper, we aimed to study the effect of the molecular structure of the cyanine dye on the acid corrosion process of copper metal. This investigation throw some light on the effect on linkage position of the hydroxystyryl to the quaternary heterocyclic moiety, either at the 2-position (2-(2-hydroxystyryl)quinolinium-1-ethyl iodide (*I*)) or the 4-position (4-(2-hydroxystyryl)quinolinium-1-ethyl iodide (*II*)) and on the effect of the size of the dye molecule by inducing extra benzene ring to the pyridinium cation.



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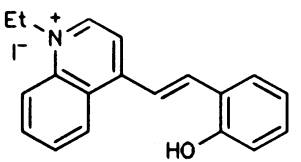

II

EXPERIMENTAL

Cyanine dyes *I* and *II* were prepared according to the method described before[6], and recrystallized from ethanol. Their purity was checked by TLC, elemental analysis and spectral data. The effect of the investigated cyanine dyes *I* and *II* on the electrochemical corrosion behaviour of copper metal (using special pure 99.9% electrolytic copper metal) in 2 M nitric acid solution was carried out in two ways: (i) Adding the dye compound to the corrosion medium in different concentrations ($10^{-5} - 2 . 10^{-3}$ mol dm^{-3}), and (ii) formation of a dye thin film at the copper metal surface (by treatment of the metal surface in aqueous dye solutions for suitable time intervals; afterwards the copper specimens are thoroughly washed with bidistilled water and dried) before their immersion in the corrosive medium.

Weight loss measurements. The effect of cyanine dyes on the corrosion process of copper metal, applying the above two ways, has been studied using weight loss technique[7]. Each experiment was carried out using 50 ml of the aerated corrosive solution and without stirring at 30 ± 0.1 °C. All corrosion tests were made in duplicate.

Polarization studies. Anodic galvanostatic polarization of copper electrodes, applying the above two ways, has been measured. The polarization cell used in this purpose has been described elsewhere[8]. Potentials were measured with a Muirhead D-972-A potentiometer using a saturated calomel reference electrode.

Potential–time relations. Open circuit potentials of copper electrodes as a function of time were followed up to examine the characteristics of potential–time curves under open circuit conditions in presence of the investigated cyanine dyes.

RESULTS AND DISCUSSION

Weight Loss Measurements

The effect of cyanine dyes concentrations added to the corrosion medium (2 M HNO_3) on the weight loss of copper specimens was investigated; the data obtained are recorded in Table I. It is shown that the higher the concentration of dye solution in corrosive medium the lower will be the loss in weight (i.e. the greater is the inhibition percentage). The inhibition effect of dye molecules may be attributed to their higher adsorbability on the copper surface[9], which inhibits the corrosion process by different values according to its concentration. It is clear that by increasing the immersion time in corrosive medium, the inhibition effect of cyanine dye molecules is decreased. The higher

TABLE I
Effect of cyanine dye concentration c on the weight loss of copper metal in 2 M nitric acid solution

c, mol dm^{-3}	Weight loss[a], mg dm^{-2}					
	45 min		120 min		240 min	
	I	*II*	*I*	*II*	*I*	*II*
$2 . 10^{-3}$	244 (71)	305 (63)	785 (38)	844 (33)	1 915 (31)	2 040 (27)
$1 . 10^{-3}$	262 (69)	320 (62)	840 (34)	892 (29)	2 440 (13)	2 115 (25)
$5 . 10^{-4}$	314 (63)	365 (57)	898 (29)	965 (23)	2 616 (7)	2 190 (22)
$1 . 10^{-4}$	371 (56)	408 (51)	1 040 (18)	1 120 (11)	2 823 (–)	2 442 (7)
$5 . 10^{-5}$	640 (25)	682 (19)	1 405 (–)	1 195 (5.0)	3 110 (–)	2 616 (13)
$1 . 10^{-5}$	767 (10)	865 (–)	1 462 (–)	1 293 (–)	3 315 (–)	2 893 (–)
0.0	851	844	1 270	1 262	2 810	2 820

[a] Values in parentheses indicate inhibition percentages.

and lower inhibition values for dye *I* are 71% and 31% after 45 and 240 min of immersion, respectively. This behaviour may be due to some desorption process to the dye molecules after a long time of immersion in the aggresive medium.

The treatment of copper metal surface, for a fixed time, at different concentrations of aqueous dye solutions before its immersion in the corrosive medium decreases the weight loss, as shown in Table II. This effect is attributed to the formation of a protective dye thin film which retards the attack of the corrosive nitric acid molecules on the copper metal surface. It is clear that the protection of the dye film depends on the concentration of the treatment solution. In the case of the two investigated dyes, the film formed in $2 \cdot 10^{-3}$ mol dm^{-3} dye resists the aggresiveness of the medium for a longer time (up to 24 min), while the film formed after treatment with lower concentra-

TABLE II
Effect of immersion time in 2 M nitric acid solution on the weight loss of copper metal previously treated at different cyanine dye concentrations c for 5 h

c, mol dm^{-3}	Weight loss[a], mg dm^{-2}					
	45 min		120 min		240 min	
	I	*II*	*I*	*II*	*I*	*II*
$2 \cdot 10^{-3}$	298 (65)	361 (57)	860 (33)	886 (30)	2 085 (26)	2 116 (25)
$1 \cdot 10^{-3}$	321 (62)	366 (56)	892 (31)	925 (27)	2 460 (13)	2 160 (23)
$5 \cdot 10^{-4}$	350 (59)	417 (50)	945 (27)	966 (24)	2 772 (–)	2 213 (22)
$1 \cdot 10^{-4}$	435 (49)	480 (43)	1 002 (22)	1 202 (5.0)	2 816 (–)	2 520 (11)
$5 \cdot 10^{-5}$	660 (23)	660 (21)	1 390 (–)	1 264 (–)	3 016 (–)	2 910 (–)
$1 \cdot 10^{-5}$	783 (8.0)	802 (4.0)	1 416 (–)	1 310 (–)	3 218 (–)	3 060 (–)
0.0	855	840	1 295	1 270	2 930	2 827

[a] Values in parentheses indicate inhibition percentages.

tion of dye solution ($5 \cdot 10^{-5}$ mol dm^{-3}) have a lower resistivity to the aggresiveness of medium up to 45 min. Generally the efficiency of the protective film depends mainly on the time of immersion in the corrosion medium.

The treatment time effect of dyes solution ($2 \cdot 10^{-3}$ mol dm^{-3}) on the weight loss of copper metal shows that the efficiency of the protective film is increased with time up to 10 h, then began to decrease. This behaviour may be attributed to the increase of the adsorbed dye molecules in the protective film up to 10 h as aggregates. Afterwards, re-orientation of the molecules to vertical ones takes place[10], leading to uncovered surface area, which facilitates the attack of the corrosive medium (cf. Table III).

The presence of $2 \cdot 10^{-3}$ mol dm^{-3} dye solution in the corrosive medium, gave an inhibition percentage slightly higher than that obtained by the pretreated metal at the

TABLE III
Effect of the treatment time t in cyanine dye solution ($2 \cdot 10^{-3}$ mol dm^{-3}) on the weight loss of copper metal in 2 M nitric acid solution

t, h	Weight loss[a], mg dm^{-2}					
	45 min		120 min		240 min	
	I	*II*	*I*	*II*	*I*	*II*
40	486	577	920	983	2 580	2 310
	(43)	(33)	(28)	(23)	(9.0)	(19)
25	417	499	890	860	2 510	2 160
	(51)	(42)	(30)	(33)	(11)	(24)
15	345	403	844	710	2 360	1 998
	(59)	(53)	(34)	(44)	(16)	(29)
10	277	301	760	800	2 009	1 870
	(67)	(65)	(40)	(37)	(29)	(34)
5	312	372	920	855	2 120	2 106
	(63)	(56)	(28)	(33)	(25)	(25)
1	540	630	1 120	920	2 875	2 275
	(36)	(27)	(12)	(28)	(–)	(20)
0.0	850	862	1 280	1 285	2 825	2 840

[a] Values in parentheses indicate inhibition percentages.

same concentration before immersion in the corrosive medium. This can be explained by the oxidation of liberated iodide ion from the dye molecules by nitric acid to iodine which hindered the corrosion process[11].

For application of these dyes as corrosion inhibitors, the pretreatment method of the metal surface by the dye solution ($2 \cdot 10^{-3}$ mol dm^{-3}) for 10 h before use is preferably recommended, as the differences in the inhibition percentages are not pronounced relative to those obtained by addition of the dyes solution to the corrosive medium (for dye *I* from 71 to 67% and dye *II* from 63 to 65%) (cf. Tables I – III). This is to overcome any contamination problems of the dye with the corrosive media in the container.

It is obvious from the weight loss measurements that cyanine dye *I* gave an inhibition action on the corrosion of copper in nitric acid higher than that of dye *II*. This behaviour may be attributed to the difference in molecular structure of the two investigated dyes, as the conjugation is increased in dye *II* relative to dye *I*. Followingly, the π electron density between the electron donnating *o*-hydroxyl group and the positive quaternary hetero nitrogen atom is increased. This is reflected on the adsorbability of the dye *II* molecules on copper surface which has a negative standard potential[12].

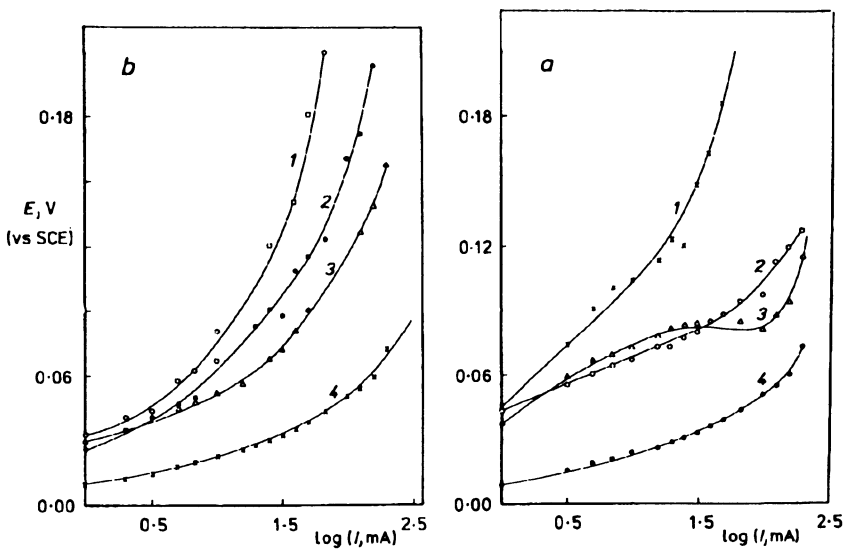

FIG. 1

The effect of dye concentration on the anodic galvanostatic polarization curves of copper electrode in 2 M nitric acid solution at 30 ± 0.1 °C for dye *I* (*a*) and dye *II* (*b*). Dye concentration: *1* 2 . 10^{-3}, *2* 0.5 . 10^{-3}, *3* 0.1 . 10^{-3}, *4* 0 mol dm^{-3}

Polarization Studies

The effect of the investigated dyes concentration on the anodic galvanostatic polarization curves of copper electrode in 2 M nitric acid solution as a corrosive medium has been studied. It is shown in Fig. 1 that the anodic potential in the presence and absence of dye is shifted to more positive values by increasing the current densities. This behaviour indicates that the corrosion process is inhibited by the application of external current. In the presence of the studied dyes, the potential shifts at a consedared current is to more positive values. The higher the dye concentration the greater the shift. This behaviour explains the inhibitive action of these dyes.

From the curves illustrated in Fig. 1, it is clear that, the potential shift in case of dye *I* is more positive than that of dye *II*, which supports the weight loss measurements.

The inhibition of copper corrosion process by using the formation of cyanine dye film before immersion in nitric acid solution is greatly affected by the dye concentration in the treatment solution. From Fig. 2, it is obvious that the higher is the concentration of the dye in a treatment solution, the greater is the shift to more positive potential, supporting the data obtained in weight loss measurements given in Table II.

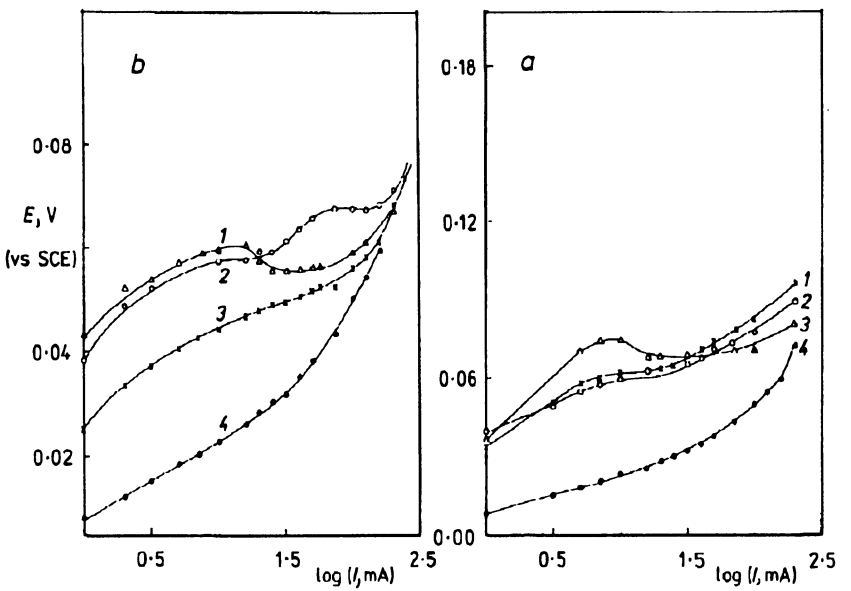

FIG. 2

The anodic galvanostatic polarization curves of copper electrode previously treated in different dye concentrations before immersion in 2 M nitric acid solution at 30 ± 0.1 °C. Electrode previously treated in: *1* 2 . 10^{-3} mol dm^{-3}, *2* 0.5 . 10^{-3} mol dm^{-3}, *3* 0.1 . 10^{-3} mol dm^{-3} of dye *I* (*a*) or dye *II* (*b*); *4* untreated electrode

From the curves in Fig. 3, it is clear that the anodic potential is greatly affected by the time of copper electrode treatment in 2 . 10^{-3} mol dm^{-3} dye solution before its immersion in corrosive medium. The previously treated electrode for 10 h gave the higher positive potential shift. This behaviour is in agreement with the data obtained in weight loss measurement (cf. Table III). It is evident that dye *I* has an inhibition action greater than that of dye *II*.

Open Circuit Potential–Time Relationships

The effect of studied cyanine dyes on the open-circuit potential variation with time (Fig. 4) was investigated. The potential of copper electrode was shifted to more positive values for up to 15 min in case of dye *II* and 20 min in case of dye *I*, then followed a slight shift to less positive and finally the steady state values were reached. The potential shift to more positive values explains the inhibition action of these dyes.

The steady state potential in the presence of the dye in corrosive medium is more positive than that in the case of the formation of dye film before the immersion in corrosive medium. This behaviour is in agreement with the weight loss measurement.

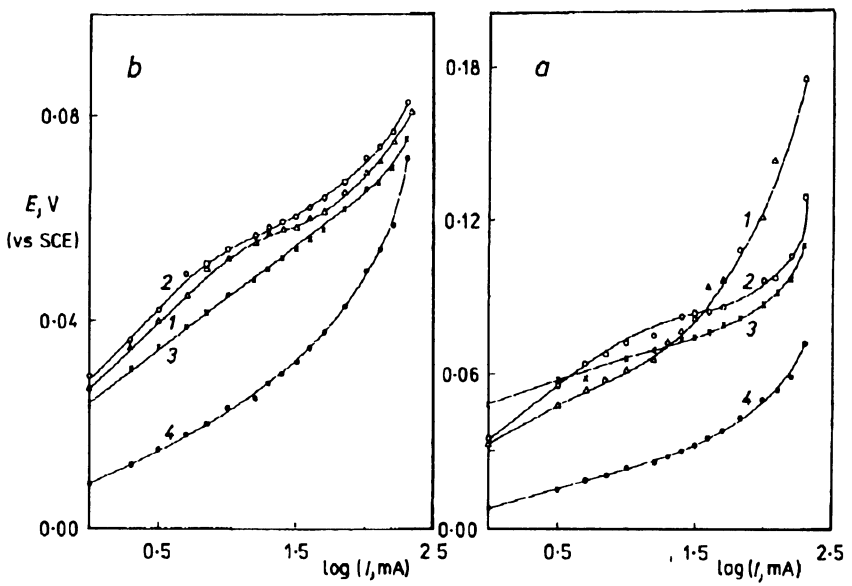

FIG. 3

The effect of treatment time in 2 . 10^{-3} mol dm^{-3} dye *I* (*a*) or dye *II* (*b*) solution on the anodic galvanostatic polarization of copper electrode in 2 M nitric acid solution at 30 ± 0.1 °C. Electrode treated for: *1* 25 h, *2* 10h, *3* 5 h; *4* untreated electrode

The steady state potential in case of using dye *I* is slightly more positive than that of dye *II*, supporting the weight loss data.

Cathodic Protection

Inhibition action of the studied cyanine dyes is further supported by investigating the effect of cathodic current on the performance of the investigated dyes as inhibitors in the acidic corrosion of copper metal. The results in Table IV show that 386 mA dm^{-2} cathodic current is required to afford complete protection of copper in 2 M nitric acid. It is evident that, the cathodic current required for complete protection of copper previously treated in 2 . 10^{-3} mol dm^{-3} dye solution for time intervals is decreased as the treatment time increases up to 10 h (198 mA dm^{-2} in case of dye *I* and 215 mA dm^{-2} in case of dye *II*). These results give another confirmation to the re-orientation process of the adsorbed dye molecules after 10 h of treatment (cf. Table III).

The protective current on using dye *I* is slightly lower than that of dye *II*. This give an evidence that the inhibition effect is more pronounced with dye *I*.

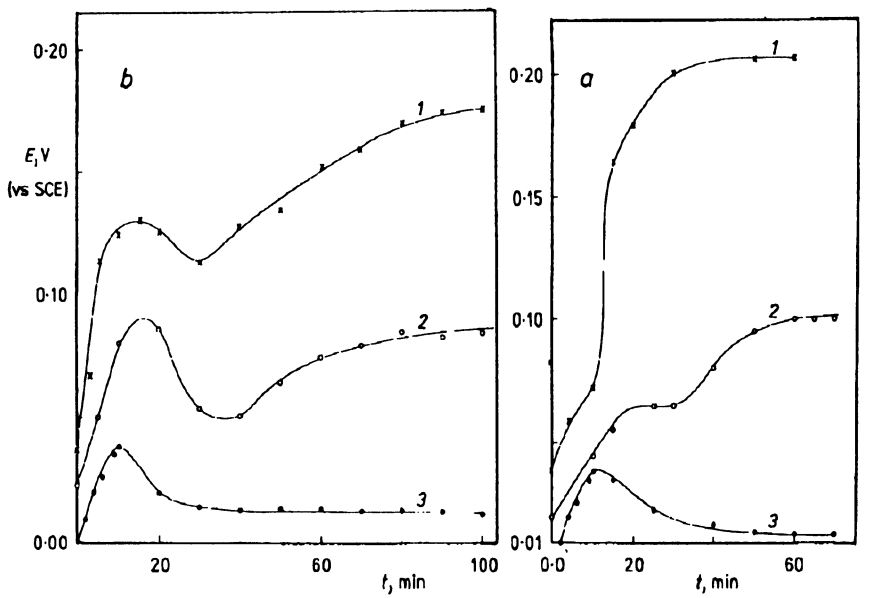

FIG. 4

Potential–time relation of copper electrode in 2 M nitric acid at different conditions for dye *I* (*a*) and dye *II* (*b*). *1* Copper electrode in 2 M nitric acid containing 2 . 10^{-3} mol dm^{-3} dye solution; *2* copper electrode previously treated in 2 . 10^{-3} mol dm^{-3} dye solution before immersion in 2 M nitric acid; *3* copper electrode only in 2 M nitric acid

It is clear that the inhibition effect of the adsorbed dye film in not changed under the effect of cathodic current. Therefore, the cathodic protection of previously treated copper metal, in relatively lower concentration of cyanine dye *I* up to 10^{-4} mol dm^{-3} for 10 h, can be considered as a practical application.

TABLE IV
Cathodic protective current required for copper metal previously treated in 2 . 10^{-3} mol dm^{-3} solution of cyanine dyes for time *t* intervals before immersion in 2 M nitric acid as corrosive medium

t, h	Cathodic protective current, mA dm^{-2}		Potential, mV	
	I	*II*	*I*	*II*
0.0	386	386	−152	−152
1.0	341	361	−131	−140
5.0	271	282	−109	−115
10.0	198	215	−76	−94
15.0	303	341	−117	−121
25.0	352	375	−128	−139
40.0	372	382	−132	−144

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