

## THE EFFECT OF THE MOLECULAR STRUCTURE OF CYANINE DYE ON THE CORROSION OF LOW-CARBON STEEL IN HYDROCHLORIC ACID SOLUTION\*

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Received November 9, 1992

Accepted July 15, 1993

The effect of two different cyanine dyes 2-(2-hydroxystyryl)quinolinium-1-ethyl iodide (*I*) and 4-(2-hydroxystyryl)quinolinium-1-ethyl iodide (*II*) on the electrochemical corrosion behaviour of low-carbon steel (0.05% C, 0.04% Si, 0.023% S, 0.004% Cu) in HCl solution has been studied. Weight loss measurements, galvanostatic polarization curves, open-circuit potential variation of steel electrode with time and the cathodic protective current values show that the investigated cyanine dyes have an anticorrosive character. The inhibition effect depends mainly on the structure of the studied dye molecules, and is more pronounced in case of pretreated carbon steel with the dye solution before immersion in the corrosion medium than that obtained by addition of the dye to the corrosive medium.

The electrochemical corrosion behaviour of iron and carbon steel was the subject of study by several authors<sup>1-10</sup>. Driver et al.<sup>1,2</sup>, investigated the corrosion behaviour during the inhibition measurements of steel in acid solution. They found that the corrosion process is greatly affected by the type of organic additives. The effect of substituted triazolo compounds namely, 4-amino-5*H*-3-mercapto-1,2,4-triazole (*a*), 4-amino-5-methyl-3-mercapto-1,2,4-triazole (*b*) and 4-amino-5-ethyl-3-mercapto-1,2,4-triazole (*c*) on the corrosion of steel in acidic medium was investigated at different temperature<sup>3</sup>. Masias et al.<sup>4</sup> studied the effect of acylthiourea and some of its substituents as corrosion inhibitors of steel in acid corrosive medium. The effect of styrene-derivatives as inhibitors in the corrosion of steel St3 was studied<sup>5</sup>. Benzimidazole derivatives of different structures were used as corrosion inhibitors of steel in acidic medium by Chervinskii<sup>6</sup>.

\* Part III in the series Cyanine Dyes as Corrosion Inhibitors; Part II: Collect. Czech. Chem. Commun. 58, 2003 (1993).

In a previous communications 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<sup>11</sup>. The effect of the molecular structure of the cyanine dyes on the acid corrosion of metallic copper was subject of our studies<sup>12</sup>. In this article, we aimed to study the effect of the last two cyanine dyes (*I* and *II*) on the corrosion behaviour of low carbon steel in hydrochloric acid solution.

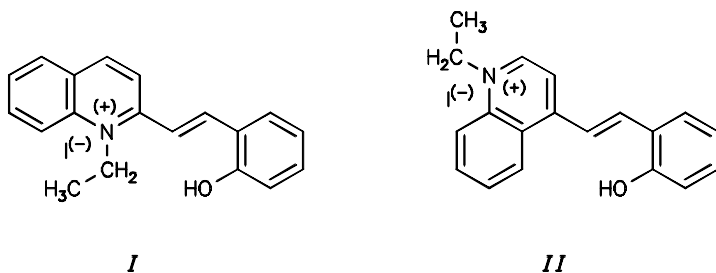
## EXPERIMENTAL

The investigated cyanine dyes *I* and *II* were prepared according to the method described before<sup>13</sup>, and recrystallized from ethanol. Their purity was checked by TLC, elemental analysis and spectral data.

The effect of cyanine dyes (*I* and *II*) on the corrosion of low-carbon steel in 2 M HCl was carried out by using two techniques: (i) adding different concentrations of the dyes to the corrosive medium, and (ii) formation of a dye thin film at the steel surface (by treatment of the metal surface in aqueous dye solutions for different times, the steel sheets being thoroughly washed with twice distilled water and dried) before their immersion in the corrosive medium.

*Low-carbon steel specimens* having a thickness of 2 mm and dimensions of 1 × 5 cm were pretreated to remove any oxide layer or corrosion products from the surface using the following solutions: *a*) degreasing solution; NaOH (100 g/l), Na<sub>2</sub>CO<sub>3</sub> (40 g/l), sodium silicate (10 g/l); *b*) etching solution, H<sub>2</sub>SO<sub>4</sub> (70 g/l). The effect of cyanine dyes on the corrosion process of low-carbon steel, applying the two procedures given above, has been studied using weight loss technique<sup>14</sup>. Each experiment was carried out using 50 ml of the aerated corrosive solution without stirring at 30 ± 0.1 °C. All corrosion tests were made in duplicate.

*Anodic galvanostatic polarization curves* of low-carbon steel electrode have been measured. The polarization cell used in this purpose has been described elsewhere<sup>15</sup>. Potentials were measured with a Muirhead D-972-A potentiometer using a saturated calomel electrode (SCE) reference electrode. Open circuit potential of low-carbon steel electrodes as a function of time was monitored to examine the characteristics of potential–time curves under open circuit conditions in the presence of the investigated cyanine dyes. The effect of cathodic current on the performance of the investigated dyes (*I* and *II*) in the acid corrosion process of low-carbon steel was studied<sup>12</sup>.



## RESULTS AND DISCUSSION

*Weight Loss Measurements*

Data recorded in Table I represent the effect of investigated cyanine dyes (*I* and *II*) concentrations, in case of their addition to the corrosive medium (2 M HCl), on the weight loss of low-carbon steel specimens. It is obvious that by increasing the dye concentration in corrosive medium, the loss in weight is decreased (i.e. the inhibition percentage increase). The inhibition action of cyanine dye molecules may be attributed to their high adsorbability on the carbon steel surface<sup>16</sup>, which inhibits the corrosion process in dependence on its concentration. It is clear that the adsorption layer of dye molecules prevent the attack of aggressive ions to the metal surface for a limited time only, i.e. the inhibition percentage for dye *I* are 68% and 30% after 10 and 20 h of immersion, respectively. This behaviour may be explained by some desorption of dye molecules under the aggressiveness of the medium after a long time of immersion.

TABLE I

The effect of cyanine dye concentration *C* on the weight loss of low-carbon steel in 2 M HCl solution

<i>C</i> (Dye) mol/dm <sup>3</sup>	Weight loss <sup>a</sup> , mg/dm <sup>2</sup>					
	10 h		15 h		20 h	
	<i>I</i>	<i>II</i>	<i>I</i>	<i>II</i>	<i>I</i>	<i>II</i>
2 · 10 <sup>-3</sup>	361 (51)	342 (55)	540 (35)	521 (35)	783 (15)	766 (15)
1 · 10 <sup>-3</sup>	390 (47)	366 (52)	787 (29)	587 (27)	820 (11)	793 (14)
5 · 10 <sup>-4</sup>	416 (44)	419 (45)	627 (25)	593 (26)	836 (9.0)	801 (13)
1 · 10 <sup>-4</sup>	516 (30)	506 (34)	644 (23)	631 (22)	951 (-)	910 (2.0)
5 · 10 <sup>-5</sup>	620 (16)	665 (13)	778 (6.0)	742 (8.0)	1 015 (-)	1 002 (-)
1 · 10 <sup>-5</sup>	672 (9.0)	788 (-)	806 (3.0)	785 (2.0)	1 031 (-)	1 021 (-)
0.0	742	763	831	805	918	926

<sup>a</sup> Values in parentheses indicate the inhibition percentages.

The preliminary treatment of carbon steel 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 due to the formation of a dye thin film at the metal surface, retarding the attack of aggressive molecules. The protection of the dye film depends on the concentration of the treatment solution; thus, the film formed in  $2 \cdot 10^{-3}$  mol/l resists the aggressiveness of the medium for a longer time (20 h) than that formed by treatment in lower concentration (10 h).

As shown in Table III, the time of treatment in dye solution ( $2 \cdot 10^{-3}$  mol/l) play an important role. The inhibition percentage increases with time up to 10 h, then began to decrease. This behaviour may be explained by the increase of the amount of adsorbed dye molecules in the protective film up to 10 h as aggregates. After this time, reorientation of the dye molecules to vertical ones takes place, leading to uncovered surface area which facilitates the attack of the aggressive ions of medium.

TABLE II

The effect of immersion time in 2 M HCl solution on the weight loss of low-carbon steel after preliminary treatment at different cyanine dye concentration  $C$  for 10 h

$C$ (Dye) mol/dm <sup>3</sup>	Weight loss <sup>a</sup> , mg/dm <sup>2</sup>					
	10 h		15 h		20 h	
	<i>I</i>	<i>II</i>	<i>I</i>	<i>II</i>	<i>I</i>	<i>II</i>
$2 \cdot 10^{-3}$	244 (68)	202 (73)	427 (48)	416 (48)	652 (30)	614 (35)
$1 \cdot 10^{-3}$	295 (61)	280 (63)	442 (49)	410 (49)	679 (27)	660 (30)
$5 \cdot 10^{-4}$	360 (53)	342 (54)	510 (37)	482 (40)	688 (26)	674 (29)
$1 \cdot 10^{-4}$	441 (42)	415 (45)	542 (34)	538 (33)	711 (23)	701 (26)
$5 \cdot 10^{-5}$	482 (37)	474 (37)	623 (24)	602 (25)	832 (-)	941 (-)
$1 \cdot 10^{-5}$	630	599	761	703	982 (-)	974 (-)
0.0	765	750	818	805	928	950

<sup>a</sup> Values in parentheses indicate the inhibition percentages.

It can be seen from the weight loss measurements (Tables I and II) that the pretreatment of low carbon steel in different concentration of dye solution before its immersion in the corrosion medium, gave an inhibition percentage higher than that obtained by the addition of the same dye concentrations to the corrosive medium. This behaviour may be attributed to the competition between the aggressive ions of corrosive medium and the adsorption of cyanine dye at the metal surface, leading to a decrease in the adsorbability of protective dye molecules relative to that obtained by treatment of the metal surface in a dye solution before the immersion in the corrosive medium.

It is clear from the weight loss measurements that cyanine dye *II* gave higher inhibition action on the corrosion of low carbon steel in HCl solution than dye *I*. This behaviour may be due to the different molecular structure of studied dyes, as the conjugation is increased in dye *II* relative to dye *I*. Followingly, the  $\pi$ -electron density

TABLE III  
The effect of treatment time  $t$  in cyanine dye solution ( $2 \cdot 10^{-3}$  mol/dm<sup>3</sup>) on the weight loss of low carbon steel metal in 2 M HCl solution

$t$ , h	Weight loss <sup>a</sup> , mg/dm <sup>2</sup>					
	10 h		15 h		20 h	
	<i>I</i>	<i>II</i>	<i>I</i>	<i>II</i>	<i>I</i>	<i>II</i>
40	425 (42)	395 (46)	616 (26)	606 (28)	805 (14)	791 (15)
30	365 (51)	350 (52)	585 (30)	572 (32)	737 (21)	733 (21)
20	340 (54)	322 (56)	566 (33)	544 (35)	715 (24)	713 (23)
15	302 (59)	292 (60)	515 (39)	507 (40)	699 (26)	683 (27)
10	256 (65)	215 (70)	480 (43)	472 (44)	657 (30)	640 (31)
5	347 (53)	322 (56)	542 (35)	512 (39)	875 (7.0)	881 (5.0)
1	482 (35)	455 (38)	627 (25)	667 (21)	890 (5.0)	962 (-)
0.0	740	732	840	842	939	932

<sup>a</sup> Values in parentheses indicate the inhibition percentage.

between the electron donating *o*-hydroxyl group and the positive quaternary heteronitrogen atom is increased in dye *II*. This increases the adsorption power of dye *II* molecules on the carbon steel metal surface which has a negative potential<sup>17</sup> and vacant spaces in *d* orbitals, explaining the higher inhibition percentage.

### Polarization Curves Studies

The effect of studied dye concentration on the anodic polarization curves of steel electrode in 2 M HCl solution has been studied. It is evident from Fig. 1 that the potential in presence and absence of dye is shifted to less negative values by increasing the applied current densities. This indicates that the corrosion process is inhibited by the application of external current. In the presence of the investigated cyanine dyes this potential shift is more pronounced than that in its absence. The higher the dye concentration, the greater the shift to less negative values. This behaviour explains the dependence of inhibition action on the concentration of dyes as shown in the weight loss measurements (Table I). By application with the current 10 mA, the potential is  $-0.175$  and  $-0.135$  V in presence of dye *I* and *II*, respectively, at  $2 \cdot 10^{-3}$  mol/l concentration, which supports the finding that dye *II* is a more effective inhibitor than dye *I*.

It is obvious from Fig. 2 that the inhibition of steel corrosion process by using the formation of cyanine dye protective film before immersion in corrosive medium is greatly affected by the dye concentration in the treatment solution.

The potential is greatly affected by the time of steel electrode pretreatment in  $2 \cdot 10^{-3}$  mol/l dye solution before its immersion in corrosive medium (Fig. 3). The treatment of steel electrode for 10 h gave the highest shift of potential to less negative value. This

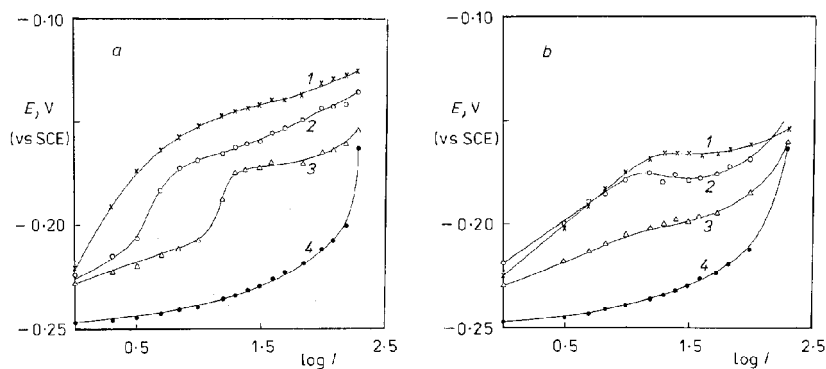


FIG. 1

The effect of dye concentration on the anodic polarization curves ( $I$  in mA) of low carbon steel electrode in 2 M HCl solution at  $30 \pm 0.1$  °C. *a* Dye *II*, *b* dye *I*. 1  $2 \cdot 10^{-3}$  mol/dm<sup>3</sup>, 2  $0.5 \cdot 10^{-3}$  mol/dm<sup>3</sup>, 3  $0.1 \cdot 10^{-3}$  mol/dm<sup>3</sup>, 4 HCl only

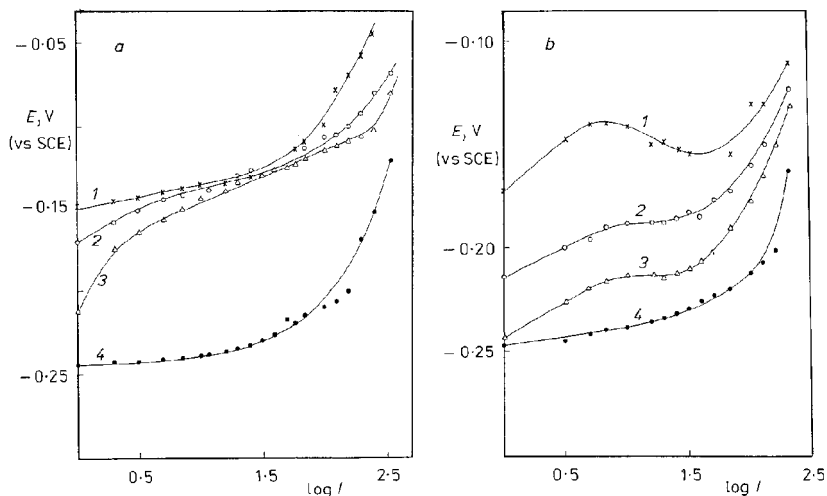


FIG. 2

Polarization curves ( $I$  in mA) of low carbon steel electrode previously treated in different dye concentrations at  $30 \pm 0.1$  °C. *a* Dye II, *b* dye I. 1 Electrode treated in  $2 \cdot 10^{-3}$  mol/dm<sup>3</sup>; 2 electrode treated in  $0.5 \cdot 10^{-3}$  mol/dm<sup>3</sup>; 3 electrode treated in  $0.1 \cdot 10^{-3}$  mol/dm<sup>3</sup>; 4 untreated electrode

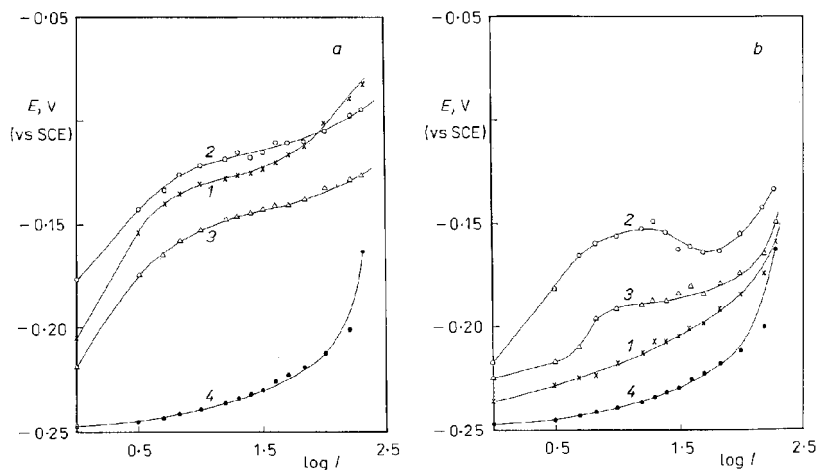


FIG. 3

The effect of treatment time in  $2 \cdot 10^{-3}$  mol/dm<sup>3</sup> dye solution on polarization curves ( $I$  in mA) of low-carbon steel electrode in 2 M HCl solution at  $30 \pm 0.1$  °C. *a* Dye II, *b* dye I. 1 Treatment for 25 h; 2 treatment for 10 h; 3 treatment for 5 h; 4 untreated electrode

behaviour is in agreement with the data obtained in weight loss measurements (Table III). Treatment of steel electrode for 10 h by dye *I* solution shifts the potential to  $-0.157$  V while in case of using dye *II* the potential shift is to  $-0.122$  V, thus confirming the higher inhibition action of dye *II*.

### Open Circuit Potential–Time Relations

Curves illustrated in Fig. 4 show the effect of investigated cyanine dyes by applying the above two ways (addition of  $2 \cdot 10^{-3}$  mol/l of the dyes to the corrosive medium or formation of protective thin film of dye by treatment in  $2 \cdot 10^{-2}$  mol/l dye solution for 10 h before its immersion) on the open-circuit potential variation with time. The potential of low carbon steel electrode is shifted to less negative values up to 10 min after immersion in case of dye *II* and 20 min in case of dye *I*, then followed by shift to a more negative values (in absence of inhibitors) and finally it reaches the steady state values.

The potential shift to less negative values explains the inhibition effect of these dyes.

The steady state potential in case of the formation of dye film before the immersion in corrosion medium is slightly less negative than that in presence of the dye in corrosion medium. This behaviour confirms the weight loss measurements.

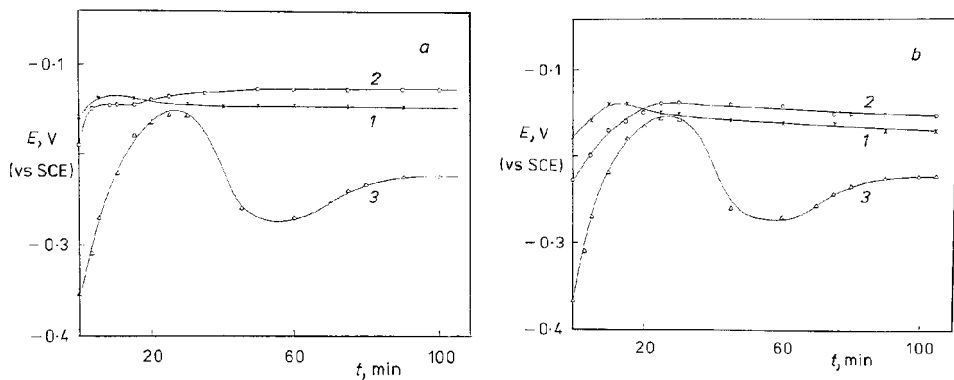


FIG. 4

Potential–time relationship of low-carbon steel electrode in 2 M HCl solution at different conditions. **a** Dye *II*, **b** dye *I*. 1 Low carbon steel electrode in 2 M HCl containing  $2 \cdot 10^{-3}$  mol/dm<sup>3</sup> dye; 2 low carbon steel electrode previously treated in  $2 \cdot 10^{-3}$  mol/dm<sup>3</sup> dye before immersion in 2 M HCl; 3 low carbon steel electrode in 2 M HCl only



By using dye *II*, it was found that the steady state potential is slightly less negative than that in case of dye *I* ( $-0.13$  V and  $-0.15$  V for dye *II* and dye *I*, respectively). These values support the higher inhibition action of dye *II* as compared to dye *I*.

### Cathodic Protection

Inhibition effect of the investigated cyanine dyes is further supported by the effect of cathodic current on the performance of the studied dyes as inhibitors in the acid corrosion of low carbon steel. The results recorded in Table IV show that  $393 \text{ mA/dm}^2$  cathodic current is required to afford complete protection of low carbon steel in  $2 \text{ M HCl}$ .

It is obvious that the cathodic current required for complete protection of steel previously treated in  $2 \cdot 10^{-3} \text{ mol/l}$  solution for various time intervals is decreased as the treatment time increases up to 10 h ( $242 \text{ mA/dm}^2$  for dye *I* and  $214 \text{ mA/dm}^2$  for dye *II*) then the current again increases. These results give another confirmation of the reorientation process of the adsorbed dye molecules after 10 h of treatment, and the fact that dye *II* is better inhibitor than dye *I*.

Finally, it is admitted that the inhibition effect of the adsorbed dye film is not changed under the effect of cathodic current. Therefore, the cathodic protection of previously treated low-carbon steel in relatively lower concentration of the studied cyanine dyes up to  $5 \cdot 10^{-4} \text{ mol/l}$  for 10 h can be considered as a practical application.

TABLE IV

Cathodic protective currents for low carbon steel previously treated in  $2 \cdot 10^{-3} \text{ mol/dm}^3$  solution of cyanine dyes for given time intervals  $t$  before immersion in  $2 \text{ M HCl}$  solution as corrosive medium

$t, \text{ h}$	Cathodic protective current, $\text{mA/dm}^2$		Potential, $\text{mV}$	
	<i>I</i>	<i>II</i>	<i>I</i>	<i>II</i>
0.0	393	393	-149	-149
1.0	372	342	-136	-122
5.0	328	312	-121	-109
10.0	242	214	-116	-92
15.0	281	263	-122	-116
25.0	317	299	-131	-126
40.0	337	341	-144	-148

*The author is grateful to Dr Zarif H. Khalil professor of organic chemistry for his help during the preparation of organic compounds.*

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