

## EFFECT OF SOME TRIMETHINE MERCYANINE DYES ON THE CORROSION OF ALUMINIUM AND ALUMINIUM MANGANESE

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(Received October 2, 1989; revised June 10, 1990)

The effect of some trimethine merocyanine dyes on the corrosion of Al and Al-Mn alloy was studied by Mylius, weight-loss and hydrogen evolution methods. The retardation of temperature rise by the added compounds was found to depend on the type of the compound and its concentration. All the compounds showed high inhibition effect. At the first stage of corrosion,  $T=0.5^\circ$ , the inhibition with Al is greater than with Al-Mn. The corrosion rate calculated from hydrogen evolution method was found to be smaller than from the weight-loss method. The order of inhibition for the compounds was found to be consistent with their electronic structures and the nature of substituents involved.

**Key words:** Trimethine merocyanine dyes, Al and Al-Mn alloy, Corrosion, Inhibitors.

### Introduction

Numerous investigations have been carried out to clarify the mechanism and nature of the corrosion inhibition caused by organic and inorganic substances [1-7]. The effect of potassium thiocyanate, sodium azide, thiourea, thiosemicarbazide and  $\alpha$ -amino acids on the corrosion of Al in trichloroacetic acid was investigated using weight-loss technique [4]. According to Talati and Daraji [5], the inhibitive efficiency of triphenyl methane dyes for Al in phosphoric acid was found to increase with inhibitor concentration but decreases with acid concentration and temperature. The inhibitive effect of some hydrazone compounds on the corrosion of Al in HCl and NaOH solutions was studied by thermometric and weight-loss methods [6]. Unni *et. al* [8] used butylamine as inhibitor for corrosion of Al-Mn alloy. The steady state corrosion potential was shifted to more negative values by the addition of inhibitors. Shams El-Din [9] obtained a satisfactory agreement between results of the weight-loss measurements and those of the thermometric method of Mylius [10] for the dissolution reaction of aluminium and zinc in hydrochloric acid solutions. The effect of some alcohols, ketones, aldehydes and amino compounds on the corrosion rate of aluminium alloys using both the Mylius and weight-loss measurements was studied [11].

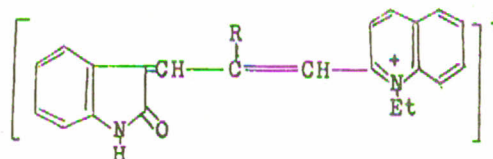
In this paper the effect of some trimethine merocyanine dyes containing 2-oxindolo moiety on the corrosion of Al and Al-Mn alloy in acidic medium was studied by Mylius, weight-loss and hydrogen evolution methods.

### Experimental

The specimens of Al and Al-Mn alloy were degreased in a mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_3\text{PO}_4$  (15 g/l) at  $85^\circ$  for 5 min., then washed and dipped in pickling solution of 100 ml concentrated HCl/l for one minute [12]. Finally the specimens were washed in bidistilled water and dried.

The organic compounds under investigation ( $I_a$ ) were

prepared [13]. The purity of each compound was checked by TLC and confirmed by microanalysis and infrared spectra.



where  $R = \text{H}(I_a)$ ,  $R = \text{CH}_3(I_b)$ ,  $R = \text{C}_6\text{H}_5(I_c)$ ,  $R = \text{C}_6\text{H}_4\text{CH}_3(I_d)$  and  $R = \text{C}_6\text{H}_4\text{Cl}(I_e)$

**Mylius method.** A specimen of dimension  $1 \times 10$  cm was immersed in 30 ml of 3.0 N HCl at  $30^\circ$  containing different concentration of the organic compounds (0.10 - 6.0 mg). The inhibitor solution was prepared by dissolving the required amount in 0.5 ml absolute ethanol which was then mixed in HCl to observe the inhibition effect. The rise of temperature with time was followed as described by Mylius [10]. The reaction number (R.N.) of each experiment was calculated using the relation  $\text{R.N.} = (T_m - T_0)/t \text{ C. min}^{-1}$ , where  $T_m$  and  $T_0$  are the maximum and initial temperatures respectively and  $t$  is the time in minutes taken to reach  $T_m$ . The inhibition effect (A) was calculated by applying the equation;  $A = [(R.N.)_{\text{free}} - (R.N.)_{\text{inh}}]/(R.N.)_{\text{free}} \times 100$ , where  $(R.N.)_{\text{free}}$  and  $(R.N.)_{\text{inh}}$  are the reaction numbers of specimen dissolution in absence and presence of the inhibitor respectively.

**Weight-loss and hydrogen evolution measurements** [9]. The corrosion process was carried out for 30 min. using a specimen of Al or Al-Mn with surface area  $4.0 \text{ cm}^2$  in 250 ml of 3.0 N HCl in absence and presence of different concentrations of organic compounds. The hydrogen gas evolved was collected and the volume corrected to S.T.P. conditions. The corroding sample was withdrawn, washed, dried and weighted. The loss in weight was thus determined and the corrosion rate calculated using the equation  $K = (W \times 10^4)/4t$ , where  $K$  is the rate of corrosion in  $\text{gm m}^{-2} \text{h}^{-1}$ ,  $W$  is the loss in weight and  $t$  is the time



of immersion in minutes. On the other hand, the corrected hydrogen volume  $V_H$  was converted into a mass of Al using the relation  $W = (V_H \times 27 \times 2)/(22414 \times 3)$  where 27 is the atomic weight of Al [9]. In both two methods the inhibition efficiency was obtained using the relation given in the literatures [3,4,6,9].

**Results and Discussion**

The increase in temperature with time for the corrosion of Al in 3.0 N HCl containing different concentrations of the compound  $I_a$  is shown in Fig. 1 as a representative of result. The values of reaction number (R.N) and inhibition effect (A) are reported in Tables 1 and 2 for the compounds studied ( $I_{a-e}$ ). The A values were found to increase with the concentration (C) of the inhibitor. The shape of the A-C relations (Fig. 2) look like those of an adsorption isotherm [1]. The observed high inhibition effect can be attributed to the cationic nature of the inhibitors. The corrosion potentials of Al and Al-Mn are more negative than the zero charge point (z.c.p.) of Al(-0.4 V) as reported earlier [14]. This makes the adsorption of cationic surfactants more effective than the non ionic or anionic ones. The corrosion potentials of Al are more negative than those of Al-Mn by about 45 mV which may enhance the adsorption of cationic inhibitors of Al more than on Al-Mn (Tables 1 and 2). The incubation period needed for the corrosion process to proceed and the temperature to rise with time can be characterized by the  $t_{1/2}$  values,  $t_{1/2} = (T_m - T_o)/2$ , where  $T_m$  and  $T_o$  have the same definitions given before. The increase in  $t_{1/2}$  in the presence of inhibitors can be interpreted as a function of the adsorption. The values of  $t_{1/2}$  were plotted against the concentration of the inhibitors ( $I_{a-e}$ ). The  $t_{1/2}$ -C relations were

similar to A-C relations (Fig.2) as both of  $t_{1/2}$  and A are functions of adsorption [1].

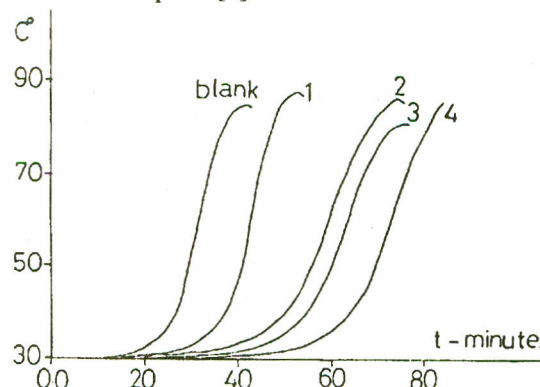


Fig. 1 : Effect of inhibitor ( $I_a$ ) concentration on T - t curves of Al 1-0.0033 2-0.0166 3-0.033 4-0.100

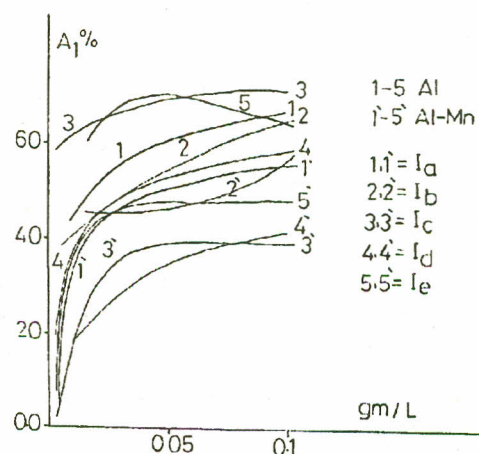


Fig. 2 : Effect of inhibitors ( $I_a$ ) concentration of  $A_1$  for Al and Al-Mn.

TABLE 1. R.N. AND "A", RELATIVE DECREASE IN R.N., OF Al IN HCl USING DIFFERENT CONCENTRATION OF INHIBITORS ( $I_{a-e}$ ).

Conc. g/l	$I_a$		$I_b$		$I_c$		$I_d$		$I_e$	
	R.N.	A%	R.N.	A%	R.N.	A%	R.N.	A%	R.N.	A%
0.5 ml alcohol	2.048	—	2.048	—	2.048	—	2.048	—	2.048	—
0.00333	1.086	47.0	0.955	53.4	0.753	63.2	1.714	16.3	1.115	45.6
0.0166	0.676	67.0	0.694	66.1	0.582	71.6	1.119	45.4	0.915	55.3
0.0333	0.664	67.6	0.582	71.5	0.568	72.3	0.676	67.0	0.611	70.2
0.1000	0.655	68.0	0.603	70.6	0.470	77.1	0.871	57.5	0.757	63.0

TABLE 2. R.N. AND "A", RELATIVE DECREASE IN R.N., OF Al-Mn ALLOY IN HCl USING DIFFERENT CONCENTRATION OF INHIBITORS ( $I_{a-e}$ ).

Conc. g/l	$I_a$		$I_b$		$I_c$		$I_d$		$I_e$	
	R.N.	A%	R.N.	A%	R.N.	A%	R.N.	A%	R.N.	A%
0.5 ml alcohol	3.410	---	3.410	---	3.410	---	3.410	---	3.410	---
0.00333	3.186	6.60	3.219	5.6	---	---	---	---	---	---
0.0166	2.129	37.60	2.357	30.9	---	---	2.538	25.6	1.482	56.54
0.0333	1.411	58.62	0.740	78.3	2.131	37.5	2.224	34.8	0.879	74.22
0.1000	1.344	60.60	1.366	59.9	1.806	47.0	1.573	53.9	1.273	62.70
0.2000	---	---	1.200	64.8	1.255	63.2	---	---	---	---

Moreover, the effect of compounds ( $I_{a,e}$ ) on the different stages of corrosion was investigated using the mathematical treatment developed by F.El-Cheikh *et.al* [15]. The rise in temperature ( $\Delta T$ ) as a function of the corrosion rate can be represented by the following equation over a wide range of temperatures,  $t = X + Y \ln \Delta T$ , or  $t = X + 2.303 Y \log \Delta T$ , where  $\Delta T = T_m - T_0$  at time  $t$ ,  $X$  is the time needed for temperature to reach  $\Delta T = 1.0$ , while  $Y$  is the time consumed in raising the temperature from  $31^\circ$  to  $40^\circ$  or to magnify  $\Delta T$  ten times. The values of  $1/X$  can be considered as a function of the corrosion rate of the most outer layers of the Al specimens and  $1/Y$  represents a function of the dissolution of the internal layers. Thus, the relative increase in corrosion resistance of the specimens (inhibition effect,  $A$ ) can be given as:

$$A_1(\Delta T = 0.5^\circ) = (1 - X/X') \times 100$$

$$A_2(\Delta T > 0.5^\circ) = (1 - Y/Y') \times 100$$

where  $X$  and  $Y$  are constants in the free acid and  $X'$  and  $Y'$  in the presence of additives.

The plot of  $\log \Delta T$  vs  $t$  was found to be linear for the most additives, but in some cases, the straight lines exhibit a break at  $T^*$  (c.f. Tables 3 and 4). Therefore, two values for  $A_{0.5^\circ < T < T^*}$  ( $A_2$ ) and  $A_{T > T^*}$  ( $A_3$ ) were calculated  $A_2$  was always lower than  $A_1$  and  $A_3$  is lower than  $A_2$ . This reflect the relation between adsorption and temperature. As the temperature increases, the adsorption is suggested to decrease and thus the

inhibition effect is decreased too. This fact confirms the adsorption mechanism of inhibition. On the other hand, the competition between the renewal rate of the corroding metal surface and the adsorption rate of the inhibition play a significant role on the continuously renewing metal surface. At  $\Delta T > 0.5^\circ$ , the renewal rate is increasing while that of adsorption is decreasing. This must lead to lower inhibition effect. The inhibition of Al-Mn at  $\Delta T > 0.5^\circ$  by the inhibitors ( $I_{a,e}$ ) was found to be higher than at  $\Delta T = 0.5^\circ$ , i.e.  $A_2 > A_1$ . The potential of Al- Mn becomes more negative after the activation incubation period [1,8,14]. This fact may lead to higher adsorption on the active Al-Mn surface than on the outer passive layer. It is obvious that the determination of  $A$  (Table 3) from the  $\Delta T$ - $t$  relations is restricted to each stage of dissolution  $A_1$ ,  $A_2$  and  $A_3$ . In the R.N. method (Table 2), the values of  $A$  cover the first and further stages of dissolution.

The inhibition of Al and Al-Mn corrosion by inhibitors ( $I_{a,e}$ ) was also studied using weight-loss and hydrogen evolution methods. Full details of calculations and techniques are given in the experimental section. The rate of corrosion calculated from the hydrogen evolution method  $K_{H_2}$  was found to be smaller to some extent than  $K_w$  calculated directly from the weight-loss data as Fig.3 indicated for Al. The same observation was found in case of Al-Mn. This was attributed to the existence of a passive oxide film on Al and Al-Mn surface. At the beginning of corrosion the reaction between

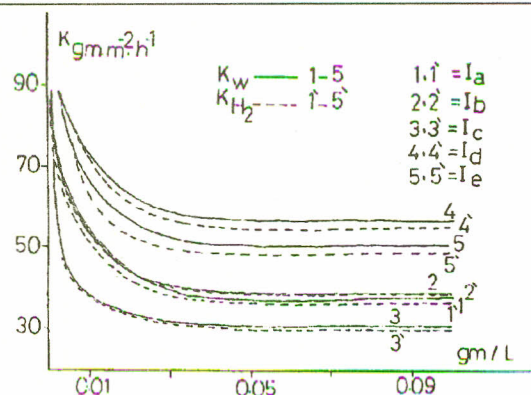
TABLE 3: EFFECT OF SOME TRIMETHINE MEROCYANINE DYES ( $I_{a,e}$ ) ON THE DIFFERENT STAGES OF CORROSION OF Al IN 3.0N HCl.

Conc., g/l	X	Y	T*	Y''	A <sub>1</sub> %	A <sub>2</sub> %	A <sub>3</sub> %
0.5ml alcohol	15.0	15.2	32.9	9.5	----	----	----
$I_a$							
0.0033	22.0	18.5	34.3	10.5	31.8	17.8	----
0.0166	30.0	21.0	35.5	18.5	50.0	27.6	17.8
0.0330	34.5	21.5	37.0	18.5	56.5	29.3	17.8
0.100	44.0	21.5	37.0	18.0	65.9	29.3	15.6
$I_b$							
0.0033	24.0	20.0	33.8	12.7	37.5	24.0	----
0.0166	26.0	36.5	34.8	15.0	42.3	58.3	----
0.0330	23.0	54.5	34.2	19.0	34.8	72.1	20.0
0.100	42.0	25.5	37.6	17.5	64.3	40.0	13.1
$I_c$							
0.0033	36.0	22.5	34.3	14.5	58.3	32.4	----
0.0166	41.0	21.0	35.6	17.5	63.4	27.6	13.1
0.100	52.5	25.0	37.0	20.0	71.4	39.2	24.0
$I_d$							
0.0033	16.0	8.0	----	----	6.3	----	----
0.0166	19.5	14.5	35.0	12.5	23.1	----	----
0.100	25.5	20.0	37.4	15.5	41.2	24.0	2.0
$I_e$							
0.0033	16.0	13.0	----	----	6.3	----	----
0.0166	27.0	18.0	34.5	14.0	44.4	15.6	----
0.100	29.0	21.5	40.0	16.5	48.3	29.3	7.9



TABLE 4. EFFECT OF SOME TRIMETHINE MERCYANINE DYES ( $I_{a-e}$ ) ON THE DIFFERENT STAGES OF CORROSION OF Al-Mn IN 3.0 N HCl.

Conc., g/l	X	Y	T*	Y <sup>∞</sup>	A <sub>1</sub> %	A <sub>2</sub> %	A <sub>3</sub> %
0.5ml alcohol	7.60	2.66	---	---	---	---	---
$I_a$							
0.0033	8.00	6.00	---	---	5.00	55.7	---
0.0166	13.00	11.50	39.5	5.50	41.50	76.9	51.6
0.100	17.00	17.50	---	---	55.30	84.8	---
$I_b$							
0.0033	9.50	5.50	---	---	20.00	51.6	---
0.0166	13.85	7.85	---	---	44.70	65.7	---
0.100	18.5	17.00	---	---	58.90	84.4	---
$I_c$							
0.033	12.0	7.00	40.5	6.50	36.70	62.0	59.1
0.100	12.5	14.50	41.5	9.50	39.50	81.7	72.0
0.200	14.0	23.50	46.0	13.50	45.70	88.7	80.3
$I_d$							
0.0166	14.0	6.00	40.0	5.00	45.70	55.7	46.8
0.033	14.0	8.50	42.0	6.00	45.70	68.7	55.7
0.100	17.5	15.00	43.0	9.00	56.60	82.3	70.4
$I_e$							
0.0166	19.5	13.50	44.0	8.00	61.00	80.3	66.8
0.033	25.0	24.00	50.0	12.00	69.60	88.9	77.8
0.100	21.0	17.50	48.0	11.00	63.80	84.8	75.8


 Fig. 3. Effect of inhibitor ( $I_{a-e}$ ) concentration on the corrosion rate of Al in HCl as measured by hydrogen evolution and weight loss.

$Al_2O_3$  and HCl is almostly chemical and not accompanied by  $H_2$  evolution according to the equation :



Accordingly, the quantity of  $H_2$  gas collected during corrosion was always smaller than the dissolved amount of Al by about 3-4%. This difference corresponds to the ratio of  $Al_2O_3$  dissolved at first stage during the corrosion. Consequently, the values of  $A_{H_2}$  are to some extent higher than  $A_w$ . In general, the observed inhibition effect of cationic mercyanine dyes ( $I_{a-e}$ ) may be attributed to the ease of their adsorption at the metal surface through their active centres nitrogen and oxygen in addition to the delocalized - electrons of the rings involved.

In case of Al, the compound  $I_c$  ( $R = C_6H_5$ ) shows high inhibition efficiency than the other compounds. The compounds  $I_a$  ( $R = H$ ) and  $I_b$  ( $R = CH_3$ ) are also better than  $I_c$  ( $R = C_6H_4Cl$ ) and  $I_d$  ( $R = C_6H_4CH_3$ ). The compound  $I_c$  is slightly better than  $I_d$ . This is obviously electronic, substituent and steric effects. The presence of phenyl group in  $I_c$  should increase the rate of charge migration through the whole compound. Consequently, a high decrease in the corrosion rate should be expected relative to  $I_a$  and  $I_b$  as the data in Tables 1 and 3 indicated. The introduction of  $C_6H_4Cl$  ( $I_c$ ) and/or  $C_6H_4CH_3$  ( $I_d$ ) group(s) seems to be highly affected on the coplanarity of the parent compound resulting a decrease in the rate of conjugation and adsorption relative to the compound  $I_c$ . The order of the compound  $I_b$  after  $I_c$  is due to the absence of steric effect and to the electron releasing nature of  $CH_3$  group which may increase the basic strength of the compound and the adsorption process.

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