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Disperse Dyes as Corrosion Inhibitors for Aluminum Alloy in Trichloroacetic Acid System

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The corrosion of aluminum alloy in trichloroacetic acid containing disperse dyes has been studied. In trichloroacetic acid (TCA), the corrosion rate increases with the acid concentration. At constant acid concentration, the inhibition efficiency of dyes increases with the inhibitor concentration. Similarly, at constant inhibitor concentration, the inhibition efficiency decreases with the increase of acid concentration. In 0.01 M trichloroacetic acid for 24 h immersion period, at 4 mM inhibitor concentration the inhibition efficiency of inhibitors increases in the order: coralene violet 3R Ex (C.I. disperse violet 99) (95.80 %) < coralene yellow Br. REL (C.I. disperse orange 61) (91.98 %). As temperature increases, percentage of inhibition increases in coralene violet 3R Ex and coralene yellow Br. REL almost in all case. Plot of log (θ /1- θ) *vs.* log C results in a straight line suggest that the inhibitors cover both the anodic and cathodic regions through general adsorption following Langmuir isotherm. The curves show little anodic but significant cathodic polarization.

Key Words: Corrosion, Aluminum alloy, Trichloroacetic acid, Disperse dyes.

INTRODUCTION

Any process of deterioration and consequent loss of a metallic material, through an unwanted chemical or electrochemical attack by its environment, starting at its surface is called corrosion[1]. Aluminum alloy is known to exhibit passive behaviour in aqueous solutions. The corrosion of the metal has been reported to depend on processes associated with the passivating surface oxide film such as metal ion transfer to the metal/oxide interface, metal ion and oxygen ion transfer to the oxide/solution interface, ion migration in the oxide film and electron transfer from the metal to acceptor species in solution[2]. Different kinds of dyes are known, *viz.*, heterocyclic dyes, xanthenes dyes, anthraquinone dyes and azo dyes. Of all the

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dyes, azo dyes are a class of compounds that are strongly coloured. In fact, about half of the dyes in industrial use today are azo dyes, which are mostly prepared from diazonium salts[3]. Talati and Gandhi[4] studied the xanthenes and azo dyes as corrosion inhibitors for aluminum alloy in trichloroacetic acid (TCA). Ebenso[5] studied (Part Two of the series) methyl red (MR) and halide ions are being investigated as inhibitors for the corrosion of aluminum alloy in H_2SO_4 solutions both individually and in conjunction. The present studies reports on the inhibitive action of coralene violet 3R Ex. and coralene yellow Br. REL on the corrosion of aluminum alloy in TCA solutions using gravimetric as well as polarization method.

EXPERIMENTAL

Rectangular specimens of the size 5.0 cm × 2.0 cm × 0.18 cm having an area of 0.2414 sq. dm of 2S grade aluminum alloy (Al = 98.02 %; Mg = 0.37 %; Si = 0.49 %; Fe = 0.68 %; Mn = 0.16 % and Cu = 0.082 %) with small hole of about 5 mm diameter near the upper edge, were used for the determination of the corrosion rate. The specimens were polished according the method described earlier[6,7] using tripoli composition. The specimens were degreased by immersion in AR grade acetone and dried in warm air using air dryer and are preserving in dessicater till use. The test specimens were immersed in 0.01, 0.05 and 0.10 M TCA solution with and without inhibitors. Various dyes like coralene violet 3R Ex. and coralene yellow Br. REL were used as inhibitors in 1, 2, 3 and 4 mM concentration. One specimen only was suspended by a glass hook, in each beaker containing 230 mL of the test solution and was open to the air at room temperature for 24 h. After the tests, specimens were cleaned with chromic-phosphate mixture solution[8]. Triplicate experiments were performed in each case and the mean value of the weight loss data were presented in mg/sq. dm.

To study the effect of temperature on corrosion rate, the specimen were immersed in 230 mL in 0.05 M TCA, with 1, 2, 3 and 4 mM of dye inhibitor concentration at solution temperatures of 313, 323 and 333 K for a period of 2 h. For the purpose of temperature effect study, thermostate assembly with accuracy of ± 0.5 ºC was used. Wesley[9] and ASTM[10] pointed out that the thermostatic control within ± 1 ºC usually are considered satisfactory. Form the data inhibition efficiency (I.E.), energy of activation (Ea), heat of adsorption (Q_{ads}) and free energy of adsorption (ΔG^o_{ads}) were calculated and shown in Table-2.

For polarization study, metal specimens of rectangular design having an area of 0.02585 dm^2 is exposed to corrosive solutions. Aluminum alloy is used as a working electrode, Ag/AgCl is used as reference electrode and auxiliary platinum electrode was placed in a 100 mL corrosive media through which external current was supplied automatically from computerized polarization instrument. The change in potential was measured by potentiostate/galvanostate (Auto lab polarization Model-273). Galvanostatic polarization has been taken with and without inhibitors in 0.01 M TCA. It curves shows polarization of both the anodes and cathodes.

Inhibition efficiency (I.E.) in percentage has been calculated as follows:

$$\text{I.E.} = (\text{Wu} - \text{Wi/Wu}) \times 100 \qquad (1)$$

where Wu is the weight loss of the metal in uninhibited acid and Wi is the weight loss of a metal in inhibited acid.

Energy of activation (Ea) has been calculated from the slopes of log p *vs.* 1/T (p = corrosion rate, T = absolute temperature) and also with the help of Arrhenius equation[11].

$$\log p_2/p_1 = \text{Ea}/2.303\ \text{R}[(1/T_1)-(1/T_2)] \qquad (2)$$

where p_1 and p_2 are the corrosion rate at temperature T_1 and T_2, respectively.

The values of heat of adsorption (Q_{ads}) were calculated by the following equation[11].

$$Q_{ads} = 2.303\ \text{R}[\log(\theta_2/1-\theta_2)-\log(\theta_1/1-\theta_1)] \times [T_1 \times T_2/T_2-T_1] \qquad (3)$$

where θ_1 and θ_2 [θ = (Wu–Wi)/Wi] are the fraction of the metal surface covered by the inhibitors at temperature T_1 and T_2, respectively.

The values of the free energy of adsorption (ΔG^o_{ads}) were calculated with slope from the following equation[12].

$$\log C = \log(\theta/1-\theta)-\log B \qquad (4)$$

where log B = -1.74 - ($\Delta G^o_{ads}/2.303$ RT) and C is inhibitor concentration.

The enthalpy of adsorption (ΔH^o_{ads}) and entropy of adsorption (ΔS^o_{ads}) are calculated using the following eqns. 5 and 6.

$$\Delta H^o_{ads} = \text{Ea} - \text{RT} \qquad (5)$$

$$\Delta S^o_{ads} = \Delta H^o_{ads} - \Delta G^o_{ads} \qquad (6)$$

RESULTS AND DISCUSSION

The results are presented in Tables 1-3. To assess their protective value, various dyes (coralene violet 3R Ex. and coralene yellow Br. REL) were added to solutions of TCA. The pH of plain 0.01 M TCA was found to be 2.02 while the inhibited acid (0.01 M TCA + 1 mM inhibitors) were observed to lie in the range of 1.99 (coralene yellow Br. REL) to 2.00 (coralene violet 3R Ex.). *i.e.* the inhibitors have no effect on the pH of the acid.

Generally, aluminum alloy dissolves in acid solutions due to hydrogen evolution type of attack.The reaction-taking place at the micro electrodes of the corrosion cell being represented as under,

$$\text{Al} \longrightarrow \text{Al}^{3+} + 3e^- \qquad \text{(anode) (7)}$$

$$\text{H}^+ + e^- \longrightarrow \text{H} \qquad \text{(cathode) (8)}$$

followed by the reaction,

$$\text{H} + \text{H} \longrightarrow \text{H}_{2(g)} \qquad (9)$$

TABLE-1
EFFECT OF ACID CONCENTRATION ON CORROSION LOSS (mg/sq. dm) AND INHIBITION EFFICIENCY (%) OF ALUMINUM IN TRICHLOROACETIC ACID CONTAINING DIFFERENT DYES AS INHIBITORS
Effective area of specimen: 0.2414 sq. dm; Immersion period: 24 h; Temp. 301±1 K

Inhibitor	Inhibitor conc. (mM)	Acid concentration					
		0.01 M		0.05 M		0.10 M	
		Corrosion loss (mg/sq dm)	I.E. (%)	Corrosion loss (mg/sq dm)	I.E. (%)	Corrosion loss (mg/sq dm)	I.E. (%)
Blank	–	118.88	–	1189.3	–	2452.09	–
Coralene violet 3R Ex.	1	21.96	81.53	307.32	74.16	1353.31	44.81
	2	13.26	88.85	313.50	73.64	1289.06	47.63
	3	15.33	87.10	290.31	75.59	1220.16	50.24
	4	4.97	95.80	266.05	77.63	1174.55	52.10
Coralene yellow Br. REL	1	24.03	79.90	320.99	73.01	1368.76	44.18
	2	14.91	87.46	282.46	76.25	1249.34	49.05
	3	14.91	87.46	274.97	76.88	1075.98	56.12
	4	9.53	91.80	245.23	79.38	1040.91	57.55

The following secondary reaction can also take place in acid solutions[13].

$$2M + 2H^+ \longrightarrow H_2 + 2M^+ \qquad \text{(anode)} \quad (10)$$

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \qquad \text{(cathode)} \quad (11)$$

If therefore only the hydrogen evolution type of attack is predominate and no other factors influence the corrosion process, corrosion by the strong acid should be maximum.

In the course of dissolution of aluminum alloy in TCA the reaction in the initial stages appear to be

$$3Cl_3CCOOH + Al \longrightarrow [Cl_3CCOO]_3Al + 3H^+ \qquad (12)$$

TCA gets reduced to acetic acid and hydrochloric acid by potassium amalgam or on electrolysis between electrodes of amalgamated zinc[14].

$$Cl_3CCOOH + 6H^+ \longrightarrow CH_3COOH + 3HCl \qquad (13)$$

During corrosion of aluminum alloy it is, therefore, possible that reaction[14] is followed by the reduction of TCA to dichloroacetic acid as a first stage.

$$Cl_3CCOOH + 2H^+ \longrightarrow CHCl_2COOH + 3HCl \qquad (14)$$

Further reduction of dichloroacetic acid to monochloroacetic and finally to acetic acid.

Effect of acid concentration: The effect of acid concentration on the inhibitive efficiency (I.E.) of the various dyes is shown in Table-1. At constant inhibitor concentration, the I.E. decreases with the increase in acid concentration (Table-1).

TABLE-2
EFFECT OF TEMPERATURE ON CORROSION RATE (CR), INHIBITIVE EFFICIENCY (%), ENERGY OF ACTIVATION (Ea), HEAT OF ADSORPTION (Q_{ads}) AND FREE ENERGY OF ADSORPTION (ΔG^o_a) FOR ALUMINIUM IN 0.05 M TRICHLOROACETIC ACID (TCA) CONTAINING INHIBITORS

System	Temperature (K)						Mean Ea from eqn.2 (kJ mol^{-1})	Ea from Arrhenius plot (kJ mol^{-1})	Q_{ads} (kJ mol^{-1})		Mean value (kJ mol^{-1})		
	313		323		333				313-323 K	323-333 K	(ΔG^o_a)	(ΔH^o_a)	(ΔS^o_a)
	CR (mg/dm^2)	I.E. (%)	CR (mg/dm^2)	I.E. (%)	CR (mg/dm^2)	I.E. (%)							
A	194.70	–	310.68	–	426.68	–	33.83	32.61	–	–	–	–	–
B	57.90	70.26	87.51	72.41	95.28	77.67	21.20	20.70	8.83	8.83	-27.67	6.78	0.108
C	33.14	82.98	58.00	89.33	111.85	73.79	52.90	50.55	-9.47	-9.47	-29.24	56.07	0.265

A = Trichloroacetic acid; B = Trichloroacetic acid + coralene violet 3R Ex.; C = Trichloroacetic acid + coralene yellow Br. REL

TABLE-3
POLARIZATION DATA AND INHIBITION EFFICIENCY OF ORGANIC DYES FOR ALUMINUM IN 0.01 M TRICHLOROACETIC ACID
Surface area of specimen: 0.02585 sq. dm; Inhibitor concentration: 1 mM

System	E_{corr} (mV)	Corrosion current density from intersection of anodic and cathodic Tafel lines I_{corr} (A/cm^2)	Tafel slope (mV/decade)			Inhibition efficiency	
			Cathodic (-βc)	Anodic (+βa)	B (mV)	Polarization method (%)	Weight loss method (%)
Blank	-755	0.0820	6250	230	96	–	–
Coralene violet 3R Ex.	-735	0.0150	1163	129	50	81.71	81.53
Coralene yellow Br. REL	-775	0.0165	976	121	47	79.88	79.90

βa = Anodic Tafel constant; βc = Cathodic Tafel constant.

Effect of inhibitor concentration: At constant acid concentration, the I.E. of the dyes increases with the inhibitor concentration, which is shown in Table-1.

Effect of temperature: The effect of temperature on the corrosion of aluminum alloy is shown in Table-2. It shows that the increase in corrosion rate may be due to the adsorption's of the adsorbed molecules-inhibitor and/or aggressive at higher temperature and thus exposing the fresh metal surface to further attack[15] which results in intensification of the kinetics of electrochemical reaction[16] and thus explains the higher corrosion rate at elevated temperature. In 0.05 M TCA at 4 mM inhibitor concentration, the I.E. for coralene violet 3R Ex. and coralene yellow Br. REL the I.E. increased with raising the temperature except in the case of coralene yellow Br. REL, I.E. decreased at 333 K.

Mean activation energy value were calculated by using eqn. 2 for aluminum alloy in 0.05 M TCA is 33.83 kJ mol^{-1} while in acid containing inhibitors, the mean Ea values are found to be lower than that of uninhibited system except coralene yellow Br. REL (Table-2). The higher values of mean Ea indicate physical adsorption of the inhibitors on metal surface[17], which leads to an increase in the energy barrier for the corrosion process[18]. The lower value of Ea in inhibited acid may probably be accounted for by an increase in the surface area of the metal covered by inhibitor molecules with rise in temperature. The values of Ea calculated from the slope of Arrhenius plot and using eqn. 2 are almost similar.

From Table-2, it is evident that in coralene yellow Br. REL the values of Q_{ads} are negative. The negative values of Q_{ads} show that the adsorption and hence the inhibition efficiency decreases with a rise in temperature[19] while in coralene violet 3R Ex. the Q_{ads} value are positive. The positive value show that the adsorption and hence the I.E. increases with rise in temperature[20].

The mean free energy of adsorption (ΔG^o_a) values are negative almost in all cases and lie in the range of -27.67 (coralene violet 3R Ex.) to -29.24 kJ mol^{-1} (coralene yellow Br. REL). The negative mean value of ΔG^o_{ads} suggest that the inhibitor molecules are strongly adsorbed on the metal surface. The values also indicate a spontaneous adsorption of the inhibitor molecules and usually characterize their strong interactions with the metal surface.

The enthalpy changes (ΔH^o_a) are positive indicating the endothermic nature of the reaction[21] suggesting that higher temperature favours the corrosion process. The entropy (ΔS^o_a) values are positive confirming that the corrosion process is entropically favourable[22].

Polarization behaviour: The polarization behaviour of aluminum alloy in 0.01 M TCA at 1 mM inhibitor concentration under galvanostatic conditions at different current densities in presence and absence of inhibitors.

The values of corrosion current densities in the presence and absence of inhibitor were obtained from the graph while percentage efficiency was calculated using the relation:

$$\text{I.E. } (\%) = [i_{corr}(u) - i_{corr}(i)/i_{corr}(u)] \times 100 \qquad (15)$$

The curves show very little anodic but significant cathodic polarization. However, the addition of inhibitors does not significantly change the Tafel slopes. Thus the open circuit potentials and galvanostatic polarization data suggest that the inhibitors function through general adsorption on cathodic as well as anodic sites on the metal surface.

Mechanism: Usually, corrosion inhibitors containing atoms of nitrogen, sulfur or oxygen have electron donating ability and their action is attributed to the adsorption of the inhibitor molecules on the metal surface through an unshared pair of electrons belonging to the functional atom[23]. Coralene violet 3R Ex. and coralene yellow Br. REL are disperse dyes and azo class. Adsorption of the compound may be due to the interaction of between π-electrons of benzene ring with the positively charged aluminum alloy surface. The interaction of the lone pairs of electrons of nitrogen atoms of the azo group and the amino group with the positively charged aluminum alloy metal surface may also play significant role on the adsorption of the compound on the aluminum alloy surface.

Conclusion

The corrosion rate increases with an increase in acid concentration. At constant acid concentration, the inhibition efficiency of dye increases with increasing inhibitor concentration. As the temperature increases corrosion rate increases in plain acid. The mean free energy of adsorption, ΔG^o_{ads} negative, suggesting that the inhibitor molecules are strongly adsorbed on the metal surface. These values of ΔG^o_{ads} indicate the spontaneous nature of the adsorption of the inhibitor and are usually characteristic of strong adsorption. log $(\theta/1-\theta)$ *vs.* log C (inhibitor concentration) shows straight line, which indicate that the inhibition action appears to be the chemisorptions and inhibitors cover both anodic and cathodic region through general adsorption following Langmuir isotherm. Coralene violet 3R Ex. shows better I.E. (95.80 %) at 4 mM inhibitor concentration in 0.01 M acid concentration. There is a good agreement in the value of I.E. calculated using weight loss data and polarization technique with marginal variation due to limitations of the technique itself.

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