ORGANIC CORROSION INHIBITORS FOR TIN IN HYDROCHLORIC ACID

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The inhibitive effect of benzaldehyde, salicylaldehyde, *p*-anisaldehyde, cinnamicaldehyde and cyclohexanol on the corrosion of tin in 6.0 M hydrochloric acid was studied by weight-loss and galvanostatic methods. It has been found that all the aldehydes give high performance while cyclohexanol appears to be the worst one. Cinnamicaldehyde is the excellent inhibitor even at low concentration (2 mM). All the inhibitors used are found to retard the corrosion by predominantly acting on local cathodes. The effect of time and temperature on inhibitor efficiency has been also studied. The values of activation energy in the absence and presence of inhibitors were evaluated.

Key words: Tin, Inhibitors, Corrosion.

INTRODUCTION

Polar organic compounds like aldehydes [1,2] and ketones [1] are effective inhibitors in the acid dissolution of metal. These compounds are electron-rich and can act as electron donors. Many studies were carried out on the inhibitive effect of some organic and inorganic compounds [3-6]. The action of these compounds as inhibitors was reported to be satisfactory. Crotty [7] stated that the corrosion of zinc in sulphamic acid is inhibited by addition of cinnamicaldehyde, laurylaldehyde and/or heptaldehyde. Machu [8] attributed inhibition to increased ohmic resistance resulting from physical adsorption over the entire surface.

In our earlier publications [9,10], corrosion studies of tin in acidic media were made with the addition of inorganic compounds.

In this article we reporte the effect of benzaldehyde, salicylaldehyde, *p*-anisaldehyde, cinnamicaldehyde and cyclohexanol on the retardation of corrosion of tin in hydrochloric acid solution.

EXPERIMENTAL

Tin foil of 0.1 mm thickness (99.5 %, As not more than 0.0025 %, BDH chemicals Ltd poole, England) was used for this study. Tin sheet of 10 cm^2 surface area (1 x 5 cm. dimensions) was degreased for one minute in an alkali bath of 15 g/l Na_2CO_3 + 15 g/l Na_3PO_4. This was followed by rinsing with running bidistilled water and thoroughly drying. The corrosion rate of tin was determined using the weight-loss teachinque [11]. All corrosion tests were made in duplicate. All chemicals used from A.R or BDH and were used without further purification. The inhibition efficiency was calculated using the equation.

$$I = \frac{W_1^i - W_2}{W_1} \times 100$$

where I is the percentage inhibition efficiency, W_1 and W_2 are the weight loss in the absence and presence of inhibitor respectively. The anodic and cathodic potentials for specimens with 2.0 cm^2 surface area were measured using Tinsley galvanometer type M.S.2, 45F All the experiments were performed in an air thermostatically maintained at $25^o \pm 0.1$.

RESULTS AND DISCUSSION

The corrosion of tin was found in increase with increasing the HCl concentration (1.0   8 0 M). The results are given in Table 1. By plotting log V against log C straight line was obtained with order 1.4 which indicates the degree of aggression.

Table 1. Effect of hydrochloric acid concentration on the corrosion of tin at 25°

Conc./M	1	2	3	4	5	6	7	8
V_{corr}/mg/ dm^2/h.	11.0	27.0	49.0	76.0	107	135.5	173	215

The effect of benzaldehyde, salicylaldehyde *p* anisaldehyde, cinnamicaldehyde and cyclohexanol concentration on the corrosion rate of tin in 6.0 M HCl was studied covering the range 2   50 mM (Table 2). All the compounds show an inhibition effect. The aldehydes possess higher inhibition than cyclohexanol. The order was found to be; cinnamicaldehyde > *p*-anisaldehyde > salicylaldehyde ⩾ benzaldehyde ≫ cyclohexanol, in which cinna-

micaldehyde has the best effect and cyclohexanol is the least one. The order is in accord with the electronic structure of each compound. The ethylenic double bond in cinnamicaldehyde could increase the activity of the carbonyl group which consequently increases its adsorption. The donor character of $-OCH_3$ group in *p*-anisaldehyde increases the rate of electron transfer through the aromatic ring which facilitates the attraction with the positively charged metal surface. The expected hydrogen bond between the hydrogen of aldehyde and the oxygen of ortho $-OH$ of salicylaldehyde may result a decrease in the polarity of the functional group and subsequently in the adsorption process relative to *p*-anisaldehyde and cinnamicaldehyde compounds. The absence of any substituent in benzaldehyde compound would show as expected a decrease in its inhibition effect. The order of cyclohexanol as the worst one is quite acceptable due to the absence of any conjugation in its electronic structure. The possible transition is only available from the free electrons located on the oxygen of the hydroxy group.

The cathodic and anodic polarization curves of tin in 6.0 M hydrochloric acid in absence and presence of 5 mM of the additives are shown in Fig. 1. It is obvious that all
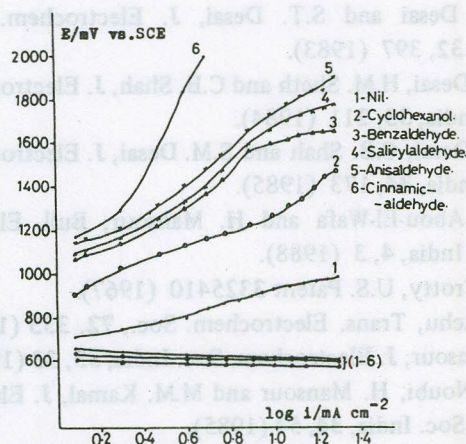

Fig. 1. The influence of current density on cathode and anode potentials of tin in 6.0 M HCl in the absence and presence of 5 mM of inhibitors.

the compounds are cathodic inhibitors. Cinnamicaldehyde shows a considerable increase in cathodic polarization whereas benzaldehyde, salicylaldehyde and *p*-anisaldehyde polarize the cathode to a less extent. The polarization with cyclohexanol is very low relative to the other compounds. This is in good agreement within the order previously mentioned. Anodic Tafel slopes have practically a constant value (35 mV/decade) while the cathodic slope (230 mV/decade) in 6.0 M hydrochloric acid is changed to 410,560,

Table 2. Influence of inhibitor concentration on the corrosion rate of tin in 6.0 M HCl (values in brackets show % inhibition).

Compound C/mM	V_{corr}/mg/dm^2/h.				
	Cyclo-hexanol	Benzal-dehyde	Salicyl-aldehyde	*p*-anisal-dehyde	Cinnamic-aldehyde
0.0	135.5	135.5	135.5	135.5	135.5
2.0	111.0 (18.1)	50.5 (62.7)	48.5 (64.2)	36.5 (73.0)	19.0 (85.9)
4.0	1.03.0 (24.0)	39.5 (70.8)	42.0 (69.0)	32.5 (76.0)	16.5 (87.8)
5.0	95.5 (29.5)	29.5 (78.2)	27.0 (80.0)	19.5 (85.6)	10.5 (92.2)
6.0	96.0 (29.1)	30.0 (77.8)	24.5 (81.9)	16.5 (87.8)	6.0 (95.5)
8.0	90.5 (33.2)	21.5 (84.1)	23.5 (82.6)	9.5 (93.0)	1.0 (99.2)
10.0	89.5 (33.9)	19.5 (85.6)	17.0 (87.4)	4.5 (96.6)	1.0 (99.2)
20.0	84.0 (38.0)	15.0 (88.9)	10.0 (92.6)	3.0 (97.7)	0.5 (99.6)
30.0	75.5 (44.2)	10.5 (92.2)	6.0 (95.5)	0.5 (99.6)	0.5 (99.6)
40.0	68.0 (49.8)	7.0 (94.8)	5.5 (95.9)	0.5 (99.6)	1.0 (99.2)
50.0	(50.9)	(95.2)	(97.0)	(99.2)	(99.6)

Table 3. Effect of time on the corrosion of tin in 6.0 M HCl in the absence and presence of 5 mM of inhibitors (values in brackets show % inhibition)

Compound	V_{corr}/mg/dm^2					
Time/h.	½	1	2	3	4	5
Nil	53.0	135.5	220.5	303.0	392.0	485.0
Cyclohexanol	39.5 (25.4)	95.5 (29.5)	148.5 (32.6)	199.0 (34.3)	254.0 (35.2)	305.0 (37.1)
Benzaldehyde	17.5 (66.9)	29.5 (78.2)	37.0 (83.2)	47.5 (84.3)	52.0 (86.7)	55.0 (88.6)
Salicylaldehyde	17.0 (67.9)	27'0 (80.0)	35.5 (83.9)	43.0 (85.8)	49.0 (87.5)	52.5 (89.1)
p-anisaldehyde	14.5 (72.6)	19.5 (85.6)	26.5 (88.0)	30.5 (89.9)	35.0 (91.0)	36.5 (92.4)
Cinnamicalde-hyde	9.0 (83.0)	10.5 (92.2)	12.0 (94.5)	13.0 (95.7)	13.5 (96.5)	14.5 (97.0)

Table 4. Influence of temperature on the corrosion of tin in 6.0 M HCl in the absence and presence of 5 mM of inhibitors (values in brackets show % inhibition).

Temperature/^{O}C Compound	V_{corr}/mg/dm^2/h.			
	25	30	40	50
Nil	135.5	218.0	685.0	1675.0
Cyclohexanol	95.5 (29.5)	189.0 (13.3)	764.0 (−11.5)	2512.5 (−49.9)
Benzaldehyde	29.5 (78.2)	34.5 (82.2)	39.0 (94.3)	46.5 (97.2)
Salicylaldehyde	27.0 (80.0)	35.0 (81.9)	37.5 (94.5)	42.0 (97.5)
p-anisaldehyde	19.5 (85.6)	22.0 (88.6)	25.5 (96.2)	28.0 (98.3)
Cinnamicaldehyde	10.5 (92.2)	12.0 (93.8)	13.5 (98.0)	16.0 (99.0)

1-Nil.
2-Cyclohexanol.
3-Benzaldehyde.
4-Salicylaldehyde.
5-Anisaldehyde.
6-Cinnamicaldehyde.
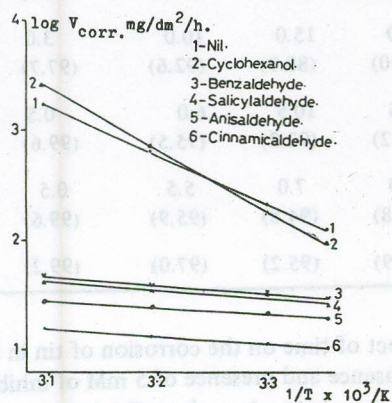
Fig. 2. log V_{corr} − 1/T plot.

620,640 and 1660 mV/decade in presence of cyclohexanol, benzaldehyde, salicylaldehyde, p-anisaldehyde and cinnamicaldehyde respectively. This indicates that these compounds have a protection effect.

The effect of immersion time (½ − 5.0 h.) on the rate of corrosion of tin in 6.0 M HCl in presence of 5 mM additives was investigated (Table 3). It is found that all the additives have inhibition effect which increase with increasing the time of immersion. The order is as given before. This behaviour may be attributed to the improvement in the adsorption character of the additive with time.

The effect of temperature (25–50°) on the performance of additives in 6.0 M HCl was studied (Table 4). It is observed that the efficiency of benzaldehyde, salicylaldehyde, p-anisaldehyde and cinnamicaldehyde as inhibitors increase with temperature while with cyclohexanol, the efficiency sharply decreased with temperature. The conclusion is that the adsorption of the aldehydes increases with temperature. The values of activation energy 9.64 and 1.53, 1.53, 1.32, 1.35 and 12.39 k.cal./mol, which were evaluated from 1/T vs. log corrosion rates plots in absence and presence of the additives respectively, indicate that all the aldehydes act as inhibitors while cyclohexanol act as accelerator at higher temperatures. The results are in consistent within the reported data [12,13].

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