TOLUIDINES AS CORROSION INHIBITORS FOR 3S ALUMINIUM IN TRICHLOROACETIC ACID

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Inhibition of corrosion of 3S aluminium in trichloroacetic acid by toluidines has been studied. In general, at constant acid concentration, inhibitor efficiency increases with concentration of the inhibitor and the period of immersion. At 1.0—1.5% concentration of the inhibitor the efficiency is in the order: p-toluidine <o-toluidine <aniline <m toluidine. The inhibitive efficiency of the inhibitors in the range 30-50°C is in the order: p-toluidine <o-toluidine <m-toluidine <aniline. The value of the energy of activation in uninhibited 0.2N TCA is 22 4 kcal/mole whereas in the presence of inhibitors the values are lower and range from 13.7 (aniline) to 17.0 (p toluidine) kcal/mole. All the four inhibitors increase the corrosion potential from -505 mV (in 0.1N TCA) to less negative values and appear to be mixed type inhibitors with somewhat preponderent action on the local anodes.

Aluminium is a highly reactive metal[1] ($\Delta G^{\circ}_{Al_2O_3} = -376.8$ cal). However, the metal resists attack by many a neutral or near-neutral environments due to the formation of a protective film of aluminium oxide. The oxide, being amphoteric in nature, dissolves in solutions which are strongly acid or strongly alkaline. In the manufacture of chlorosubstituted acetic acids it is observed that no metal satisfactorily withstands corrosion. The uses of chlorosubstituted acetic acids in cellulose industry also brings in serious corrosion problems.

Although corrosion of aluminium in acetic and chlorosubstituted acetic acids is studied by a number of workers[2—10] the data are not so plentiful. In earlier communications[11—20] the inhibition of corrosion of 2S (99.8% Al), 3S (Al-1.3% Mn), B26S (Al-3.9% Cu) and M57S (Al-2% Mg) aluminium in aqueous solutions of trichloroacetic acid (TCA) using different colloids, inorganic salts and organic amines has been reported. In the present communication, the inhibition of corrosion of 3S aluminium in TCA by toluidines has been studied.

EXPERIMENTAL

Rectangular (5×4 cm) specimens of 3S aluminium (supplied by Indian Aluminium Co. Ltd., Bombay) with a small hole of about 2 mm dia. near the upper edge of the specimen, were used for the determination of the corrosion rate. The amounts of Fe, Si and Mn in the alloy were determined according to the method of Vogel[21]. The percentage composition of the alloy was found to be as follows:

Mn 1.3; Fe 0.68; Si 0.65; Cu ≤ 0.15; Zn ≥ 0.10; Al remainder.

The specimens were polished according to the method described earlier[22,23]. The test specimens were exposed to 0.1–0.2N trichloroacetic acid solutions containing controlled additions of toluidiness in the range 0.0 to 1.5%. One specimen only was suspended by a glass hook in each beaker which contained 230 ml of the test solution and was open to the air, at 30° ±0.5°C (unless otherwise specified). Duplicate experiments were performed in each case and the values of the weight losses have been reported. After the tests, the specimens were cleaned with a chromic-phosphoric acid mixture[24,25].

For the collection of polarization data, metal coupons of circular design with a diameter of 2.84cm, and a handle 1.81 cm long and 0.5 cm wide, were used. The handle and the back of the test coupon as well as the auxiliary platinum electrode were coated with a mixture of perspex and wax from chloroform solution, leaving only the circular portion of apparent surface area of 6.156 sq.cm. exposed to the corrosive medium The concentration of the inhibitor employed was that which gave maximum inhibition in the absence of applied current. The change in potential was measured against a seturated calomel electrode. The test cell was an H-type cell with the Luggin's capillary as nearer to the electrode surface as possible. The c.d. was varied in the range 1.624×10^{-5} to $8\ 120 \times 10^{-4}$ Amp/cm².

OBSERVATIONS

The specimens immersed in acid solutions containing small amounts (0.1–0.3%) of inhibitor suffered pitting type of attack when the extent of inhibition was less than 55%. However in those cases, wherein the extent of inhibition was more than 55% but less

than 90%, there was no pitting and the specimens appeared dull metallic with slight etching in some cases. With the extent of inhibition greater than 90% the specimens were almost as bright as before.

RESULTS AND DISCUSSION

(A) EFFECT OF INHIBITOR CONCENTRATION

Fig. 1 shows the effect of inhibitor concentration on inhibitive efficiency of aniline and the three toluidines in 0.1N TCA. It is evident that the efficiency increases with inhibitor concentration.

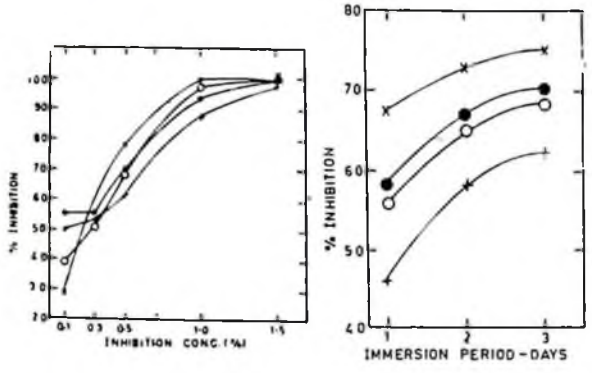


FIG 1. EFFECT OF INHIBITOR CONC. & FIG 2 EFFECT OF IMMERSION PERIOD ON INHIBITOR EFFICIENCY. X-X ANILINE; ●-● O-TOLUIDINE; o-o m- AND + + p-TOLUIDINE

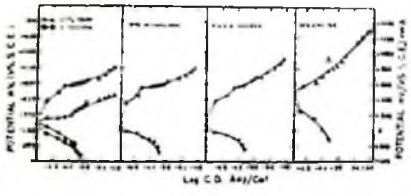


FIG 3 EFFECT OF C.D ON CATHODE AND ANODE POTENTIALS (1.0% INHIBITOR)

Addition of 0.1% aniline to 0.1N TCA decreased the extent of corrosion by ~28%. Further increase in concentration increased its efficiency and there was 100% protection from attack with 1.5% of aniline. With other inhibitors also there was an increase in efficiency with inhibitor concentration, the ranges of inhibitive efficiencies being 38.9% to 100% in the case of m-toluidine, 55.2% to 99.6% with o-toluidine and 50.5% to 97.4% for p-toluidine.

A comparison of the inhibitive efficiencies of the four compounds studied in 0.1N TCA shows that at lower concentrations (0.1%) of the inhibitor, the order of efficiency is: Aniline (28.2%) <m-toluidine <p-toluidine <o-toluidine (55.2%). At higher (1.0–1.5%) concentrations the efficiency is in the order: p-toluidine <o-toluidine <aniline <m-toluidine.

(B) EFFECT OF EXPOSURE PERIOD

In order to examine the effect of immersion period on inhibitor efficiency, the extent of corrosion was measured for different exposure periods ranging from 1 to 3 days in 0.1N TCA inhibited with 0.5% of inhibitor. The results given in Fig.2, indicate that, in the case of aniline the efficiency slightly increased from 67.7% for 1 day to 77.5% for 3 days immersion period. In the case of ortho-, meta-and p-toluidine the efficiency increased up to 2 days and then almost remained constant. For an immersion period of 1 day the efficiencies of the compounds tested are in the order: p-toluidine (46.5%) <m-toluidine <o-toluidine <aniline (67.7%). For the 3 d exposure period the efficiencies of the inhibitors are: p-toluidine 62.4% <m-toluidine > o-toluidine <aniline (77.5%). The increase in efficiency with time may be attributed to an increase in adsorption of the inhibitor with time.

(C) EFFECT OF TEMPERATURE:

In order to study the effect of temperature on inhibitor efficiency the corrosion of 'S aluminium was studied in 0 2N TCA, with and without 1.5% inhibitor, at 20°, 30°, 40° and 50°C. In 0.2N TCA (uninhibited), the extent of corrosion increased from 7.8 mg/dm² at 20°C to 625.0 mg/dm² at 50°C. i.e. there was an 80-fold increase in corrosion with 2.5-fold increase in temperature (Table 1). This may be due to an increase in the rate of reduction of TCA to dichloroacetic and hydrochloric acids with rise in temperature:

$$CCl_3COOH + 2H \rightarrow CHCl_2COOH + HCl \qquad (1)$$

In 0.2N TCA containing 1.5% inhibitor, aluminium did not suffer any corrosion at 20°C. At other temperatures the weight losses ranged from 1.8 to 7.5 mg/dm² (30°C), 3.8 to 20.0 mg/dm² (40°C) and 7.2 to 43.8 mg/dm² (50°C). This gave an efficiency of 100% at 20°C; 88.0—97.2% at 30°C; 90.6—98.2% at 40°C and 93.0—98.8% at 50°C. This results indicate that although the extent of inhibition remains almost constant, the extent of corrosion is doubled for every 10°C rise in temperature.

In the range 30—50°C, the efficiency of the inhibitors is in the order: p-toluidine <o-toluidine <m-toluidine < aniline. The values of the energy of activation E, for the corrosion process in inhibited

as well as unihibited acid were calculated following the equation :

$$\log \frac{g_2}{g_1} = \frac{E}{2.303T} \left\{ \frac{1}{T_1} - \frac{1}{T_2} \right\} \quad \ldots\ldots(2)$$

where g_1 and g_2 are the corrosion rates (mg/dm²/3hr) at temperatures T_1 and T_2 (°K) respectively. The values of E, given in Table I, agree with those calculated from the slope of the plot of log g vs $\frac{1}{T}$. The mean values of E are found to be in the order : analine (13.7) <m-toluidine (14.9) <o-toluidine (15.2) <p-toluidine (17.0) <uninhibited TCA (22.4 kcal/mole).

From the Table it is apparent that for each of the compounds studied, the energy of activation has alomst a constant value in the range 30—50°C and the value is lower in inhibited than in uninhibited acid. The nearly equal values of E for all the inhibitors indicate that they are similar in their mechanism of action. The higher value of E (viz 22.4 kcal/mole) in uninhibited acid shows that the temperature coefficient of the reaction in uninhibited acid is very high, probably because of the reduction of TCA according to eq. (1). The lower values of temperature coefficient as well as the corrosion rate in presence of inhibitors suggest that the compounds are powerful inhibitors and are of practical interest when retardation of corrosion at elevated temperature is disired. Such substances, like the catalysts which do not change the temperature coefficient of reaction are firmly held on the metal surface by forces of specific adsorption or chemisorption[26]. The decrease in the value of E is probably accounted for by the increase in the surface area of the metal covered by the inhibitor molecules with a rise in temperature[27]. When there is specific adsorption of the inhibitor on the metal, the corrosion reaction can proceed by diffusion of the corrosive species through fine pores of the protective layer formed. The kinetics of the corrosion process then acquire the character of a diffusion process, which explains the low temperature coefficient of the reaction.

TABLE-I Values of corrosion loss and energy of activation for 3S aluminium in 0.2N trichloroacetic acid (Surface area of specimen, 40 cm²; Immersion period, 3 hrs; Inhibitor concentration, 1.5%)

Inhibitor	Corrosion loss (mg/dm²) at 20°	30°	40°	50°C	Energy of activation, kcal/mole, for the temperature range 20—30°	30—40°C	40—50°C	Mean E	'E' (Arrhenius plots)
Nil	7.8	62.5	212.5	625.0	(37.3)+	23.1	21.7	22.4	21.5
Aniline	nil	1.8	3.8	7·2	*	14.3	13.2	13.7	13.7
o-toluidine	nil	6.0	12.5	28.6	*	13.8	16.7	15.2	15.1
m-toluidine	nil	5.8	12.0	26.8	*	13.8	16.1	14.9	15.5
p-toluidine	nil	7.5	20.0	43.8	*	18.4	15.7	17.0	16.9

* E Values are not calculated as there is no corrosion at 20°.

\+ Values in brackets are not considered for calculating the mean value of E.

(D) STEADY STATE POTENTIALS :

Specimens of 3S aluminium, when immersed in uninhibited 0.1N TCA developed a corrosion potential of -505 mv (vs.S.C.E.). In the presence of inhibitors the potential was found to increase (became less negative), the values being, -480, -480, -450 and -460 mv respectively in presence aniline, o-toluidine, m-toluidine and p-toluidine. This indicates that the inhibitors have somewhat preponderent action on the local anodes, it being more so in the case of m-toluidine.

(E) POLARIZATION BEHAVIOUR :

The polarization behaviour of aluminium in 0.1N trichloroacetic acid under galvanostatic conditions at different current densities in presence and absence of inhibitors is shown in Fig. 3. 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 :

$$I = \frac{i_{corr}\text{ (without inhibitor)} - i_{corr}\text{ (with inhibitor)}}{i_{corr}\text{ (without inhibitor)}} \times 100$$

From the polarization data shown in Fig. 3 it is evident that under the influence of impressed current the cathodes in inhibited acid are polarized to a greater extent than in uninhibited acid. Maximum cathodic polarization is observed in aniline followed by ortho-, meta- and p-toluidine. During anodic polarization the anodes are polarized to a greater extent in uninhibited acid than in inhibited acid. Taking into consideration the data in Fig. 3 and Table II, it may be generalized that the four inhibitors act as mixed type inhibitors. Good correlation appears to exist between the inhibitor efficiencies calculated from the weight loss data and those calculated by extrapolation of cathodic Tafel line as well as from intersection of cathodic and anodic Tafel lines.

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TABLE-II Tafel parameters and inhibitor efficiencies for 3S aluminium in 0.1N trichloroacetic acid

Inhibitor (conc. 1.0%)	Open circuit potential (mV)	Tafel slope (V/decade) Anodic	cathodic	Energy Transfer coefficient (cathodic)	Corrosion Current A/cm² from Intersection of cathodic and anodic Tafel lines (a)	Extrapolation of cathodic Tafel line (b)	Inhibitor efficiency (%) calculated from (a)	(b)	weight loss data
Nli	-505	0.32	0 24	0.23	3.25×10^{-5}	5.00×10^{-7}	—	—	—
Aniline	-480	0. 0	0.50	0.12	0.90×10^{-6}	0.20×10^{-7}	97.2	96.0	99.1
o-toluidine	-480	0.25	0.18	0.33	0.80×10^{-6}	5.00×10^{-8}	97 5	90.0	93.8
m-toluidine	-450	0.23	0.20	0.30	1.80×10^{-6}	2.00×10^{-8}	94.4	96.0	97.1
p-toluidine	-460	0.36	0.25	0.24	6.00×10^{-6}	7.50×10^{-8}	81.5	85.0	87.6

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