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ANILINE AS CORROSION INHIBITOR FOR ALUMINUM IN TRICHLOROACETIC ACID

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ABSTRACT

Aniline was studied as a corrosion inhibitor for aluminum in trichloroacetic acid (TCA) solution. The inhibition efficiency depended on the concentration of acid and the inhibitor. Inhibition efficiency of TCA solutions increased with aniline concentration, but decreased with rise in temperature, this corresponded to surface coverage of the metal by the inhibitor. The degrees of surface coverage, θ, were calculated and found to increase with the inhibitor concentration. The results show also that, the nhibitors were adsorbed on the aluminum surface according to Langmuir adsorption isotherm. Polarization study reveals that the inhibitors function as a little anodic, but significant cathodic inhibitor.

KEYWORDS*:* Corrosion, Aluminum, Trichloroacetic acid, Aniline, Adsorption.

INTRODUCTION

Corrosion is clearly a multidisciplinary field of science and engineering. Corrosion is a natural phenomenon, which can be considered either chemical or electrochemical in nature. It is an inevitable and serious problem for various industries. Corrosion process degrades the metallic properties of metal/alloys and renders them to be rejected from the special structures of industrial importance. Since metal have a high electric conductivity, their corrosion is usually of an electrochemical in nature. Aluminum and its alloy show high resistivity towards a wide variety of corrosive environments. This is may be due to the formation as protective, tightly adherent and at times invisible oxide film on the metal surface. The film is generally stable in solutions of pH 4.5- 8.5.[1] Acid solutions mainly HCl and H_2SO_4 are generally used for the removal of undesirable scale and rust in several industrial processes. For this reason some sorts of inhibitors are generally used to control metal dissolution as well as acid consumption.[2] Most of the well-known acid inhibitors are organic compounds containing polar nitrogen, oxygen or sulfur atoms in a conjugated system have particularly been reported to exhibit corrosion inhibiting efficacy.[3-8] The efficiency of N-organic compounds as corrosion inhibitors depends on the possibility of the transfer of one pair of electrons from the organic compounds and formation of coordinate bonds with the metal or alloys.[9] Therefore, the inhibition efficiency strongly depends on the structure and chemical properties of the layers that are formed under the particular experimental condition. Nitrogen containing organic compounds has been used extensively as corrosion inhibitors for the corrosion of metals in acid solutions. At the same time, there is very little information about the inhibition of aluminum corrosion in TCA solutions using such organic compounds as inhibitors.[10-14] Some researcher used amino acetanilides[15], ansidines[16] and Nitro aniline[17] as corrosion inhibitors for aluminum corrosion in acid solution. Desai et al.[18] studied the corrosion inhibition behavior of aluminium in TCA in the absence and presence of anisidine isomers and their blends using weight loss and Polarization technique. Therefore, the purpose of the present work is to investigate the effect of aniline on the corrosion of aluminum in TCA solution, using gravimetric and galvanostate polarization technique.

EXPERIMENTAL PROCEDURE

Aluminum sheets of the 2S type aluminum (Al = 98.02%; Mg = 0.37%; Si = 0.49%; Fe = 0.68%; Mn = 0.16; and Cu = 0.082%) were used in this study. Each sheet, which was 0.18 cm in thickness, was mechanically press-cut into coupons of dimension 2 x 5 cm with small hole of about 5 mm diameter near the upper edge. These coupons were used in the "as cut" condition, inhibition efficiency without further polishing, but were degreased in absolute ethanol, dried in acetone, weighed and stored in a moisture-free desiccator prior to use. All chemicals and reagents used were of analytical grade and used as source without further purification. The aggressive media were, respectively, 0.01, 0.05 and 0.1 M TCA solutions. Aniline was used inhibitor in the concentration range 5 to 20mM.

Weight loss method

The test specimens were immersed in 0.01, 0.05 and 0.1 M TCA solution with and without inhibitors. Only one specimen was suspended by a glass hook, in each beaker containing 230 ml of the test solution and was open to air at room temperature for 24 h duration. After the test, the specimens were cleaned with chromic-phosphate mixture solution.[19] Triplicate experiments were performed in each case and the mean values of the weight loss data are presented in Table 1.

To study the effect of temperature on corrosion rate, the specimen was immersed in 230 ml in 0.05 M TCA, with aniline as inhibitor concentration 5, 10, 15, and 20mM at solution temperatures of 313, 323 and 333 K for a period of 2 h. To study the effect of temperature, thermostat assembly with an accuracy of ± 0.5^{oaks} was used. Wesley[20] and ASTM[21] pointed out that thermostatic controls to within ± 1°C usually are considered satisfactory. Inhibition efficiency (η %), energy of activation (E_a), heat of adsorption (Q_{ads}) free energy of adsorption ($\Delta G^0{}_{ads}$), enthalpy of adsorption ($\Delta H^0{}_{ads}$) and entropy of adsorption ($\Delta S^0{}_{ads}$) were calculated and shown in Table 2 & 3.

Polarization

For polarization study, metal specimens of rectangular design having an area of 0.0932 dm^2 were exposed to corrosive solutions. Aluminum metal was used as a working electrode, SCE was used as reference electrode and the auxiliary graphite electrode was placed in a 350 ml corrosive medium through which external current was supplied automatically from the computerized polarization instrument. The change in potential was measured by potentiostate / galvanostate (Gamry-Make, USA) on potentiostate mode with 5 mV/ sec scan rate. Polarization has been taken with and without inhibitors in 0.01 M TCA. Curves show polarization of both the anodes and cathodes.

RESULTS AND DISCUSSION

The results are presented in Tables 1 to 4 and Figures 1 to 2. To assess the effect of corrosion of aluminum in TCA, aniline is used as inhibitors.

Specific conductivity of 0.01, 0.05 and 0.1 M acid concentration was found to be 3.25 x 10^{-3}, 16.79 x 10^{-3} and 30.30 x 10^{-3} milimohs / cm respectively. This suggests that specific conductivity increase with increase of acid concentration. The addition of inhibitors decreases the specific conductivity. Specific conductivity for aniline at 5mM inhibitor concentration in 0.01 M acid concentration is 0.66 x 10^{-3} milimohs / cm.

The corrosion rate of aluminum metal in TCA was increased with the acid concentration which was shown in Table 1. The inhibition efficiency (η %) and degree of surface coverage (θ) at each concentration of aniline was calculated by comparing the corrosion loss in the absence (W_u) and presence of aniline (WI) using the relationships.

$$\eta\% = \left(\frac{Wu - Wi}{Wi}\right) X100 \qquad (1)$$

$$\theta = \left(\frac{Wu - Wi}{Wi}\right) \qquad (2)$$

As a constant inhibitor concentration, the inhibition efficiency decreases with the increase in acid concentration. At 20 mm inhibitor concentration, the inhibition efficiency of aniline is 99.99, 75.79 and 22.29 % with respect to 0.01, 0.05 and 0.1 M acid concentration respectively. At a constant acid concentration, the inhibition efficiency of the aniline increases with the inhibitor concentration, e.g. aniline in 0.01 M TCA the inhibition efficiency was found to be 90.24, 96.86, 97.21 and 99.99 % with respect to 5, 10, 15 and 20mM inhibitor concentration respectively (Table 1).

Table :1 Effect of acid concentration on corrosion loss (CL) and inhibition efficiency (η %) of aluminum in TCA.

Temp. 301 ± 1 K, Immersion Period: 24 h, Effective Specimen area: 0.2414 dm^2

Inhibitor	**I.C. mM**	**Acid Concentration**					
		0.01 M		**0.05 M**		**0.1 M**	
		C. L. mg / dm^2	**I. E %**	**C. L. mg / dm^2**	**I. E %**	**C. L. mg / dm^2**	**I. E %**
I	II	III	IV	V	VI	VII	VII
Blank	-	118.88	-	1189.3	-	2452.09	-
aniline	5	11.60	90.24	425.29	64.24	1943.04	20.76
	10	3.73	96.86	375.39	69.95	1937.40	20.99
	15	3.31	97.21	319.80	73.11	1926.61	21.43
	20	0.01	99.99	287.93	75.79	1905.52	22.29

The temperature has significant influence on a metal corrosion rates. The effect of change in temperature on the corrosion rates of aluminum in 0.05 M TCA, the corrosion of aluminum was increased with rising temperatures. Corrosion rate was measured in 0.05 M TCA containing 5, 10, 15 and 20mM inhibitor concentration at a solution temperature of 313, 323 and 333 K for an immersion period of 2h. In 0.05 M TCA solution with 20mM inhibitor concentration, the inhibition efficiency for aniline was decreased corresponds to 70.22, 65.33 and 35.92 % in 313, 323 and 333 K respectively (Table 2).

Table 2: Effect of temperature on corrosion rate (CL), inhibitive efficiency (η %), for aluminum in 0.05M TCA contain aniline at different inhibitor concentration.

Immersion Period : 2 h,Effective Specimen area : 0.2488 dm²

Inhibitor concentration	Temperature K					
	313		323		333	
	C. R. mg/ dm²	I. E %	C. R. mg/ dm²	I. E %	C. R. mg/ dm²	I. E %
Blank	194.70	-	310.68	-	426.68	-
5	78.70	59.58	162.70	47.63	298.26	30.10
10	68.65	64.74	143.60	53.78	281.74	33.97
15	60.37	68.99	124.36	59.97	272.65	36.10
20	57.99	70.22	107.71	65.33	273.41	35.92

In the present study general type of corrosion occurs predominately and less pitting. Plotting of log θ/1-θ versus log C(M), straight lines were obtained, indicating that the adsorption of the added inhibitors followed the Langmuir adsorption isotherm (Fig.1). Therefore, adsorption of these compounds is assumed to occur uniformly over the metal surface.

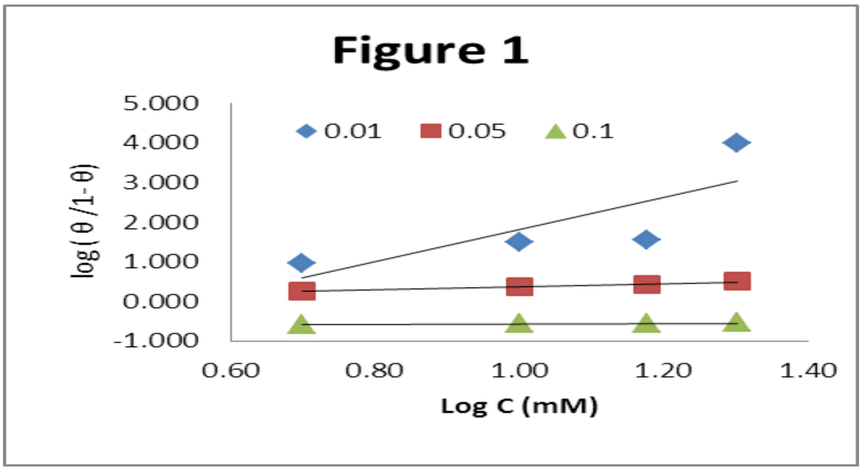


Figure 1 : Plot of log (θ / 1-θ) Versus log C(M) for aromatic amines in 0.05 M TCA.

The values of the free energy of adsorption (ΔG^0_{ads}) were calculated with slope of the following equation.[22]

$$LogC = L\log\left(\frac{\theta}{1-\theta}\right) - LogB \qquad (3)$$

Where

$$LogB = -1.74 - \left(\frac{\Delta G^0_{ads}}{2.303RT} \right)$$

and C is the inhibitor concentration. The mean ΔG^0_a values are negative almost in all cases and lie in the range of -22.02 to -24.63 kJ. mol^{-1} shown in Table 3. The most efficient inhibitor shows more negative ΔG^0_a value. This suggests that they be strongly adsorbed on the metal surface. This statement was supported by the work of Talati and Darji.[23] The values of heat of adsorption (Q_{ads}) were calculated by the following equation.

$$Q_{ads} = 2.303R\left[Log\left(\frac{\theta_2}{1-\theta_2} \right) - Log\left(\frac{\theta_1}{1-\theta_1} \right) \right] X \left[\left(\frac{T_1T_2}{T_2-T_1} \right) \right] \qquad (4)$$

From Table 3, it is evident that in all cases, the (Q_{ads}) values are negative and ranging from -18.14 to -82.05 kJ.mol^{-1}. The negative values show that the adsorption, and hence the inhibition efficiency, decreases with a rise in temperature.[24]

Table 3: Energy of activation (Ea), heat of adsorption (Qads) and free energy of adsorption (ΔG^0a) for aluminum in 0.05M TCA contain aniline.

System	Mean Ea from Eq (2) kJ.mol^{-1}	Ea from Arrhenius plot kJ.mol^{-1}	Qads (kJ.mol^{-1})		Mean Value (kJ.mol^{-1})		
			313 – 323 K	323 - 333 K	ΔG^0a	ΔH^0a	ΔS^0a
Blank	33.83	32.61	-	-	-	31.18	-
5	57.63	55.37	-24.64	-78.80	-24.63	54.985	0.2525
10	61.23	58.69	-38.33	-68.60	-23.18	58.585	0.2591
15	65.49	62.66	-33.25	-82.05	-22.57	62.84	0.2707
20	67.68	64.44	-18.84	-94.97	-22.02	65.035	0.2758

Mean 'E_a' value was calculated by using eq. (5) for aluminum in 0.05 M TCA is 33.83 kJ.mol^{-1} while in acid containing inhibitor, the mean E_a values are found to be higher than that of an uninhabited system (Table 3). Higher values of mean sea indicate physical adsorption of the inhibitors on metal surface[25], which leads to an increase in the energy barrier for the corrosion process. The values of a calculated from the slope of an Arrhenius plot (Figure 2) and using eq. (5) are almost similar. Energy of activation (Ea) has been calculated from the slopes of log p versus 1/T (p = corrosion rate, T = absolute temperature) and also with the help of Arrhenius equation.

$$Log\frac{P_2}{P_1} = \frac{Ea}{2.303R}\left[\left(\frac{1}{T_1} \right) - \left(\frac{1}{T_2} \right) \right] \qquad (5)$$

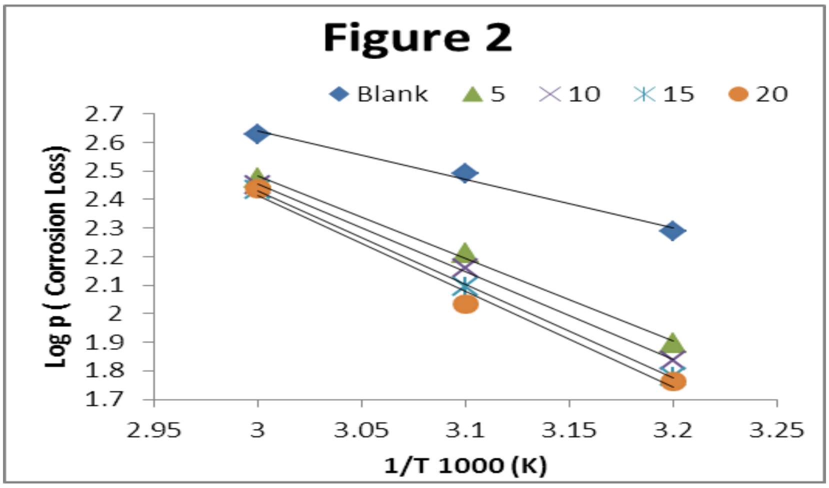


Figure 2 : Arrhenius plots for corrosion of Aluminum in 0.05 M TCA in absence and presence of inhibitor.

Where p_1 and p_2 are the corrosion rate at temperature T_1 and T_2 respectively. The enthalpy of adsorption (ΔH^0_{ads}) and entropy of adsorption (ΔS^0_{ads}) were calculated using the following equation (6) and (7).

$$\Delta H^0 ads = Ea - RT \qquad (6)$$

$$\Delta S^0{}_{ads} = \frac{\Delta H^0{}_{ads} - \Delta G^0{}_{ads}}{T} \qquad (7)$$

The enthalpy changes (ΔH^0_a) are positive, indicating the endothermic nature of the reaction suggesting that higher temperature favors the corrosion process.[26] The entropy (ΔS^0_a) values are positive, confirming that the corrosion process is entropically favorable.[27]

The value of the corrosion potential with inhibitors were found become more negative than the without inhibitors. Polarization study reveals that the inhibitors function as little anodic, but significant cathodic inhibitors, the curve of aniline showed that inhibitor functions as a mixed inhibitor. The values for the Tafel parameters obtained from this plot with and without inhibitors are given in Table 4. The values of corrosion current densities in the presence and absence of inhibitor were obtained from the graph while percentage efficiency (η %) was calculated using the Equation (8). The inhibition efficiency from Tafel plots agrees well (within ± 10 %) with the values obtained from weight loss data.

$$\eta(\%) = \left[\frac{i_{corr}(u) - i_{corr}(i)}{i_{corr}(u)}\right] \times 100 \qquad (8)$$

Table 4: Polarization data and inhibition efficiency of aniline for aluminum in 0.01 M TCA.

Inhibitor Concentration: 20 mM, Effective Specimen area: 0.0932 dm²

System	Ecorr mV	Icorr A/cm²	Tafel slope (mV / decade)			Inhibition efficiency %	
			-βc	+βa	B mV	Pol. method	Wt. loss method
Blank	-755	0.0820	6250	231	97	_	_
Aniline	-730	0.0090	3667	202	63	89.02	90.24

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

$$Al \rightarrow Al^{+3} + 3e^{-} \quad (9) \quad \text{(anode)}$$

$$H^{+} + e^{-} \rightarrow H \quad (10) \quad \text{(cathode)}$$

followed by the reaction,

$$H + H \rightarrow H_2 \quad (11)$$

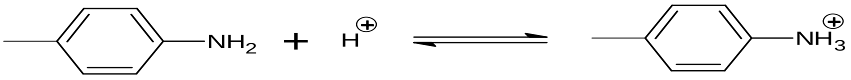
The following secondary reaction can also take place in acid solutions.[28]

$$2M + 2H^{+} \rightarrow H_2 + 2M^{+} \quad (12) \quad \text{(anode)}$$

$$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O \quad (13) \quad \text{(cathode)}$$

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.

It was observed that the percentage of inhibition increase with increase of inhibitor concentration and it decreases with increase of acid concentration. This may be due to that the inhibitor changes in to onium ion in more acidic medium and thus may not be available as a free molecule for adsorption. The inhibitors change in cationic form i.e. onium ion as follows.



Immediately afterwards, as the corrosion reaction starts, the anilinium type ion may become electrostatically attached to the anode points, or it is possible that the alkalinity produced at the cathodic sites favors the free base.

$$—RNH^{+}_{3\,(sol)} \leftrightarrow —RNH_2 + H^{+\leftrightarrow} —RNH_2 : M$$

Which would then be generally adsorbed on the metal surface.[29] It may be assumed that the inhibitory function through general adsorption covering both the cathodic and anodic points, although in the initial stages they might get attached to the cathodic points. The adsorption can take place via the functional nitrogen atom or the delocalized or ה- electrons of the aromatic amine.

CONCLUSIONS

- At all concentration of acid, as the inhibitor concentration increases inhibition efficiency increases and corrosion rate decreases.
- As the temperature increases corrosion rate increases in plain acid.
- Addition of inhibitors in corrosive media indicates that as the temperature increases corrosion rate increases while inhibition efficiency decreases.
- In all cases, the value of heat of adsorption (Q_{ads}) and the value of free energy of adsorption (ΔG^{0}_{a}) is negative. The value of change of entropy (ΔH^{0}_{a}) and entropy of adsorption (ΔS^{0}_{a}) is positive.
- A mean value of 'Ea' in inhibiting acid is higher than the value of 'Ea' in acid only.

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