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ADSORPTION BEHAVIOR AND THERMODYNAMICS INVESTIGATION OF ANILINE-N-(p-METHOXYBENZYLIDENE) AS CORROSION INHIBITOR FOR Al-Mg ALLOY IN HYDROCHLORIC ACID.

V.A. Panchal, A.S. Patel and N.K. Shah*

Chemistry Department, School of Sciences, Gujarat University, Ahmedabad, Gujarat - 380009

ABSTRACT

The interfacial behavior of Aniline-N-(p-methoxybenzylidene) (ANPMB) between Al-Mg alloy and hydrochloric acid has been investigated by using weight loss method at a temperature range from 35°-65° C. The results showed that ANPMB is an excellent corrosion inhibitor for Al-Mg alloy in acidic medium. Inhibition efficiency increased with increase in the concentration of ANPMB but decreased with rise in temperature. The activation (E_a) of corrosion and other thermodynamic parameters (such as heat of adsorption (Q_A), entropy of adsorption ($\Delta S°_A$) and free energy of adsorption ($\Delta G°_A$)) were calculated to elaborate the mechanism of corrosion inhibition. From the thermodynamic parameters, the $\Delta G°_A$ values are negative that suggest that the adsorption is of chemisorption type between the metal and inhibitor molecules. A plot of log θ/1-θ vs log C_{inh} gives a straight line indicating that the inhibitor function through adsorption following Langmuir isotherm. At 0.8% concentration of ANPMB, > 99% inhibition was observed.

Key words: Al-Mg alloy, Hydrochloric acid, Inhibitor, Corrosion.

INTRODUCTION

Corrosion of aluminium and its alloys have been a subject of numerous studies due to their high technological values and wide range of industrial applications especially in aerospace and house hold industries. Aluminium and its alloys, however, are reactive materials and are prone to corrode [1].

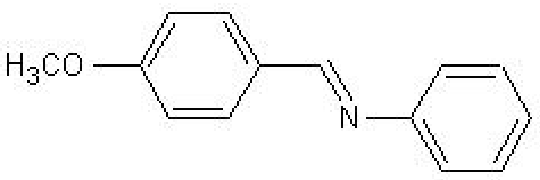
Thermodynamically aluminium is a highly reactive metal ($E°_{Al^{+3}/Al}$ = –1.676 V) [2] and because of its high affinity for oxygen ($\Delta G°_{Al2O3}$ = –1582 $kJmol^{-1}$) [3], aluminium surfaces are usually covered with thin but tightly adherent and protective film of aluminium oxide. The film is stable in solutions of pH 4.5 to 8.5, but because of its amphoteric nature, it fails to protect aluminium in strongly acid and strongly alkaline media [4]. Addition of magnesium to aluminium gives strain-hardenable alloys with increase in mechanical properties and improvement in resistance to corrosion [5, 6]. Al-Mg alloys are important materials for use in many applications such as for automobiles, containers, electric devices, etc., and are wildly used in marine-atmosphere.

Acids have long been used in removing the scale from metal surfaces and also in pickling. Hence to avoid attack on the base metal during scale-removal and cleaning metal surfaces with acidic solutions, the use of inhibitors become necessary. The applicability of organic compounds as corrosion inhibitors for metals in acidic media has been recognized for a long time.

Aldehydes and amines are fairly good inhibitors for metals and alloys in acids and other corrosive media [7, 8]. The inhibition efficiency of Schiff bases is much greater than corresponding aldehydes and amines. This is due to the presence of a > C = N – group in azomethine [9]. From this point of view, the inhibitor (Schiff base) has been synthesized and the performance of this inhibitor in retarding the corrosion of Al-Mg alloy in hydrochloric acid has been studied.

Synthesis of Schiff base

The Schiff base was synthesized by condensation of aniline with p-methoxybenzaldehyde to the procedure described by Jaeger [10]. ANPMB (m.p., 63°C, registry number, 836-41-9) is light yellow crystalline substance, insoluble in water but soluble in ethanol.



Aniline-N-(p-methoxybenzylidene) (ANPMB)

RESULTS and DISCUSSION

Adsorption behavior, thermodynamic parameters and activation energy in the presence of inhibitor have been evaluated.

Adsorption behavior

Adsorption is primary and important step in inhibition by organic based film forming corrosion inhibitors. Adsorption results from the polar or charged nature of the organic molecule / ionic species first establishing a physisorption surface film which may further stabilize through chemisorption to form a donor type bond [11]. If it is assumed that the inhibition of corrosion is due to the surface coverage (θ) by the inhibitor molecules then value of $\frac{W_u - W_i}{W_u}$ is a measure of the surface coverage θ [12]. The relationship between the coverage of an interface with an adsorbed species and the concentration of the species in solution is given by Langmuir adsorption isotherm [13].

$$\theta = \frac{KC_{inh}}{1 + KC_{inh}}$$

where, K is the Langmuir adsorption constant or adsorption coefficient.

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*Corresponding author: nishchem2004@yahoo.co.in

Table-1 : Adsorption behavior

C (%)	C* (mole/litre x 10^{-2})	log C* (mole/l)	Weight loss (mg)	θ	θ/1- θ	log (θ/1- θ)
0.15	0.7109	-2.1481	55	0.8693	6.6511	0.8228
0.20	0.9478	-2.0232	40	0.9049	9.5152	0.9784
0.30	1.4218	-1.8471	28	0.9334	14.0150	1.1465
0.40	1.8957	-1.7222	17	0.9596	23.7524	1.3757

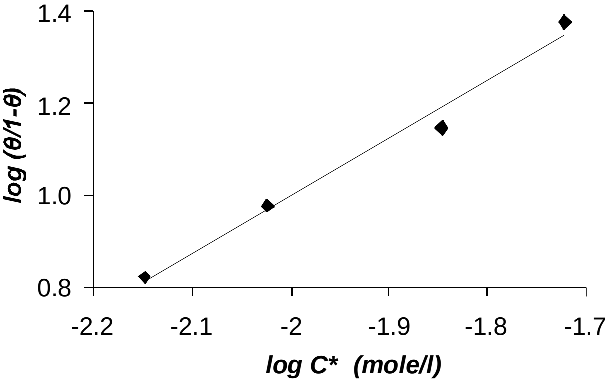

Fig.1 : Langmuir plots for ANPMB in 2.0 M hydrochloric acid at 35°C.

A plot of log θ/1-θ vs log C_{inh}(inhibitor concentration) (Fig-1) was drawn (from data given in Table-1) straight line was observed indicating that the inhibitor was adsorbed onto the metal surface following Langmuir isotherm.

Thermodynamic Parameters

If it is assumed that the inhibitor is adsorbed on the metal surface in the form of a monolayer film, covering at any instant a fraction, θ, of the metal surface in an uniform random manner, then the heat of adsorption, Q_A, can be calculated as per Hoar and Holiday [14]. The values of the free energy of adsorption, $\Delta G°_A$, were calculated following Abdel and Saiyed equation [15]. From the values of heats of adsorption and free energy of adsorption, values of the entropy of adsorption $\Delta S°_A$ were calculated. The values of Q_A, $\Delta G°_A$, and $\Delta S°_A$ for the temperature range 35°-65°C are given in Table-2. From the results, it is evident that for ANPMB, the heats of adsorption and free energy of adsorption are negative, further, the Q_A value is less negative while the free energy of adsorption is more negative in the case of a good inhibitor like ANPMB, which suggests that there is a strong interaction of the inhibitor molecules with the metal surface resulting in the spontaneous adsorption. It is observed that at higher concentration of inhibitor, $\Delta G°_A$ values are more negative, which suggest that the chemisorption of the inhibitor on the metal is a spontaneous process. The metal-inhibitor bonds are strong enough to provide excellent inhibition even at higher temperature.

The adsorption is a spontaneous process which is further supported by positive values of the entropies of adsorption, $\Delta S°_A$. It may be generalized from the present studies, that an efficient inhibitor is characterized by a relatively greater decrease in free energy of adsorption (become more negative), positive values of entropy of adsorption and less negative value of heat of adsorption as compared to free energy of adsorption.

Activation energy (E_a)

E_a is the apparent activation energy. It is the difference between the average energy of active molecules and the average energy of all the molecules.

A low activation energy means a fast reaction and a high activation energy means a slow reaction [16]. A high activation energy corresponds to a reaction rate that is very sensitive to temperature. Conversely, a small activation energy indicates a reaction rate that varies only slightly with temperature [17]. If a reaction has zero activation energy, its rate is independent of temperature. In some case E_a is found to be negative which indicates that the rate decreases as the temperature is raised; such behavior is a signal that the reaction has a complex mechanism.

In the present work the E_a values have been calculated from the plot of log ρ (corrosion rate) vs 1/T (Table-3 and Fig-2). In the uninhibited acid, the E_a value was 14.3 kcal/mol. The value of E_a at 0.8% of ANPMB was found to be 16.2 kcal/mol. The E_a value in inhibited acid thus varied and depended upon the ability of the inhibitor to reduce the corrosion rate. According to Putilova et al [18] the E_a value is higher in inhibited solutions and can be compared with unstable catalyst poisons whose adsorption fall off appreciably with rise in temperature and indicate physical adsorption on the metal surface. The extent of inhibition is likely to decrease with increasing temperature because of desorption of the inhibitor which would expose larger surface areas to the corrosion solution.

At 0.8% inhibitor concentration, weight losses were determined at 35°C, 45°C, 55°C and 65°C for an immersion period of 30 minutes. In plain acid the loss of metal due to corrosion increased from 1120 mg/dm^2 at 35°C to 7608 mg/dm^2 at 65°C (Table-3). In inhibited acid also the weight loss due to corrosion was found to increase with temperature but as compared to uninhibited acid it was much less upto 65°C, and the inhibition efficiencies were found to be 99.3% at 35°C and 98.8% at 65°C in ANPMB. However, when the inhibitor is present in sufficient amount it can confer ~ 98% to 99% protection in the temperature range 35° - 65°C.

Table-2 : Thermodynamic parameters :

Inhibitor (%)	Temp (^oC)	2.0M HCl		
		ΔG^o_A (kcal mol^{-1})	ΔS^o_A (cal mol^{-1})	Q_A (kcal mol^{-1}) (35^0-65^oC)
0.8	35	-7.5	36.1	-3.6
	45	-7.8	35.9	
	55	-7.8	35.0	
	65	-7.9	34.1	

Table : 3 Activation Energy and effect of temperature.

Inhibitor concentration (%)		Weight loss (mg/dm^2) at a temperature of				Energy of activation, E_a (kcal/mol)
		35°C	**45°C**	**55°C**	**65°C**	**35° - 65°C**
Nil (HCl only)	1	1072	2410	4980	7682	14.3
	2	1104	2453	4932	7562	
	3	1184	2335	4817	7581	
	avg.	**1120**	**2399**	**4910**	**7608**	
0.8	1	8	13	37	85	16.2
	2	8	19	48	74	
	3	8	16	43	104	
	avg.	**8 (99.3%)**	**16 (99.3%)**	**43 (99.1%)**	**88 (98.8%)**	

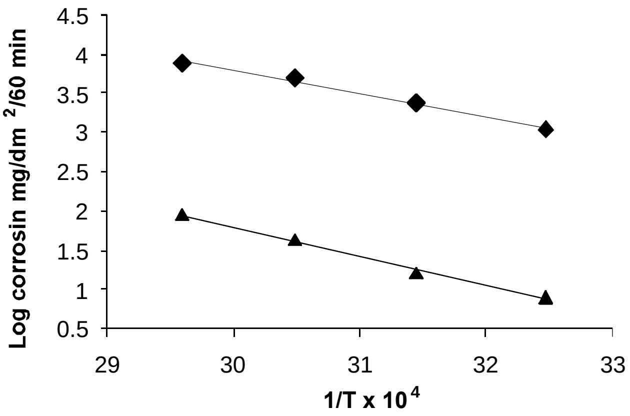

Fig.2 : Arrhenius plots for Al-Mg alloy in 2.0 M hydrochloric acid in the presence and absence of inhibitor ANPMB.

♦....♦ 2.0 M hydrochloric acid alone

▲...▲ inhibitor ANPMB (0.8%) in 2.0 M hydrochloric acid.

Mechanism of inhibition

Organic compounds containing one or more polar units, which may be regarded as the reaction centre/centres for the chemisorption process function as corrosion inhibitors. The adsorption bond strength is determined by the electron density on the atom (e.g., N, S, O, etc.) acting as the reaction centre and by the polarisibility of the unit. Thus, organic corrosion inhibitors are adsorbed on the bulk metal, M, forming a charge transfer complex between their polar atoms and the metal;

$$M + R_n X \rightarrow M : XR_n.$$

The size, shape and orientation of the molecule, and the electronic charge on the molecule determine the degree of adsorption and that way the effectiveness of the inhibitor.

The structure of the inhibitor shows that it is having three anchoring site (one iminic group > C = N –, and two aromatic rings, among the one having methoxy $-OCH_3$ group attached) and they show good inhibitive power when present in sufficient amounts. It is assumed that the compound form onium ions in acidic media and move to the cathodic regions, then adsorption will take place through the iminic nitrogen (> C = N –) and also through the delocalized π-electrons of the benzene moiety, and gives good protection.

The results show that ANPMB is the effective inhibitor and this may be traced to the fact that the $-OCH_3$ group (+R, –I) supplies electron density to the aromatic benzaldehydic ring and thus the delocalized π-electrons of this ring help in the chemisorption of the compound with stronger bonds and gives better protection.

CONCLUSION

1) ANPMB confers 98-99% protection to Al-Mg alloy in hydrochloric acid at 0.8% inhibitor concentration.
2) The adsorption follows Langmuir isotherm.
3) The heat of adsorption and free energy of adsorption are negative while the entropy of adsorption is positive. The free energy of adsorption are more negative in the case of very good inhibitor. The positive values of the entropy of adsorption suggest that the adsorption is a spontaneous process.
4) Activation energy is higher in the presence of inhibitor compared to that in plain acid.

The presence of iminic group (> C = N –) and methoxy group ($-OCH_3$) in the molecule, appeared to be the main factor enhancing chemisorption of an inhibitor.

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