Adsorption of Acridine on Aluminium Base Alloys in Dilute Hydrochloric Acid Solution — Kinetic and Thermodynamic Parameters.

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The study is concerned with corrosion of aluminium base alloys in 0.1 N HCl and its inhibition using acridine. The influence of temperature (28 to 70°C) on corrosion of alloys Al 3 S, Al-1% Ni-0.5% Fe and Al-0.1% Zr was studied. It is observed that acridine is effective for Al-1% Ni-5% Fe, the maximum inhibition effeciency value being 89 to 99%. The corrosion reaction is found to be second order with respct to HCl Al-0.1% Zr alloy is found to be more resistant than Al-1% Ni-0.5% Fe alloy in 0.1N to 1N HCl however, in presence of acridine its corrosion rate increases with increase in concentration of acridine, while Al-1% Ni-0.5% Fe alloy exhibits decrease in corrosion rates. The latter alloy exhibits maximum inhibition efficiency values followed by Al3S and Al-0.1% Zr alloys. It is found that Al-0.1%Zr abd Al-1% Ni-0.5% Fe alloys obey Langmuir and Freundlich dsorption isotherms. While the activation energy value in plain 0.1N HCl increases in order of Al-1% Ni-0.5% Fe, Al3S and Al-0.1% Zr alloys, reverse is the trend in presence of acridine.

Kinetic and thermodnamic parameters using Langmuir and Gibbs-Helmholtz equations have been calculated. The heat of adsorption values for Al3S and Al-0.1 % Zr alloys are found to be 8 and 11 k.cal/mole respectively. A higher value of heat of adsorption is observed for Al-0.1% Zr alloy as compared to Al3S corresponding to higher values of entropy of adsorption (55 to 62 cal/mole and 49 to 63 cal/mole) and free energy of adsorption (-8 to -9 k.cal/mole and -9 to -10 k.cal/mole).

The addition of small amounts of Ti, Zr, Be and misch metal to aluminium improves grain refining and results in increased mechanical strength[1-4]. It is of interest to investigate their behaviour in hydrochloric acid solution. Several investigators have reported earlier on the effect of certain organic inhibitors on the corrosion of selected aluminium base alloys in dilute hydrochloric acid solution[5-9] In the earlier investigations[10-12] commercial and experimental aluminium base alloys were corrosion tested in 0.1 N HCl solution with acridine as inhibitor at various temperatures. These results yielded various models for adsorption isotherms, activation energy and heat of adsorption values.

In the present work, Al-1% Ni-0.5% Fe and Al-0.1% Zr alloys have been corrosion tested in different concentractions of HCl solution upto 1N and in 0.1 N HCl solutions with various concentractions of acridine upto 1 gm/litre. These results have been utilised to determine the order of reaction, inhibitor efficiencies and the relation between adsorption and concentration. The results on the effect of temperature on the corrosion rate yielded values such as activation energy, heat of adsorption, free energy and entropy of adsorption.

EXPERIMENTAL

Al3S sheets were obtained from Trade. Al-1% Ni-0.5% Fe and Al-0.1% Zr alloys of nominal compositions were made by induction melting and were cold rolled and vacuum annealed at 450°C for 4 hours. Other experimental details were the same as these reported in an earlier paper [13] The chemicals used were of A.R. Grade.

In the present studies, corrosion of experimental aluminium base alloys of composition 1% Ni-0.5% Fe and Al-0.1% Zr have been studied in 0.1N to 1N HCl and in 0.1N HCl with various concentractions of acridine (upto 1 gm/litre) at 28° C for 6 hours. Besides these two experimental alloys, Al3S alloy has also been corrosion tested in 0.1N HCl containing 1 gm/litre acridine at various temperatures of 28 to 70°C for 6 hours.

RESULTS AND DISCUSSION

Corrosion rates in plain HCl solutions:

Table 1 gives the corrosion rates of Ai-1% Ni-0.5% Fe and Al-0.1% Zr alloys in various concentractions of HCl solutions at 28° C. The corrosion rates obtained in these solutions in case of Al-1% Ni-0.5% Fe alloy are found to be higher by more than two orders than Al-0.1 Zr alloy.

TABLE 1

CORROSION RATES OF ALUMINIUM BASE ALLOYS AT 28°C.

Type of aluminium alloy	[HCl] (N)	Corrosion rate (mdd)	R-C relationship
Al-1% Ni-0.5% Fe	0.10	5648	
	0.25	15050	
	0.50	51234	$R = K.C^2_{HCl}$
	0.75	126100	
	1.00	365280	
Al-0.1% Zr	0.10	22.0	
	0.25	38.5	
	0.50	63.3	$R = K.C^2_{HCl}$
	0.75	139.4	
	1.00	466	

* based in 6 hours test

* order of reaction is 2 in both cases.

It is observed that the corrosion rate R is proportional to the square of the concentrations of HCl for both these alloys, thus indicating that the reaction is of second order. Similar observation has been made for Al-0.7% Be and Al-0.2% misch metal alloys.

Corrosion rates in HCl solutions with additions of acridine:

The two experimental alloys in question have also been corrosion tested in 0.1N HCl in presence of various concentrations of acridine from 0.25 gm /litre (1.4×10^{-5} M) to 1 gm/litre (5.6×10^{-5} M) at 28°C. It has been observed from Table 2 that the corrosion rates of Al-1% Ni-0.5% Fe alloy are found to be severely brought down by additions of acridine. While with increasing ion concentration of acridine inhibition efficiency remains high for Al-1% Ni-0.5% Fe alloy is decreases in the case of Al-0.1% Zr alloy. However, the value

TABLE 2

CORROSION OF ALUMINIUM ALLOY IN PRESENCE OF ACIDINE (WIGHT LOSS MEASURED DURING 6 HOURS) CORRODANT CONCENTRATION 0.1 M HCl; TEMPERATURE 28°C.

Type of aluminium alloy	Inhibitor conc(molarity $Cx10^5$	Corrosion rate (mdd) R	Inhibitor efficiency (%)	Surface coverage θ
Al-1% Ni -0.5% Fe		5648		
	1.4	25.10	99.56	0.9956
	2.8	23.61	99.58	0.9958
	4.2	20.54	99.63	0.9963
	5.6	18.07	99.68	0.9968
Al -0.1% Zr	-	22.03		
	1.4	3.69	83.26	0.8326
	2.8	6.97	68.40	0.6840
	4.2	9.47	57.00	0.5700
	5.6	16.45	25.33	0.2533

of absolute corrosion rate is case of Al-1% Ni-0.5% Fe alloy is slightly higher than in Al-0.1% Zr alloy.

The observed decrease in inhibition efficiency with increase in concentration of acridine in case of Al-0.1% Zr alloy indicates that description may be involved. Simple models of adsorption are found to be satisfied when the plots of $\log \frac{\theta}{1-\theta}$ versus log C and log θ versus log C are plotted to yield Langmuir and Freundlich adsorption isotherms repectively, where θ is the fraction of the active site of the metal surface covered by the inhibitor, $1 - \theta$ is the fraction of the active sites reacting with the medium and C is the molar concentration of inhibitor acridine. It is found that Al-1% Ni-0.5% Fe alloy obeys Langmuir and Freundlich adsorption isotherms.

Kinetic and thermodynamic parameters:

Table - 3 gives the corrosion rates in 0.1N HCl at 28, 45, 55 and 70°C and in presence of $5.6 \times 10M^{-5}$ acridine. The inhibition efficiency and hence the surface coverage values are calculated for every temperature.

It is seen from this table, amongst the three alloys studied, that Al-1% Ni-0.5% Fe alloy exhibits highest efficiency values followed by Al3S and Al-0.1% Zr alloys. There is successive increase in these values for Al3S and Al-0.1% Zr

TABLE 3

CORROSION RATES, INHIBITION EFFICIENCIES, ACTIVATION ENERGIES AND HEAT FREE ENERGY AND ENTROPY OF ADSORPTION VALUE OF ALUMINIUM BASE ALLOYS IN 0.1 N HCl SOLUTION.

Type of aluminium alloy	Temperature° C	Corrosion rates (mdd) based on 6 hours test in		Inhibition efficiency %	Surface coverage θ	Activation Energy E K.Cal/mole	Heat of adsorption ΔH K.Cal/mole	Free energy adsorption-ΔG K.cal/mole	Entropy of adsorption ΔS Cal/mole/°K
		0.1N HCl	0.1N HCl + 5.6×10^{-5} M acridine						
Al3S	28	44.90	14.85	66.92	0.6692			8.71	53.68
	45	152.33	99.31	34.80	0.3480	14.91‡	7.45	8.36	49.71
	55	440.53	228.77	48.06	0.4806	17.70*		8.97	53.85
	70	891.12	440.00	50.62	0.5062			9.58	58.41
Al-1% Ni-0.5% Fe	28	5648	18.07	99.68	0.9968			11.77	
	45	7570	149.89	98.02	0.9802	1.77‡	—	11.25	-
	55	7690	401.74	94.77	0.9477	19.57*		10.93	
	70	8557	897.35	89.51	0.8951			10.91	
Al-0.1% Zr	28	22.03	16.45	25.33	0.2533			7.64	55.95
	45	144.69	122.31	15.46	0.1546	20.50‡		7.67	59.21
	55	292.36	213.48	26.98	0.2698		10.95	8.36	62.33
	70	901.73	583.35	35.30	0.3530	16.31*		9.03	58.25
Al1S[a]	28	8.48	25.24	-	-			-	-
	45	98.75	64.48	34.82	0.3482	27.63‡		8.36	79.62
	55	239.07	100.00	58.17	0.5817		16.96	9.27	79.96
	70	778.63	195.36	74.90	0.7490	10.60*		10.20	79.18
DTD182B[a]	28	138.10	19.80	85.60	0.8560			9.37	48.00
	45	1209.30	114.80	90.50	0.9050	22.60‡		10.19	48.71
	55	3776.30	318.40	91.50	0.9150		5.30	10.60	48.47
	70	10497.80	629.40	94.00	0.9400	18.80*		11.60	49.27
Al/0.2%[a] misch metal	28	32.90	31.31	4.80	0.048			6.52	39.87
	45	156.49	78.72	49.70	0.4970	16.67‡		8.76	44.90
	55	378.02	174.40	53.26	0.5326		5.52	9.14	44.69
	70	1050.30	397.10	62.19	0.6219	14.29*		9.81	44.69

TABLE 3(contd.)

Type of aluminium alloy	Temperature ° C	Corrosion rates (mdd) based on 6 hours test in: 0.1N HCl	0.1N HCl + 5.6×10^{-5}M acridine	Inhibition efficiency %	Surface coverage θ	Activation Energy E K.Cal/mole	Heat of adsorption ΔH K.Cal mole	Free energy adsorption $-\Delta G$ K.cal/mole	Entropy of adsorption ΔS Cal/mole/°K
Al-0.7%[a]	28	197.10	41.46	78.96	0.7896			9.09	38.66
	45	531.04	48.53	90.86	0.9086	17.54‡		10.23	40.18
	55	1259.00	109.60	91.29	0.9129	1.74*	2.55	9.12	35.57
	70	3765.50	293.23	92.21	0.9221			11.22	40.14

‡. in 0.1 M HCl plain* In 0.1N HCl + 5.6 x 10^{-5}M acridine.
a: The data is from an earlier study "12"

alloys from 45°C onwards upto 70°C studied. The inhibition efficiency value is found to decrease with increase in temperature for Al-1% Ni-0.5% Fe alloy. Al3S and Al-0.1% Zr alloys exhibits lower inhibition efficiency values from 28 to 45° C. This decrease in inhibtion efficiency values with increase in temperature could be due to desorption process.

The plots of log (corrosion rate in mdd) vs 1/T with and without the presence of acridine enabled to evaluate the activation energy values and the plots of log $\frac{\theta}{1-\theta}$ vs 1/T enabled to evaluate heat of adsorption values according to the relevant Langmuir adsorption isotherm expressed by $\frac{\theta}{1-\theta}$ e Q/RT, where
A = temperature dependent constant characteristic of the adsorption system,
C = bulk concentration of the adsorbent in moles/litre,
Q = heat of adsorption,
T = temperature in °K.

It is seen from Table 3 that in 0.1N HCl, it is found that the lowest activation energy value of 1.77 K.cal/mole is obtained for Al-1% Ni-0.5% Fe alloy, followed by Al3S (14.9 K.cal/mole) and Al-0.1% Zr alloys (20.50 K.cal/mole). This is well reflected in their corrosion rate values. However, in 0.1N HCl in presence of 5.6×10^{-5} M acridine, the trend is found to be reverse. It is observed that in case of Al-0.1% Zr alloy, the activation energy is found to be lower in presence of acridine than in plain 0.1N HCl. This has been explained by Riggs[17] in that the decrease arise from a shift of the corrosion reaction from the uncovered surface to the adsorbed site directly. Putilova[18] explains this mechanism as due to an increase in surface area of metal covered by inhibitor molecules as temperature rises. Similar observation of lower activation energy values have been made by Desai and coworkere[5,6], Talati and Modi[7] when they studied inhibition by cyclohexane derivatives of Al2S in HCl solutions. In an earlier paper[11], such lower values of activation energy in 0.1N HCl solution in presence of 5.6×10^{-3}M acridine have been obtained for Al1S, Al-0.2% misch metal and Al-0.7% Be alloys. The heat of adsorption values for Al3S are found to be lower than Al-0.1% Zr alloys and inhibitor efficiency higher. This indicates that adsorption is easier on the alloys and the low values of heat of adsorption indicate that it is physical adsorption.

Using the values obtained experimentally from the Langmuir adsorption equation, it was possible to calculate the apparent free energy of adsorption and entropy of adorption at the various temperatures studied for these alloys. According to the Langmuir type adsorption $\log C = (\log\theta/1-\theta) - \log B$, where C is concentration of acridine in moles/litre and is surface coverage of the inhibitor . The apparent free energy of adsorption (ΔG) estimated from the B factor using the equation[16] $\log B = -1.74 - (\Delta G/2.3RT)$. The values of entropy of adsorption ΔS calculated from the Gibbs-Helmoltz equation $\Delta G = \Delta H - T\Delta S$. It is seen from Table 3 that higher values of heat of adsorption are observed for Al-0.1% Zr alloy than Al-1% Ni-0.5% Fe alloy with correspondingly higher values of free energy and entopy of adsorption. The values of free energy of adsorption are found to be more

negative for Al-1% Ni-0.5% alloy followed by A13S and Al-0.1% Zr alloys. It has been observed from the results in Table 3 that more negative values of free energy of adsorption are correspondingly proportional to higher rates of corrosion viz., Al-1% Ni-0.5% Fe > DTD 1828 > Al-0.7% Be > A13S Al-0.2% misch metal > Al-0.1%Zr > A11S. The data for the last 4 alloys in the table are from an earlier study[11,12]

The values of entropy of adsorption are found to be varying from 49 to 63 cal/mole for A13S and Al-0.1% Zr alloys and 35 to 80 cal/mole for alloys A11S, DTD 1828, Al-0.2% misch metal and Al-0.7% Be. The variation of 35 to 80 cal/mole for the above alloys is understandable in view of the temperature limits of 28 to 70° C in the experiments. It may be surmised that significant change in the mechanism of corrosion process is envisaged.

CONCLUSIONS

1. The corrosion reaction of Al-1% Ni-0.5% Fe and Al-0.1% Zr alloys is of the second order w.r.to HCl.

2. Al-0.1% Zr alloy is found to be more corrosion resistant than Al-1% Ni-0.5% Fe alloy in 0.1N to 1N HCl concentration.

3. The inhibition efficiency values for Al-1% Ni-0.5% Fe alloy increases with increase in corrosion rates, while it is inverse for Al-0.1% Zr alloy.

4. Al-0.1% Zr and Al-1% Ni-0.5% Fe alloys are found to obey Langmuir and Freundlich adsorption isotherms.

5. Al-1% Ni-0.5% Fe alloy exhibits maximum inhibition efficiency values followed by A13S and Al-0.1% Zr alloys.

6. While the activation energy in plain 0.1N HCl is found to be in increasing order of Al-1% Ni-5% Fe, A13S and Al-0.1% Zr alloys, reverse is the trend in presence of acridine.

7. The heat of adsorption for A13S are found to be lower than Al-0.1% Zr alloy the inhibition efficiency higher, and are inversely proportional. The low values of heat of adsorption indicate that it is physical adsorption.

8. Higher heat of adsorption value is observed for Al-0.1% Zr alloy than Al-1% Ni-0.5% Fe alloy with correspondingly higher values of free energy and entropy of adsorption. More the negative value of heat of adsorption, higher are the corrosion rates observed.

9. The values of free energy of adsorption are found to be more negative for Al-1% Ni-0.5% Fe alloy followed by A13S and Al-0.1% Zr alloys.

10. A small variation in the value of the entropy of adsorption of 35 to 80 cal/mole obtained for these alloys is consonant with the expectation that no change in corrosion mechanisms is involved.

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REFERENCES

1. Nyriam D. Eborall, J. Institute of Metals, 76 (1949/1950) 296.

2. "ALCOA aluminium and its alloys", Aluminium Company, of America, 51 (1947).

3. Yuri Lakhtin, "Enginnering Physical Metallurgy and Heat Treatment", (Mir publishers, Moscow,) 378 (1974).

4. D.A. Dodson, Canadian Metals July (1953) 24-27

5. M.N. Desai and Y.B. Desai, Trans. of the SAEST, 10(3) (1975) 175.

6. M.N. Desai, P.M. Chayya and M.H. Gandhi, Trans. of the SAEST, 4(3) (1969) 75.

7. J.D. Talati and R.M. Modi, Trans. of the SAEST, 2(2) (1976) 265.

8. K. Ramakrishnan and N. Subramanyan, Trans. of the SAEST, 6 (1971) 87.

9. O.T. Woo, H. Unglik and K.T. Aust, Canadian Metallurgical Quarterly, 14-3 (1975) 275.

10. K.N. Adhe and P.R. Shibad, J. Electrochem Soc., India 28-3 (1979) 71.

11. Idem, Ibid, 29-3 (1980) 129.

12. Idem, presented at the symposium on "Corrosion and its control in power and chemical Induistries", organised by Dept. of Atomic Energy, December 15-17, 1982 at M.S. University of Baroda, Baroda.