



EVALUATION OF CORROSION BEHAVIOUR OF ALUMINUM IN DIFFERENT ENVIRONMENT

Musa Husaini, Bishir Usman and Muhammad Bashir Ibrahim

Department of Pure and Industrial Chemistry, Faculty of Physical Sciences,
Bayero University, P.M.B. 3011, Kano. Nigeria

Corresponding author: musahusaini36@gmail.com; mbibrahim.chm@buk.edu.ng

ABSTRACT

The corrosion behaviour of aluminum in hydrochloric, nitric, sulfuric and phosphoric acids was investigated using weight loss method. The results shows that the corrosion rate of aluminium in HCl, H₃PO₄, H₂SO₄ and HNO₃ are 39.1200, 1.5000, 0.7111 and 0.6500 mg cm⁻² h⁻¹ respectively. The corrosion rate was found to increase with increase in concentration and temperature. The thermodynamic and kinetic parameters were evaluated and enthalpy ΔH was found to be positive indicating the endothermic nature of the reactions. The study further reveals that the rate of corrosion in different environment follows the following order. HCl > H₃PO₄ > H₂SO₄ > HNO₃.

Keywords: aluminum, weight loss, corrosion rate, thermodynamic and kinetic parameters

INTRODUCTION

Corrosion is the deterioration of a material, usually a metal, because of reaction with its environment (Rosliza *et al.*, 2010). Metal interaction with environment is a process that cannot be disregarded when the issue of corrosion and its effect comes to play. The metal in the combined state tends to revert back to its most stable natural state on exposure to certain environmental conditions (Ajanaku *et al.*, 2015). Corrosion process has affected a number of industries resulting into loss and damages of many materials and life (Barbara and Robert, 2006). The effect of corrosion on aqueous environment of sea water, salt water and rain water, can be felt when pipes corroded with toxic metals into the environment thereby causing health complications to the living system (Holsen *et al.*, 1991). Other causes can be hazardous, which may results in loss of capital, loss of equipment and alienation of workforce, fire and explosion etc. (Holsen *et al.*, 1991). When metals are exposed to aggressive environments such as, the use of acid solutions for pickling, chemical and electrochemical etching of metal, industrial acid cleaning, cleaning of oil refinery equipment, oil well acidizing and acid descaling, they usually lead to loss of the metal due to corrosion (Ating *et al.*, 2010; Bishir *et al.*, 2017). The problem of metallic corrosion has received significant concerns. It has been estimated that approximately 5% of an

industrialized nations income is spent on corrosion prevention, maintenance and replacement of products lost or contaminated due to corrosion reactions (Abiola, 2002). The study of aluminum corrosion in different acidic and alkaline environments has attracted considerable attention in view of its important applications (Eduok *et al.*, 2012). Aluminum is highly electropositive and considered as one of the most important metals due to its economic and technical importance as well as the wide range of industrial and domestic applications such as reflectors, decorative products, buildings, airspace, aircraft, architectural, packaging, construction, a wide range of household items (Hurlen *et al.*, 1984). Aluminium is remarkable for its low density and its ability to resist corrosion because of hard, tough film of oxide it forms on the surface through the phenomenon called passivation (Abdel-Gaber *et al.*, 2006). Acid medium such as HCl, HNO₃, H₂SO₄ and H₃PO₄ used for industrial maintenance operations often cause the structure position of aluminum to corrodes. It is in this regard that different acids used in industrial application need to be assessed and evaluate their corrosion effects in order to find the best acid that could be used in cleaning, pickling, descaling and all other industrial applications that need the use of acid. Therefore the aim of the present work is to investigate the corrosion rate of aluminum in different acidic environments using weight loss method.

MATERIAL AND METHODS

Sample Preparation

Aluminum sheets (Al 99% purity) were obtained from Metal Focus Fabrication Technology Incubation Centre Kano State, Nigeria. Each sheet was pressed cut into 2 x 3 x 0.1 cm³. The coupons were polished with 240, 640, 800 and 1000 grade of different emery paper respectively. The coupons were degreased in ethanol and dried in acetone, then kept in desiccator prior to use.

Corrosive Media Preparation

A stock solution of analytical grade hydrochloric acid (36.5%, 1.18g/L), nitric acid (68%, 1.51 g/L), sulfuric acid(98%, 1.84 g/L) and phosphoric acid (85%, 1.68 g/L) were prepared by using double distilled water. The acid solutions of required concentrations of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4M were prepared by appropriate dilutions.

Weight loss Measurement

During the weight loss experiments, aluminum coupons were weight (w_1) and suspended completely in 0.2M solutions of different acids in 100ml beaker respectively. The volume of the solution was kept at 50ml. The coupons were retrieved after 30, 60, 120, 150, 180 and 210 min, washed with distilled water, dried with acetone and reweighed (w_2). The immersion time with relatively higher weight loss was adopted as optimum immersion time. From the weight loss data, corrosion rate in $\text{mgcm}^{-2}\text{h}^{-1}$ was calculated using equations 1 and 2 (Khandelwal *et al.*, 2011)

$$\Delta w = w_1 - w_2 \quad (1)$$

$$\text{Corrosion rate (mg cm}^{-2}\text{ h}^{-1}) = \frac{\text{Weight loss}}{\text{Area} \times \text{Time}} \quad (2)$$

Where w_1 and w_2 are the weight of coupons before and after immersion in the corrodent medium respectively.

Effect of Concentration

To study the effect of corrodent concentration the prepared weighted aluminium coupon was immersed in 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4M corrodent maintained at 308K for 3hrs immersion time. The final weight was taken and the weight loss was calculated. The concentration with relatively higher weight loss was considered as the optimum concentration.

Effect of Temperature

To study the effect of temperature, the prepared weighted aluminium coupon was immersed in 1.4M corrodent concentration at 308, 313, 318, 323 and 328K for 3hrs. The final weight was taken, the weight loss and corrosion rate was calculated.

RESULTS AND DISCUSSION

The Effect of Immersion Time

The result obtained from Table 1 shows that the weight loss of aluminium in HCl, HNO₃, H₂SO₄ and H₃PO₄ increased with increase in immersion time. At least immersion time of 30min the weight loss of aluminum in HCl, HNO₃, H₂SO₄ and H₃PO₄ are 0.0018, 0.0011, 0.0014 and 0.0016g while at highest immersion time of 3hrs the weight loss increased to 0.0199, 0.0063, 0.0068 and 0.0119g. Increase of the rate of weight loss of the metal in the given acids indicates the instability of protective film for the longer contact period. Increased in weight loss with immersion time is due to the interaction that occur between the acid and the metal surface in solution, which tend to destroy the metal surface gradually with time thereby increasing the weight loss of the metal. Weight loss in constant concentration of the corrodent increased with increase in immersion time. Similar work was done by Patil and Sharma (2011) during the study of corrosion kinetics of iron in acid and base medium and reported that the weight loss increases with increase in immersion time and the result of the weight loss in acid medium was 0.0152, 0.0308, 0.0469 and 0.0626g at 2, 4, 6 and 8hrs.

Table 1: Weight loss of Aluminum Corrosion at Different Immersion Time

Time (min)	Weight Loss(g)			
	HCl	HNO ₃	H ₂ SO ₄	H ₃ PO ₄
30	0.0018	0.0011	0.0014	0.0016
60	0.0040	0.0019	0.0020	0.0038
90	0.0063	0.0023	0.0029	0.0053
120	0.0098	0.0043	0.0046	0.0074
150	0.0140	0.0056	0.0057	0.0098
180	0.0199	0.0063	0.0068	0.0119

The Effect of Concentration

The result of changes in concentration (Table 2) shows that as the concentration of the acids increase the weight loss and corrosion rate

increases, this is due to the fact that the rate of chemical reaction increases as the concentration of active species increases.

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At least acid concentration of 0.2M the weight loss and corrosion rate of aluminium in HCl, HNO₃, H₂SO₄ and H₃PO₄ are (0.0205, 0.0062, 0.0069 and 0.0120g) and (1.1388, 0.3444, 0.3833 and 0.6667 mg cm⁻² h⁻¹). While at highest acid concentration of 1.4M the weight loss and corrosion rate increased to (0.3515, 0.0117, 0.0128 and 0.0270g) and (19.5277, 0.6500, 0.7111 and 1.5000 mg cm⁻² h⁻¹). The dissolution rate of aluminium depend on the concentration of the corrosive media, this could be attributed to increase in

concentration of the acid anions in the more concentrated solution, which readily react with aluminum ion present in the solution. Similar observation was reported by Rathod and Vashi (2016) who investigated the effect of ammonium dichromate on the corrosion of aluminum in phosphoric acid and the result showed that the corrosion rate increased with increase in the concentration of the acid and the result of the corrosion rate was found to be 389.7, 454.0, 486.2 and 525.6 mg/dm² in 1.0, 1.25, 1.50 and 1.75 M H₃PO₄.

Table 2: Corrosion rate of Aluminum at Different Acids Concentration

Concentration (mold m ⁻³)	Weight Loss (g)				Corrosion Rate (mg cm ⁻² h ⁻¹)			
	HCl	HNO ₃	H ₂ SO ₄	H ₃ PO ₄	HCl	HNO ₃	H ₂ SO ₄	H ₃ PO ₄
0.2	0.0205	0.0062	0.0069	0.0120	1.1388	0.3444	0.3833	0.6667
0.4	0.0340	0.0075	0.0078	0.0160	1.8888	0.4167	0.4333	0.8889
0.6	0.0690	0.0082	0.0085	0.0154	3.8333	0.4556	0.4722	0.8556
0.8	0.1380	0.0090	0.0096	0.0218	7.6666	0.5000	0.5333	1.2111
1.0	0.2151	0.0098	0.0104	0.0234	11.9500	0.5444	0.5778	1.3000
1.2	0.2760	0.0102	0.0115	0.0250	15.3333	0.5667	0.6389	1.3889
1.4	0.3515	0.0117	0.0128	0.0270	19.5277	0.6500	0.7111	1.5000

The Effect of Temperature

The results in Table 3 shows that the rate of corrosion increases with increase in temperature. High temperature produce more severe corrosion condition. At the lowest temperature (303K) used, the weight loss and corrosion rate of aluminium in HCl, HNO₃, H₂SO₄ and H₃PO₄ are (0.3102, 0.0090, 0.0101 and 0.0201g) and (17.2333, 0.5000, 0.5611 and 1.1167 mg cm⁻² h⁻¹). With increasing the temperature to 328K the weight loss and corrosion rate increased to (0.5811, 0.0270, 0.0299 and 0.0602g) and (32.2833, 1.5000, 1.6611 and 3.3444 mg cm⁻² h⁻¹). Increase in temperature usually increases the solubility of

the protective films through increase in the average kinetic energy of the constituent particles. As the average kinetic energy increases the particles move faster and collide more frequently which result in the increase of the reaction rate as reported by Olasehinde *et al.* (2013) and Ahmad *et al.* (2014). Similar observation was reported by Rathod and Vashi (2016) who investigated the effect of ammonium dichromate on the corrosion of aluminum in phosphoric acid and the result showed that the corrosion rate increased with increasing temperature and the corrosion rate was found to be 92.95, 175.18 and 425.45 mg/dm² at 313,323 and 333K.

Table 3: Corrosion rate of Aluminum in Acid at Different Temperature

Temperature (K)	Weight loss(g)				Corrosion rate (mg cm ⁻² h ⁻¹)			
	HCl	HNO ₃	H ₂ SO ₄	H ₃ PO ₄	HCl	HNO ₃	H ₂ SO ₄	H ₃ PO ₄
303	0.3102	0.0090	0.0101	0.0201	17.2333	0.5000	0.5611	1.1167
308	0.3515	0.0117	0.0128	0.0270	19.5277	0.6500	0.7111	1.5000
313	0.3951	0.0134	0.0170	0.0330	21.9500	0.7444	0.9444	1.8333
318	0.4521	0.0181	0.0200	0.0403	25.1166	1.0055	1.1111	2.2388
323	0.5002	0.0221	0.0254	0.0493	27.7888	1.2277	1.4111	2.7388
328	0.5811	0.0270	0.0299	0.0602	32.2833	1.5000	1.6611	3.3444

In all the three given parameters above HCl, shows the high reactivity over HNO₃, H₂SO₄ and H₃PO₄. In the effect of immersion time the weight loss at 3hrs of HCl, HNO₃, H₂SO₄ and H₃PO₄ are 0.0338, 0.0063, 0.0068 and 0.0119g. In the effect of concentration the corrosion rate at 1.4M solution of HCl, HNO₃, H₂SO₄ and

H₃PO₄ are 39.1200, 0.6500, 0.7111 and 1.5000 mg cm⁻² h⁻¹. In the effect of temperature the corrosion rate of HCl, HNO₃, H₂SO₄ and H₃PO₄ at 328K are 42.43, 1.2278, 1.7222 and 7.2278 (mg cm⁻² h⁻¹). The reactivity of the acids follow the variation pattern HCl > H₃PO₄ > H₂SO₄ > HNO₃.

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The highest reactivity of HCl is due do the fact that HCl is a typical reducing acid across its entire concentration range. Its strongly acidic character and the harmful effect of the chloride ion combine to make it a very severe corrosive. The HNO₃ has the least reactivity in the variation pattern because it's strong oxidizing acid that form a thin layer of aluminum oxide to coat the surface of aluminum through the process called passivation (Ahmed *et al.*, 2009; Singh *et al.*, 1981). While Pure H₃PO₄ has no effective oxidizing power and is classified as a non-oxidizing acid, so it shows higher reactivity with aluminum than H₂SO₄ because concentrated H₂SO₄ (above 87% by weight) at room temperature is oxidizing in nature (Laque and Copson 1963).

Thermodynamic and Kinetic Parameters

The apparent activation energies (*E_a*) were calculated from Arrhenius (equation 3) (Shivakumar and Mohana 2013; Hegazy *et a.*, 2012) and the results are presented in Table 4.

$$\ln(C_R) = B - \frac{E_a}{RT} \quad (3)$$

Where B is a constant, R is the universal gas constant, and T is the absolute temperature. The plot of ln (C_R) Vs reciprocal of absolute temperature (1/T) gave a straight line with slope = -E_a/R, from which the activation energy values for the corrosion process was calculated.

The Thermodynamic parameters enthalpy and entropy of activation were calculated using the transition state equation (Putilova *et al.*, 1960; Hegazy *et al.*, 2013).

$$\ln \left(\frac{C_R}{T} \right) = \ln \left(\frac{R}{Nh} \right) + \left(\frac{\Delta S_a}{R} \right) - \left(\frac{\Delta H_a}{RT} \right) \quad (4)$$

Where *h* is Plank's constant and *N* is Avogadro's number. A plot of ln (C_R/T) vs 1/T gave a straight show with slope = -ΔH_a/R and intercept = ln(R/Nh) +ΔS_a /R. The calculated values of enthalpy and entropy from the plots were presented in Table 4.

Table 4: Activation Parameters for the Corrosion of Aluminum in Different Acid solutions

Acids (M)	E _a (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
HCl	20.44	17.82	-175.02
H ₃ PO ₄	35.40	32.78	-193.06
H ₂ SO ₄	36.14	33.52	-196.50
HNO ₃	36.36	33.80	-196.69

From Table 4, the values of energy of activation for the corrosion of aluminium in HCl, HNO₃, H₂SO₄ and H₃PO₄ are 20.44, 35.40, 36.14 and 36.36 kJ mol⁻¹. HCl has the least value of E_a while HNO₃ has the highest, this is considered as good evidence supporting the highest and lowest corrosion rates recorded in the HCl and HNO₃ system. The E_a values of all the acid are greater than 20 kJ mol⁻¹ this suggested that the whole process is controlled by surface reaction as reported by Bouklah *et al.* (2005). The values of the entropy change (ΔS) for the corrosion of aluminium in HCl, HNO₃, H₂SO₄ and H₃PO₄ are -175.02, -193.06, -196.50 and -196.69 Jmol⁻¹K⁻¹. The ΔS values are large and negative, this implies that the activated complex in the rate determining step represents association rather than dissociation indicating that a decrease in disorder takes place. The values of enthalpy change (ΔH) for the corrosion of aluminium in HCl, HNO₃, H₂SO₄

and H₃PO₄ are 17.82, 32.78, 33.52 and 33.80 kJ mol⁻¹.The positive signs of ΔH reflect that transition state (the activated complex) is endothermic process. Similar observation was reported by Ahmed *et al.* (2011) who studied the galvanic corrosion of aluminum Alloy (Al2024) in 1.0 M nitric acid and the result obtained for activation energy (E_a), enthalpy change (ΔH) and entropy chasnge (ΔS) were 50.54 kJ mol⁻¹, 47.91 kJ mol⁻¹ and -85.63 J mol⁻¹ K⁻¹

CONCLUSION

Based on the results of weight loss measurements conclusions are drawn in this study; Weight loss increases with increase in immersion time in all acids environment. The corrosion rate increases with increase in the concentration and temperature. Corrosion rate of aluminum in different environment follows the order HCl > H₃PO₄ > H₂SO₄ > HNO₃.

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