The Republic Of Yemen
Taiz University

مجلة بحوث جامعة تعز
سلسلة الآداب والعلوم الإنسانية والتطبيقية مجلة دورية محكمة

الجمهورية اليمنية
جامعة تعز
نيابة الدراسات العليا والبحث العلمي

Effect of Sodium Tungstate, Sodium Molybdate and Thiourea on Corrosion of Aluminum in Oxalic Acid Solution

S.R. Selim
Chemistry Department Faculty of Science , Al-Azhar University, Cairo - Egypt
Kh. A. S. Galeb , and G. M. A. Al-Maleeh
Chemistry Department Faculty of Science , Taiz University Taiz -Yemen

Abstract

Corrosion of aluminum in oxalic acid had been investigated by using wt-loss technique in absence and in presence of 0.001 M concentration of different additive compounds (sodium tungstate [ST], sodium molybdate [SM] and thiourea [TU]) at different temperature. It is noticed from the observed thermodynamic parameters derived from wt-loss measurements that ΔH_{ad} for the adsorption of ST, SM, and TU resulted in a positive value (endothermic), the adsorption typed is physical - chemical adsorption. The dissolution of aluminum in oxalic acid is decreasing as the concentration of the acid increased due to the collective properties of organic acid were the oxalic acid behave as dimmer molecular at different concentration. The dissolution of aluminum in oxalic acid decreased after short period due to fast formation of oxide passive layer [$Al_2O_3.3H_2O$].

Introduction

The importance of aluminum is refer to widely used for industrial processes and humane uses, nontoxic and its good corrosion resistance etc…, so that the corrosion studies of aluminum and its alloy become topic in recently years [1-5]. These remarkable combinations of qualities make it a preferred choice for many critical applications in food handling, buildings, heat exchange and electrical transmission [6]. The inhibition effects of molybdate and tungstate on the corrosion in acids solution were investigated, the results reveal that both molybdate and tungstate are very good inhibitors with little concentration [7]. The effect of addition of halides is also reported [8]. Byran's studies on the corrosion of aluminum in citric acid and tartaric acid [9] indicates that the rate

of attack of aluminum in organic acid is not proportional to H-ion concentration but is related to the rate of diffusion of the acid through the corresponding film of corrosion products. It showed that corrosion become raped in the region of pH = 7.0. Aluminum resists corrosion in many environments because of the formation of a protective oxide film on the metal surface [10], oxalic acid (0.1 N) has a severe corrosion effect on Al at 25 ^{o}C. The film is the generally stable in solution of pH 4.5-8.5 [11], but it dissolves in strong acids and strong alkaline media, therefore in such cases, the metal shows a high rate of corrosion. Inhibition of the corrosion of aluminum in (HCl) by sulfonic acid, sodium sulfonate derivatives, and sodium alkyl sulfate has been studied [12] too. Thermodynamic functions for both dissolution and adsorption processes were determined [13].

Experimental:

The chemical composition of aluminum metal used is [AL 91.1%, Zn 5.7%, Mg 1.7%, Cu 1.5% (Germany)]. Oxalic acid $C_2H_2O_4.2H_2O$ assay 99 % Himedia , India company. The additives (ST, SM and TU El-Nasr Company Egypt) had been used as inhibitors. All solutions were prepared from ordinary distilled water, thermo-stated to within +/- 0.1 ^{O}C of the indicated temperature. The specimens are polished according to the methods described earlier [14,15] the corroded media is prepared as (0.1, 0.2, 0.4, 1.0 M) oxalic acid.

Type of additive	**Abbreviation**	**Molecular formula**
Sodium Tungstate	ST	$Na_2 WO_4 2H_2O$
Sodium Molypdate	SM	$Na_2 MoO_4.2H_2O$
Thiourea	TU	NH_2 - CS - NH_2

The additives prepared as 0.001M in 0.1M oxalic acid solution. Al sample were used in the form of sheet (2 X 2) cm, the sample were chemically

cleaned [16] weighted and suspended in 50 ml of test solution. then weighted again at the end of the reaction after drying.

Results and Discussion:

The weight loss of the aluminum sample that immersed in different oxalic acid concentrations was measured as (mg/cm^2) at 25°C. The dissolution of aluminum in oxalic acid decreased as acid concentration increased. The effect of acid concentration at 25°C on the dissolution of aluminum is recorded in Table (1) and showed in Fig. (1).

Weight-loss – time curves of Al in 0.1 M oxalic acid in presence of (0.001 M) of different additives (ST, SM, and TU), at 25 °C are illustrated in (Fig. 2) and the treated data is listed in Table (1). The surface coverage area (Ө) and the inhibition efficiency (IE %) were calculated as [17] ;

$$\Theta = (W_O - W) / W_O \qquad (1)$$

$$IE\ \% = [(W_O - W) / W_O] \times 100 \ ; \qquad (2)$$

W_O and W indicate the weight loss in absence and presence of additives.

The corrosion rate (r) is calculated as [18];

$$R\ (mpy) = 3448\ W(mg) / d\ (g/cm^3) \times A\ (cm^2) \times t\ (hr), \qquad (3)$$

Where A = specimen area, d = density and; t = exposure time.

The decreasing of corrosion rate of aluminum by increasing of oxalic acid concentration may be due to the collective properties where the oxalic acid has dimmer structure at high concentrations [19] and the adsorpition of the formed aluminum complex. Fast formation of the protective oxide passive layer [$Al_2O_3.3H_2O$] [20] appears after short period, then the passive layer dissolved again and the corrosion increased gradually.

The effect of temperature is studied, weight-loss – time curves of Al in 0.1 M oxalic acid in absence and presence of (0.001 M) of different temperatures were illustrated in (Fig. 3.1) and the treated data is listed in Table (2). It observed that the corrosion rate is increased by rising the temperature.

The study of the temperature effect allowed to investigating the thermodynamic activation and adsorption parameters.

The activation energy of corrosion reaction investigated according to Arrhenius equation [21];

$$K_r = A\, e^{-E^*/RT} \qquad (4)$$

Where the specific rate constant $(K_r) = dW/dt$. (5)

$$\log K_r = \log A - (E^* / 2.303\, RT) \qquad (6)$$

$$E^* = 2.303\, RT \times [\log A - \log K_r] \qquad (7)$$

where K_r is obtained from the slope of wt-loss – t (Fig. 3.2)

Other activation thermodynamic functions; free energy of activation ΔG^*, entropy of activation ΔS^* and enthalpy of activation ΔH^*, which recorded in Table (3) were calculated from transition state equation [22,23] as following;.

$$K_r = (RT/Nh)\, \mathrm{Exp}^{-\Delta G^*/RT} \qquad (8)$$

Or $K_r/T = R/Nh\ \mathrm{Exp}^{-\Delta G^*/RT}$

Where h is Blanck's constant and R is universal gas constant and N is Avogadro's number.

$$\log K_r/T = \log R/Nh - \Delta G^* / 2.303RT \qquad (9)$$

By taken $N = (N_{as})$ number of molecules that associated in reactions, log $(R/N_{as}h)$ item can be obtained from the intercept of $(\log K_r/T - 1/T)$ curve (Fig. 4) and N_{as} can be investigated.

ΔH^* and ΔS^* can be given as follows;

$$\Delta H^* = E^* + RT \qquad (10)$$

$$\Delta S^* = (\Delta H^* - \Delta G^*) / T \qquad (11)$$

The activation thermodynamic calculated values were listed in (Table 3).

It was found that can be applied the Langmuir adsorption isotherm [24], where free energy of adsorption ΔG^o_{ad} can be determined from;

$$\log (\Theta/1-\Theta) = \log C\beta - (\Delta G^o_{ad} / 2.303RT), \qquad (12)$$

where β is the adsorption equilibrium constant and C is the additive concentration, The parameter log $C\beta$ obtained from the intercept of $(\log (\Theta/1-\Theta) - 1/T)$ (Fig. 5).

At equilibrium of adsorption processes has;

adsorption rate = desorption rate; the free energy is equal to Zero.

$$\Delta G = 0 \qquad \text{and where,} \qquad (13)$$

$$\Delta G = \Delta G^o_{ad} + 2.303RT \log K \qquad (14)$$

So that we can write,

$$\Delta G^{o}_{ad} + 2.303RT \log K = 0 \qquad (15)$$

Hence; $\Delta G^{o}_{ad} = - 2.303RT \log K$ (16)

The thermodynamic parameters of adsorption can be calculated by using Van't Hoff; isochore relationship [25].

$$d(\ln K/dT) = - \Delta H_a/R \qquad (17)$$

or $K = \mathrm{Exp}^{-\Delta Gad/RT}$ (18)

and where; $\Delta G_{ad} = \Delta H_{ad} - T\Delta S_{ad}$

so that, $K = \mathrm{Exp}^{\Delta Sad/R} . \mathrm{Exp}^{-\Delta Had/RT}$ (19)

$$\ln K = \Delta S_{ad}/R - \Delta H_{ad}/RT \qquad (20)$$

or $\log k = \Delta S_{ad}/2.303R - \Delta H_{ad}/2.303RT$ (21)

By applied equations (12 and 21), we got the calculated adsorption thermodynamic values ΔG_{ad} , ΔS_{ad} and ΔH_{ad} that recorded in Table (4), where ΔS_{ad} can be investigated from the intercept of (Log k – 1/T) curve. The enthalpy of adsorption (ΔH_{ad}) can be calculated by substituted ΔS_{ad} value in equation (21).

By applied Eq. (9) we can get the number of molecules (N_{as}) that associated in reactions.

It is observed that in presence of inhibitor the associated molecules (N_{as}) were increased as the molecular weight of the inhibitor increased.

The calculated values of (N_{as}) are found as:

1) in 0.1M oxalic acid solution = 1.55×10^{36} molecules
2) in presence of 0.001M ST = 1.44×10^{38} molecules
3) in presence of 0.001M SM = 5.58×10^{36} molecules
4) in presence of 0.001M TU = 1.47×10^{36} molecules

Conclusion

- The dissolution of aluminum in oxalic acid decreased as acid concentration increased may be due to the result of dimerization of oxalic acid and to the adsorpition of the formed aluminum complex.
- The corrosion rate is increased by rising the temperature.
- IE % at 25 ^{O}C in the order SM > TU > ST.

- **IE % decrease by temperature increase.**
- **ΔH^* and ΔH_{ad} values indicates that the majority adsorpition type is physical adsorpition.**
- **The corrosion rate is affected by the molecular structure of additives.**
- **The passive oxide layer [$Al_2O_3.3H_2O$] is moderate stable in 0.1 M oxalic acid solution.**
- **The associated molecules (N_{as}) increased as the temperature increased and the coverage area (Θ) increased as (N_{as}) increased.**
- **The adsorption is subordinate to Langmuir adsorption isotherm**

REFERANCES

1- **R. Rosliza, W.B. Wan Nik and H.B. Senin** ***Materials Chemistry and Physics*, 107,281-288 (2008).**

2- X.F. Liu Corrosion Science, 49 , ***3494-3513*** **(2007).**

3- K.H. Na, S.I.Pyun, and H.P. Kim Corrosion Science, 49 , ***220-230*** **(2007).**

4- Ajit Kumar Mishra and R. Balasubramaniam Materials Chemistry and Physics, 103 385-393 (2007).

5- F. Andreatta, H. Terryn and J. H. W. de Wit ***Electrochimica Acta, 49, 2851-2862 (2004*****).**

6- Corrosion of Aluminum and Aluminum Alloys, edited by J. R. Davis (ASM International, OH, 1999).

7- Z. Szklarsk – Smialowska, corro. Sci. 41 ,9 . 1743-1767 (1999)

8- E.E. Ebenso Materials Chemistry and Physics, 79. 58-70 (2003).

9- J.M.Byran. Dept. Sci. Ind. Research (Brit.) Food invesest. Board, 1937, 201-207 (1936).

10- N.D. Tomashov, Theory of Corrosion and Corrosion Protection of Metals. (Eds. B.H. Tyteh. I.Geld and H.S. Priser). Macmillan, N.Y. 613 (1966).

11- W.W. Binger, in Corrosion Resistance of Metals and alloys (Eds. F.L. Laque and H.R. Copson). Reinhold , N.Y. 183 (1963).

12- A.K. Maayta, N.A.F. Al-Rawashdeh, Corros. Sci., 46, 1129-1140 (2004).

13- S.S. A. El Rehim, H. H. Hassan and M. A. Amin. ***Materials Chemistry and Physics, 78, 337-348 (2003*****).**

14- J.D. Talati, M.N. Desai and A.M. Trivedi, Werkstoffe und Korros. (Mannheim), 10, 20 (1959).

15- J.D. Talati and R.M. Modi. Br. Corros. J, 10, 103 (1975).

16- F.A. Champion, Corrosion Testing Procedures, London, 191 (1975).

17- A.A ksut and S.Bilgic, Corros. Sci., 33, 379 (1992).

18- W.H. Allor, Handbook of Corrosion Teesting and Evaluation, 173, 9 (1983).

19- S.A. Soliman, Al-Azhar Bull. Sci. Vol. 17, 27-41, (2006).

20- G. Charlot, L. Analyse Qualitativ et les Reactions en Solution, 2nd ed. Masson, Paris (1957).

21- I.Z. Selim, J. Moter, Sci. Technol., 14,313 (1998).

22- K. K. Sharma, L. K. Sharma, A Textbook of Physical Chemistry, 500 (1977).

23- A. A. Taha, I. Z. Selim and A. A. Khedr, Egypt. J. Chem., 38, 141 (1995).

24- G.M. Docresm R.A.Sulula, and B.F.Larrickk, J. Electrochem. Soc.,130, 981 (1983).

25- M. A. Alwahab ,M. F. Baker, and K. A. E. Fattah, Thermo Chemical . Acta, 405,435 (2003).

Tables

Table (1): Effect of acid concentration on dissolution of aluminum in absence and in presence of 0.001M different additives at 25 ^{o}C

Medium	Conc. (M)	W (mg/cm^2)	θ	IE(%)	Corr.rate (mpy)
Free Oxalic acid	0.1 0.2 0.4 1.0	0.8 0.7 0.6 0.5	-	-	51.081 44.696 34.331 31.925
ST in 0.1 M Oxalic	0.001	0.7	0.125	12.5	44.696
SM in 0.1 M Oxalic	0.001	0.6	0.25	25	34.331
TU in 0.1 M Oxalic	0.001	0.6	0.25	25	39.555

Table (2): Effect of temperature on dissolution of aluminum in 0.1M oxalic acid in absence presence of 0.001M single additive.

additive	T (^{o}K)	Wt-loss (mg/cm^2)	θ	IE(%)	Corr.rate (mpy)
blank	298	0.8	-	-	51.039

	303	0.9			57.419
	308	1.2			76.558
	313	1.4			89.318
	318	1.6			102.078
ST	298	0.7	0.125	12.5	44.659
	303	0.8	0.111	11.1	51.039
	308	1.1	0.0833	8.33	70.178
	313	1.3	0.0714	7.14	82.938
	318	1.5	0.0625	6.25	95.698
SM	298	0.6	0.23	25	38.659
	303	0.7	0.222	22.2	44.659
	308	1	0.166	16.6	63.799
	313	1.2	0.142	14.2	76.558
	318	1.4	0.125	12.5	89.318
TU	298	0.62	0.225	22.5	39.555
	303	0.75	0.167	16.7	47.849
	308	1.1	0.0833	8.33	70.178
	313	1.3	0.0714	7.14	82.938
	318	1.5	0.0625	6.25	95.69

Table (3): The thermodynamic activation parameters for corrosion of aluminum in 0.1M oxalic acid in absence and in presence of 0.001M different additives at different temperature.

additive	T (^oK)	ΔE^* (kJ/mol.)	ΔH^* (kJ/mol.)	ΔS^* (J/mol./degree)	ΔG^* (kJ/mol.)
blank	298	29.852	32.330	16.897	27.294
	303	30.111	32.630	16.758	27.552
	308	29.852	32.413	16.622	27.293
	313	29.916	32.518	16.488	27.357
	318	29.94	32.591	16.357	27.389
ST	298	18.887	21.364	16.899	16.328
	303	18.315	20.834	16.760	15.755
	308	18.318	20.878	16.624	15.758
	313	18.543	21.145	16.490	15.984
	318	18.803	21.447	16.359	16.245
SM	298	25.826	28.304	12.165	24.679
	303	25.693	28.212	12.026	24.568
	308	25.526	28.087	11.890	24.424
	313	25.559	28.161	11.756	24.481
	318	25.790	28.434	11.625	24.737
TU	298	30.655	33.132	16.880	28.102
	303	30.480	32.999	16.741	27.926
	308	30.233	32.794	16.605	27.679
	313	30.468	33.070	16.471	27.915
	318	30.681	33.325	16.339	28.129

Table (4): The thermodynamic adsorption parameters for corrosion of aluminum in 0.1M oxalic acid in absence and in presence of 0.001M different additives at different temperature.

additive	T (^{o}K)	ΔH_{ad} (KJ/mol.)	ΔS_{ad} (J/mol./degree)	ΔG_{ad} (KJ/mol.)
ST	298	-38.138	-21.774	-31.649
	303	-38.439	-21.774	-31.41
	308	-38.259	-21.774	-31.553
	313	-38.445	-21.774	-31.630
	318	-38.682	-21.774	-31.758
SM	298	-30.113	5.257	-31.680
	303	-30.503	5.257	-32.096
	308	-30.084	5.257	-31.703
	313	-30.092	5.257	-31.738
	318	-30.184	5.257	-31.856
TU	298	-57.048	16.324	-61.913
	303	-57.072	16.324	-62.019
	308	-55.988	16.324	-61.016
	313	-56.462	16.324	-61.571
	318	-56.986	16.324	-62.178

Figures

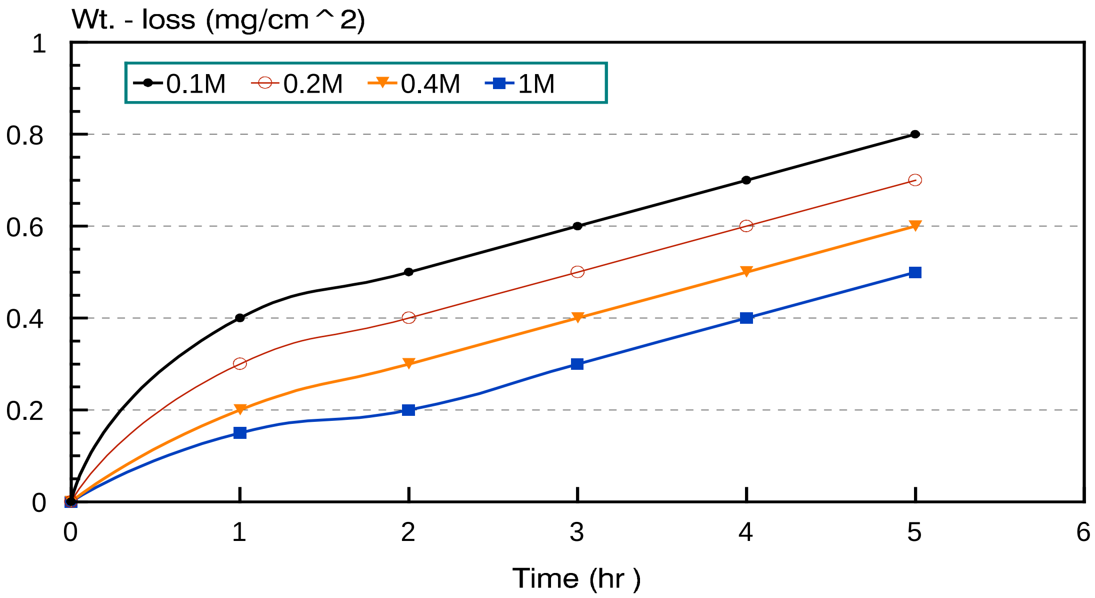


Fig.(1) Weight loss - Time Curves of Aluminum of Different Concentration Oxalic acid

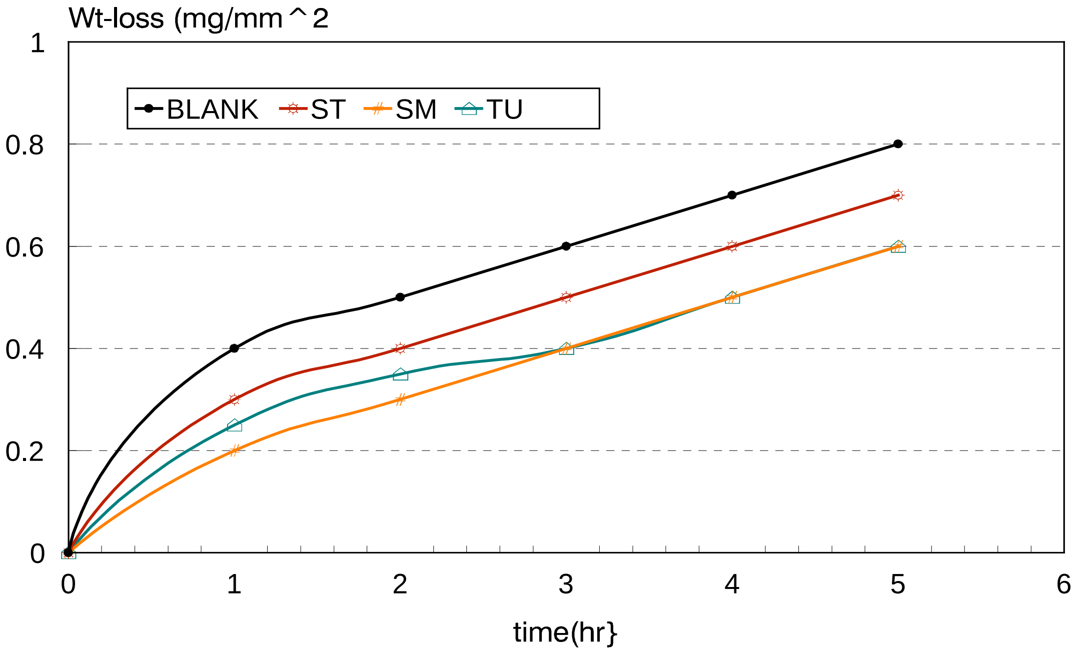


Fig.(2) Weight loss - Time Curve of Aluminum In 0.1M Oxalic acid with different additive

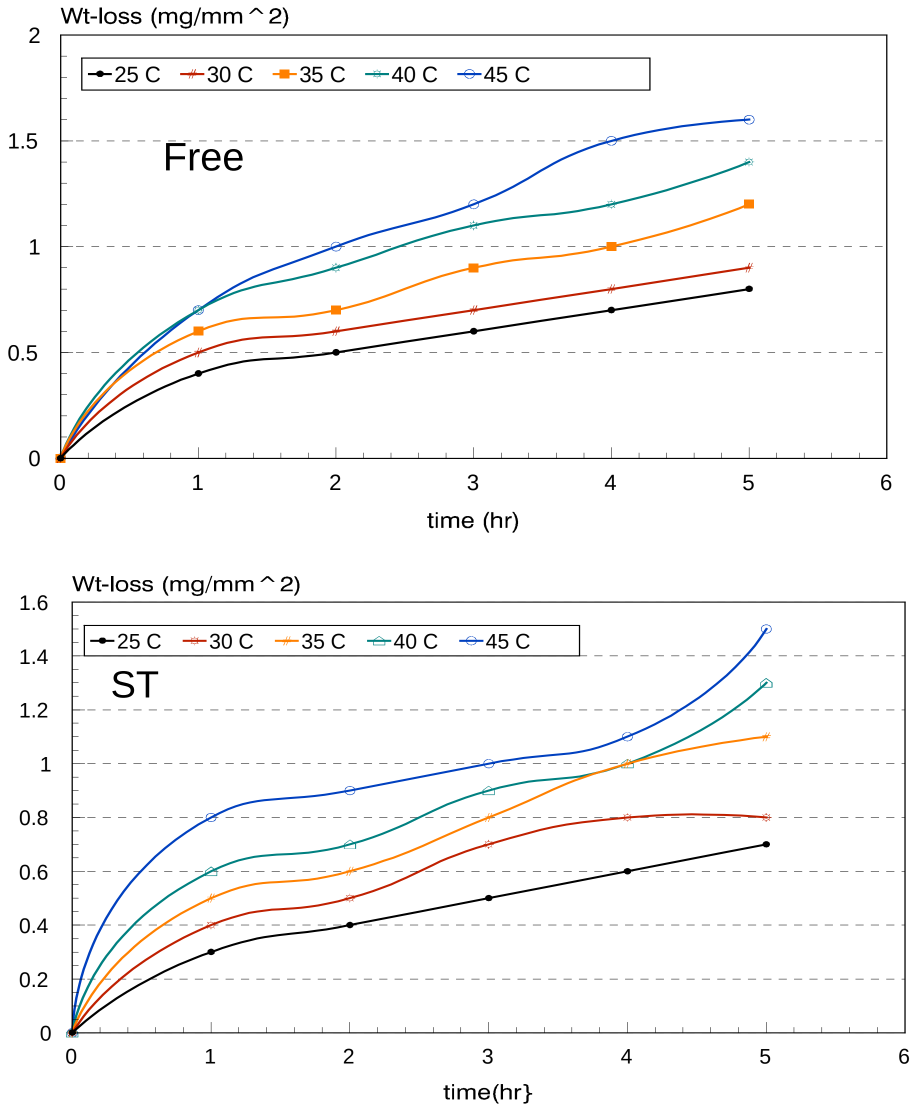


Fig. (3.1.1) Effect of temperature on dissolution of aluminum in 0.1M oxalic acid in absence and presence of 0.001M single additive.

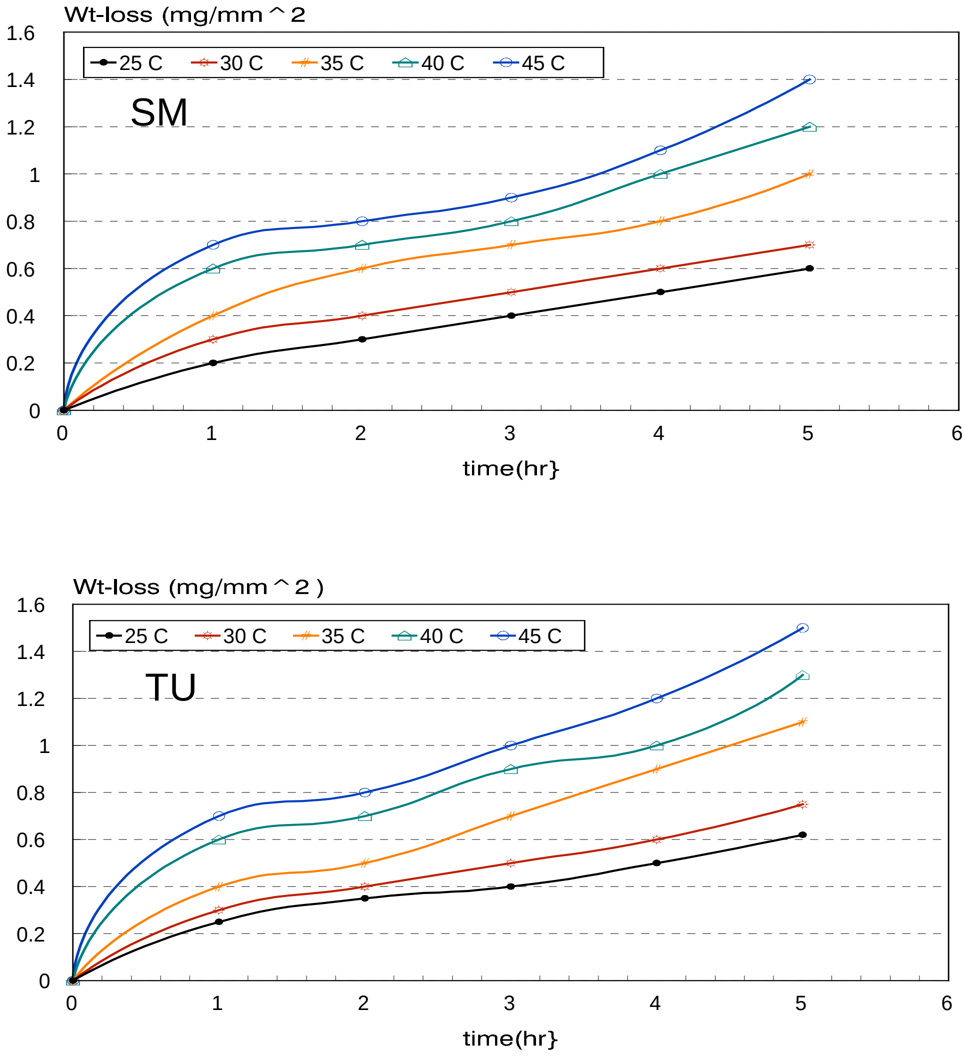
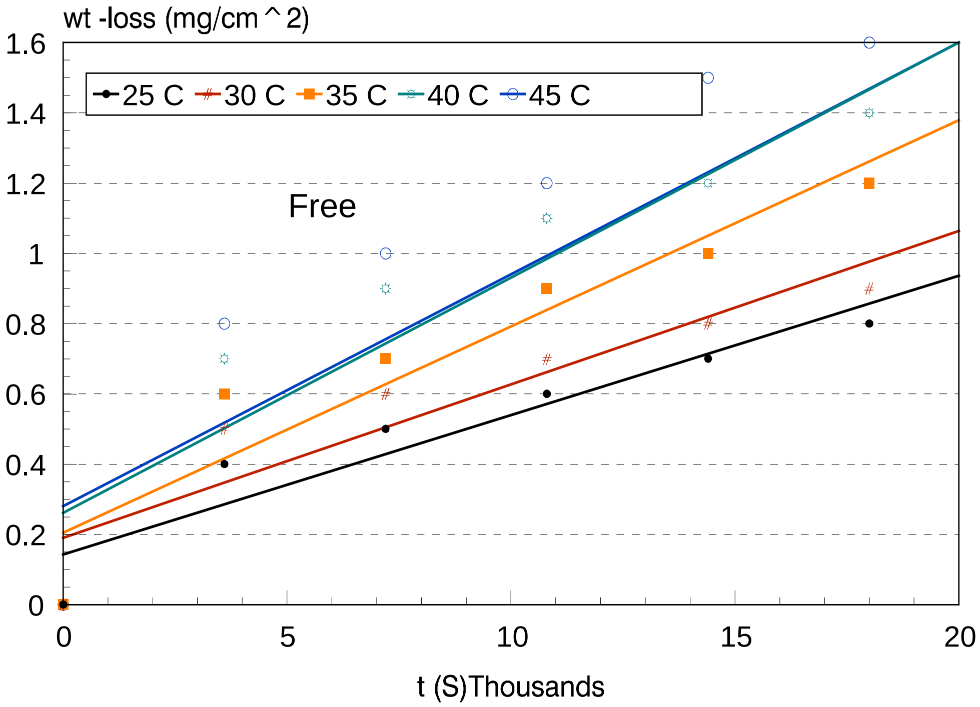


Fig. (3.1.2) Effect of temperature on dissolution of aluminum in 0.1M oxalic acid in absence and presence of 0.001M single additive.


wt -loss (mg/cm ^ 2)
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
25 C
30 C
35 C
40 C
45 C
Free
0
5
10
15
20
t (S)Thousands

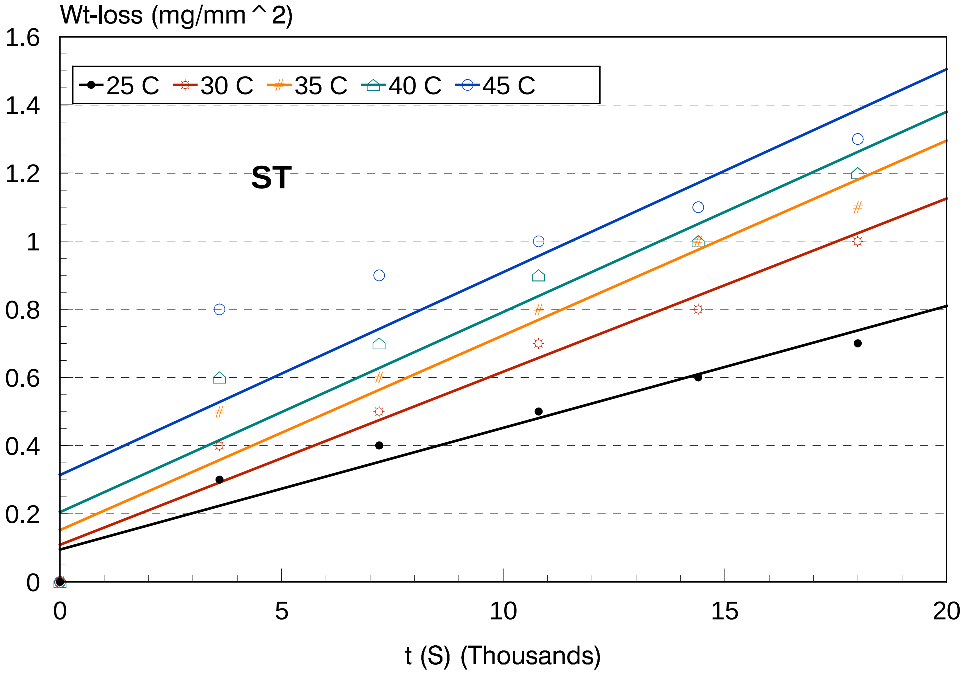

Wt-loss (mg/mm ^ 2)
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
25 C
30 C
35 C
40 C
45 C
ST
0
5
10
15
20
t (S) (Thousands)

Fig. (3.2.1) Effect of temperature on dissolution of aluminum in 0.1M oxalic acid in absence and presence of 0.001M single additive.

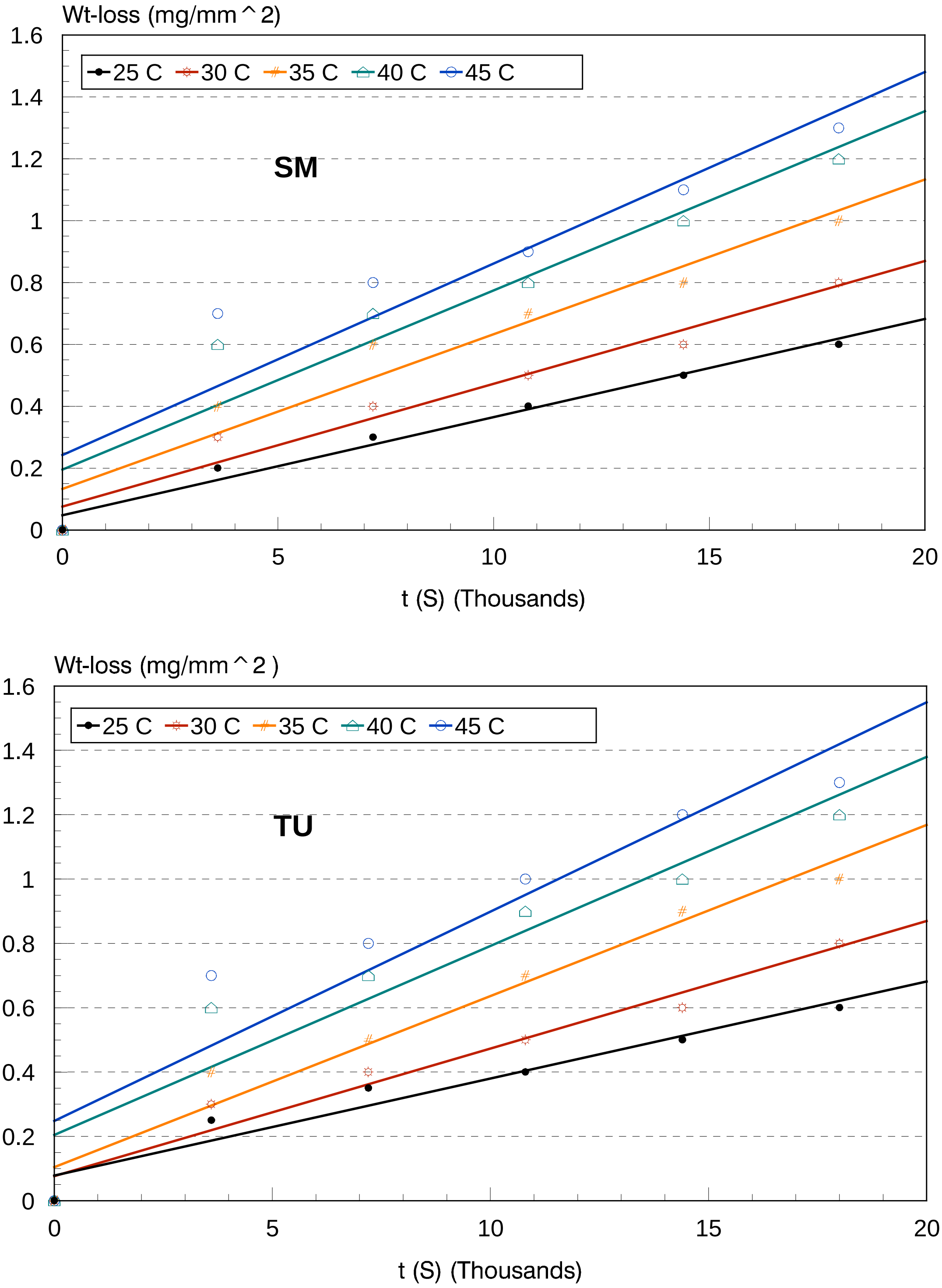


Fig. (3.2.2) Effect of temperature on dissolution of aluminum in 0.1M oxalic acid in absence and presence of 0.001M single additive.

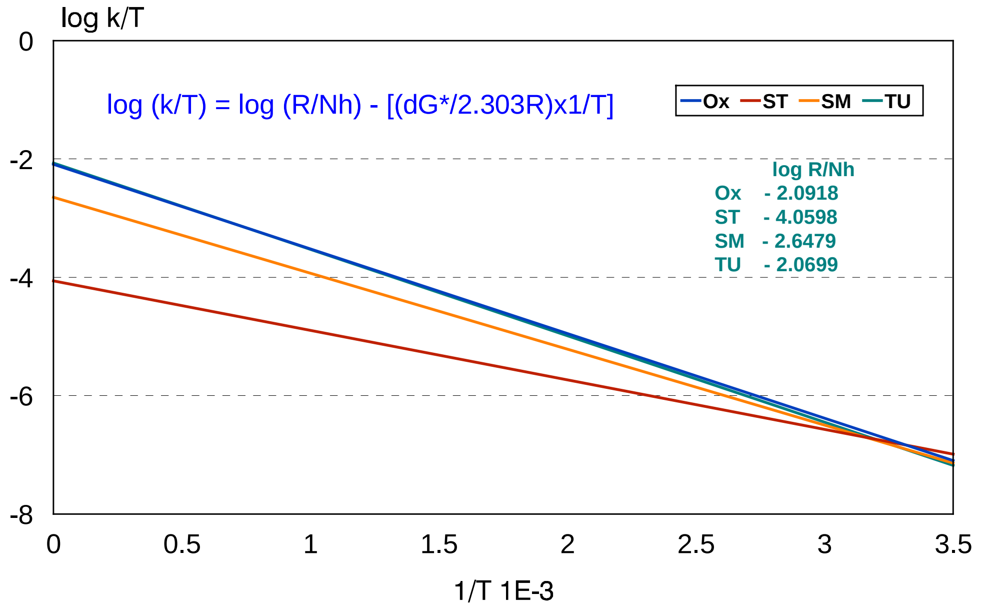


Fig. (4) Evaluation of log (R/Nh) intercept and free energy

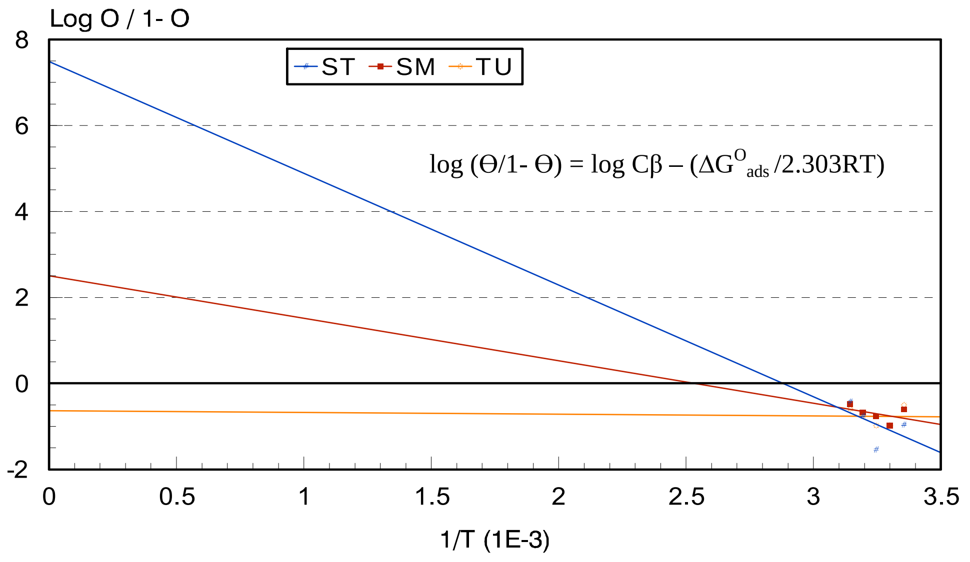


Fig. (5) Evaluation of log Cβ intercept and adsorption energy ΔG^{O}_{ad}