
THERMODYNAMIC PARAMETERS OF INHIBITION OF ALUMINUM DISSOLUTION IN OXALIC ACID SOLUTIONS USING SOME ORGANIC COMPOUNDS

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Abstract

Corrosion of aluminum in oxalic acid has been done by using wt-loss technique and polarization technique in presence of different concentrations of different organic derivatives of (5-Acetyl, 3-Cyano, 6-Methyl, 2-Thiopyridone, ...) such as (... , 4-p Anisyl [A₁]), (... ,4-p Bromo phenyl [A₂]), (... , 4-p Toly, [A₃]), (... ,4-p Nitro phenyl [A₄]) and (... ,4-p Chloro phenyl [A₅]) at different temperatures. It is noticed from the observed thermodynamic parameters derived from wt-loss measurements that ΔH for the adsorption of A₁, A₂, A₃ and A₅ resulted in a negative value (exothermic), the adsorption typed is chemical adsorption, whereas A₄ acquired physical adsorption and accelerated the dissolution of aluminum. This behavior is also observed at high temperatures for A₅ compound. From the polarization method studied the dissolution of aluminum in oxalic acid is decreasing as the concentration of the acid increased due to the formation of oxide passive layer (Al₂O₃. 3H₂O), the application of Evans diagram showed that the used compounds A₁, A₂, A₃ and A₅ can act as anodic inhibitors.

Introduction

Corrosion of aluminum and its alloys have recently become a topic of considerable importance with the increasing use of aluminum for industrial processes. Researches carried out on samples of aluminum⁽¹⁾ containing 0.6%Fe and 0.54%Si placed in 0.1N concentration of HCl, HNO₃, H₂SO₄, H₂C₂O₄, HOAc and tartaric acid for 15 weeks showed decreasing attack in the order given. The rate of attack 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. Byran studies on the corrosion of aluminum in citric acid and tartaric acid⁽²⁾ showed that corrosion became rapid in the region of pH= 7.0 , the rise being much more abrupt with citric acid .Oxalic acid (0.1N) has a severe corrosion affect on Al at 25°C. Aluminum resists corrosion in many environments because of the formation of a protective oxide film on the metal surface⁽³⁾. The film is generally stable in solution of pH 4.5-8.5⁽⁴⁾ 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⁽⁵⁾. In view of the high toxicity of chromates, used to inhibit

the corrosion of aluminum alloys in industry owing to humid atmospheres of different aggressiveness, viable alternatives are being researched to replace them⁽⁶⁾. Also molybdate species, have been used as corrosion inhibitors to replace hexavalent chromium in anodising processes⁽⁷⁾. The effect of addition of halides is also reported⁽⁸⁾.

Experimental:

The chemical composition of aluminum metal used is Al 99%, Fe 0.2% ,Cu 0.2%,Si 0.2%,Ti 0.03% and Zn 0.08% (Riedel – De Haan –Germany). Oxalic acid $C_2H_2O_4.2H_2O$ assay 99% prolabo. El-Nasr company for chemicals and drugs. The following additives have been tested as inhibitors:

A1: 5-acetyl, 3-cyano, 6-Methyl, 4-p Anisyl, 2-Thiopyridone.

A2: 5-acetyl, 3-cyano, 6-Methyl, 4-p Bromo phenyl, 2-Thiopyridone.

A3: 5-acetyl, 3-cyano, 6-Methyl, 4-p Tollyl, 2-Thiopyridone.

A4: 5-acetyl, 3-cyano, 6-Methyl, 4-p Nitro phenyl, 2-Thiopyridone.

A5: 5-acetyl, 3-cyano, 6-Methyl, 4-p Chloro phenyl, 2Thiopyridone.

All solutions were prepared from ordinary distilled water, thermo-stated to within $\pm 0.1^\circ C$ of the indicated temperature. The specimens are polished according to the methods described earlier^(9,10), the corrosion of aluminum in 0.1 M oxalic acid was carried out by using weight-loss and polarization techniques. In case of weight-loss technique, Al samples were used in the form of sheets (1x1.5x0.01cm), the samples were chemically cleaned⁽¹¹⁾, weighed and suspended in 50 ml of test solution. In polarization technique⁽¹²⁾ an electrolytic cell of Pyrex glass vessel of 250 ml capacity consists of aluminum electrode (working electrode), Pt. electrode (auxiliary electrode) and SCE as a reference electrode were used.

Results and Discussion:

Weight-loss Technique:

The weight loss was measured as (mg/cm^2) of the aluminum sample, immersed in 0.1M oxalic acid solution, the corrosion rates were determined at various temperatures and various concentrations of oxalic acid in presence and absence of different additives (A₁ – A5). The surface coverage θ and the inhibition efficiency (%IE) of the additives are calculated as⁽¹³⁾;

$$\Theta = (W_o - W) / W_o \quad (1)$$

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

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

The corrosion rate (r) is calculated as ⁽¹⁴⁾;

$$r \text{ (mpy)} = 534 \times W \text{ (mg)} / d \text{ (g/cm}^3\text{)} \times A \text{ (cm}^2\text{)} \times t \text{ (min)}, \quad (3)$$

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

$$\text{The specific rate constant } (K_r) = W/t. \quad (4)$$

According to Arrhenius equation ⁽¹⁵⁾;

$$\text{Log } K_r = \text{log } A - (E_a / 2.303 RT) \quad (5)$$

The values of activation thermodynamic functions for dissolution of aluminum in oxalic acid in the absence and presence of the additives were calculated as ⁽¹⁶⁾;

$$K_r = (kT/h) \text{ Exp } [-\Delta G_a / RT] \quad (6)$$

$$\Delta H_a = E_a - RT \quad (7)$$

$$\Delta S_a = [\Delta H_a - \Delta G_a] / T \quad (8)$$

Where k is Boltzmann constant and h is Blank's constant.

Weight-loss – time curves of Al in 0.1 M oxalic acid in presence of (1.0×10^{-4} M) of different additives at 30°C are illustrated in Fig. 1. Similar behavior was obtained at 40°, 50°, and 60°C and the data are recorded in table (1). The effects of temperature on the inhibition efficiency of additives ($A_1 - A_5$) given in Fig. 2, show that compound A_4 promotes corrosive action in presence of oxalic acid medium.

From the Langmuir adsorption isotherm ⁽¹⁷⁾;

$$\text{log } (\theta/1 - \theta) = \text{log } C\beta - (\Delta G_{\text{ads}}^0 / 2.303RT), \quad (9)$$

where; β is the adsorption equilibrium constant and C is the additive concentration.

The values of enthalpy of adsorption can be calculated from the relation ⁽¹⁶⁾;

$$\text{log } k = \text{log } k_o - (\Delta H_{\text{ads}} / 2.303 RT) \quad (10)$$

$$k = \theta / [C(1 - \theta)] \quad (11)$$

where k_o is a coefficient connected with the entropy of adsorption and k is the adsorption coefficient.

The calculated values of thermodynamic parameters that obtained from weight-loss measurements are listed in Table 2. It is noticed that, ΔH of the adsorption of the additives (A_1, A_2, A_3 , and A_5) have negative value. This indicates that the adsorption processes are exothermic and they can be typed as chemical adsorption for the high value of ΔH .

Polarization Method:

The polarization curves of aluminum dissolution in oxalic acid medium are given in (Fig. 3), illustrate that aluminum is dissolved as aluminum oxalate⁽¹⁸⁾. A discharge

process of the hydronium ion and an ionization of (H_{ads}) proceed reversibly^(1,12) in which case both hydrogen ions and water molecules participate as electron donors.

The corrosion rate (mpy) is calculated from Faradic relationship^(14,17);

$$\text{Rate (mpy)} = 0.1285 \times I_{cor} \times \text{Eq.wt} / d, \quad (12)$$

d: density and I_{cor} :corrosion current.

The dissolution of aluminum in oxalic acid is decreasing as the concentration of acid increased –as shown in figures (3-a and 4) due to fast formation of oxide passive layer $[Al_2O_3 \cdot 3H_2O]^{(18)}$, and may be due to the result of dimerization of oxalic acid, and the adsorption of the formed aluminum complex, (the data are recorded in table 3). The effect of temperatures given in fig. 3-b, show that the temperature increases as the rate of dissolution of Al increases, till $\geq 60^\circ C$, where oxalic acid is approached near its degradation temperature.

From the polarization curves of aluminum in (0.1 M) oxalic acid in absence and in presence of additives are illustrated in Figs.(5 & 6), it is possible to evaluate the surface coverage θ and the inhibition efficiency (%IE) of the additives as calculated from Faradic relation⁽¹⁴⁻¹⁶⁾.

$$\theta = (I_o - I) / I_o, \quad \%IE = \theta \times 100 \quad (13)$$

The effects of additives on the dissolution of aluminum in 0.1 M oxalic acid at different temperatures are given in table (4).

The obtained results show that the solution which contains compound A4 is a corrosive medium, such behavior is also observed at high temperatures for A₁ and A5.

At $E = E_{cor}$, the corrosion resistance (R_{cor}) is defined as^(19,20)

$$R_{cor} = (\partial E / \partial I)_{E=E_{cor}} \quad (14)$$

I_{cor} can be used to express the corrosion rate (mpy) where;

$$\text{(mpy) is proportional to } I_{cor},$$

$$\text{where; } I = (1/R_{cor}) E_{cor}, \quad (15)$$

$(1/R_{cor})$ can be used to express the rate constant of reaction.

$$\text{i.e. } K_r \equiv (1/R_{corr}). \quad (16)$$

So that;

$$\log (1/R_{corr}) = \log K_r = \log A - (\Delta E_a / 2.303 RT) \quad (17)$$

Hence, the activation thermodynamic parameters of the driven cell can be calculated by using Eqs.(6,7,8 and 17). The adsorption thermodynamic functions obtained from Eqs.(9, 10, 11, 12), illustrate the effect of temperatures on the activation and adsorption thermodynamic parameters of the driven cell listed in table (5). ΔG and ΔH values for (A4 and A5) have positive sign. In the other hand (A1, A2

and A3) which have negative sign for ΔG and ΔH indicate chemical adsorption whereas the major adsorption factor for (A4 and A5) is physical adsorption where they accelerate the dissolution process.

The third type of thermodynamic functions which can be obtained are related to the electrode potential ⁽²¹⁾ where;

$$\Delta G = - n F \Delta E, \quad \Delta E = E_{inh} - E_b, \quad (18)$$

$$\text{And ; } \Delta S = (\partial E / \partial T)_p \quad (19)$$

$$\Delta H = \Delta G + T \Delta S \quad (20)$$

$(\partial E / \partial T)_p$ = temperature coefficient, $n = 3$, F = Faraday constant, E_{inh} and E_b are electrode potentials in presence and in absence of additives respectively. Values of the change in the thermodynamic functions of the corrosion reactions in the driven cell at different temperatures are listed in table (6)

Evans diagrams

By applied Evans diagram principle⁽²²⁾ for free oxalic acid solutions at different concentrations at I_0 exchange current (Fig. 7), shows that:

- 1)- The corrosion current I_{corr} decreases as the oxalic acid concentration increases, where the anodic (de-electronation) curves at high concentration are sitting inside the closed area of 0.1M oxalic acid. The de-electronation potential is shifted to less negative value.
- 2)- The cathodic potential (electronation) is shifted towards less negative value, but at higher concentration (1.0 M) oxalic acid, the electronation potential is strongly shifted to more negative value.
- 3)- The cathodic area corroded till 0.3 M oxalic acid and still constant till 0.7 M, but at 1.0 M the increasing in the concentration inhibit the dissolution of cathodic area.
- 4)- Increasing the concentration of oxalic acid inhibits the dissolution of anodic area in all cases, which is in agreement with anodic corrosion resistance R_p (fig. 4), where R_p increased as the concentration of oxalic acid increased.
- 5) It is clear that the dissolution processes of aluminum in oxalic acid solution under polarization conditions is anodically controlled.

The dissolution of aluminum in 0.1 M oxalic acid solution in the presence of additives at different concentrations is studied under driven cell conditions (Fig. 5), to clarify the behavior of aluminum electrode. The dissolution of aluminum in oxalic acid solution is found to be anodically controlled and the effect of additives is studied under anodic polarization (Fig. 6).

The Evans diagram applications of dissolution of aluminum in 0.1 M oxalic acid solution in the presence of additives at different temperatures under anodic polarization are shown in (fig. 8), indicate that:

- 1) A4 compound exhibits and accelerates the dissolution of aluminum at all. The de-electronation curve is sitting out side the closed area of 0.1M solution and the de-electronation potential is shifted to more negative value.
- 2) Compound A5 behaves in the same manner but at high corrosion current. Therefore A4 and A5 act as salt in for oxalate solution.
- 3) The behavior of A4 is explained to be due to the presence of (-NO₂) group with high electron acceptor, and form complex compounds with the corrosion products.
- 4) The behavior of A₁, A₂, and A₃, show that;
 - i) They inhibit the corrosion processes where the anodic (de-electronation) curves are located inside the closed area of 0.1M solution.
 - ii) The de-electronation potential is shifted towards less negative value.

From the interpretation of Evans diagrams we notice that the data is in good agreement with that obtained from the interpretation of the thermodynamic functions.

Table 1: data obtained from weight loss – time curves.

Comp.	T (K)	W _o (mg/cm ²)	W (mg/cm ²)	θ	EI %
A 1	303	2.30	1.04	0.5478	54.78
	313	3.12	2.20	0.2949	29.49
	323	4.16	3.54	0.1490	14.90
	333	4.70	4.26	0.0936	9.36
A 2	303	2.30	1.46	0.3652	36.52
	313	3.12	1.87	0.4006	40.06
	323	4.16	2.29	0.4495	44.95
	333	4.70	3.54	0.2468	24.68
A 3	303	2.30	0.67	0.7061	70.61
	313	3.12	1.46	0.5321	53.21
	323	4.16	2.70	0.3510	35.10
	333	4.70	3.22	0.3149	31.49
A 5	303	2.30	1.77	0.2304	23.04
	313	3.12	2.86	0.0833	8.33
	323	4.16	3.95	0.0505	5.05
	333	4.70	corrosive	----	

Table (2): The activation and adsorption thermodynamic parameters from weight-loss

Add.	T (K)	Activation parameters				Adsorption parameters		
		ΔE_a J/mole	ΔG_a J/mole	ΔH_a J/mole	ΔS_a J/mole. K	ΔG_{ads} J/mole	ΔH_{ads} J/mole	$T\Delta S_{ads}$ J/mol
A 1	303	75879	83457.9	73360	-33.33	-132847	-131950	896.8
	313	76386	84299.8	73784	-33.6	-134462	-133536	926.4
	323	77613	85863.6	74927	-33.86	-136421	-135465	956.0
	343	79474	88065	76706	-34.11	-139182	-138196	985.6
A 2	303	45871.3	82638	43352.2	-129.6	-22788	-22870	-81.51
	313	46691.3	84755.9	44089	-129.9	-23931	-24015	-84.2
	323	47664.9	87030.1	44979.5	-130.1	-25233	-25320	-86.89
	343	47938.0	88606.4	45169.5	-130.4	-23486	-23575	-89.58
A 3	303	84538	84528.4	82019	-8.282	-91965	-93938	-1973
	313	85375	85449.8	82773	-8.552	-93053	-95091	-2038
	323	86600	86761.2	83914	-8.814	-94029	-96133	-2103
	343	88585	88835.9	85816	-9.067	-96491	-98659	-2168
A4	303	47851.9	81149.2	45332.8	-118.2	Acts as corrosive at all		
	313	48858.4	83339.2	46256.2	-118.4			
	323	49431.7	85098.6	46746.4	-118.7			
	343	50165.5	87021	47397	-118.9			
A 5	303	62887	82132.4	60367	-71.83	-136844	-135691	1153
	313	63680	83645.7	61078	-72.1	-138257	-137066	1191
	323	64859	85547.3	62174	-72.36	-141234	-140005	1229
	343	65792	87204.5	63023	-72.62	-136844	-135691	1153
blank	303	36855.3	81570.1	34336.2	-155.8			
	313	37264.4	83539.5	34662.2	-156.1			
	323	37576.9	85414.9	34891.6	-156.4			
	343	38414.2	87817.6	35645.6	-156.6			

Table 3: Effect of concentrations of oxalic acid solution on the dissolution of aluminum at 30° C.

concentration	I_{corr} (mA/cm ²)	R_{corr} Ω	Rate (mpy)
0.1M	15	4.404	6.424
0.3M	4	4.839	1.713
0.5M	2	21.299	0.856
0.7M	0.9	42.478	0.385
1.0M	0.5	91.300	0.214

Table (4): The effect of additives concentration and temperatures on the dissolution of aluminum in 0.1 M oxalic acid (polarization).

Temp.	0.1 M free		Efficiency % of additives				
	I_{corr} mA/cm ²	Rate (mpy)	A 1	A 2	A 3	A 4	A 5
30°C	15	6.425	96.7	78.67	97	Corr.	80
40°C	40	17.133	62.5	62.5	94	Corr.	Corr.
50°C	76	32.553	Corr.	86.84	80.26	Corr.	Corr.
60°C	72	30.840	Corr.	75.6	765.7	Corr.	Corr.

Table (5): The activation and adsorption thermodynamic parameters calculated from driven cell.

Add.	T (K)	Activation parameters				Adsorption parameters		
		ΔE_a J/mole	ΔG_a J/mole	ΔH_a J/mole	ΔS_a J/mole.K	ΔG_{ads} J/mole	ΔH_{ads} J/mole	$T\Delta S_{ads}$ J/mol
A 1	303	151085	83557	148566	214.55	-105101	-105103	-1.788
	313	148036	78363	145433	214.28	-101803	-101805	-1.847
	323	150412	78598	147727	214.02	-105344	-105345	-1.906
	343	150333	76380	147565	213.76	-108484	-108486	-1.965
A 2	303	42790.4	79110	40271.3	-128.1	-6695.8	-6697.5	-1.788
	313	42461.7	80065	39859.4	-128.4	-4849.9	-4851.7	-1.847
	323	43251.2	82140	40565.8	-128.7	-6775.5	-6777.4	-1.906
	343	42514.2	82692	39745.6	-128.9	-6890.9	-6892.8	-1.965
A 3	303	91757.3	68785	89238.2	67.502	-70400	-70405	-5.181
	313	104041	80395	101439	67.232	-70838	-70843	-5.352
	323	106244	81928	103559	66.970	-69478	-69484	-5.523
	343	108781	83796	106013	66.717	-70891	-70896	-5.694
A4	303	34243.5	75321	31724.3	-143.8	10028	10027.4	-0.57
	313	32679.1	75196	30076.8	-144.1	10406.9	10406.3	-0.588
	323	33467.2	77427	30781.7	-144.4	9804.33	9803.72	-0.607
	343	34111.9	79518	31343.3	-144.6	10229.7	10229.0	-0.626
A 5	303	36932.6	77488	34413.5	-142.1	9490.23	9489.88	-0.342
	313	35561.5	77539	32959.2	-142.4	9853.78	9853.42	-0.354
	323	36672.7	80076	33987.3	-142.6	9231.02	9230.66	-0.365
	343	36628.8	81461	33860.2	-142.9	9701.08	9700.70	-0.376
blank	303	57269.1	76822	54750	-72.84			
	313	57737.8	78021	55135.5	-73.11			
	323	57548.1	78564	54862.7	-73.37			
	343	57297.4	79048	54528.9	-73.63			

Table (6): The change in the thermodynamic functions of the corrosion reactions in driven cell at different temperature.

Add	T (k)	$(\partial E/\partial T)$ V/degree	ΔE (V)	ΔG J/mole	T ΔS J/mole	ΔH J/mole
A 1	303	0.00072	0.019	-5500.5	63.157	-5437.3
	313		0.030	-8685	65.242	-8619.8
	323		0.042	-12159	67.326	-12092
	343		0.039	-11291	69.411	-11221
A 2	303	0.00062	0.019	-5500.5	54.385	-5446
	313		0.029	-8395.5	56.18	-8339
	323		0.040	-11580	57.975	-11522
	343		0.036	-10422	59.77	-10362
A 3	303	0.00062	0.022	-6369	54.385	-6314.6
	313		0.031	-8974.5	56.18	-8918.3
	323		0.042	-12159	57.975	-12101
	343		0.039	-11291	59.77	-11231
A 4	303	0.00059	0.011	-3184.5	51.754	-3133
	313		0.021	-6079.5	53.462	-6026
	323		0.032	-9264	55.17	-9209
	343		0.027	-7816.5	56.878	-7760
A 5	303	0.00062	0.009	-2605.5	57.017	-2548.5
	313		0.020	-5790	58.899	-5731.1
	323		0.031	-8974.5	60.781	-8913.7
	343		0.027	-7816.5	62.662	-7753.8

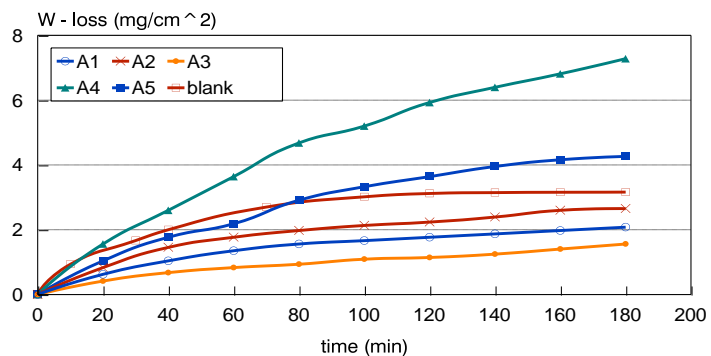


Fig 1: Weight loss - time curve of aluminium in 0.1 M oxalic acid with different additives at 30 C

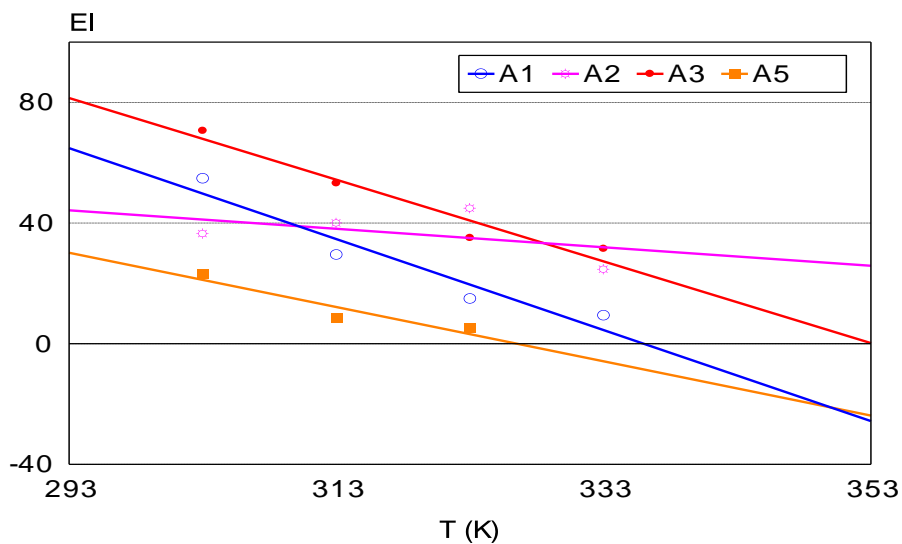


Fig. 2: The effect of temperatures on the inhibition efficiency of the additives.

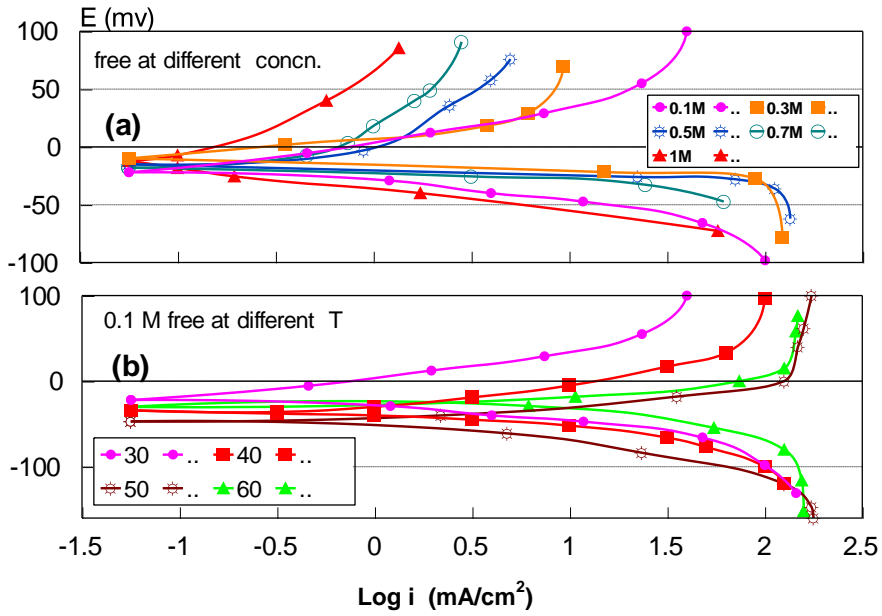


Fig. 3: The polarization curves:
 a)- Effect of oxalic acid concentrations,
 b)- Effect of temperatures on aluminum dissolution in 0.1 M oxalic acid.

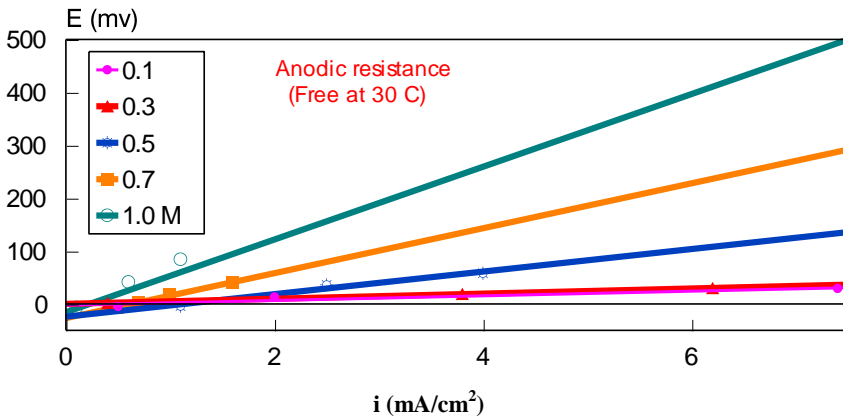


Fig. 4: Anodic resistance of corrosion of aluminum in different concentrations of oxalic acid.

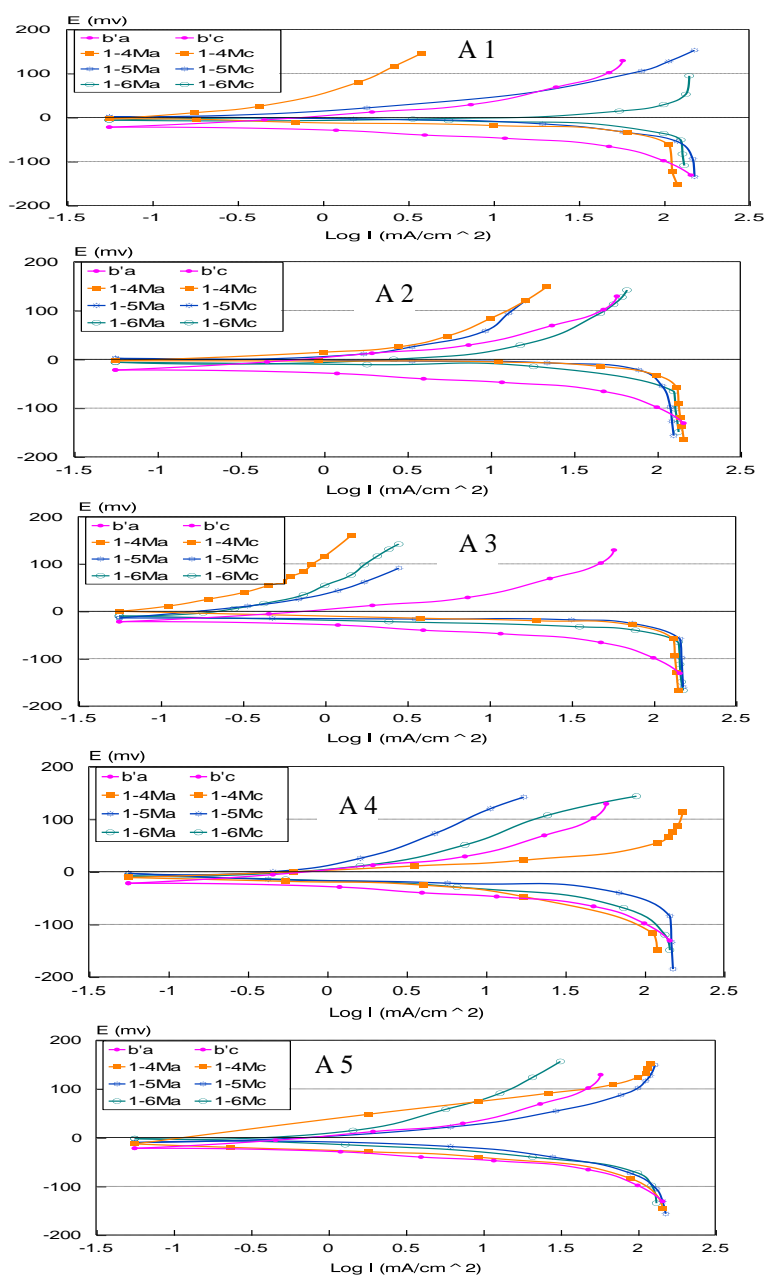


Fig 5: Polarization curves of the dissolution of aluminum in 0.1 M oxalic acid in presence of different concentrations of different additives. (1-4Ma = 0.0001 M anodic polarization) and so on.

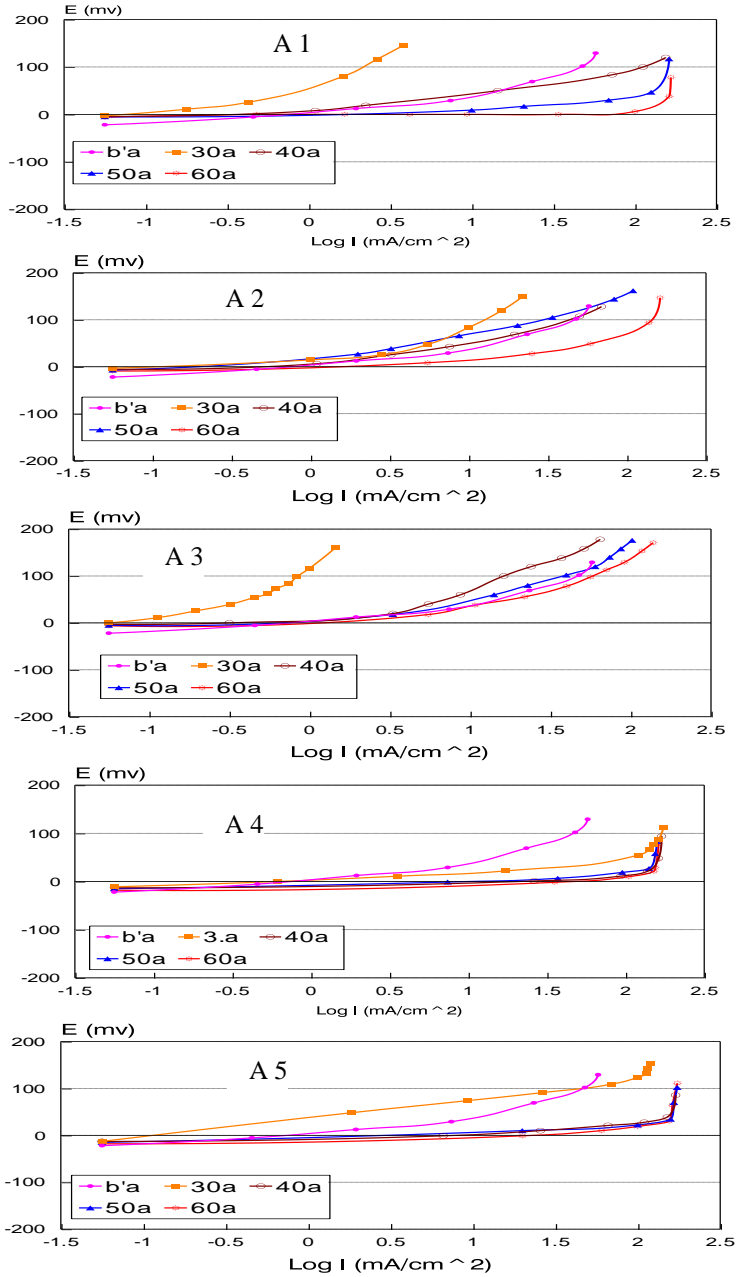


Fig 6: Anodic polarization curves of the dissolution of aluminum in 0.1 M oxalic acid in presence of ($1.0 \times 10^{-4}\text{M}$) of different additives at different temperatures.

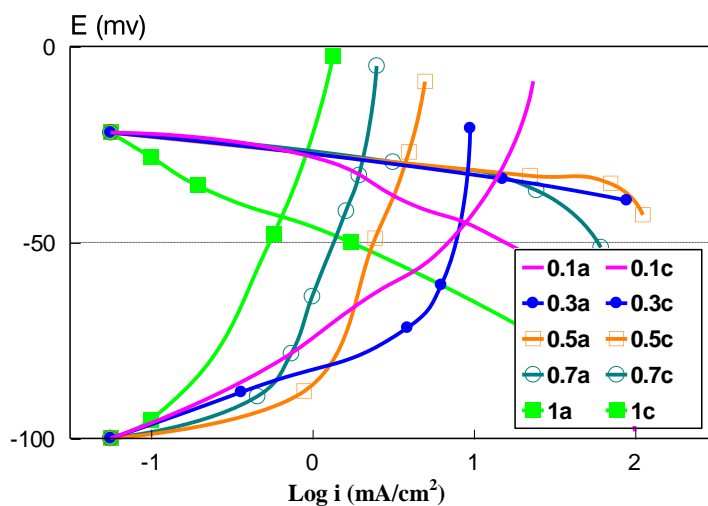


Fig. 7: Evans diagram of the dissolution of Al in oxalic acid solutions.

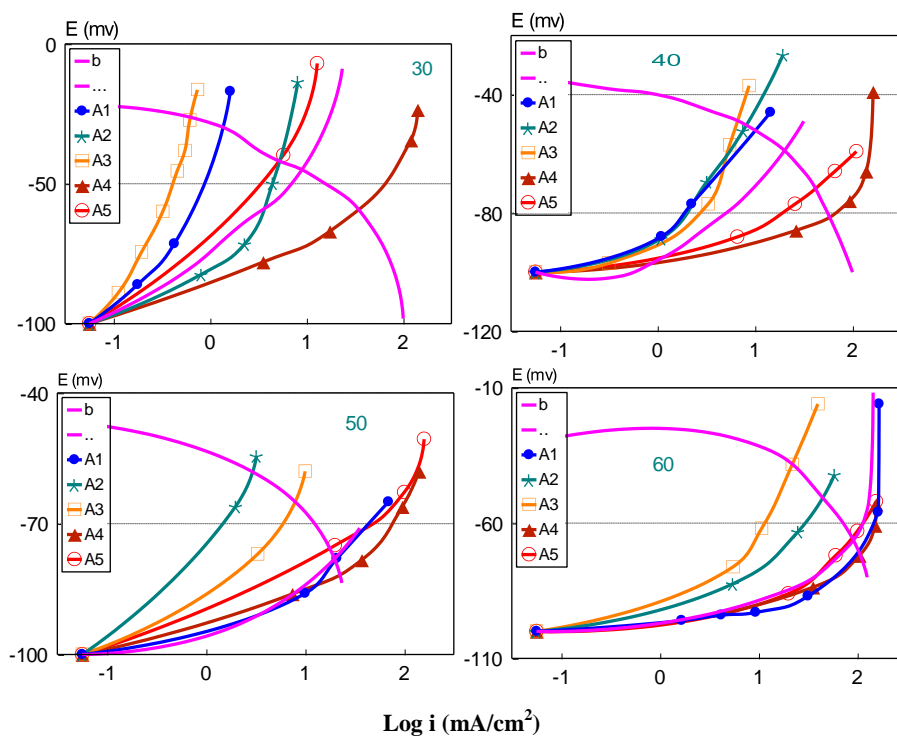


Fig. 8: Evans diagram applications in the presence of additives at different temperatures.

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