Effect of Some Organic and Inorganic Compounds on Corrosion Inhibition of Aluminum in Alkaline Solution

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Abstract— Corrosion of aluminum in potassium hydroxide has been investigated by using weight loss and open- circuit techniques in the absence and presence of chlotrimazole (CTM) and potassium iodate (PI) as inhibitors at varying concentrations and different temperatures. The inhibition efficiency was found to increase as the concentration of inhibitor goes on increasing, while the increase in temperature resulted in a dramatic lowering of inhibition at all inhibitors concentration. Adsorption of both CTM and PI onto the surface of aluminum was fitted well to the Langmuir isotherm model over whole concentration and temperature ranges. Thermodynamic parameters were calculated and the most possible mechanism for the physical adsorption of the investigated inhibitors was also proposed.

Index Terms— Corrosion, Inhibition, Aluminum, KOH, CTM, PI

1 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]. Organic and inorganic compounds are widely used as corrosion inhibitors to control the dissolution of the protective oxide film on the surface of aluminum in alkaline solution; in order to minimize metal loss and the consumption of the alkaline solution. Thus, organic and inorganic compounds are usually added to alkaline media as corrosion inhibitors in industrial processes such as alkaline cleaning, pickling and etching, and to improve efficiency in devices such as aluminum alkaline battery [7]. The nature of inhibitor adsorption depends on the number and types of adsorption sites on the metal surface as well as the type of interaction between the organic molecule and the metallic surface[8].Chlotrimazole [1-[(2-chlorophenyl)-diphenylmethyl] imidazole] is a non toxic, cheap and environmental friendly antifungal drug that is use in the treatment of fungal disease. It contains reactive centers like N atoms containing lone pairs of electrons and aromatic rings with delocalize π electron systems which can aid the adsorption onto metal surfaces. Furthermore, it has a high molecular weight (molecular weight- 344. 845amu) and likely to effectively cover more surface area (due to adsorption) of the aluminum metal thus preventing corrosion from taking place[9]. Potassium iodate is anti-microbial and oxidizing properties (molecular weight- 214 amuun) .

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In the present study, the effect of chlotrimazole and potassium iodate on the corrosion inhibition of corrosion process of aluminum in 1M potassium hydroxide solution have been investigated using chemical and electrochemical measurements.IJSER staff will edit and complete the final formatting of your paper.

2 MTETERIALS &METHODS

The purity of aluminum metal is 99 %, (Germany), pure potassium hydroxide E. Merck company (Germany). Chlotrimazole and Potassium iodate as the organic and inorganic inhibitors respectively.

Medium	Type of inhibitors	Abbreviation	Molecular formula
100 mmol Potassium hydroxide	Chlotrimazole	CTM	$C_{22}H_{17}ClN_2$
	Potassium iodate	PI	KIO_3

All solutions were prepared from ordinary distilled water, thermo-stated to within ± 0.1 °C of the indicated temperature. The specimens are polished according to the methods described earlier [10,11] the corroded media is prepared as (0.5, 1.0, 1.5, 2.0 M) Potassium hydroxide .

An aqueous solution of 1 M potassium hydroxide was used as a bank solution. The inhibitors was added to the alkaline in concentrations ranging (0.005, 0,015, and 0.025 g). The tested specimens were used in the of sheets of dimension (2cm × 2cm). The exposed area, 4 cm^2 for weight loss and (1cm × 1cm). The exposed area, 1 cm^2 for open circuit, the sample were chemically cleaned [12] weighted and suspended in 100 ml of test solution and then weighted again at the end of the reaction after drying. In the weight loss measurement and the potential of the aluminum specimens against a saturated calomel electrode (SCE) were simultaneously recorded with time by open-circuit measurements.

3 RESULTS & DISCUSSION

3.1 Weightt- loss technique

The weight loss of the aluminum metal that immersed in different potassium hydroxide concentrations was measured as (mg/cm²) at 25°C. The dissolution of aluminum in potassium hydroxide increased as alkaline
concentration increased. The effect of alkaline concentration at 25 °C on the dissolution of aluminum are shown in Fig. 1 and illustrated in Table 1.

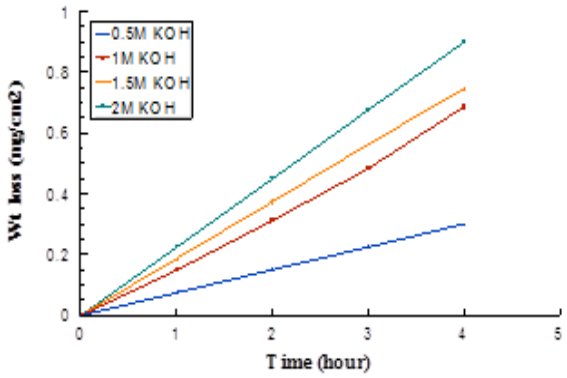

Fig. 1.Weight loss–time curves of aluminum dissolution in potassium hydroxide solutions with varying concentration at 25 °C.

TABLE 1
DATA OF WEIGHT LOSS AND CORROSION RATES OBTAINED FROM WEIGHT LOSS MEASUREMENTS FOR ALUMINUM IN DIFFERENT CONCENTRATION OF POTASSIUM HYDROXIDE SOLUTION AT 25 °C.

	Time (hour)	wt loss (mg/cm²)	R_{Corr} (mg.cm².h⁻¹)	R_{Corr} (mpy)
	1	0.075	0.0188	23.92
0.5	2	0.151	0.0189	24.08
	3	0.225	0.0188	23.92
	4	0.301	0.0188	24.00
	1	0.167	0.0418	53.27
1.0	2	0.338	0.0423	53.91
	3	0.498	0.0415	52.95
	4	0.686	0.0429	54.71
	1	0.187	0.0468	59.65
1.5	2	0.374	0.468	59.65
	3	0.562	0.0468	59.76
	4	0.746	0.0466	59.49
	1	0.225	0.0563	71.77
2.0	2	0.449	0.0561	71.61
	3	0.675	0.0563	71.77
	4	0.898	0.0561	71.61

The weight loss – time curves of aluminum in 1M potassium hydroxide in the absence and presence of different concentration (0.005g, 0.015g, 0.025g) of different inhibitors (CTM and PI), at 25 °C are presented in Fig. 2 and 3, and the relevant calculated values are listed in Table 2. It is clear that the corrosion rate decrease with increasing their concentrations in solution.

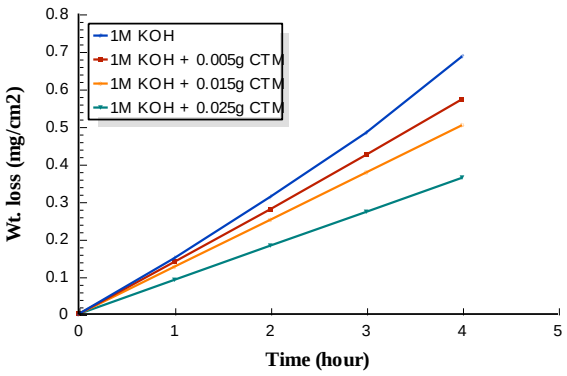

Fig. 2. Weight loss – time curves of aluminum dissolution in 1M potassium hydroxide solution at 25 °C in the absence and presence of CTM for various concentrations.

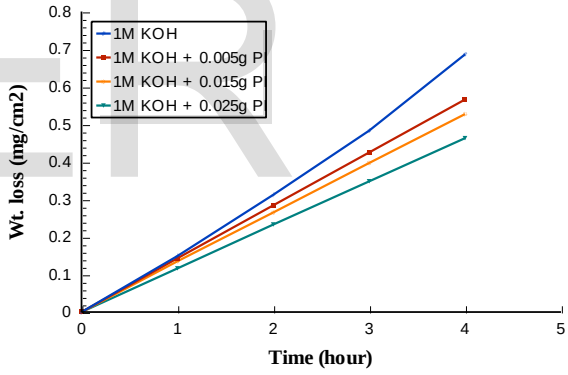

Fig. 3. Weight loss – time curves of aluminum dissolution in 1Mpotassium hydroxide solution at 25 °C in the absence and presence of PI for various concentrations.

The surface coverage area (Θ) and the inhibition efficiency (IE %) were calculated as [13].

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

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

Wo and W refer to the values of weight loss in absence and presence of inhibitors, respectively.

The corrosion rate (R) is calculated as,

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

A, d, and t are specimen area, density and exposure time, respectively.

TABLE 2

DATA OF WEIGHT LOSS, CORROSION RATE, SURFACE COVERAGE AND INHIBITION EFFICIENCY OBTAINED FROM WEIGHT LOSS MEASUREMENTS FOR ALUMINUM IN1M POTASSIUM HYDROXIDE WITHOUT AND WITH VARIOUS CONCENTRATION OF DIFFERENT INHIBITORS AT 25 °C

Medium	Conc.	Wt. loss (mg/cm²)	Θ	IE%	R_{Corr} (mpy)
KOH	1M	0.686	0	0	54.71
CTM	0.005g	0.503	0.2667	26.67	40.11
	0.015 g	0.463	0.3251	32.51	36.92
	0.025 g	0.363	0.4708	47.08	28.95
PI	0.005g	0.572	0.1662	16.62	45.62
	0.015 g	0.557	0.1881	18.81	44.42
	0.025 g	0.463	0.3251	32.51	36.92

The effect of temperature on the corrosion parameters of aluminum in 1M potassium hydroxide in presence of (0.015 g) for all inhibitors was studied at different temperatures (25, 35, 45, 55 °C) as illustrated in Fig. 4, and 5 and listed in Table 3. It can observed that the corrosion rate is increased by rising the temperature.

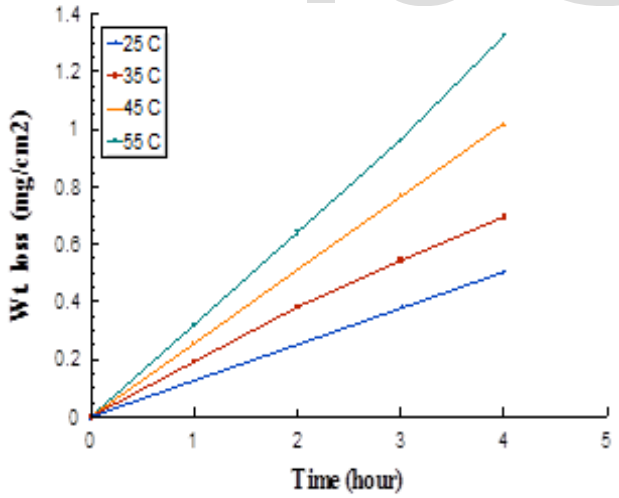

Fig. 4. Weight loss – time curves of aluminum dissol tion in 1M potassium hydroxide with CTM (0.015g) at different temperatures.

TABLE 3

DATA OF WEIGHT LOSS, CORROSION RATE, SURFACE COVERAGE AND INHIBITION EFFICIENCY OBTAINED FROM WEIGHT LOSS MEASUREMENTS FOR ALUMINUM IN1M POTASSIUM HYDROXIDE WITHOUT AND WITH 0.015 G OF DIFFERENT INHIBITORS AT DIFFERENT TEMPERATURES.

Medium	T (°K)	Wt–loss (mg/cm²)	Θ	IE(%)	R_{Corr} (mpy)
KOH	298	0.686	–	–	54.7
	308	0.896			71.1
	318	1.261			100.1
	328	1.602			127.8
CTM	298	0.463	0.3251	32.51	36.92
	308	0.695	0.224	22.4	55.4
	318	1.021	0.19	19.0	81.4
	328	1.324	0.174	17.4	105.6
PI	298	0.557	0.232	23.2	44.4
	308	0.693	0.227	22.7	55.3
	318	1.036	0.178	17.8	82.6
	328	1.385	0.135	13.5	110.4

The study of the temperature effect allowed to investigating the thermodynamic activation and adsorption parameters. The activation energy (ΔEa *) of corrosion reaction is calculated according to the Arrhenius dependence [15]:

$$k_r = A \exp(-\Delta Ea^*/RT) \quad (4)$$

where k_r is the specific rate constant and is equal to the ratio (dW/dt).

$$\log kr = \log A - (\Delta E a^*/2.303RT) \quad (5)$$

$$\text{or } \Delta E a^* = 2.303\ RT \times (\log A - \log k_r) \quad (6)$$

Accordingly, the value of kr is simply obtained from the slope of weight loss versus time curves. Plotting of log kr versus 1/T for the aluminum corrosion in the presence and absence of inhibitors. Fig. 6 gives a straight line whose slope is equal to ΔE* with an intercept of log A. The Gibb's free energy of activation (ΔG*) was computed from the transition– state equation [16,17] as follows:

$$kr = (RT/Nh) \exp(-\Delta G^*/RT) \quad (7)$$

$$\text{or} \quad \log kr/T = \log(R/Nh) - (\Delta G^*/2.303RT) \quad (8)$$

where h is the Blanck's constant, R is the universal gas constant, and N is Avogadro's number. Hence, plotting of log kr/T versus 1/T gives a straight line whose slope is equal to (–ΔG*/2.303R) with an intercept of log(R/Nh). Fig. 7 show plots of log kr/T versus 1/T for the aluminum corrosion, in the presence and absence of inhibitors. Values of ΔG* were obtained from the magnitude of slope according to the following formula:

$$\Delta G^* = -2.303R \times (\text{Slope}) \quad (9)$$

The corresponding enthalpy (ΔH^*) and entropy (ΔS^*) of activation were then calculated using equation (10) and (11), respectively:

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

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

The values of thermodynamic activation parameters, estimated without and with inhibitors for the aluminum corrosion in 1M potassium hydroxide solution are listed in Table 4.

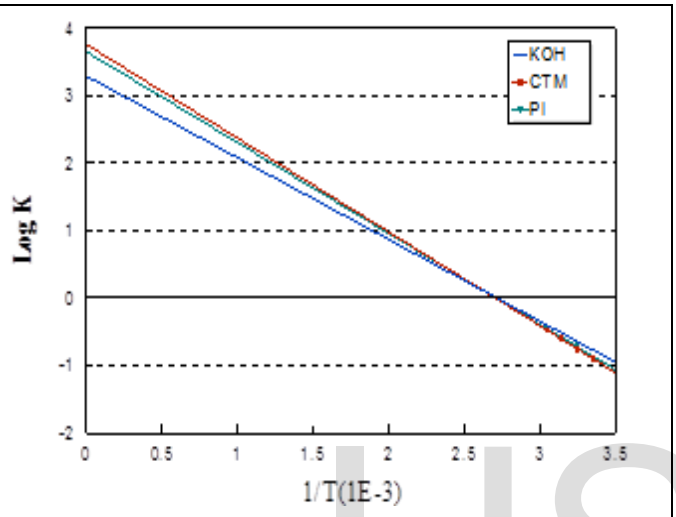

Fig. 6. Arrhenius plots of Al in 1M potassium hydroxide without and with 0.015g of all inhibitors

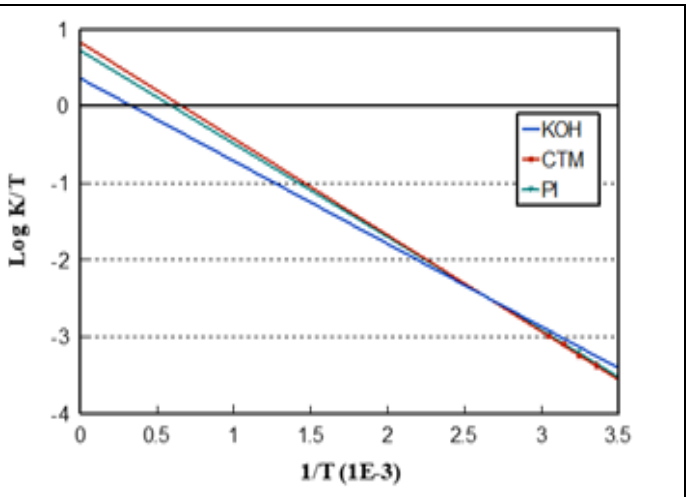

Fig. 7. Evaluation of log(R/Nh) intercept and free energy for aluminum in 1M potassium hydroxide without and with 0.015g of all inhibitors at different temperatures.

TABLE 4

THERMODYNAMIC ACTIVATION PARAMETERS FOR THE CORROSION OF ALUMINUM IN 1M POTASSIUM HYDROXIDE IN ABSENCE AND PRESENCE OF 0.015G DIFFERENT INHIBITORS AT DIFFERENT TEMPERATURES.

Medium	T (^oK)	ΔE_a^* (kJ/mol.)	ΔH^* (kJ/mol.)	ΔS^* (J/mol./degree)	ΔG^* (kJ/mol.)
KOH	298	23.154	25.631	17.04	20.553
	308	23.274	25.835	16.766	20.671
	318	23.143	25.787	16.500	20.540
	328	23.194	25.921	16.243	20.594
CTM	298	26.581	29.059	17.022	23.986
	308	26.632	29.198	16.747	24.040
	318	26.494	29.136	16.482	23.895
	328	26.632	29.359	16.243	24.037
PI	298	25.868	28.346	23.972	21.202
	308	25.686	28.247	23.697	20.948
	318	25.813	28.457	23.432	21.006
	328	25.836	28.562	23.147	20.961

From Langmuir adsorption isotherm can be employed to investigate the adsorption of inhibitors on aluminum surface [18]. The Gibb's free energy of adsorption (ΔG^o_{ads}) was evaluated by applying the empirical formula illustrated below:

$$\text{Log } (\Theta /1- \Theta) = \log C\beta - (\Delta G^o_{ads} /2.303RT) \quad (12)$$

where β is the adsorption equilibrium constant and C is the concentration of inhibitor. The parameter log Cβ was obtained from extrapolation of the log (Θ /1– Θ) versus 1/T plots to log (Θ /1– Θ) = 0 , as clearly depicted in Fig. 8 showing the dependence of inhibitors adsorption on temperature for aluminum metal

The values of enthalpy (ΔH_{ads}) and entropy (ΔS_{ads}) of adsorption were calculated from equation (13) and (14), respectively [19]:

$$\log k = \log ko - (\Delta H_{ads} /2.303RT) \quad (13)$$

$$\log k = (\Delta S_{ads} /2.303R) - (\Delta H_{ads} /2.303RT) \quad (14)$$

where k_o is a coefficient connected with the entropy of adsorption and k is the adsorption coefficient. The thermodynamic adsorption parameters (ΔG_{oads} , ΔS_{ads} and ΔH_{ads}) for dissolution of aluminum in potassium hydroxide in the absence and presence of inhibitors were summarized in Table 5

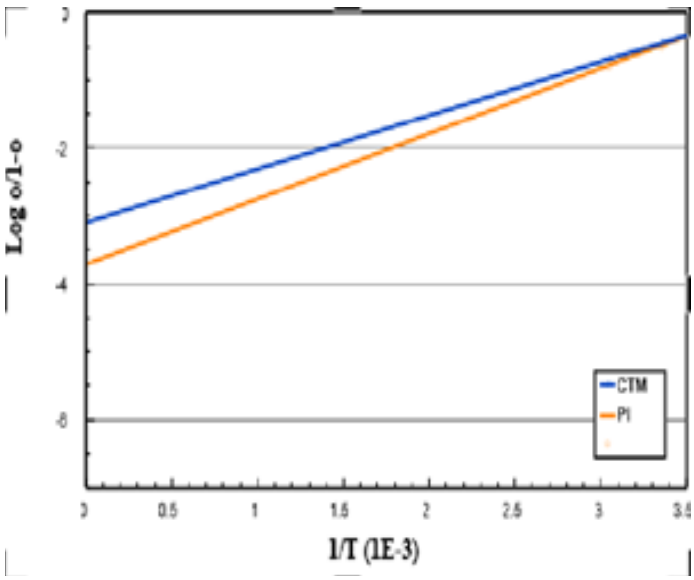

Fig. 8: Evaluation log Cβ intercept and adsorption energy ΔG^{o}_{ads} for aluminum in 1M potassium hydroxide with 0.015g of all inhibitors at different temperatures.

However, more information may be deduced from values of ΔG_{ads}. Generally, it has been found that if the value of ΔG_{ads} is up to –20 kJ mol^{-1}, the adsorption can be regarded as physisorption, and consequently the inhibition acts due to the electrostatic interaction between the charged molecules and the charged metal, while chemisorptions are predominantly seen for those adsorptions whose ΔG_{ads} values are around or higher than – 40 kJ mol^{-1}. The chemisorption occurs as a result of the charge sharing or transferring from inhibitor molecules to the metal surface to form a covalent bond, which is the fact behind the inhibition action of this type of adsorption [20,21]. In the light of this concept, the adsorption of these inhibitors on the aluminum metal the lower values of ΔGads range from –14.9 to –18.7 kJ mol^{-1} of CTM and PI inhibitors are due to physisorption. The negative values of (ΔG_{ads}) indicate the inhibitor is spontaneous adsorbed on the aluminum surface for all inhibitors.

3.2 Open- circuit potential measurements

The open– circuit potential of the aluminum metals immersed in potassium hydroxide solution at different concentration (0.5, 1, 1.5 and 2 M), were measured as a function of time, till the steady– state values were attained. In the absence of inhibitors, the steady – state potentials are approached to be more negative values by increasing the potassium hydroxide concentration is shown in Fig. 9

In the presence of inhibitors (CTM and PI) at varying concentrations (0.005, 0.015 and 0.025g), the steady– state potential (Figs. 10 and 11). The values of the immersion potential (Eim.) and steady– state potential (Es.s.) in the absence and presence of deferent concentrations of inhibitors are listed in Table 5. It can be noted that the extent of the potential rise is inversely dependent on the concentration of inhibitors. This may be due to the complex formation between inhibitor and corrosion product that is dissolved in the medium and the formation of a protective layer in the interfacial metal– corrosive medium.

Figs. 12 to 14 show the temperature dependence of steady–state potential in the absence and presence of different inhibitors. Generally, the higher the temperature within the range of 25 – 55 °C, the higher is the potential measured for aluminum electrode, suggesting a very high rate of the complementary anodic reaction under these conditions,

$$Al \rightarrow Al^{+3} + 3e \qquad (15)$$

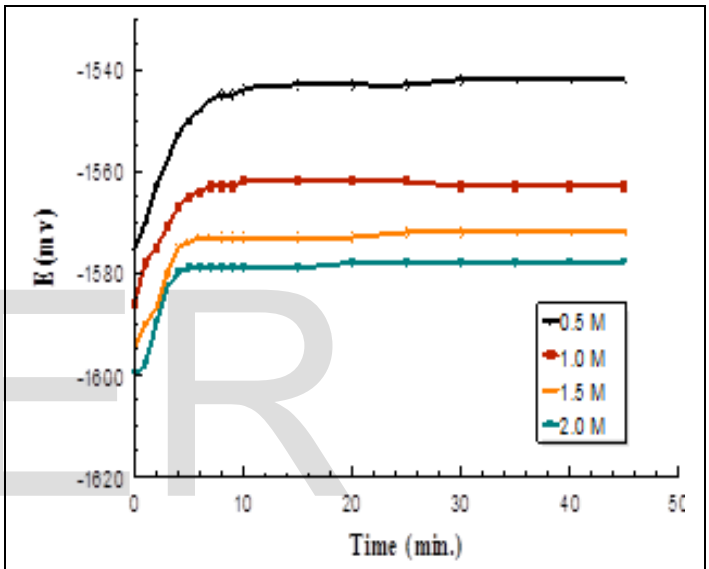

Fig. 9. Potential – time curves for aluminum in different concentrations of potassium hydroxide..

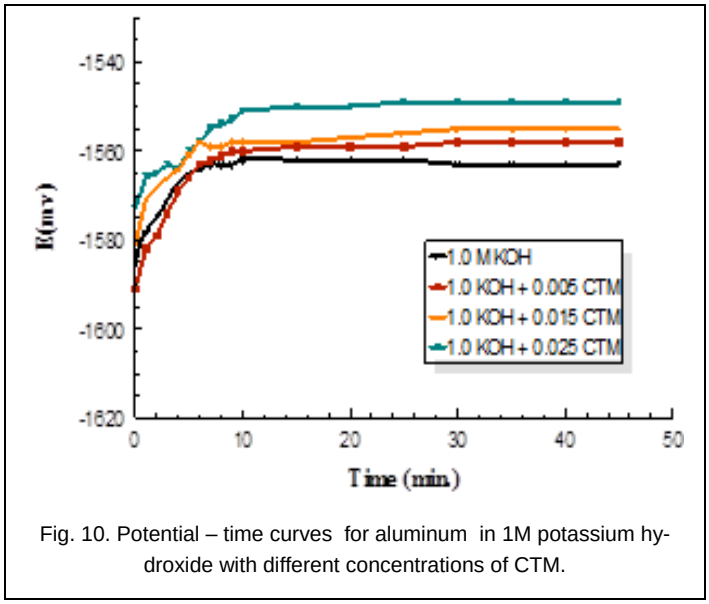

Fig. 10. Potential – time curves for aluminum in 1M potassium hydroxide with different concentrations of CTM.

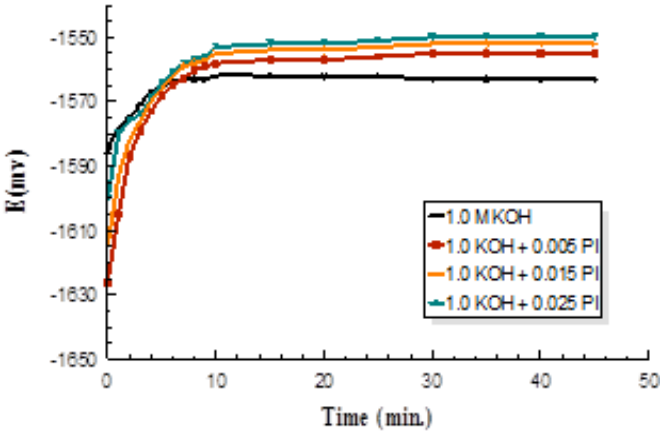

Fig. 11. Potential – time curves for aluminum in 1M potassium hydroxide with different concentrations of PI.

TABLE 5
VALUES OF EIM. AND ES,S FOR ALUMINUM METAL IN 1M POTASSIUM HYDROXIDE IN ABSENCE AND IN PRESENCE OF DIFFERENT CONCENTRATION INHIBITORS

Inhibitors	Concentration	Aluminum metal	
		E_{im}(mv)	$E_{s.s}$(mv)
KOH	1M	–1586	– 1563
CTM	0.005	–1591	–1558
	0.015	–1581	–1555
	0.025	–1573	–1549
PI	0,005	–1626	–1555
	0.015	–1615	–1552
	0.025	–1600	–1550

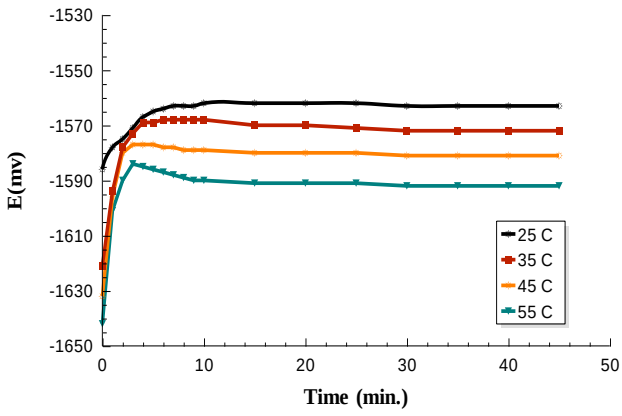

Fig. 12. Potential – time curves for aluminum in 1M potassium hydroxide at different temperatures.

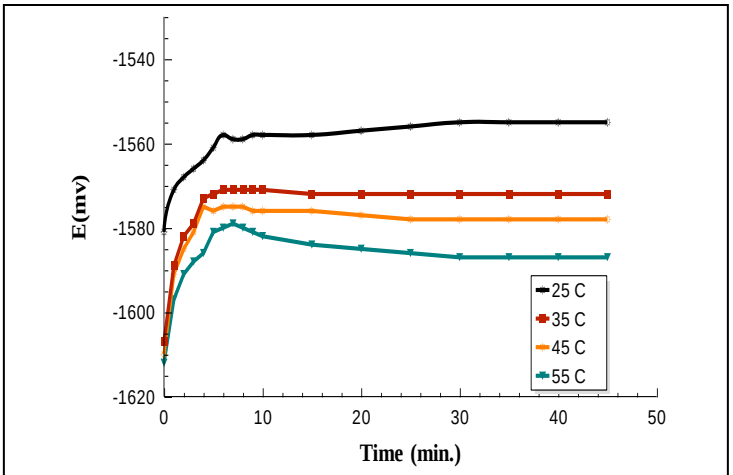

Fig. 13. Potential – time curves for aluminum in 1M potassium hydroxide with 0,015g CTM at different temperatures.

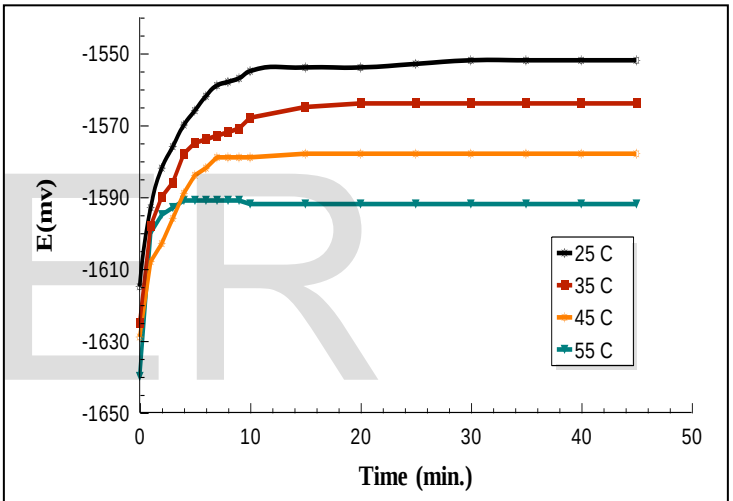

Fig. 14. Potential – time curves for aluminum in 1M potassium hydroxide with 0.015g PI at different temperatures.

ture with respect to SCE, can be considered as a relative emf of single aluminum electrode. The temperature coefficient of the emf is defined as $(\partial E/\partial T)p$. While, the changes in the thermodynamic parameters can be calculated as [22,23]:

$$\Delta S^* = nF(\partial E/\partial T) \quad (16)$$

$$\Delta G^* = -nF\Delta E_{cell} \quad (17)$$

$$\Delta E_{cell} = E_b - E_{inh} \quad (18)$$

$$\Delta H^* = \Delta G + T\Delta S \quad (19)$$

$$\Delta E^* = \Delta H - RT \quad (20)$$

where, n = 3 for aluminum, F is Faraday constant, and E_b and E_{inh} are the measured potential in the absence and presence of inhibitors, respectively. The changes in the thermodynamic parameters at different temperature in the steady state are illustrated in Table 6.

TABLE 6
THE THERMODYNAMIC ACTIVATION PARAMETERS FOR STEADY STATE OF ALUMINUM IN 1M POTASSIUM HYDROXIDE IN ABSENCE AND IN PRESENCE OF DIFFERENT INHIBITORS AT DIFFERENT TEMPERATURES.

Inhibitor	T (°K)	$-\Delta E_a^*$ (kJ/mol.)	ΔG^* (kJ/mol.)	$-\Delta H^*$ (kJ/mol.)	$-\Delta S^*$ (J/mol./degree
KOH	298	85298	0	82820	277920
	308	85555	2606	82994	
	318	85811	5211	83168	
	328	85489	8396	82762	
CTM	298	87835	2316	85680	295290
	308	88678	290	90660	
	318	91278	868	93034	
	328	95576	1447	95408	
PI	298	96779	3184	94303	307135
	308	101002	2316	98442	
	318	105804	868	103160	
	328	109738	289	107011	

4 CONCLUSION

Herr, it is important from the present study to conclude the following points of interest:

- The dissolution of aluminum in potassium hydroxide solution increased as the alkaline concentration increased. The corrosion rate is increased by rising the temperature.
- Clotrimazole and potassium iodate show a good inhibition property for corrosion of aluminum in 1M potassium hydroxide and the inhibiting efficiency of these inhibitors follows the order: CTM > PI.
- Inhibition efficiency decrease as the temperature rises.
- ΔH* and ΔHad values indicate that the adsorption process is mainly of physical type.
- The corrosion rate is increased with rising temperature.

ACKNOWLEDGMENT

The authors wish to thank every to body who helped me directly or indirectly throughout this study.

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