

Polyethylene Glycol Compounds As Corrosion Inhibitors for Aluminium in 0.5M Hydrochloric Acid Solutions

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Abstract: Inhibition of corrosion of aluminium in 0.5 M HCl solution using polyethylene glycol compounds (PEG with different molecular weight, 600, 2000, 6000 g mol⁻¹) has been studied using weight loss measurements, galvanostatic, and potentiodynamic anodic polarization techniques. The results drawn from these techniques are comparable and exhibit small discrepancy. The percentage of inhibition efficiency was found to increase with increasing the concentration of inhibitors and the decrease of temperature. The inhibiting action of these compounds depends on the chemical structure, the concentration of the inhibitors, and the temperature. The efficiency of inhibition increases in the order: PEG600 < PEG2000 < PEG6000 in the studied concentration range. Inhibition is attributed to the adsorption of these compounds on the aluminium surface. The adsorption process fitting a Temkin adsorption isotherm. It was found that PEG compounds protect aluminium surface pitting attack in chloride containing solution by shifting the pitting corrosion potential to more noble direction.

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1. Introduction

Aluminium (Al) and its alloys are widely used in technology because of their low density and good resistance to corrosion. Hydrochloric acid solutions are used for pickling, chemical and electrochemical etching of Al. It is very important to add a corrosion inhibitor to decrease the corrosion of Al in such solutions. Various studies have been made to study the corrosion of Al and its inhibition by organic compounds in acid solutions [1-7]. The inhibition efficiency of such compounds is due to the adsorption on the metal surface. The adsorption process depends mainly on certain physico-chemical properties of the molecule such as functional groups, steric factors, aromaticity, electron density at the donor atoms, π -orbital's character of donating electrons [8,9] and also on the electronic structure of the molecules. The inhibition efficiency increases with increasing the number of aromatic rings [10,11]

The aim of the present work is to study the inhibiting action of polyethylene glycol compounds with different molecular weights on the corrosion of aluminium in 0.5 M hydrochloric acid using different techniques, e.g., weight loss, galvanostatic and potentiodynamic anodic polarization

2. Experimental

The working electrode employed in this work were made of aluminium (99.95% Koch Light Laboratories, Colnbrook Bucks, UK). For weight loss

measurements, corrosion inhibition tests were performed using coupons measuring 1 x 2 x 0.1 cm³ prepared from pure aluminium. The aluminium coupons were polished with emery papers, then degreased with acetone and washed with distilled water. The coupons were dried and kept in a desiccator. The weight loss (g cm⁻²) was determined at different immersion times at 30°C by weighing the cleaned samples before and after hanging the coupon into 50 cm³ of the corrosive solution. For electrochemical measurements, the investigated materials were cut as cylindrical rods, welded with Cu-wire for electrical connection and mounted into glass tubes of appropriate diameter using Araldite to offer an active flat disc shaped surface of (0.785 cm²) geometric area, to contact the test solution. Prior to each experiment, the surface pretreatment of the working electrode was performed by mechanical polishing (using a polishing machine model POLIMENT I, BUEHLER POLISHER) of the electrode surface with successive grades of emery papers down to 1200 grit up to a mirror finish. The electrode was then, rinsed with acetone, distilled water, and finally dipped in the electrolytic cell. A conventional electrochemical cell of capacity 100 cm³ was used containing three compartments for working, platinum spiral counter and reference electrodes. A Luggin-Haber capillary was also included in the design. The reference electrode was a normal calomel one used directly in contact with the working solution.

The experiments were carried out in aerated stagnant and containing various concentrations of the three polymers. All solutions were prepared from analytical grade chemical reagents using doubly distilled water and were used without further purification. The potentiodynamic current–potential curves were recorded by changing the electrode potential automatically from -2.0 to 2.0 V at a scan rate of 1 mV sec⁻¹. Both cathodic and anodic polarization curves were recorded galvanostatically using EG & G model 363 potentiostat/ galvanostat corrosion measurement system and digital millimeters (Fluke-73) were used for accurate measurements of potential and current density. Solutions were not decreased to make the conditions identical to weight loss measurements. All the experiments were carried out at 25 ± 1 °C by using ultra circulating thermostat.

The chemicals and solutions were provided by Sigma Aldrich, Germany. Hydrochloric acid (HCl), polyethylene glycol and sodium chloride were provided by El Gomhoria Co., Egypt. Used water was Deionized Double distilled water (DDI) with a resistivity of 18MΩcm. All purchased Chemicals were used without additional purification.

The inhibitors were polyethylene glycol (PEG) with different molecular weight 600, 2000, 6000 g mol⁻¹ for compound I, compound II and compound III, respectively.

3. Results and Discussion

3.1. Weight loss measurements

The corrosion behavior of (Al) in an aqueous environment is characterized by the extent to which it dissolves in the solution. The degree of dissolution, of course, dependent on the surface area of the metal exposed and the time of exposure; hence the amount of corrosion is given with respect to area and time. The resulting quantity, corrosion rate, is thus a fundamental measurement in corrosion science. Corrosion rates can be evaluated by measuring either the concentration of the dissolved metal in solution by chemical analysis or by measuring is directly related to the extent of corrosion and does not rely on any assumptions about reactions occurring during corrosion. The weight losses given by:

$$\Delta W = W_1 - W_2 \quad (1)$$

Where W_1 and W_2 are the weights of specimen before and after reaction, respectively. The inhibition or acceleration efficiency %I was computed from the equation:

$$\%I = \frac{\Delta W - \Delta W_i}{\Delta W} \times 100 \quad (2)$$

Where ΔW and ΔW_i are the weight losses per unit area in absence and presence of the additive, respectively.

The corrosion rate in mpy was calculated from the equation:

$$mpy = \frac{534W}{DAT} \quad (3)$$

Where

W = weight loss, in mg; D = density of specimen in g cm⁻³

A = area of specimen, in sq. inch.

T = exposure time, in hours.

Fig.1 represents the weight loss- time curve for pure aluminium in 0.5M HCl acid in absence and present of different concentration of compound III (PEG 6000) compound as an example. Similar curves were obtained for the other two compounds (not shown) As shown from these figures, by increasing the concentration of polymer compounds, the weight loss of aluminium samples are decreased. This mean that the presence of these polymer compounds retards the corrosion of aluminium in 0.5M HCl acid or in other words, these compounds act as inhibitors [12]. The linear variation of weight loss with time in uninhibited and inhibited 0.5M HCl indicates the absence of insoluble surface films during corrosion. In the absence of any surface films, the inhibitors are first adsorbed on to the metal surface and there after impede corrosion either by merely blocking the reaction sites (anodic and cathodic) or by altering the mechanism of the anodic and cathodic partial processes. The percentage of inhibition efficiency (%I.E) of polymer compounds were determined by using the equation.

$$\%IE = (1 - I_{edd} / I_{free}) \quad (4)$$

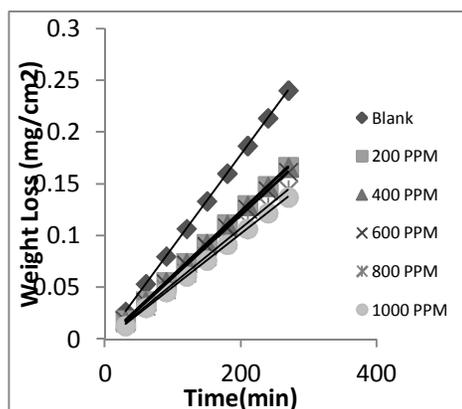


Fig. 1: Weight loss-time curves for the corrosion of aluminum in 0.5 M HCl solution in the absence and presence of different concentrations of compound (III) at 30°C

The calculated values of %I.E are given in Table 1. It is clear from this table, the order of the

inhibition efficiency of polymer compounds decreasing as following:



Table 1: Percentages of Inhibition of aluminum dissolution at 210 min. immersion in 0.5 M HCl in the presence of different concentration of different polymeric compounds at 30 °C

Concentration ppm	% Inhibition (I.E %)		
	I	II	III
200	25.7	28.9	36.9
400	33.6	40.6	44.6
600	41.9	45.5	52.4
800	53.8	55.9	60.8
1000	62.2	68.2	70.4

3.2. Effect of temperature and activation parameters

The effect of temperature on the rate of dissolution of Al in 0.5 M HCl solution containing 1000ppm of three compounds was tested by weight loss measurements over temperature range from 30-60° Similar figures were obtained to figure 1 (not shown).

The effect of increasing temperature on the inhibition efficiency are listed in Table 2. The increasing in the temperature has a reverse relationship with the percentage of inhibition this means that the adsorption of polymeric compounds on the metal surface is physically.

Table 2: Percentage of Inhibition efficiency of aluminum dissolution in 0.5 M HCl in the presence of 1000 ppm concentrations of the different polymer compounds at different temperatures and at 210 min. immersion.

Temperature, K	% inhibition (I.E %)		
	I	II	III
303	62.2	68.2	70.4
313	55.8	60.5	64.6
323	47.6	52.6	58.4
333	42.6	46.4	49.8

The results of table (2) show that the percentage of inhibition is decreased with increasing the temperature, this behavior can be explained on the basis that, the increase of the temperature leads to desorption of the adsorbed molecules of the inhibitors from the metal surface.

The apparent activation energy E_a^* , the enthalpy of activation ΔH^* and the entropy of activation ΔS^* for the corrosion of aluminum samples in 0.5M HCl solutions in the absence and presence of 1000 ppm of poly ethylene glycole compounds were calculated from Arrhenius- type equation:

$$\text{Rate} = A \exp (-E_a^*/RT) \quad (5)$$

and transition – state equation:

$$\text{Rate} = RT/Nh \exp (\Delta S^*/R) \exp (-\Delta H^*/RT) \quad (6)$$

where A is the frequency factor h is the plank's constant, N is Avogadro's number and R is the universal gas constant. A plot of log rate vs. 1/T (Fig.2) give straight lines with slope of $-E_a^*/2.303R$

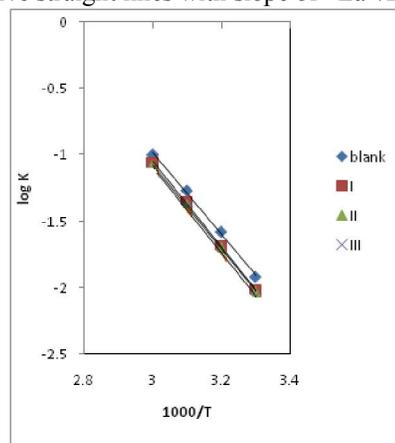


Fig. 2: Log corrosion rate-1/T curves for aluminum dissolution in 0.5 M HCl in absence and presence of 1000ppm of polymer compounds

Figures (3) represent plots of the log rate $\log r_{at}/T$ vs. 1/T are obtained straight lines with slope of $(-\Delta H^*/2.303R)$ and an intercept of $\log[(RT/Nh) - (\Delta S^*/2.303R)]$.

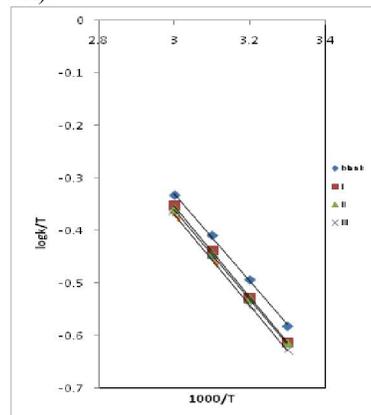


Fig.3: log (corrosion rate/T) -(1/T) curves for aluminum dissolution in 0.5 M HCl in absence and presence of 1000 ppm of polymer compounds

The calculated values of the apparent activation energy, E_a^* , activation entropies, ΔS^* and activation enthalpies, ΔH^* are given in table (3).

Table 3: Activation parameters of aluminum dissolution in 0.5 HCl solution in the absence and presence of 1000 ppm polymer compounds

Inhibitors	Activation parameters		
	$E_a^*, KJ mol^{-1}$	$\Delta H^*, KJ mol^{-1}$	$-\Delta S^*, J mol^{-1}$
Free acid	52.32	51.36	90.56
I	55.21	53.54	85.6
II	57.92	55.49	83.79
III	60.56	56.12	80.21

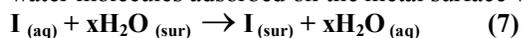
From the results of Table (3), it is clear that the presence of the tested compounds increase the activation energy values and consequently decreased the corrosion rate of the aluminium. These results indicate that these tested compounds act as inhibitors through increasing activation energy of aluminium dissolution by making a barrier to mass and charge transfer by their adsorption on aluminium surface. The positive signs of ΔH^* reflect the endothermic nature of the aluminium dissolution process. The values of ΔH^* are different for studied compounds which means that their structure affect the strength of its adsorption on the metal surface.

The negative values of ΔS^* in the absence and presence of the inhibitors implies that, the activated complex is the rate determining step and represents association rather than dissociation. It also reveals that an increase in the order takes place in going from reactants to the activated complex[13]. The order of the inhibition efficiency of polymeric compounds as gathered from the increase in E_a^* and ΔH^* values and decrease in ΔS^* values are:



3.3. Adsorption isotherm

Organic molecules like polymeric compounds molecules inhibit the corrosion process of (Al) in (HCl) solution by adsorption on metal surface. Theoretically, the adsorption process can be regarded as a single substitutional process in which an inhibitor molecule, I, in the aqueous phase substitutes an "x" number of water molecules adsorbed on the metal surface vis,



Where, x is known as the size ratio and simply equals the number of adsorbed water molecules replaced by a single inhibitor molecule. The adsorption depends on the structure of the inhibitor, the type of the metal and the nature of its surface, the nature of the corrosion medium and its pH value, the temperature and the electrochemical potential of the metal- solution interface. Also, the adsorption provides information about the interaction among the adsorbed molecules themselves as well as their interaction with the metal surface. Actually an adsorbed molecule may make the surface more difficult or less difficult for another molecule to become attached to a neighboring site and multilayer adsorption may take place. There may be more or less than one inhibitor molecule per surface site. Finally, various surface sites could have varying degrees of activation. For these reasons a number of mathematical adsorption isotherm expressions have been developed to take into consideration some of non ideal effects. Adsorption isotherm equations are generally of the form:

$$f(\theta, x) \exp(-a, \theta) = KC \quad (8)$$

Where $f(\theta, x)$ is the configurationally factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm a is a molecular interaction parameter depending upon molecule interactions in the adsorption layer and the degree of heterogeneity of the surface. All adsorption expressions include the equilibrium constant of the adsorption process, K, which is related to the standard free energy of adsorption (ΔG_{ads}^0) by:

$$K = 1/55.5 \exp(-\Delta G_{ads}^0 / RT) \quad (9)$$

Where R is the universal gas constant and T is the absolute temperature. A number of mathematical relationships for the adsorption isotherms have been suggested to fit the experiment data of the present work. The simplest equation is that due to Temkin and is given by the general equation:

$$\ln KC = a \theta \quad (10)$$

Where K is the equilibrium constant of the adsorption reaction, C is the inhibitor concentration in the bulk of the solution, a is the interaction parameter and θ is the surface coverage. The surface coverage, i.e., the fraction of the surface covered by the inhibitor molecules.

Plots of θ vs. $\log C$ (Temkin adsorption plots) for adsorption of polymeric compounds on the surface of aluminum in 0.5 M HCl acid at 30°C is shown in Fig. (4).

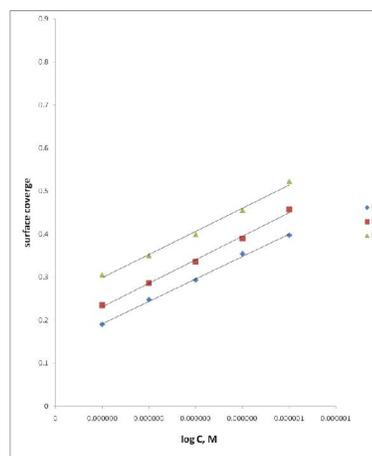


Fig. 4: Curve fitting of corrosion data for aluminium in 0.5 M HCl in presence of different concentration of polymer compounds to the Temkin isotherm at 30°C

The data gave straight lines indicating that Temkin's isotherm is valid for these systems. Temkin's isotherm is applied for ideal case of physical and chemical adsorption on a smooth surface with no interaction between the adsorbed molecules.

On the other hand, it is found that the kinetic-thermodynamic model of El Awady *et al.* [14]

$$\log \theta / (1 - \theta) = \log K' + y \log C \quad (11)$$

is valid to operate the present adsorption data. The equilibrium constant of adsorption $K = K' (1/y)$, where $1/y$ is the number of the surface active sites occupied by one polymeric compounds molecule and C is the bulk concentration of the inhibitor. The relation between $\log \theta / (1 - \theta)$ against $\log C$ is given in Fig (5).

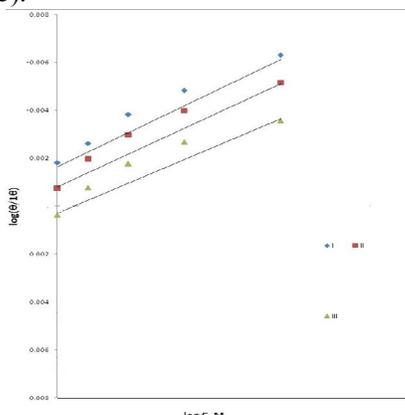


Fig. 5: Curve fitting of corrosion data for aluminum in 0.5 M HCl in presence of different concentration of polymer compounds to the kinetic model at 30°C

The calculated values of $1/y$, K' and ΔG_{ads}° . Are given in table (4).

Table 4: Inhibitor binding (K), free energy of binding (ΔG_{ads}°), number of active sites ($1/y$) and later interaction (a) for polymeric compounds at 30°C.

Inhibitors	Kinetic model			Temkin		
	$1/y$	$K \times 10^5$	$-\Delta G_{ads}^{\circ}$ KJ mol^{-1}	A	$K \times 10^6$	$-\Delta G_{ads}^{\circ}$ KJ mol^{-1}
I	0.745	24.799	43.050	4.05	31.366	47.786
II	0.849	29.978	43.151	4.24	37.725	48.251
III	0.972	53.874	43.568	4.36	55.315	48.977

Inspection of the data of these tables shows that the large values of ΔG_{ads}° . And its negative sign, indicate that the adsorption of polymeric compounds on the aluminum surface is proceeding spontaneously and is accompanied by a highly- efficient adsorption. It is worth noting that the value of $1/y$ is more than unity. This means that the given inhibitor molecules will occupy more than one active site. In general, the values of ΔG_{ads}° . Obtained from El- Awady *et al.*, model are comparable with those obtained from Temkin's isotherm.

From these results it may be generalized that the more efficient inhibitor has more negative ΔG_{ads}° . Value so that from the tabulated values of ΔG_{ads}° the order of inhibition efficiencies is as following:

PEG 6000 > PEG 2000 > PEG 600

3.4. Galvanostatic Polarization Technique.

Fig.6 represents the anodic and cathodic polarization curves of aluminum electrode in 0.5M HCl in absence and present of different concentration of compound III (PEG 6000) compound as an example. Similar curves were obtained for the other two compounds (not shown)

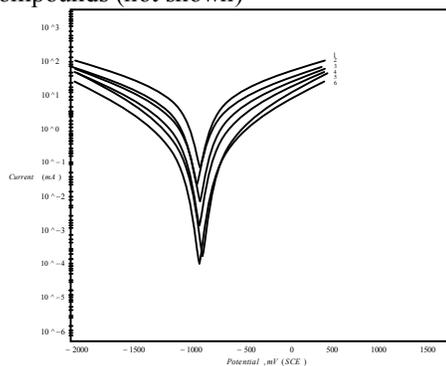


Fig. 6: Galvanostatic polarization curves of aluminum in 0.5M HCl containing different concentrations of compound III (PEG 6000) (1) 0.00 (2) 200 (3) 400 (4) 600 (5) 800 (6) 1000 ppm.

From this figure one can observe a presence, a transition region in which the potential increases (anodic polarization) or decreases (cathodic polarization) slowly with current density after this region there is a rapid linear build up of potential with current density (Tafel region).

Further inspection of the curves of Figures reveals that the presence of increasing concentration of polymer compounds cause a decrease in the rate of anodic dissolution reaction i.e. shifting the anodic current – potential curves in the anodic direction. This may be ascribed to a parallel adsorption of the organic molecules over the corroding surface[15].

From the cathodic polarization curves illustrated in Fig 6.it's clear that the increase of the additives concentration shifts the current-potential curves towards less cathodic potentials. Polymers compounds like other adsorption inhibitors are known to undergo specific adsorption i.e. they adsorb in the inner part of the double layer. In doing so the adsorbed species replace some of the H_3O^+ ion i.e. the additives block part of the surface and hence decrease the rate of hydrogen evolution reaction and consequently the rate of the overall corrosion reaction produced.

The values of corrosion current density (I_{corr}) was determined by the intersection of the extrapolated cathodic and anodic Tafel lines (linear part) with the stationary corrosion potential (E_{corr}).

The percentage inhibition efficiency (% I.E) imparted by the added inhibitor, which is defined as the percentage of the relative decrease in corrosion rate

brought about by the presence of a certain concentration of the inhibitor is given by:

$$\% \text{ I.E} = (1 - I_{\text{add}} / I_{\text{free}}) \times 100 \quad (12)$$

Where, I_{free} and I_{add} are the corrosion current densities in the absence and presence of the inhibitors, respectively.

Table (5): The effect of concentration of compound (I) on the free corrosion potential (E_{corr}), Corrosion current density (I_{corr}), Tafel slopes (β_a & β_c), inhibition efficiency (%I.E) and Degree of surface coverage (Θ) in presence of 0.5 HCl at 30° C.

Inhibitors	Concentration (ppm)	$-E_{\text{corr}}$, mV. (SCE)	I_{corr} , mAcm ⁻²	β_a , m V dec ⁻¹	β_c , m V dec ⁻¹	Θ	%I.E
(I)	0	799	155	217	89	---	---
	200	767	48.1	166	110	0.35	35.5
	400	758	46.0	168	112	0.38	38.2
	600	753	41.6	170	114	0.47	47.6
	800	724	38.7	172	116	0.54	54.3
	1000	936	45.6	212	118	0.70	70.9
(II)	0	799	155	217	89	---	---
	200	767	92.4	206	111	0.40	40.2
	400	758	86.2	207	113	0.44	44.7
	600	753	78.7	208	115	0.49	49.9
	800	724	66.8	211	117	0.52	52.6
	1000	936	40.5	219	119	0.74	74.9
(III)	0	799	155	217	89	---	---
	200	767	88.6	277	102	0.43	43.2
	400	758	80.4	280	103	0.48	48.6
	600	753	68.7	293	107	0.55	55.6
	800	724	58.2	295	110	0.62	62.9
	1000	936	35.3	298	112	0.77	77.0

An inspection of this table, it is clear that the corrosion potentials (E_{corr}) is shifted to more negative values and Tafel lines are shifted to more positive and negative potential for anodic and cathodic process, respectively, relative to the blank curve. This means that these compounds influence both anodic and cathodic process. However, the data suggested that these compounds act mainly as mixed type inhibitors. The values of anodic and cathodic Tafel slopes (β_a & β_c) are approximately constant which suggest the simple blocking of the available surface area of the metal by the inhibitor molecules. In other words, the adsorbed inhibitor molecule decreases the surface area available for the both metal dissolution and hydrogen evolution reactions without affecting the reaction mechanism [16]. The reaction between the metal covered with inhibitor molecule may take place by diffusion H^+ and Cl^- ions through the pores of the protective layer on the metal surface.

From these Table (5) and Fig (6) (5) it is clear that, the increase of additive concentrations decreases the corrosion current density (I_{corr}), and hence increase the inhibition efficiency of these compounds.

The values of inhibition efficiency of polymers compounds decrease in the following order:



3.5. Inhibition of Pitting Corrosion of aluminum

Fig.7 represents the of potentiodynamic anodic polarizations curves of aluminum electrode in 0.5M HCl+ 0.5M NaCl (as a pitting corrosion agent) in absence and present of different concentration of compound III (PEG 6000) at a scanning rate of

Tables (5) show the effect of different concentrations of polyethylene glycol compounds on the corrosion parameters such as: cathodic Tafel slop (β_c), anodic Tafel slop (β_a), corrosion potential (E_{corr}), corrosion current density (I_{corr}), percentage inhibition efficiency (%I.E) and surface coverage (θ).

1mVsec⁻¹ as an example of the additives compounds. Similar curves were obtained for the other two compounds (not shown).The potential was swept from negative potential toward anodic direction up to the pitting potential (E_{pitt}).The pitting potential was taken as the potential at which the current flowing, along the passive film increases suddenly to higher values, denoting the destruction of passive film and initiation of visible pits. It was found that the pitting potential of the aluminium electrode is shifted to more positive (noble) values with increasing the concentration of these additives. This indicates that increased resistance to pitting attack.

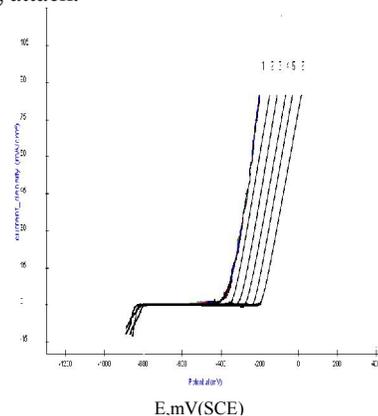


Fig. 7: Potentiodynamic anodic polarization curves of aluminum in 0.5M HCl solution + 0.5M NaCl containing different concentrations of compound (III) at a scan rate 1mVsec⁻¹. (1) 0.00 (2) 200 (3) 400 (4) 600 (5) 800 (6) 1000 ppm.

Fig. (8) represents the relationship between pitting potential and the logarithmic of the molar concentration of the added compounds. Straight lines were obtained and the following conclusion can be drawn:

- a. The increase of inhibitor concentration causes the shift of the pitting potential into more positive values in accordance with the following equation:

$$E_{\text{pitt}} = a_1 + b_1 \log C_{\text{inh}} \quad (13)$$

where, a_1 and b_1 are constants which depend on both the composition of additives and the nature of the electrode.

- b. Inhibition afforded by these compounds using the same different concentrations of the additives decreases in the following order:

PEG6000 > PEG2000 > PEG600

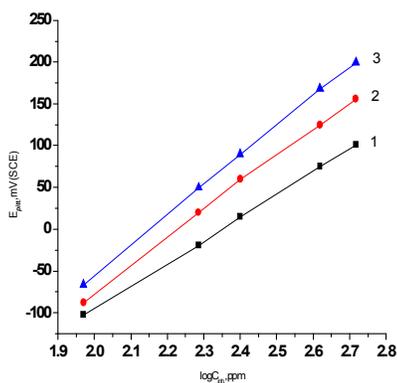


Fig. 8: The relationship between the pitting potential of aluminum and logarithm the concentration of polyethylene glycol compounds in presence 0.5 M HCL solution (1) compound I (2) compound II (3) compound III

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