INHIBITION EFFECT OF SOME POLYETHYLENE GLYCOLS (PEG) ON THE CORROSION OF ALUMINUM IN 1.0 M PHOSPHORIC ACID

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Abstract

The effect of some polyethylene glycols (PEG) as inhibitors on the corrosion of aluminum in 1.0 M H_3PO_4 has been studied using weight loss and polarization measurements in various concentrations of PEG and at different temperatures. The dissolution of aluminum in phosphoric acids increases by increasing temperatures and decreases by increasing the additive concentrations. The inhibition efficienciy values proceed according to the following order of the molecular weights of the used inhibitors PEG 4000 > PEG 2000 > PEG 1500 > PEG 400. For relatively higher molecular weights inhibitor (beginning from 1500) the type of adsorption taking place at the surface of aluminum was physical adsorption whereas for the molecular weight. = 400 had different behavior till 50ºC and then the inhibition efficiency decreasing at 60ºC indicating physical adsorptions. The lone pair of electrons of oxygen atom of hydroxyl groups play an important role in the adsorptions of additives on aluminum surface, which affected by polarization. The thermodynamic calculated values of activation and adsorption were calculated and discussed.

Introduction

Corrosion of aluminum and aluminum alloys has been the subject of numerous studies due to the importance of such materials in contemporary civilization and to their greatly industrial applications [1-3]. Many researches were devoted to study the corrosion of aluminum in different aqueous solutions [4-5]. It is very important to add corrosion inhibitors to decrease the corrosion rate of the dissolution of aluminum in such solutions[6]. The processes of adsorption of inhibitors are influenced by: the nature and surface charge of the metal, the chemical structure of organic inhibitors, the distribution of charges in the molecule and the type of electrolyte[7]. The chemisorptions are the principle type of interaction between organic inhibitors and the metal surface[8]. The adsorption of organic inhibitors mainly depends on some physicochemical properties of the molecule, related to its functional groups, to the possible steric effects and electronic density of donor atoms [9]. Recent studies have been concerned with the effect of oxygen-containing compounds such as polyethylene glycol with different molecular weights on the inhibition of aluminum corrosion[10]. The general formula of polyethylene glycol is given by "H(-OCH$_2$–CH$_2$-)$_n$OH ", for PEG 400, average value of n between 8.2 and 9.1, viscous, slightly

hygroscopic and liquid, for PEG 1500,average value of n between 29 and 36 , white, free flowing powder, for PEG 2000, average value of n between 42 and 48, white solid and for PEG 4000, average value of n between 68 and 84 and white flakes.

Experimental

The samples were made from commercial aluminum sheets having the following chemical composition: Al 99%, Fe 0.2%, Cu 0.2%, Si 0.2%,Ti 0.03% and Zn 0.08% (Riedel–De Haan–Germany). Phosphoric acid assay 88% Prolabo, Arabic laboratory equipment company. For weight loss measurements, aluminum specimens were polished and cleaned according to the methods described earlier [11-12], the corrosion of aluminum in 1.0 M H_3PO_4 was carried out by using sheets (1 x 1.5 x 0.01 cm), and suspended in 50 ml of the test solutions for a known time at a desired temperatures. All solutions were prepared from ordinary distilled water, thermo-stated to within $\pm$ 0.1ºC of the indicated temperatures. The used of polyethylene glycol (PEG) samples were prepared and delivered from EPRI[13]. The electrochemical measurements were carried out using EG & G (Prinston Applied Research) potentiostat / galvanostat Model 372 with scan rate of 1 mV/sec. from -1750 to 1000 mV. An electrolytic cell of Pyrex glass vessel capacity 250 ml consisted of aluminum electrode in the form of sheet as a working electrode. Pt. electrode as an auxiliary electrode and saturated calomel electrode (SCE) as a reference electrode were used. The organic compounds used as inhibitors were polyethylene glycols of different molecular weights (PEG 400 – PEG 1500 – PEG 2000 and PEG 4000).

Results And Discussions

1. *Weight- loss   measurements*.

Corrosion behavior of aluminum in 1.0 M H_3PO_4 has been studied intemperatures ranged from (20ºC – 60ºC). Results given in Fig. (1), concern the corrosion rate determined in the absence of inhibitor. The inhibition efficiency, %EI is defined as follows [14];

$$\% \ EI \ = \ [(W_{non \ inh,} \ -W_{inh}) \ / \ W_{non \ inh.}] \ x \ 100; \qquad (1)$$

where ; $W_{non \ inh}$ and $W_{inh,}$ are weight loss for the metal in the absence and presence of inhibitors respectively.

Fig. (2) shows the effect of addition of different concentrations of polyethylene glycols (PEG 400, PEG 1500, PEG 2000 and PEG 4000), on the dissolution of

aluminum in 1.0 M phosphoric acid solution at 30°C. The curves indicate that an increase in inhibitor concentration decreases the dissolution of aluminum. Its also noticed - from Fig. (3), which reveals the effect of temperatures on the dissolution of aluminum - that the temperature retards the inhibition effect. In general, the inhibition efficiency of these compounds increase with increasing molecular weight. This may be due to the increase in the number of ethylene oxide groups attached in molecule [15] .

The effect of temperatures on the inhibition efficiencies are shown in Fig. (4), which shows that PEG 400 has an abnormal behavior, where the temperature accelerates the inhibition effect till 50°C, then the adsorbed layer destroyed as a result of increasing the desorption process at 60°C, the data are listed in Table (1). To calculate the activation thermodynamic parameters of the corrosion reaction such as the activation energy E_a , the entropy of activation ΔS_a, free energy of activation ΔG_a and the enthalpy of activation ΔH_a, Arrhenius equation [16] was used;

$$K = W / t \qquad (2)$$

Where K is the specific rate constant and t is the immersion time

$$Log\ K = \log A - (E_a /2.303\ RT) \qquad (3)$$

Where, A is Arrhenius constant and R is the universal gas constant.

The values of activation thermodynamic functions were calculated from [17],

$$K = (kT /h)\ Exp\ [- \Delta G_a / RT\ ] \qquad (4)$$

$$\Delta H_a = E_a - RT \qquad (5)$$

$$\Delta S_a = [\Delta H_a - \Delta G_a\ ] / T \qquad (6)$$

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

From Langmuir adsorption isotherm [18] ;.

$$\log\ (\theta/1 - \theta) = \log C\beta - (\Delta G^o_{ads} /2.303RT), \qquad (7)$$

$$\theta = (W_{non\ inh,} - W_{inh}) / W_{non\ inh}$$

where; β is the adsorption equilibrium constant , C is the inhibitor concentration, and θ is the surface coverage of the metal surface by adsorbate

The values of enthalpy of adsorption can be calculated from the relation [16];

$$\log\ k = \log k_o - (\Delta H_{ads} /2.303\ RT) \qquad (8)$$

where; k is adsorption coefficient. and k_o is a constant.

The thermodynamic parameter data were summarized in Table (2) which shows that ΔH_a, ΔS_a of the dissolution reactions of aluminum in 1.0 M H_3PO_4 in presence of PEG 1500, PEG 2000, and PEG 4000 are higher as compared with those of the non-inhibited solutions, and the negative values of ΔH_{ads} mean that the adsorption reaction is an exothermic process [19] and the dissolution of aluminum is difficult in

presence of PEG additives. The values of ΔG_{ads} presented in Table (2), indicate that the inhibitors are physically adsorbed on the electrode surface [20]. Data of Table (2) obviously show that, for PEGs with high molecular weights (1500, 2000 and 4000 gm mol^{-1}), the inhibition efficiency decreases with increasing temperature, confirming physical adsorption. On the other hand, the inhibition efficiency of low molecular weight PEG (400 gm mol^{-1}), obviously enhanced with rise in temperature. These results may indicate that PEG is chemisorbed on the electrode surface. It is also, polymerization takes place on the electrode surface with rise in temperature and consequently, the inhibition efficiency increases. In addition, the values of ΔS_{ads} decrease with increase in temperature, this meaning that a stable ordered layer of the inhibitor is formed on the aluminum electrode surface [21].

2. *Polarization   Measurements*:

Anodic and cathodic Tafel polarization curves of the dissolution of aluminum in 1.0 M phosphoric acid solution was measured in the absence and presence of 0.01 M of (PEG) additives at temperatures ranged from 30°C to 60°C as shown in Fig. (5). The data clarified that the addition of PEG inhibitor compounds shifts the corrosion potential E_{corr} to more negative values, thus the cathodic sits are blocked to greater extent than the anodic sites by the inhibitor molecules except PEG 400 which shifts the corrosion potential to more positive value by increasing the temperatures. It means that this compound affects anodic reaction more than cathodic one. The electrochemical parameters ($i_{corr.}$, $E_{corr.}$, b_a b_c and %EI) associated with polarization measurements at different temperatures are listed in Table 3, where $i_{corr.}$, $E_{corr.}$, b_a , b_c and %EI are the corrosion current density, corrosion potential, anodic and cathodic Tafel slopes and inhibition efficiency, respectively. Since the corrosion rate is directly related to the corrosion current density, the inhibition efficiency (% EI) at different temperatures were calculated from the equations:

$$\theta = 1 - (i_{inh.} / i_{non\ inh.}) \qquad\qquad (9)$$
$$\% \ EI \ = \theta \ \times 100 \qquad\qquad (10)$$

Where, i_{inh} and $i_{non\ inh}$ are the corrosion current density in presence of inhibitor and in absence of inhibitor, respectively.

And the corrosion rate (mpy) is calculated from the equation [22],

$$Rate \ (mpy) = 0.1285 \ \times \ i_{corr} \ \times \ Eq.wt \ / \ d, \qquad\qquad (11)$$

where, d; is the density and i_{corr} , is the corrosion current density.

The activation and adsorption thermodynamic parameters are calculated by using equations 3, 4 and 5. From polarization measurements, the data are given in Table 4.

It is clear that (ΔH_{ads}) values have a negative signs which mean that an exothermic reaction takes place, except in case of PEG 400 which has a positive values, that indicated an endothermic reaction took place, these behaviors were identical to that obtained from weight loss measurements.

Conclusion

All examined PEG additive compounds act as good inhibitors for aluminum corrosion in 1.0 M phosphoric acid solutions at all temperatures studied. The data indicated that the inhibition efficiencies decrease as the temperatures increasing. However, for PEG 400, the inhibition efficiency increases with increasing temperature. At ambient temperature .the adsorption of such compounds is physical adsorption except for PEG 400 which undergoes chemical adsorption owing to the lowest number of functional groups of small molecular weight then at higher temperatures the adsorption would be physical. The lone pair of electrons of oxygen atoms of hydroxyl groups plays an important role in the adsorption processes of the additives on aluminum surface. The adsorption obeys the Langmuir adsorption isotherm. The data obtained from weight loss measurements agree well with those obtained from polarization measurements. The inhibition efficiencies of these inhibitors decrease in the following order: PEG 4000 > PEG 2000 > PEG 1500 > PEG 400.

Table (1) Values of corrosion rate and inhibition efficiency of 0.01M PEG additives at different temperatures.

Comp.	T (K)	$W_{noninh.}$ (mg/cm^2)	$W_{inh.}$ (mg/cm^2)	θ	EI %
PEG 400	303	14.00	11.73	0.162	16.214
	313	27.23	20.40	0.254	25.356
	323	55.33	30.73	0.445	44.460
	333	84.07	76.2 0	0.094	09.400
PEG 1500	303	14.00	07.47	0.466	46.642
	313	27.33	18.60	0.319	31.942
	323	55.33	39.70	0.282	28.248
	333	84.07	75.40	0.103	10.312
PEG 2000	303	14.00	04.87	0.652	65.214
	313	27.33	18.27	0.332	33.158
	323	55.33	34.47	0.377	37.701
	333	84.07	67.67	0.195	19.507
PEG 4000	303	14.00	08.13	0.419	71.427
	313	27.33	17.80	0.349	34.570
	323	55.33	28.53	0.484	48.436
	333	84.07	79.10	0.059	5.9117

Table (2): The activation and adsorption thermodynamic parameters for the dissolution of aluminum in 1.0 M phosphoric acid in the absence and presence of 0.01 M PEG inhibitors, from weight-loss measurements.

Add.	T (K)	Activation parameters				Adsorption parameters		
		ΔE_a kJ/mole	ΔG_a kJ/mole	ΔH_a kJ/mole	ΔS_a kJ/mole.K	ΔG_{ads} kJ/mole	ΔH_{ads} kJ/mole	$T\Delta S_{ads}$ kJ/mol
Free	303	40.354	75.816	37.835	-0.125			
	313	40.354	77.738	37.752	-0.127			
	323	40.354	78.311	37.668	-0.125			
	333	40.354	78.463	37.585	-0.122			
PEG 400	303	40.940	76.415	38.420	-0.125	-22.563	-31.232	-8.667
	313	40.940	77.077	38.337	-0.123	-24.772	-33.727	-8.954
	323	40.940	79.258	38.254	-0.126	-27.866	-37.107	-9.240
	333	40.940	79.832	38.171	-0.125	-23.058	-32.585	-9.526
PEG 1500	303	60.289	76.963	57.770	-0.063	-107.048	-114.303	-7.254
	313	60.289	77.346	57.687	-0.062	-108.963	-116.457	-7.493
	323	60.286	78.058	57.604	-0.063	-111.972	-119.705	-7.733
	333	60.289	78.799	57.520	-0.063	-112.030	-120.003	-7.972
PEG 2000	303	61.729	77.485	59.209	-0.060	-102.978	-110.024	-7.046
	313	61.729	77.646	59.126	-0.059	-102.915	-110.194	-7.279
	323	61.729	78.367	59.043	-0.059	-106.738	-114.250	-7.511
	333	61.729	79.224	58.960	-0.063	-107.509	-115.253	-7.744
PEG 4000	303	64.083	76.883	61.564	-0.050	-71.931	-83.728	-8.667
	313	64.083	77.603	61.481	-0.051	-73.526	-82.481	-8.953
	323	64.083	79.082	61.397	-0.054	-77.386	-86.626	-9.239
	333	64.083	77.978	61.314	-0.050	-72.292	-81.818	-9.525

Table (3) Electrochemical parameters for aluminum in 1.0 M H₃PO₄ at different temperatures in presence of 0.01M of different PEG additives, from polarization measurements

Inhibitor	T,K	-E $_{corr}$ (mV)	I $_{corr}$ (mA/Cm^2)	b_a (mV/dec)	$-b_c$ (mV/dec)	EI.%
Free	303	950	3.01	700.6	349.9	
	313	970	3.4	1830.9	345.4	
	323	985	3.98	1795.0	335.8	
	333	1000	4.17	1358.0	306.7	
PEG 400	303	890	1.99	1573.3	296.5	33.9
	313	885	1.86	542.6	322.2	45.3
	323	870	1.55	434.5	269.7	61.1
	333	790	0.79	368.5	253.1	81.1
PEG 1500	303	740	0.89	739.8	374.4	70.4
	313	850	1.20	208.1	261.6	64.7
	323	840	1.55	320.5	130.0	59.8
	333	870	1.78	244.3	228.1	57.3
PEG 2000	303	915	0.39	338.7	208.4	87.0
	313	965	1.09	574.2	174.7	68.0
	323	930	1.55	224.1	195.1	61.1
	333	940	2.39	500.9	161.3	42.7
PEG 4000	303	785	0.25	142.2	160.7	91.7
	313	830	0.35	128.3	135.5	89.7
	323	880	1.41	277.1	178.4	64.6
	333	855	1.55	427.4	277.1	62.8

Table (4): The activation and adsorption thermodynamic parameters, calculated from polarization measurements.

| Add.	T (K)	Activation parameters				Adsorption parameters		
		ΔE_a kJ/mol	ΔG_a kJ/mol	ΔH_a kJ/mol	ΔS_a kJ/mol.K	ΔG_{ads} kJ/mol	ΔH_{ads} kJ/mol	$T\Delta S_{ads}$ kJ/mol
PEG 400	303	17.380	83.602	14.861	0.0068	57.958	58.115	0.1566
	313	17.867	86.358	15.265	0.0078	58.624	58.785	0.1618
	323	17.340	88.104	14.655	0.0056	58.781	58.948	0.1669
	333	19.263	92.303	16.495	0.0109	57.820	57.992	0.1721
PEG 1500	303	51.734	85.797	49.215	0.1201	-16.048	-16060.318	-11.6030
	313	49.209	84.475	46.607	0.1079	-15.900	-15912.276	-11.9860
	323	50.294	86.771	47.609	0.1076	-15.847	-15860.016	-12.3689
	333	51.444	89.134	48.675	0.1076	-16.052	-16065.612	-12.7591
PEG 2000	303	24.888	82.790	22.369	0.0315	-57.467	-57461.800	5.8015
	313	25.462	85.359	22.860	0.0320	-56.378	-56372.413	5.9930
	323	24.622	86.517	21.936	0.0282	-57.367	-57361.638	6.1844
	333	25.121	89.017	22.352	0.0285	-57.079	-57072.877	6.3759
EG 4000	303	11.655	81.937	9.136	-0.0120	-59.194	-59211.639	-16.8244
	313	11.604	84.291	9.002	-0.0121	-60.529	-60546.511	-17.3797
	323	11.486	86.580	8.801	-0.0124	-58.265	-58283.409	-17.9349
	333	11.685	89.187	8.916	-0.0117	-59.853	-59872.245	-18.49026

Figures

wt-loss (mg/cm^2)
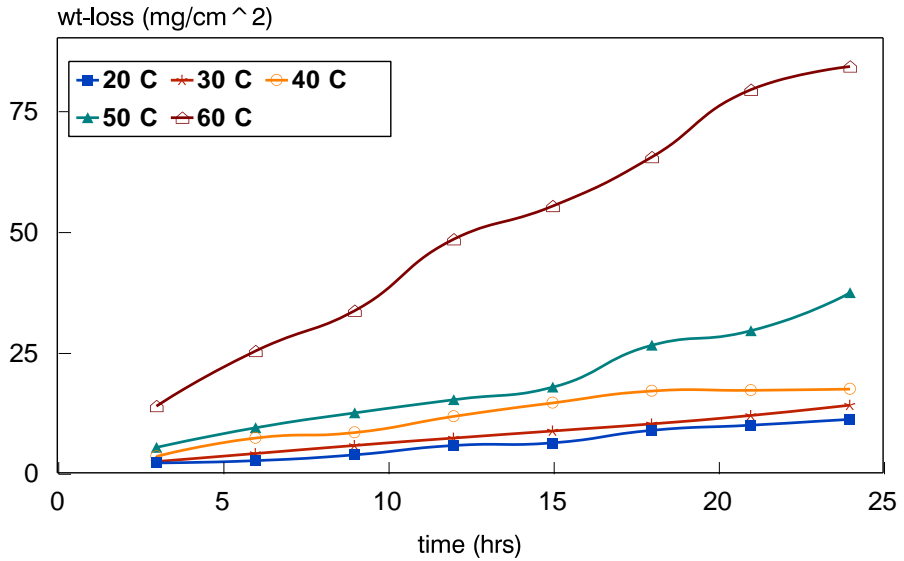
Fig. 1: The effect of time on the dissolution of aluminum in 0.1 M H$_3$PO$_4$
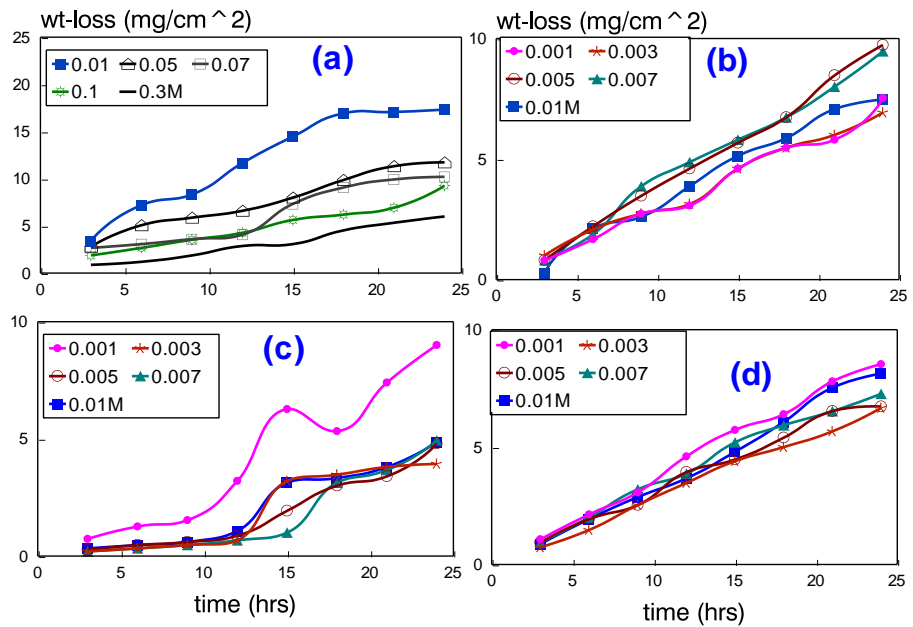at different temperatures.

Fig. 2: The effect of concentrations of PEG additives (a = 400, b = 1500, c = 2000, and d = 4000) on the corrosion of aluminum in 0.1 M H$_3$PO$_4$ at 30 ºC.
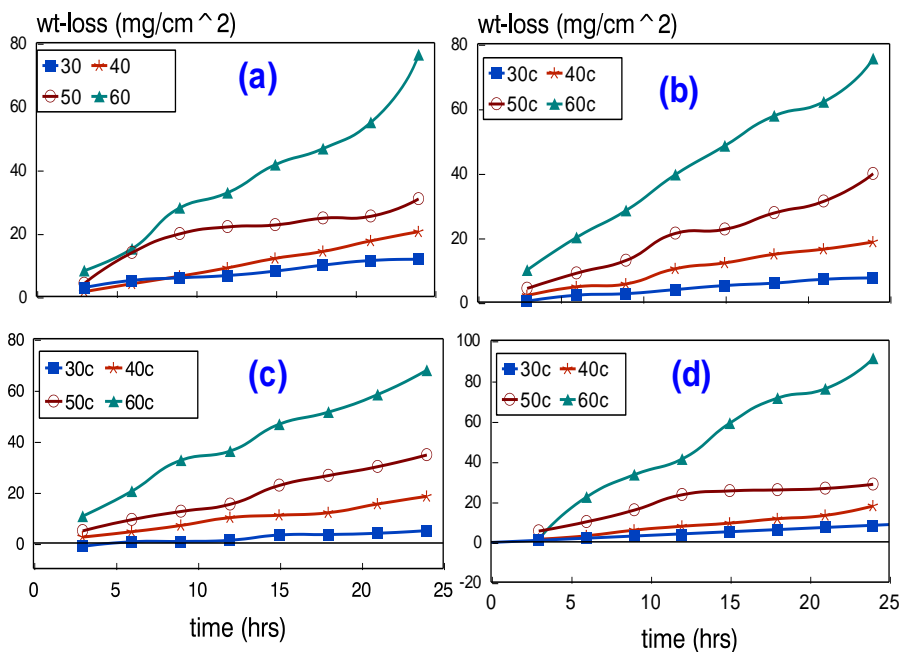
wt-loss (mg/cm^2)

wt-loss (mg/cm^2)

Fig. 3: The effect of temperatures on the dissolution of aluminum in 1.0 M H₃PO₄ in presence of 0.01 M PEG additives (a = 400, b = 1500, c = 2000, and d = 4000)
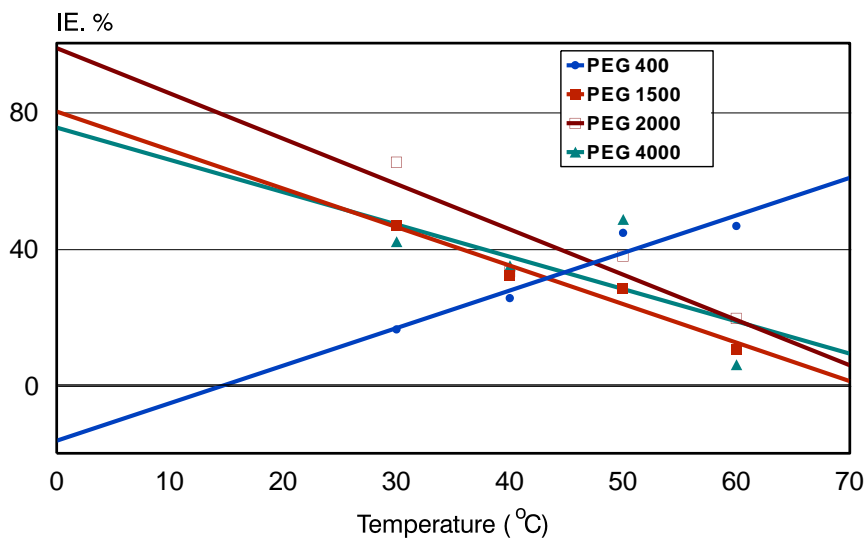
IE. %

Fig. 4: The effect of temperatures on the inhibition efficiency of PEG additives.
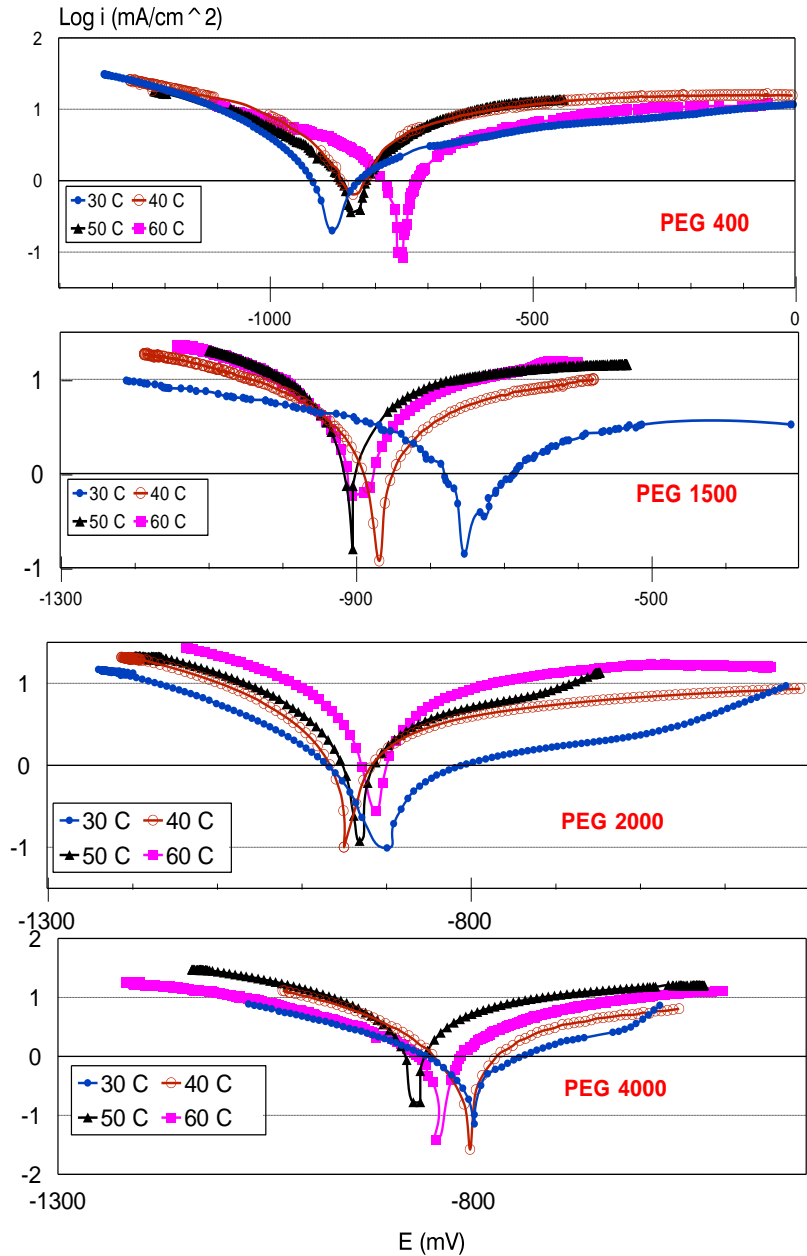
Fig. 5: Polarization curves measured for Al in 1.0 M H₃PO₄ in presence of PEG additives at different temperatures.

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