

Corrosion Inhibition of Aluminium with A Series of Aniline Monomeric Surfactant and Their Analogues Polymers in 0.5 M HCl Solution
Part I: 3-(6- Sodiamsulfonate hexayloxy) Aniline Monomeric Surfactant (MC₆) and Its Analogues Polymer

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THE INHIBITION effect of 3-(6- sodiamsulfonate hexayloxy) aniline monomeric surfactant (MC₆) and the analogues polymer poly 3-(hexayloxy sulphonic acid) aniline (PC₆) on the corrosion of aluminium in 0.5 M HCl solution was investigated with weight loss and potentiodynamic polarization techniques. The results show that the inhibition occurred through the adsorption of inhibitor molecules on the metal surface. The inhibition efficiency was found to increase with increasing of inhibitor concentration and decrease with increasing temperature. It was found that these inhibitors acted as mixed-type inhibitors with anodic predominance. The adsorption of these compounds on the metal surface obeyed the Langmuir and Frumkin adsorption isotherms. Thermodynamic functions for both the dissolution and adsorption processes were determined. The obtained results from weight loss and potentiodynamic polarization techniques are in good agreement.

Keywords: Activation energy, Adsorption, Conducting polymers, Electro-chemistry and Surfactants .

Aluminium has a remarkable economic and industrial importance owing to its low cost, light weight, high thermal and electrical conductivity. The most important feature of aluminium is its corrosion resistance due to the formation of a protective film on its surface upon its exposure to atmosphere or water⁽¹⁾. Several authors⁽²⁻⁴⁾ have studied the corrosion of aluminium and its inhibition by organic inhibitors in acid solutions. Various surfactants as well as 1, 1-(laurly amido) propyl ammonium chloride are being studied as a corrosion inhibitor for pure aluminium in acid media⁽⁵⁻⁶⁾. Many of organic compounds as electroactive-conducting polymers⁽⁷⁻¹⁵⁾, carboxylic organic acids^(16,17), fatty acids⁽¹⁸⁾ dicyandiamide and some of its related compounds⁽¹⁹⁾, triazole and thiazole derivatives^(20,21), were also found to inhibit the corrosion of aluminium.

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The inhibition of most of these compounds occurs via their adsorption on the metal surfaces which can markedly change the corrosion – resisting property of the metal ^(22, 23) and thus the study of the relations between the adsorption and corrosion inhibition is of a great importance.

Abd El-Rehim *et al.*⁽²⁴⁾ studied the effect of sodium dodecyl benzene sulphonate on the corrosion of aluminium and its alloy in 1 M HCl. The data show that the addition of this surfactant inhibits the hydrochloric acid corrosion of the aluminium samples and the inhibition occurs through adsorption of the surfactant on the metal surface and fits Frumkin adsorption isotherm.

The objective of this study is to investigate the corrosion inhibition performance of 3-(6-sodiumsulfonate hexayloxy) aniline (MC₆) and its analogues polymer (PC₆) as mixed-type inhibitors in 0.5M HCl solution. This performance will be investigated via weight loss measurements and potentiodynamic polarization techniques. In addition, this work will extend to compare the experimental data obtained from weight loss and potentiodynamic polarization technique with several adsorption isotherms at different temperatures in order to determine the thermodynamic functions for the adsorption process and to get more information about the mode of adsorption of the inhibitors on the surface of aluminium.

Experimental

Materials

3-Aminophenol provided by Aldrich Chemical Co. Sodium sulfite used in the synthetic process was obtained from Merck Chemical Co., (Germany). Concentrated hydrochloric acid was chemically pure grade products provided by Prolabo-Chemical Co., (U.K.). Double distilled water was used as a medium for the polymerization reactions. Potassium persulfate, 3-aminophenol and 1,6-dibromohexane were obtained from Aldrich Chemical Co., England.

Weight loss measurements

Aluminium metal was provided by the Egyptian Aluminium Company, Nag-Hammady, Egypt with the following chemical composition: 99.57 % Al, 0.31 % Fe, 0.07 % Si, 0.015 % Ti, 0.0016 % Zn, 0.0003 % Cr, 0.0019 % Mg, 0.0021 % Mn and 0.0007 % Cu. The dimensions of the tested samples were 2 x 2 x 0.1(cm). The samples were polished successively with fine grade emery papers, cleaned with acetone, washed with doubly distilled water and finally dried, weighed and then introduced into test solution.

Potentiodynamic polarization measurements

The working electrode was made from Al rod that has the same composition as mentioned above. The rod was axially embedded in araldite holder to offer an active flat disc shaped surface of an area of 0.785 cm². Before each experiment, the working electrode was polished successively with fine emery paper. The polished metal surface was rinsed with acetone and distilled water before dipping

it into the electrolytic cell. A platinum wire was used as the counter electrode and a saturated calomel electrode as a reference electrode to which all potentials are referred.

The electrochemical experiments were performed with Wenking PGS95, Potentiostat /Galvanostat connected to a computer. The current potential curves (I-E) were recorded with computer software (ECT). The experiments were carried out by changing the electrode potential automatically from the starting potential towards more positive values at the required scan rate till the end of the experiments.

Synthesis of monomeric 3-(6- sodiumsulfonate hexayloxy) aniline(MC₆)

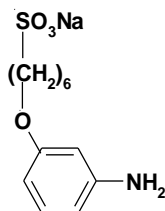
3-(6- Bromohexayloxy) aniline monomeric surfactant was prepared by an equimolar reaction, between 3 -aminophenol with 1-(6-dibromohexane), in the presence of sodium ethoxide. The product 3-(6-bromohexayloxy) aniline was reacted with sodium sulfite to produce MC₆ as mentioned by Sayyah *et al.*⁽²⁵⁾.

Synthesis of polymeric 3-(hexayloxy sulphonic acid) aniline (PC₆)

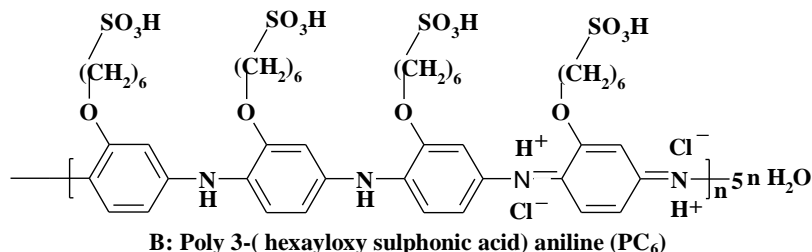
Poly 3-(hexayloxy sulphonic acid) aniline was synthesized by dissolving 0.1M of 3-(6- sodiumsulfonate hexayloxy) aniline in 25 ml of 2.0M HCl solution into a well stoppered conical flask 250 ml capacity, followed by the addition of 0.3M potassium persulfate (25 ml) to the reaction mixture under nitrogen atmosphere. The order of addition of substances was kept constant in the performed experiment. The stoppered conical flask was then placed in an automatically controlled thermostat at 25°C. The flask was shaken (50 shakings/10 s/15 min) for one hour with an automatic shaker, left for 72 hr at room temperature to continue the reaction and then filtrated with a Buchner funnel. The solid was washed with the distilled water and finally dried in vacuum at room temperature until a constant weight was reached.

Elemental and spectroscopic analysis

The elemental analysis of the prepared monomeric surfactant (MC₆) and its analogues polymer(PC₆) was carried out in the Microanalytical Laboratory at Cairo University with oxygen flask combustion and a dosimat E415 titrator (Switzerland). The data are summarized in Table 1, which show that there was a good agreement between the calculated structure and suggested structure present in Scheme 1. The number of water molecules in the polymer unit was calculated as mentioned by Sayyah. *et al.*⁽²⁶⁾.



A: 3-(6-Sodiumsulfonate hexayloxy) aniline (MC₆)



Scheme 1. Structure of monomeric surfactant (A) and its analogues polymer(B).

TABLE 1. Elemental analysis of the prepared monomeric surfactant (MC₆) and its polymer(PC₆).

Name	C %		H %		Cl %		S %		N %		N a %	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
MC ₆	48.80	48.12	6.14	5.99	-	-	10.85	10.65	4.74	4.58	7.78	7.63
PC ₆	46.26	46.92	6.26	6.54	5.70	5.75	10.28	10.36	4.49	4.53	-	-

The infrared (IR) spectroscopic analysis of the prepared monomeric and polymeric surfactants was carried out in the Micro analytical Laboratory at Cairo University with a Jasco FTIR-430 Spectrophotometer and potassium bromide disc techniques. The IR absorption bands and their assignments⁽²⁷⁾ of MC₆ and PC₆ are summarized in Table 2. The medium absorption band appearing at 409 cm⁻¹ which could be attributed to bending deformation of N-H group attached to the benzene ring in case of monomer, appearing at 500 cm⁻¹ with slight shift in case of polymer. The strong absorption band appearing at 626 cm⁻¹ which could be attributed to out-of-plane deformation of CH for 1,3-disubstituted benzene ring in case of monomer but disappears in case of polymer. The medium absorption band appearing at 755 cm⁻¹ in case of monomer due to the rocking deformation of methylene group in case of monomer, appears also with slight shift at 750 cm⁻¹ in case of polymer. The sharp absorption band appearing at 972 cm⁻¹ which could be attributed to symmetric stretching vibration of S-O or C-N group in case of monomer appears at 917 cm⁻¹ as a medium band in case of polymer. A series of absorption bands appearing in the region from 1000 to 1200 cm⁻¹ could be attributed to symmetric stretching vibration for C-O group in case of both monomer and its analogues polymer. The sharp absorption band appearing at 1408 cm⁻¹ which could be attributed to scissoring deformation of CH in methylene group in case of monomer, appears at 1457 cm⁻¹ in case of polymer. The medium absorption band appearing at 1545 cm⁻¹ which could be due to symmetric stretching vibration of C=C in quinoide structure in benzene ring, disappears in case of monomer. The broad absorption band appearing at 1624 cm⁻¹ which could be attributed to symmetric stretching vibration of C=C in case of monomer, appears as splitted band at

1616 and 1639 cm^{-1} in case of polymer. The shoulder absorption band appearing at 2930 cm^{-1} may be due to asymmetric stretching vibration for CH group in aliphatic chain in case of monomer, appears as a medium absorption band at 2928 cm^{-1} in case of polymer. The broad absorption band appearing at 3163 cm^{-1} in case of monomer for the stretching vibration of hydrogen bonded OH group in sulphonic group, appears as a medium absorption band at 3235 cm^{-1} in case of polymer. Other absorption bands and their assignments are summarized in Table 2.

TABLE 2. Infrared absorption bands and their assignments in case of monomeric surfactant and its polymer.

Wave number (cm^{-1})		Assignments ⁽²⁶⁾
MC ₆	PC ₆	
409 ^m	500 ^m	Bending deformation of NH in primary aromatic amines
626 ^s	---	Out-of-plane bending deformation of CH in 1,3-disubstituted benzene ring.
755 ^m	750 ^m	In-plane rocking vibration for CH in aliphatic chain
---	816 ^s	Out-of-plane bending deformation of CH in 1,3,4-trisubstituted benzene ring.
972 ^s	917 ^m	Symmetric stretching vibration for S-O or C-N group
1056 ^m	-	Symmetric stretching vibration for C-O group
1131 ^m	1136 ^m	
-	1197 ^m	
1328 ^w	1321 ^w	Symmetric stretching vibration for S=O group
1408 ^s	1457 ^w	Scissoring deformation for CH in methylene group
---	1545 ^m	Stretching vibration for quinoide structure in benzene ring
1624 ^b	1616 ² 1639 ^m	Stretching vibration for C=C in benzene ring
2853 ^{sh}	2845 ^w	Symmetric stretching vibration for CH group in aliphatic chain
2930 ^{sh}	2924 ^m	Asymmetric stretching vibration for CH group in aliphatic chain
3041 ^{sh}	3040 ^{sh}	symmetric stretching vibration for CH group in benzene ring
3163 ^b	3235 ^m	Stretching vibration for OH group in SO ₃ H group strongly hydrogen bond
3414 ^m	---	Symmetric stretching vibration for NH in aromatic amine
3446 ^{sh}	3479 ^m	Asymmetric stretching vibration for NH in aromatic amine

s= sharp m= medium w=weak sh= shoulder b = broad

Critical micelle concentration and contact angle

Critical micelle concentration (CMC) and contact angle were measured by using K100 Tensiometer (Kruss Type) for the hydrochloric form of synthesized monomeric and polymeric surfactants using different concentrations.

Results and Discussion*Weight loss measurements*

Figure 1 represents the straight line relation of the weight loss (in mg.cm^{-2}) as a function of the immersion time for aluminium in 0.5 M HCl solution in the absence and presence of different concentrations of 3-(6- sodiumsulfonate hexayloxy) aniline (MC_6) monomeric surfactant and its polymer (PC_6) at 30°C . The slope of each line ($\text{mg.cm}^{-2} \text{min}^{-1}$) represents the corrosion rate of aluminium at the specified conditions. From these data, the weight loss and hence rate of corrosion of aluminium enhances with the immersion time. On one hand, the dissolution of aluminium in HCl solution is slow and increases with the immersion time as indicated by increasing the weight loss by time, this may be due to the presence of a pre-immersion hydrate Al_2O_3 film on the metal surface⁽²⁸⁾. On the other hand, the addition of (MC_6) monomeric surfactant and its polymer (PC_6) retards the rate of dissolution and inhibits the acid corrosion of aluminium. The inhibition efficiency values (P%) at different inhibitor concentrations and temperatures were calculated from the following equation (1):

$$P \% = 100 \times \left(1 - \frac{W}{W_0} \right) \quad (1)$$

where W_0 and W are the weight losses per unit of time in the absence and presence of the inhibitors, respectively. The data are summarized in Table 3. As shown from Table 3, the inhibition efficiency of PC_6 was higher than that of MC_6 . The inhibition efficiency increased with increasing concentration of the two surfactants and reached a maximum value at a critical concentration ($8.47 \times 10^{-5} \text{ mol/L}$ in case of MC_6 and $4.11 \times 10^{-6} \text{ mol/L}$ in case of PC_6). Beyond this critical concentration, the efficiency tended to achieve steady state values. It was observed that, the maximum efficiency was obtained at concentration lower than the respective critical micelle concentration ($5 \times 10^{-4} \text{ mol/L}$ for MC_6 and $2.3 \times 10^{-4} \text{ mol/L}$ for PC_6). This means that, the adsorption of these surfactants on Al surface reached equilibrium before the formation of micelles (The aggregation of these surfactant long chains into fairly large charged units).

The contact angle is the angle formed when a liquid droplet is placed on the solid surface and its values vary from 0° (perfect wetting) to 180° (complete non-wetting). The values of the contact angle for MC_6 and PC_6 at 30°C are given in Table 3. The data clearly show that, the inhibition efficiency of these two inhibitors increased with the decrease in their contact angles. Moreover, it was observed that the contact angles for PC_6 were lower than that for MC_6 in all of the investigated concentration. This confirmed that PC_6 was more effective than MC_6 in inhibiting the acid corrosion of Al.

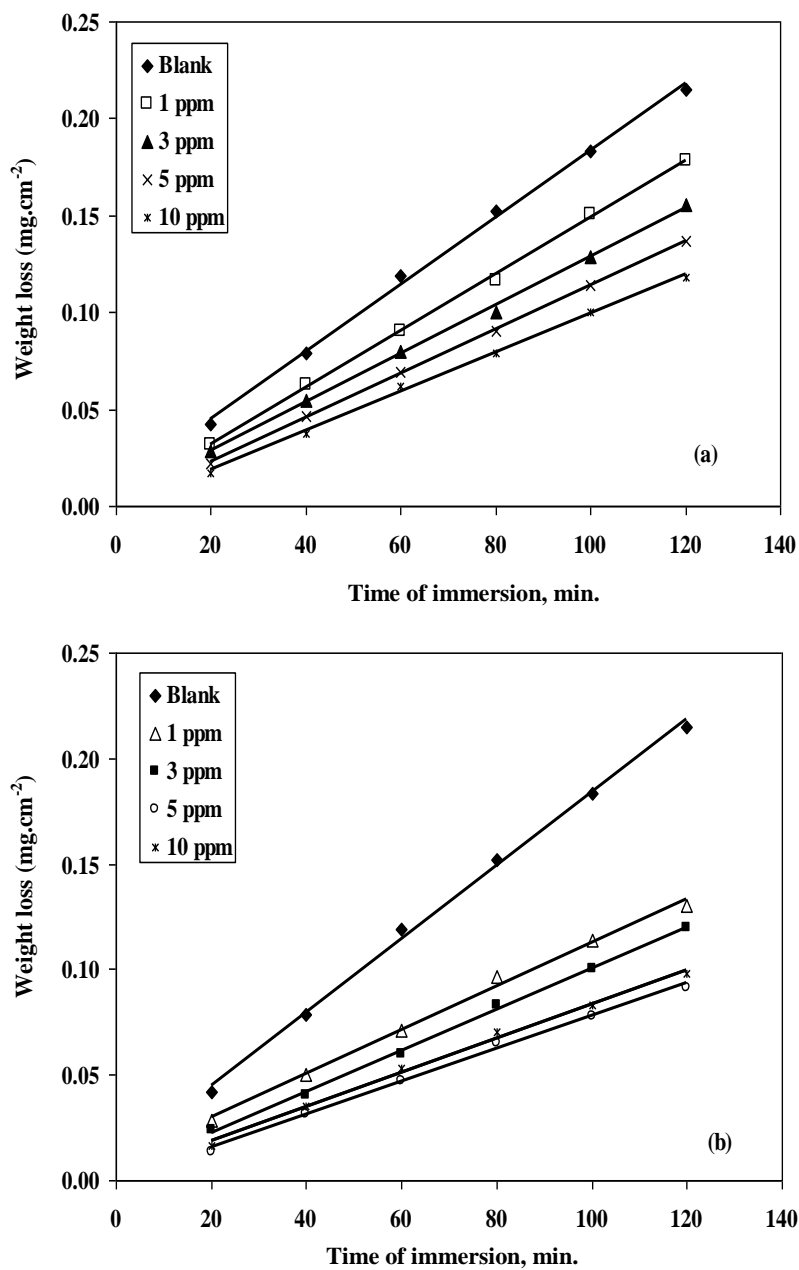


Fig.1. Weight loss vs. immersion time for aluminium in 0.5 M HCl solution in the absence and presence of different concentrations of monomeric surfactant MC₆ (a) and its polymer PC₆ (b) at 30°C.

TABLE 3. Values of the inhibition efficiency and contact angle values of aluminum in 0.5 M HCl solution containing various concentrations of monomeric surfactant (MC₆) and its polymer (PC₆) at 30°C.

Concentration (ppm)	P%				Contact angle	
	Weight loss technique		Polarization technique		MC ₆	PC ₆
	MC ₆	PC ₆	MC ₆	PC ₆		
1	20.41	30.40	18.71	25.80	98.64	91.46
3	24.53	44.70	25.72	41.97	93.25	69.8
5	27.30	56.10	28.98	56.49	73.44	0.00
10	31.14	49.70	32.26	49.82	68.63	12.10

Figure 2 shows the influence of the temperature on weight loss for Al in 0.5 M HCl in the absence and presence of 10 ppm of MC₆ and PC₆. The data show that the weight loss and the corrosion rate of the Al sample increase with increasing temperature and the addition of both inhibitor surfactants retarded the rate of dissolution in all ranges of the investigated temperatures. This may be due to the decrease in the strength of adsorption process with increasing temperature; this suggested that physical adsorption may have been the type of adsorption of the inhibitor on Al surface. The corrosion rate (in mg.cm⁻². min⁻¹) for each concentration of MC₆ and PC₆ (from 1 ppm to 10 ppm) was calculated at different temperatures and the logarithm of the corrosion rate was plotted against the reciprocal of the absolute temperature (1/T) for each concentration according to Arrhenius equation^(24, 29).

$$\text{Logarithm of the corrosion rate} = \frac{-E_a}{2.303 RT} + A \quad (2)$$

where E_a is the apparent effective activation energy, R is the universal gas constant and A is the Arrhenius pre-exponential factor. The corrosion rate for each concentration from 1 to 10 ppm of the monomeric and its polymeric surfactant was calculated at different temperatures and the logarithm of the corrosion rate was plotted against 1/T for each concentration and the value of E_a was calculated and tabulated in Table 4. An alternative formula of the Arrhenius equation is the transition state equation^(24, 29).

$$\text{Rate} = \frac{RT}{Nh} \exp \frac{\Delta S^\circ}{R} \exp \left(-\frac{\Delta H^\circ}{RT} \right) \quad (3)$$

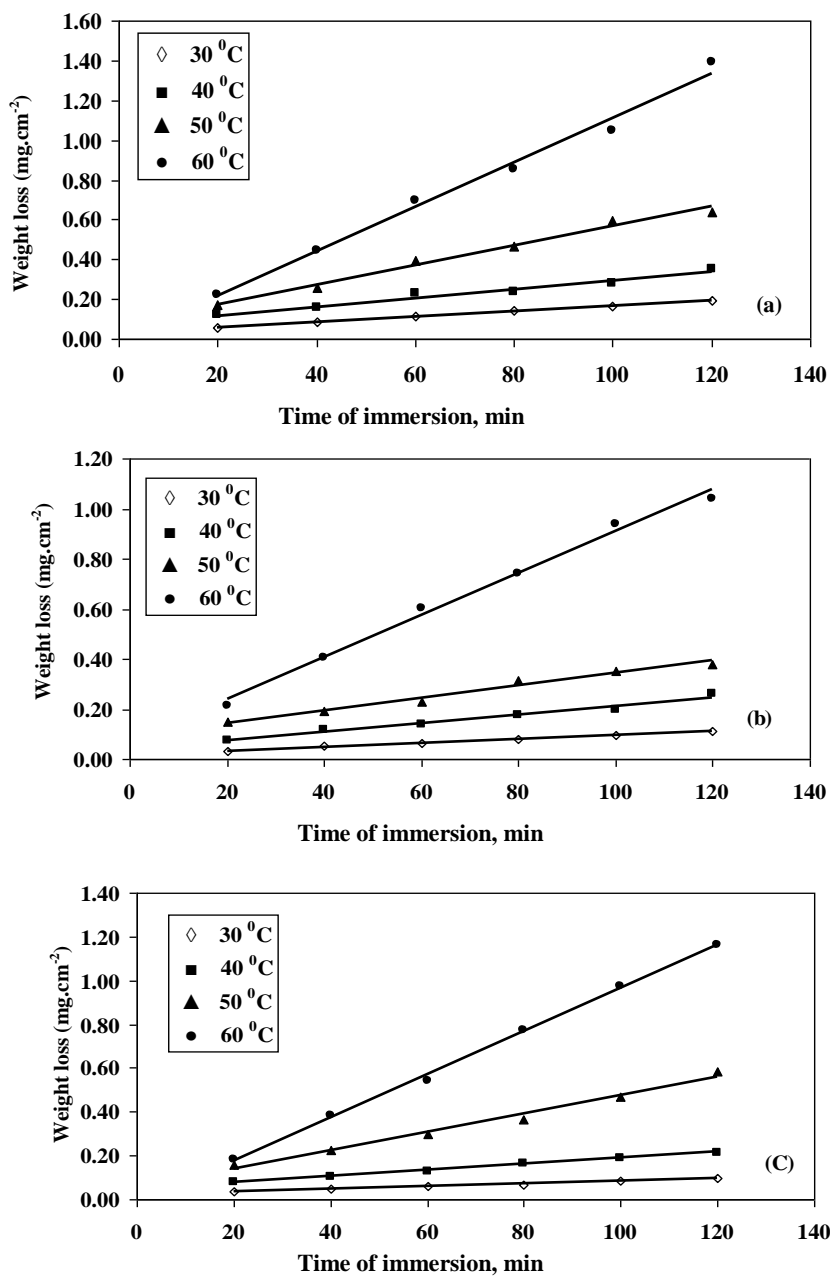


Fig. 2. Weight loss vs. immersion time for aluminium in 0.5 M HCl solution in the absence (a) and presence of 10 ppm of monomeric surfactant MC₆ (b) and its polymer PC₆ (c) at different temperatures.

where h is the Planck's constant, N is the Avogadro's number, ΔS^0 is the entropy of the activation, and ΔH^0 is the enthalpy of activation. The plot of $\log(\text{Rate}/T)$ vs. $1/T$ gives a straight line with a slope of $(-\Delta H^0/2.303R)$, from which the value of ΔH^0 was calculated and listed in Table 4. The data in Table 4 reveal that the addition of both surfactant inhibitors enhanced the values of both E_a and ΔH^0 . The enhancement may have been due to the adsorption of surfactant inhibitors on the Al surface and increased the energy barrier of the corrosion reaction as the concentrations of the inhibitors increased. This suggests that the process was activation-controlled. The activation energy value of 78.1 kJmol^{-1} for the HCl inhibitor systems suggested the fact that the inhibitors were physically adsorbed on the Al surface which was in agreement with the same earlier reports⁽³⁰⁻³³⁾.

TABLE 4. Effect of monomeric surfactant (MC₆) and its polymer (PC₆) concentrations on the thermodynamics dissolution process of Al in 0.5 M HCl solution (obtained from weight loss and polarization techniques).

Conc. ppm	E_a kJmol ⁻¹				ΔH^0 kJmol ⁻¹			
	Weight loss technique		Polarization technique		Weight loss technique		Polarization technique	
	MC ₆	PC ₆	MC ₆	PC ₆	MC ₆	PC ₆	MC ₆	PC ₆
Blank	57.4	57.4	57.3	57.3	55.5	55.5	54.7	54.7
1	61.6	63.5	63.2	64	57.9	62.1	60.6	61.3
3	64.2	69.4	65.7	71	62.8	69.3	63.2	68.4
5	67.2	80.6	66.8	78.2	64.5	77.6	64.1	75.6
10	69.1	77.7	68.2	75.1	68.3	75.8	65.5	72.4

Potentiodynamic polarization measurements

Figure 3 shows the effect of different concentrations of MC₆ and PC₆ on the potentiodynamic cathodic and anodic polarization curves for Al in 0.5 M HCl solution with scan rate of 25 mVS^{-1} at 30°C in the absence and presence of different concentrations of monomeric surfactant MC₆ and its polymer PC₆ where as Fig. 4 illustrates the influence of temperature on the potentiodynamic cathodic and anodic polarization curves of Al in 0.5 M HCl containing 10 ppm of both MC₆ and PC₆. The data clearly show that the addition of MC₆ and PC₆ enhanced both the anodic and cathodic overpotential and decreased the corresponding potential anodic (dissolution of the metal) and potential cathodic (evolution of hydrogen) current densities. The addition of each inhibitor decreased the values of I_{corr} (corrosion current), this confirmed the inhibition of the corrosion process. Moreover, the corrosion potential was displayed to more positive values in the presence of the inhibitor; this revealed that these surfactants predominantly acted as anodic inhibitors.

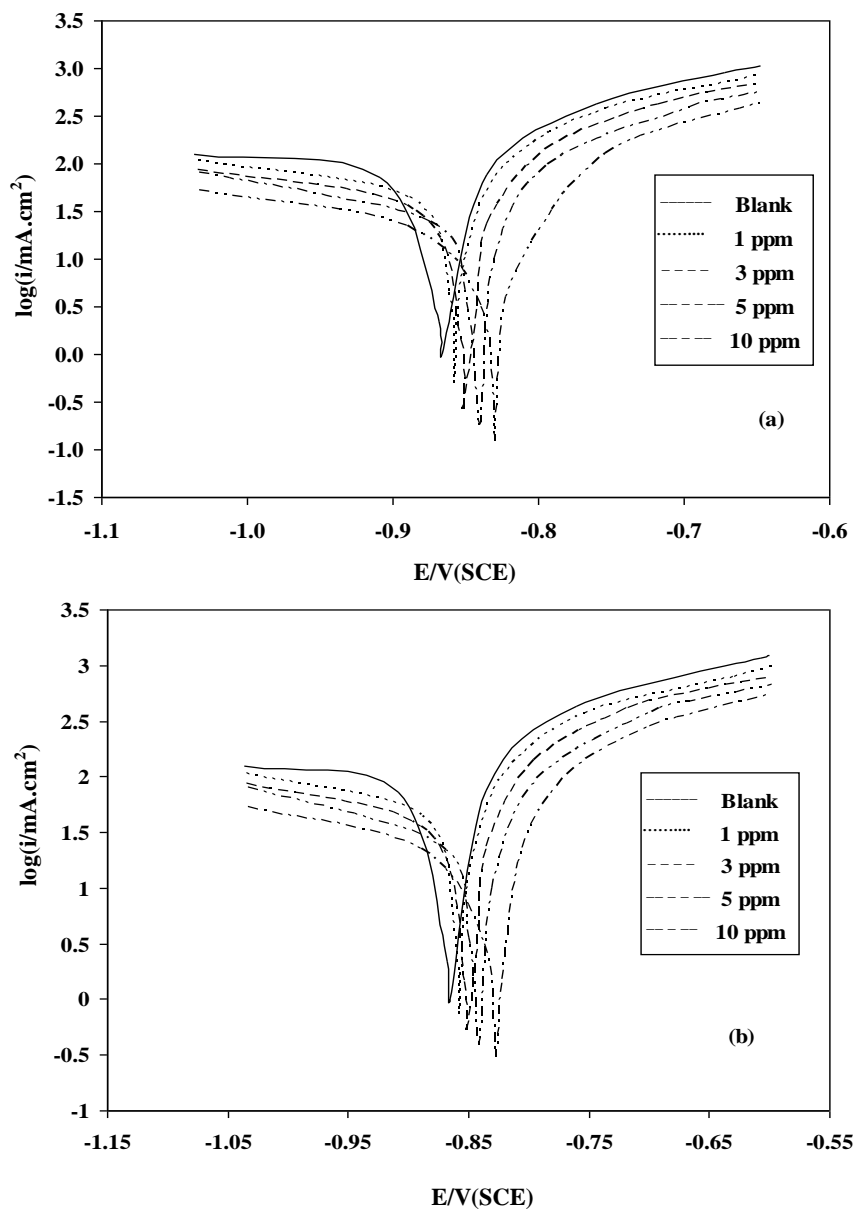


Fig. 3. Effect of MC_6 (a) and PC_6 (b) concentrations on the cathodic and anodic polarization of aluminium in 0.5 M HCl solution with a scan rate of 25 mV s^{-1} at 30°C .

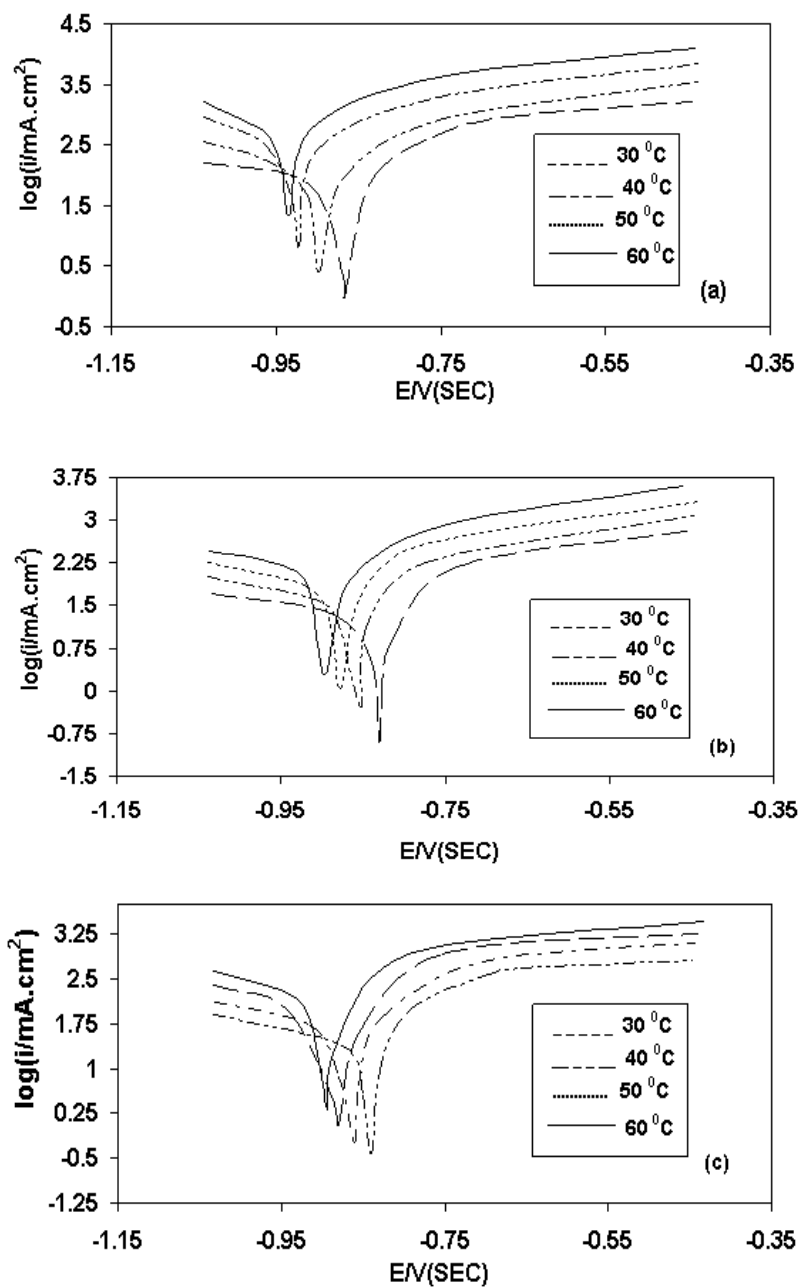


Fig. 4. Effect of temperature on the cathodic and anodic polarization of aluminum in 0.5 M HCl in the absence(a), presence 10 ppm of MC_6 (b) and 10 ppm of PC_6 (c) with a scan rate 25mVs^{-1} .

The electrochemical parameter I_{corr} , E_{corr} , the corrosion potentials (b_c) and (b_a) are cathodic and anodic Tafel slope respectively and the corrosion rate associated with the corrosion of Al in the absence and presence of different concentrations of MC_6 and PC_6 at different temperatures are listed in Tables 5 & 6. The corrosion rate is directly related to the corrosion current density I_{corr} , inhibition efficiency (P%) at different inhibitor concentrations and temperatures were calculated from the equation ⁽⁵⁾:

$$P \% = 100 \times \left(1 - \frac{(I_{\text{corr}})_I}{(I_{\text{corr}})_0} \right) \quad (4)$$

and the data are given in the Table 3, where $(I_{\text{corr}})_0$ and $(I_{\text{corr}})_I$ are the corrosion current densities in the absence and presence of inhibitor surfactants. It is seen that, the inhibition efficiency increases with the increase of the surfactant concentration up to the critical concentrations. However, the inhibition efficiency decreased with raising the temperature. The slopes of the anodic (b_a) and cathodic (b_c) Tafel lines are approximately equal. These results indicate that these inhibitors act by simply blocking the available surface area for corrosion reaction. In other words, the inhibitor decreases the surface area for corrosion without affecting the mechanism of corrosion reaction and only causes inactivation of a part of the aluminium surface with respect to the corrosive medium.

TABLE 5. The electrochemical parameters associated with polarization measurements for Al in 0.5 M HCl solution in the absence and presence of different concentrations of monomeric surfactant (MC_6) and its polymer (PC_6) at 30°C.

Conc. (ppm)	MC_6				PC_6			
	E_{corr} (mV)	I_{corr} ($\mu\text{A.cm}^{-2}$)	ba (mV.dec ⁻¹)	-bc (mV.dec ⁻¹)	E_{corr} (mV)	I_{corr} ($\mu\text{A.cm}^{-2}$)	ba (mV.dec ⁻¹)	-bc (mV.dec ⁻¹)
Blank	-0.82	95.22	0.044	0.35	-0.82	95.22	0.044	0.34
1	-0.721	77.41	0.109	0.35	-0.67	70.67	0.240	0.34
3	-0.71	69.70	0.121	0.35	-0.76	55.25	0.057	0.36
5	-0.82	67.62	0.103	0.27	-0.66	41.43	0.285	0.38
10	-0.75	64.50	0.084	0.32	-0.96	44.22	0.215	0.31
15	-0.69	63.64	0.310	0.32	-0.69	47.19	0.115	0.35
20	-0.72	56.60	0.137	0.31	-0.71	48.72	0.141	0.38
25	-0.81	54.11	0.106	0.31	-0.71	47.72	0.074	0.37
30	-0.74	72.09	0.131	0.31	-0.72	49.10	0.140	0.35
40	-0.79	77.91	0.044	0.43	-0.714	48.67	0.091	0.38

TABLE 6. The electrochemical parameters associated with polarization measurements for Al in 0.5 M HCl solution in the presence of 10 ppm of monomeric surfactant (MC_6) and its polymer (PC_6) at different temperatures.

T (k)	MC_6				PC_6			
	E_{corr} (mV)	I_{corr} ($\mu\text{A.cm}^{-2}$)	ba (mV.dec ⁻¹)	-bc (mV.dec ⁻¹)	E_{corr} (mV)	I_{corr} ($\mu\text{A.cm}^{-2}$)	ba (mV.dec ⁻¹)	-bc (mV.dec ⁻¹)
303	-0.75	64.51	0.084	0.319	-0.96	44.22	0.215	0.310
313	-1.01	256.33	-0.560	0.102	-0.90	202.00	-0.460	0.091
323	-0.97	518.24	-0.366	0.123	-0.899	417.21	-0.441	0.082
333	-0.97	771.80	-0.540	0.096	-1.22	704.32	-0.371	0.187

Adsorption isotherm

To get more information about the mode of adsorption of the inhibitors on the Al surface at different temperatures, the obtained data from the two different techniques were tested with several adsorption isotherms "Langmuir" adsorption isotherm was found to fit well with our experimental data. Figure 5 represents curve fitting of MC₆ monomeric surfactant and its analogues polymer PC₆ using data obtained from potentiodynamic polarization measurements. Similar results were obtained from weight loss technique. The adsorption isotherm relationship of Langmuir is represented by the following equation⁽³¹⁾:

$$\frac{C_i}{\theta} = \frac{1}{(K_{ads})} + C_i \quad (5)$$

where C_i is the concentration of the inhibitor in bulk solution, θ is the surface coverage (θ = P/100) inhibition efficiency and K_{ads} is the adsorption equilibrium constant.

Frumkin⁽³²⁾ isotherm was also found to fit well with the obtained experimental data. The adsorption isotherm relationship of Frumkin is represented by the following equation:

$$\ln \frac{\theta}{C_i} (1 - \theta) = \ln K_{ads} + 2a\theta \quad (6)$$

where (a) is the lateral interaction term describing the molecular interactions in the adsorption layer and the heterogeneity of the surface and measure for the steepness of the adsorption isotherm. The more positive the value of (a) is the steeper the adsorption isotherm. Curves fitting of the weight loss data for MC₆ and PC₆ are graphically represented in Fig. 6. Similar results were obtained from the data of the potentiodynamic technique.

The adsorption thermodynamic parameters (ΔH_{ads} and ΔS_{ads}) for the surfactant adsorption on Al surface in 0.5 M HCl at different temperatures were determined from the slopes and intercepts of the lines of log K_{ads} vs. 1/T plots with the following equation⁽³¹⁾:

$$\log K_{ads} = -\frac{\Delta H_{ads}}{2.303RT} + \frac{\Delta S_{ads}}{2.303R} \quad (7)$$

where ΔH_{ads} and ΔS_{ads} are the enthalpy and entropy of the adsorption process, respectively. The calculated values for ΔH_{ads}, ΔS_{ads} and ΔG_{ads} are listed in Table 7 (ΔG_{ads} = ΔH_{ads} - TΔS_{ads}). The thermodynamic functions of the adsorption process obtained from the two techniques confirm each other. The calculated values of ΔG_{ads} were low suggesting that the nature of the inhibitor adsorption was mainly physical adsorption and their negative sign indicated spontaneous interaction of the inhibitor with aluminium surface^(33,34). The negative value of ΔH_{ads} indicated that the adsorption of the inhibitors on Al surface was an exothermic process. The values of ΔH_{ads} and ΔS_{ads} were characteristic of the occurrence of a replacement process between the inhibitor species and adsorbed water molecules from the surface of metal during the adsorption of the inhibitor compound on the metal surface⁽³⁵⁾.

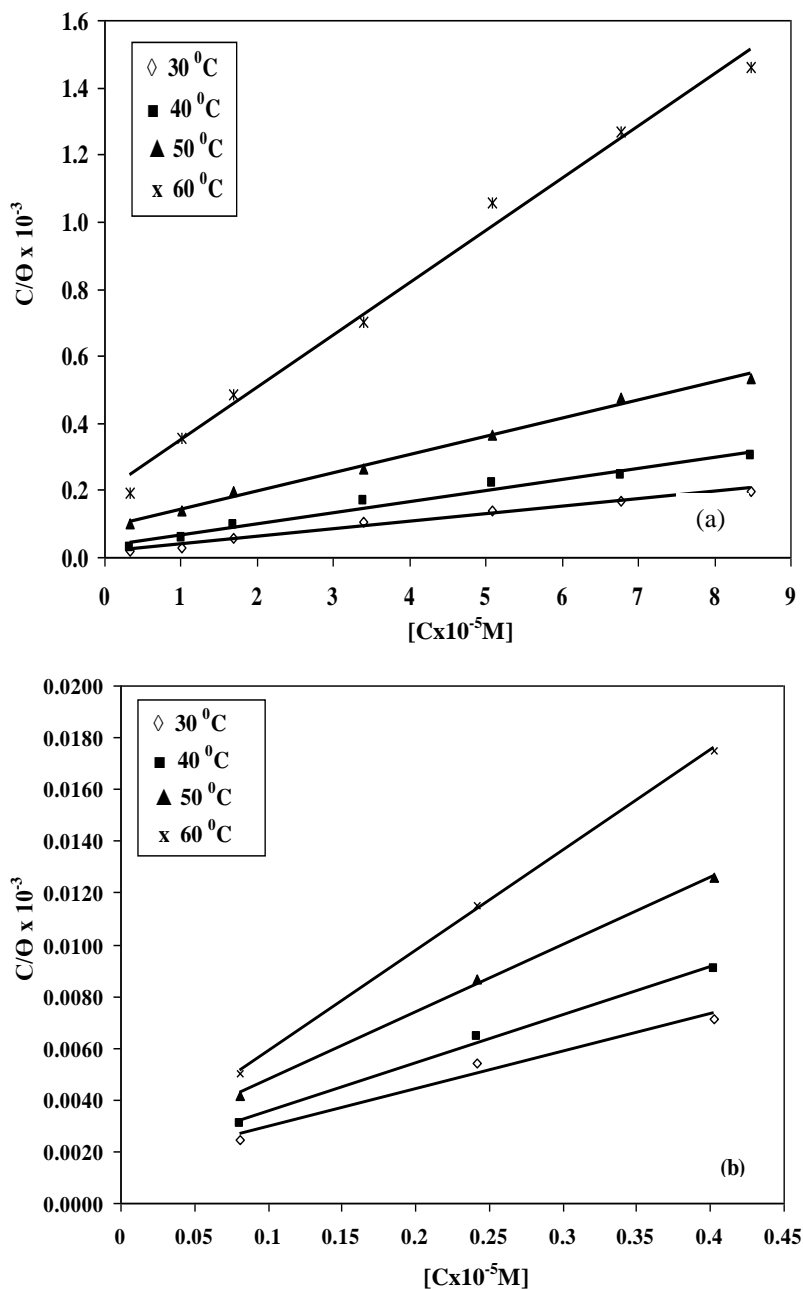


Fig. 5. Langmuir adsorption isotherm of MC₆ (a) and PC₆ (b) using potentiodynamic polarization data at different temperatures.

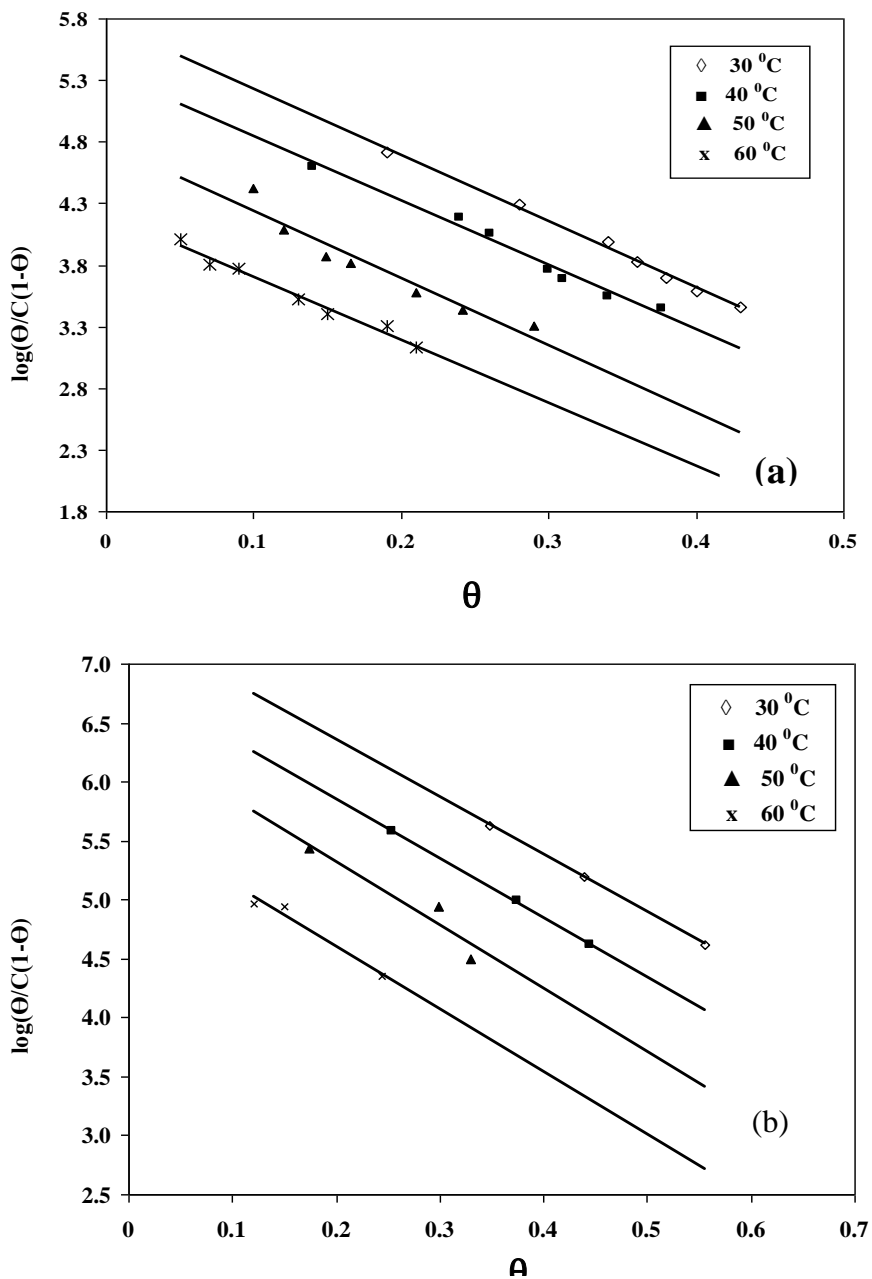


Fig.6. Curve fitting of weight loss data of Al in 0.5 M HCl solution containing various concentrations of MC₆ (a) and PC₆ (b) to Frumkin isotherm at different temperatures.

TABLE 7. The thermodynamic parameter of adsorption process obtained by applying Frumkin model and Gibbs equation ($\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S_{\text{ads}}$) on the weight loss and polarization data of Al in 0.5 M HCl in the 30-60 °C temperature range.

Technique used	Monomeric surfactant			Polymeric surfactant		
	ΔH_{ads} kJmol ⁻¹	ΔS_{ads} kJmol ⁻¹	$-\Delta G_{\text{ads}}$ kJmol ⁻¹	ΔH_{ads} kJmol ⁻¹	ΔS_{ads} kJmol ⁻¹	$-\Delta G_{\text{ads}}$ kJmol ⁻¹
Weight loss	-104.54	-0.2202	35.92	-42.12	-0.0210	35.73
Polarization	-103.39	-0.2220	37.83	-44.03	-0.0216	37.48

Conclusion

- The addition of MC₆ and PC₆ surfactants inhibits the corrosion of aluminium in 0.5M HCl solution.
- The inhibition efficiency of polymeric surfactant was higher than that of monomeric surfactant.
- The inhibition efficiency of the two surfactants increases with the increase of inhibitor concentration but decreases with the increase of temperature.
- The data obtained from weight loss and potentiodynamic polarization techniques were in good agreement with each other and fit well with the Langmuir and Frumkin isotherms.

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تثبيط تآكل الألومنيوم عن طريق سلسلة من مونيمرات الأنيلين ذات
النشاط السطحي والبوليمرات المناظرة له في محلول 0.5 مولر
حامض الهيدروكلوريك
الجزء الأول: 3-6- هيكسيلوكسي سلفونات الصوديوم) أنيلين
مونيمر والبوليمر المناظر له

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يتناول هذا البحث دراسة معدل تآكل الألومنيوم في محلول 0.5 مولر حامض
الهيدروكلوريك بطريقتي الفقد في الوزن والإستقطاب البوتنشيودينمكلي في وجود
وعدم وجود تركيزات مختلفة من مادتين لهما نشاط سطحي وهما 3-6-
هيكسيلوكسي سلفونات الصوديوم) أنيلين مونيمر (MC₆) والبوليمر المناظر له
بولي(3- هيكسيلوكسي حمض السلفونك) أنيلين (PC₆) والذي تم تحضيرهما في
المعمل وإثبات التركيب لهما باستخدام التحاليل المختلفة.

أوضحت النتائج أن تثبيط تآكل الألومنيوم في الوسط الحامضي يتم من خلال
إمتزاز المادتين ذات النشاط السطحي (MC₆) و (PC₆) على سطح الألومنيوم وان
كفاءة التثبيط تزداد بزيادة تركيزات المواد السابقة بينما تقل بزيادة درجة الحرارة.
كما وجد من النتائج المستخلصة من الطريقتين السابقتين أن المادتين ذات النشاط
السطحي (MC₆) و (PC₆) يحققا إمتزاز من نوعي Frumkin و Langmuir
على سطح الألومنيوم وان عملية الإمتزاز تلقائية كما اثبتتها قيم ΔG_{ads} السالبة
وان الإمتزاز فيزيائي والذي تم الإستدلال عليه من قيم ΔG_{ads} الصغيرة.