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The Corrosion Inhibition of Aluminium by Some of 3-alkyloxylaniline Monomeric Surfactants and Their Analogues Polymers in 0.5 M HCl Solution

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Additional information is available at the end of the chapter

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1. Introduction

Corrosion is the destructive result of reaction between a metal or metal alloy and its environment [1-3]. Metal atoms in nature are present in chemical compounds (i.e, minerals). The same amounts of energy needed to extract metals from their minerals are emitted during the chemical reactions that produce corrosion. The corrosion process (anodic reaction) of the metal dissolving as ions generates some electrons, are consumed by a secondary process (cathodic reaction). These two processes have to balance their charges. The sites hosting these two processes can be located close to each other on the metal's surface, or far apart depending on the circumstances.

The thermodynamic or chemical energy stored in a metal or that is freed by its corrosion varies from metal to metal. It is relatively high for metals such as magnesium, aluminium, and iron, and relatively low for metals such as copper, silver and gold [4].

There are several factors effects on the corrosion process, which classified to factors associated mainly with the metal such as:

1. Effective electrode potential of a metal in a solution [5].
2. Overpotential of hydrogen on the metal [6-8].
3. Chemical and physical homogeneity of the metal surface [9].
4. Inherent ability to form an insoluble protective film [10].
5. Hydrogen-ion concentration (pH) in the solution [11-16].

and factors associated mainly with the environment such as [16]:

1. Influence of oxygen in solution adjacent to the metal [18].
2. Specific nature and concentration of other ions in solution [19].
3. Rate of flow of the solution in contact with the metal [20-22].
4. Temperature [23].
5. Contact between dissimilar metals or other materials [24].

Some chemicals react with a metallic surface, or metal environment giving the surface a certain level of protection named corrosion inhibitor. Corrosion inhibitors are commonly added in small amounts to corrosion medium, either continuously or intermittently to prevent serious corrosion [25].

Some inhibitors retard corrosion by adsorption to form a thin invisible film, others form visible bulky precipitates which coat the metal and protect it from attack. Other inhibitors, when added to an environment, retard corrosion but do not interact directly with metal surface.

The four components of a corrosion cell (anode, cathode, electrolyte and electronic conductor), three may be affected by a corrosion inhibitor to retard corrosion. The inhibitor may cause:

1. Increase Polarization of the anode (anodic inhibitor).
2. Increase Polarization of the cathode (cathodic inhibitor).
3. Increase the electrical resistance of the circuit.

Four classes of inhibitors will be discussed as follow:

1. *Anodic Inhibitors* [26-28]:

Anodic inhibitors which cause a large shift in the corrosion potential which called Passivating inhibitors. They are also called dangerous inhibitors, because if used in insufficient concentrations, they cause pitting or sometimes an increase in corrosion rate. There are two types of Passivating inhibitors: (i) oxidizing anions such as chromate, nitrite and nitrate which can passivate the working electrode in the absence of oxygen; and (ii) non-oxidizing ions such as phosphate, tungstate, and molybdate which require the presence of oxygen to passivate the working electrode.

2. *Cathodic Inhibitors* [29]:

Cathodic inhibitors either slow the cathodic reaction itself, or they selectively precipitate on cathodic areas to increase circuit resistance and restrict diffusion of reducible species to the cathodes.

Some cathodic inhibitors make the discharge of hydrogen gas more difficult, and they increase the hydrogen over voltage. Another possible cathodic reaction is the reduction of oxygen.

3. *Organic and polymer inhibitors:*

Organic compounds constitute a broad class of corrosion inhibitors which can not be designed specifically as either anodic or cathodic. Anodic and cathodic effects alone are sometimes observed in the presence of organic inhibitors, but, as a general rule, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration. Both anodic and cathodic areas probably are inhibited, by different depending on the potential of the metal, chemical structure of the inhibitor molecule, and size of the molecule. The inhibition is the result of adsorption of inhibitor on the metal surface. The film formed by adsorption of soluble organic inhibitors is invisible.

Polymers are used as corrosion inhibitors for different metals. Polyaniline as an electronically conductive polymer has attracted considerable attention. Because of its excellent environmental stability in the electro-conducting form, it has many potential applications; unique electrical and optical properties [31-41]. The applications of polyaniline have been limited due to its poor processability [42], which is true for most conducting polymers. Several studies have been done in order to improve the solubility of polyaniline, among them, using functionalized protonic acids as dopant, like p-toluene-sulphonic acid, octyl-benzene-sulphonic acid, dodecyl benzene-sulphonic acid [43-45], poly(styrene) sulphonic acid [46,47], and phosphoric acid esters [48]. An alternative method to obtain soluble conductive polymers is the polymerization of aniline derivatives. The most studied aniline derivatives are alkyl [49,50], alkyloxy [51-54], hydroxy [55,56], chloroaniline [57-59]. Also, substitution at the nitrogen atom was reported by Sayyah et al. [60] to improve the solubility of polyaniline.

This study has been done in order to improve the solubility of polyaniline by using terminal side chain containing 6-12 carbon atom and the presence of the hydrophilic SO_3Na anionic group at the end of side the alkyl chain group. By this way, the solubility of poly aniline conducting polymer has been improved and have the properties of surface active agent (surfactant).

Surfactants (surface active agents) are amphiphilic molecules that consist of a non-polar hydrophobic portion, usually a straight or branched hydrocarbon chain, which is attached to a polar or ionic portion (hydrophilic). The hydrophilic molecule has a tendency to interact with or be dissolved by water and other polar substances. The hydrocarbon chain interacts weakly with the water molecules, due to the cooperative action of dispersion and hydrogen bonding between the water molecules tends to squeeze the hydrocarbon chain out of the water and hence these chains are referred to hydrophobic, while the polar or ionic head group interacts strongly with water molecules via dipole or ion-dipole interactions. Therefore, a surfactant contains both a water insoluble component and a water soluble component [61]. The balance between hydrophobic and hydrophilic parts of the molecule gives these systems their special properties, e.g. accumulation at various interfaces and association in solution (to form micelles). Adsorption of surfactant molecules at the interface between metal and solution lowers the surface tension and higher the surfactant adsorption. The degree of surfactant adsorption at the interface depends on surfactant structure and the nature of the two phases that meet the interface [62]. The surfactants can be classified based on the nature of the hydrophilic group as follow:

1. *Anionic Surfactants*

These are the most widely used class of surfactants in industrial applications due to their relatively low cost of manufacture and they are used in practice as detergent [63]. For optimum detergency the hydrophobic chain is a linear alkyl group with a chain length in the region of 12–16 carbon atoms. The most commonly used hydrophilic groups are carboxylates, sulphates, sulphonates and phosphates.

2. *Cationic Surfactants:*

The most common cationic surfactants are the quaternary ammonium compounds with the general formula $R_0R_{00}R_{000}R_{0000}NX$, where X is usually chloride ion and R represents alkyl groups [64,65]. A common class of cationic is the alkyl trimethyl ammonium chloride, where R contains 8–18 carbon atoms, e.g. dodecyl trimethyl ammonium chloride, $C_{12}H_{25}(CH_3)_3NCl$. Another widely used cationic surfactant class is dialkyl dimethyl ammonium chloride, with the alkyl groups having a chain length of 8–18 carbon atoms.

3. *Amphoteric Surfactants [66]:*

These are surfactants containing both cationic and anionic groups. The most common amphoteric are the derivatives of trimethyl glycine $(CH_3)_3NCH_2COOH$ (described as betaine). An example of betaine surfactant is lauryl amido propyl dimethyl betaine $C_{12}H_{25}CON(CH_3)_2CH_2COOH$. The main characteristic of amphoteric surfactants is solubility in solution.

4. *Nonionic Surfactants [67]:*

The most common nonionic surfactants are those based on ethylene oxide, such as ethoxylated surfactants. Several classes can be distinguished: alcohol ethoxylates, alkyl phenol ethoxylates, fatty acid ethoxylates, monoalkaolamide ethoxylates, sorbitan ester ethoxylates and ethylene oxide–propylene oxide copolymers (sometimes referred to as polymeric surfactants).

5. *Polymeric Surfactants:*

There has been considerable recent interest in polymeric surfactants due to their wide applications in the oil industry, preparation of emulsions, suspensions, stabilization, wetting spreading and adhesion.

Aluminum and its alloys have been widely used as a material in the fields of transport, storage of liquefied industrial gases, building, electrical engineering, household appliances, containers, aircraft, chemical equipments including heat exchangers, pressure vessels, condensers, rotatory dryers, tanks, portable containers, valves, and piping. Aluminium is particularly suitable for neutral or oxidizing substances such as paraffin's, alcohols, nitric acid, hydrogen peroxide,.. etc. This is because they are characterized by low density, low cost, excellent electrical and thermal conductivities, good corrosion resistance, good appearance, and high ductility [68–74].

The corrosion resistance of aluminum and its alloys comes from the continuous film that is developed on their surfaces upon exposure to the atmosphere or aqueous solutions [75]. This

film is not guaranteed to protect the aluminum surface in corrosive media. The most widely used HCl acid solution, so this medium has induced a great deal of research on aluminium [76]. Most of the effective inhibitor have hetero atom such as O, N, S containing multiple bonds in their molecules through which they can adsorb on the metal surface. The sites of these elements have higher electron density, making them the reaction centers. Other articles on the corrosion inhibition of aluminium by different type of inhibitors are summarized in Table (1).

In the present study, 3-alkyloxy aniline sodium sulfonate monomeric surfactants and their analogues polymers as mixed-type inhibitors for the corrosion of aluminium in 0.5M HCl. This performance will be investigated via weight loss 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.

Author	Metal type	Inhibitor	Medium	Method of Investigation	General Remarks
B. Muller et al. [77] (1994)	Aluminum	Low and high molecular weight Polyacrylic acids (PAAC)	Water and butyl glycol V/V 9:2 at pH=10	Atomic absorption spectroscopy (AAS) by measuring soluble Al acrylate in solution	• In the concentration range from 0.3-0.5 wt% of PAAC, low molecular weight PAAC has markedly inhibition effect than high molecular weight. • In case of the concentration range 0.05-0.1 wt%, low molecular weight PAAC has no effect where the high molecular weight of PAAC has an inhibition effect.
B. Muller et al. [78] (1995)	Aluminum	High molecular weight of styrenemaleic acid copolymers	Mixture of water and butyl glycol V/V 9:2 at pH=10	AAS by measuring soluble Al(III) acrylate in solution And volumetric measurement of hydrogen	• The inhibition efficiency is measured by volumetric measurement of the hydrogen produced by the corrosion. • The lower acid number of the copolymers, the lower is the volume of hydrogen.
Ogurtsov, N.A., et al. [79] (2004)	Aluminum alloy	Undoped and doped polyaniline (PANI)	0.1N HCl and 3.5% NaCl solutions	Electrochemical impedance spectroscopy (EIS)	• Polyaniline can provide corrosion protection of Al alloy in both NaCl and in dilute HCl solutions. • The degree of the corrosion protection of the Al alloy by the undoped PANI is higher than that of the doped PANI.

Author	Metal type	Inhibitor	Medium	Method of Investigation	General Remarks
					• Based on the obtained corrosion currents, it is possible to believe that, the thickness of the surface protective aluminum oxide layer plays a key role in the inhibiting effect.
et.al. [80] (2004)	Aluminum	Polyamide	Oxalic acid	Potentiostatic and potentiodynamic anodic polarization techniques	• The inhibition efficiency increases with increasing polyamide concentration until a critical value and then starts to decrease. • The inhibitive behavior of the polymer is due to adsorption of the polyamide compounds on the metal surface and formation of insoluble complexes. • The adsorption process is found to obey Temkin adsorption isotherm.
et al. [81] (2008)	Aluminum	Polyvinyl pyrrolidone (PVP) and Polyacrylamide (PA)	HCl	Weight loss, hydrogen evolution and thermometric techniques	• The inhibition efficiency increased with increasing inhibitor concentrations but decrease with increasing temperature. • The inhibition efficiency of PVP higher than PA which may be due to the differences in their molecular structures play a significant role in the adsorption process. • The inhibitors (PVP and PA) obey Freundlich, Temkin and Flory-Huggins adsorption isotherms. • Results obtained from the kinetic and thermodynamic parameters indicate spontaneous and physical adsorption of the inhibitors.
Amin, M. A., et al. [82] (2009)	Aluminum	Polyacrylic acids with different molecular weights ($PAA_1 = 1800$, $PAA_2 = 11,000$ and $PAA_3 = 14,000$ g mol ⁻¹)	Alkaline solutions (pH 8 and 10)	Weight loss, potentiodynamic polarization and impedance techniques.	• The polymers inhibit the alkaline corrosion of aluminium. • The inhibition efficiencies of inhibitors increase with increasing concentration, molecular weight, immersion time and act as mixed-type inhibitors.

Author	Metal type	Inhibitor	Medium	Method of Investigation	General Remarks
					• The results obtained from the chemical and electrochemical measurements are in good agreements.
Umoren, S.A., et al. [83] (2009).	Aluminum alloy 3SR	Polyvinylpyrrolidone and polyacrylamide	HCl	Weight loss, hydrogen evolution and thermometric methods	• The polymers inhibit acid induced corrosion of aluminum. • PVP was found to be a better corrosion inhibitor than PA. • Adsorption of these inhibitors follows Temkin and El-Awady adsorption isotherm models. • Kinetic/thermodynamic parameters (E_a, K_{ads}, ΔG°_{ads}) of adsorption of the studied inhibitors reveal that the adsorption was physical in nature and spontaneous.
, B., et al. [84] (2011).	Aluminum alloy	Polypyrrole (PPy) and poly(pyrrole-co-o-anisidine)	3.5% NaCl	Open circuit potential(E_{ocp}), electrochemical impedance and anodic polarization techniques.	• Thermogravimetric results were indicated that copolymer film has higher thermal stability than PPy. • The synthesized copolymer film decreased the corrosion of Al by acting as physical barrier on the surface and exhibiting anodic protective behavior. • The E_{ocp}-time curves showed that the barrier effect of copolymer coating increased during immersion period.
Oliveira, M.A.S., et al. [85] (2011).	Aluminum alloy	Polyaniline doped with poly(methylmethacrylate-co-acrylic acid) (PAni-PMMA-co-A)	NaCl, pH 5.8	Impedance studies	• The films, PAni-PMMA-co-AA and epoxy resin, formed on the Al alloy surfaces were porous and non-uniform allowing electrolyte permeation and oxidation of the metal inside the pores. • The PAni-PMMA-co-AA films offer better corrosion protection to aluminum alloy than the commercial epoxy resin films.
Zaafarany.I, [86] (2012)	Aluminum	Alginate and pectate water-soluble natural polymer	NaOH	Gasometric and weight-loss techniques	• The alginate and pectate are effective inhibitors for corrosion of aluminum in alkaline medium.

Author	Metal type	Inhibitor	Medium	Method of Investigation	General Remarks
					• Pectates are more active for corrosion inhibition than alginates, this may be due to the geometrical configuration of the functional groups, which play an important role in the magnitude of inhibition efficiency. • The natural or synthetic polymers containing the same functional groups will have the same corrosion behavior and, hence, may proceed through similar corrosion mechanism.
Ghoreishi, S.M., et al. [87] (2012).	Aluminum alloy	Poly(o-anisidine)	3.5% NaCl	Potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS).	• The homogeneous and adherent poly(o-anisidine) were successfully synthesized on Al alloy. • The EIS results are in good agreement with the potentiodynamic polarization measurements. • This study reveals that the poly(o-anisidine) coating has excellent corrosion protection properties and can be considered a potential coating material to protect aluminum alloy against corrosion.
Awad , M.K. et al. [88] (2013)	Aluminum	Poly ethylene glycol	HCl	Weight loss and polarization techniques.	• Poly ethylene glycols with different number of repeating unit can work as chemical inhibitor for corrosion aluminum surface. • The adsorption of these polymers on metal surface is physical adsorption and obeys Langmuir adsorption isotherm. • The inhibition efficiency increases with both number of repeating unit and concentration but decreases with increasing temperature.
et al. [89] (2013)	Aluminum	Water-soluble natural poly) pectates ((PEC)	HCl	Gasometric and weight loss techniques	• The inhibition efficiency was found to increase with increasing inhibitor concentration and decrease with increasing temperature.

Author	Metal type	Inhibitor	Medium	Method of Investigation	General Remarks
					• The inhibition action of PEC on Al metal surface was found to obey the Freundlich isotherm. • Factors such as the concentration and geometrical structure of the inhibitor, concentration of the corrosive medium, and temperature affecting the corrosion rates were examined. • The kinetic parameters were evaluated and a suitable corrosion mechanism consistent with the kinetic results is discussed

Table 1. Some physical data of using water soluble polymers as corrosion inhibitors

2. Experimental

2.1. Weight loss measurements

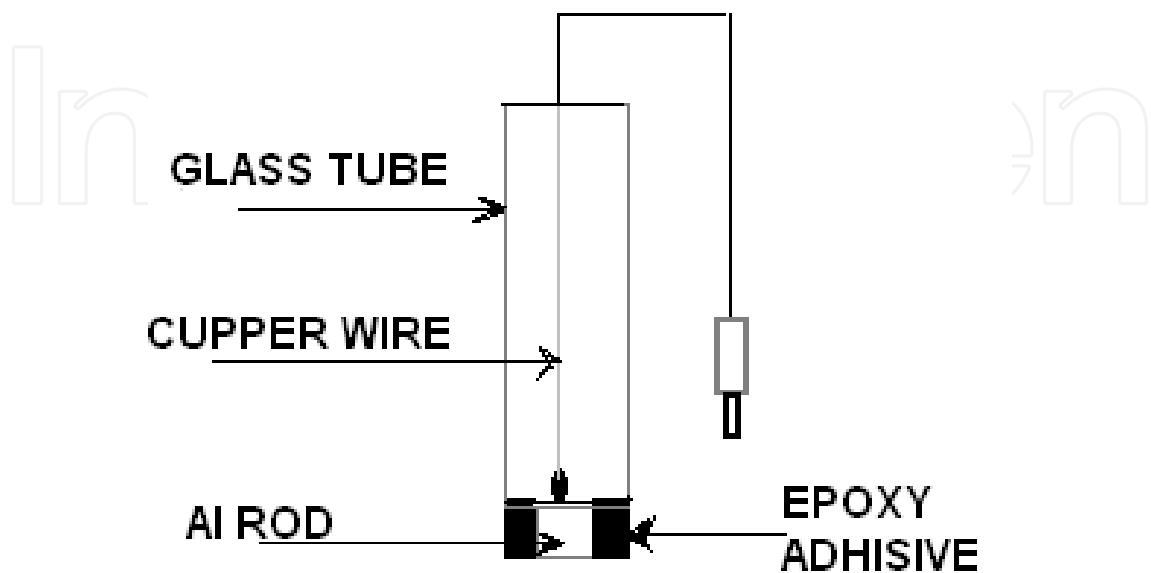
Aluminium metal provided by the Egyptian Aluminium Company, Naghammady of the following chemical composition: 99.57 % Al, 0.31 % Fe, 0.07 % Si, 0.015 % Ti %, 0.0016 % Zn, 0.0003 % Cr, 0.0019 % Mg, 0.0021 % Mn and 0.0007 Cu. The dimensions of the tested samples are 2 x 2 (cm²), 0.1cm (thickness) is used in this study. 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.

2.2. Potentiodynamic polarization measurements

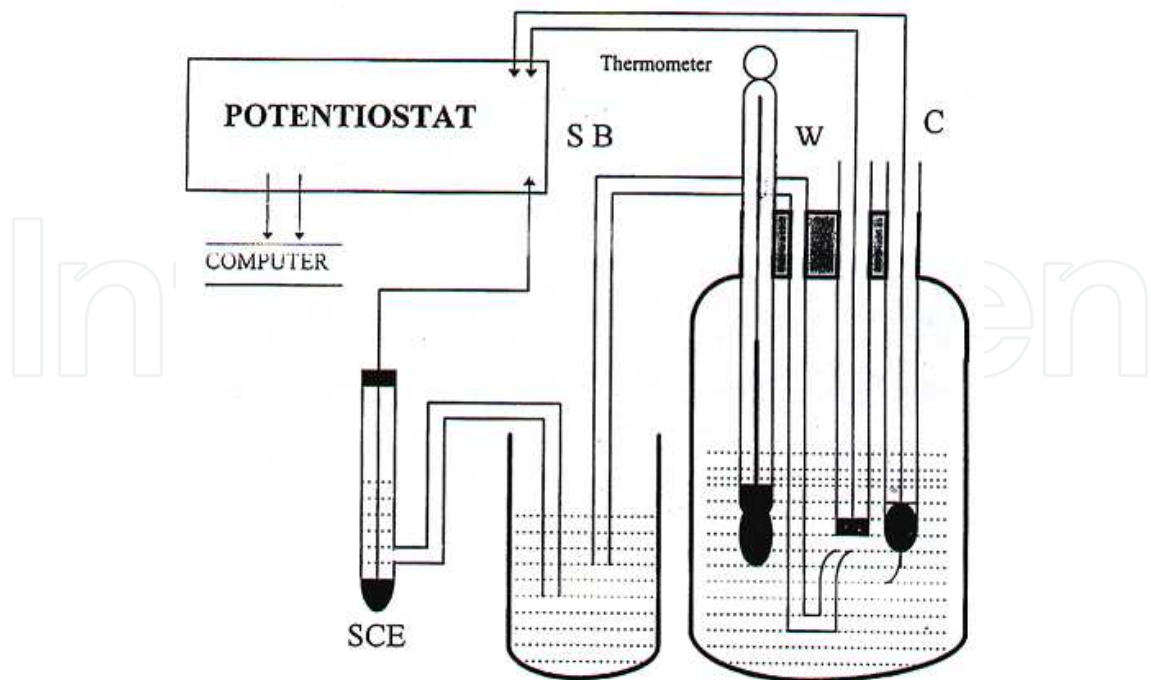
The working electrode was made from aluminium rod has the same composition as mentioned in point 2.1. The rod is axially embedded in araldite holder to offer an active flat disc shaped surface of an area 0.785 cm² as shown in scheme (1). Prior to each experiment, the working electrode was polished successively 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 are performed using the Potentiostat /Galvanostat Wenking PGS95, connected to computer. The I-E curves are recorded using computer software (model 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. The complete polarization cell is shown in scheme (2). It is a multi-necks

250 ml flask. The multiple necks were used to introduce working (W), counter (C) electrode and Luggin probe entered the cell through the clamped ball and socket joint.



Scheme 1. The working electrode.



Scheme 2. Electrode cell and the circuit diagram for Potentiodynamic polarization measurements.

2.3. 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 of chemically pure grade products provided by Prolabo-Chemical Co., (U.K.). Doubly distilled water was used to prepare all solutions. Potassium persulfate and 1,6- dibromohexane, 1,10- dibromodecane and 1, 12- dibromododecane were obtained from Aldrich Chemical Co., (England).

2.4. Synthesis of monomeric (3-alkyloxy anilines sodium sulfonate)

3-(6-Bromohexyloxy) aniline, 3-(10-bromodecyloxy) aniline and 3-(12-bromododecyloxy) aniline were prepared by the reaction of (1:1) 3-aminophenol with 1, 6- dibromohexane, 1, 10- dibromodecane and 1, 12- dibromododecane respectively, in the presence of sodium ethoxide.

3-(6-bromohexyloxy) aniline, 3-(10-bromodecane) aniline and 3-(12-bromododecane) aniline were reacted with sodium sulfite to produce 3(6- sodium sulfonate hexacyloxy) aniline (MC_6), 3(10- sodium sulfonate decyloxy) aniline (MC_{10}) and 3(12- sodium sulfonate dodecyloxy) aniline (MC_{12}).

2.5. Synthesis of polymeric surfactants

The amount of monomers of 3(6- sodium sulfonate hexacyloxy) aniline, 3(10- sodium sulfonate decyloxy) aniline and 3(12- sodium sulfonate dodecyloxy) aniline were dissolved in 25 ml of 2.0 M HCl solutions in a well stoppered conical flasks of 250 ml capacity followed by the addition of the required amounts of potassium persulfate (0.15 M) dissolved in 25 ml of (2M) HCl solutions to the reaction mixture under nitrogen atmosphere. The order of addition of substances was kept constant in all the performed experiments. The stoppered conical flasks were then placed in automatically controlled thermostat at 25°C. The flasks were shaken (50 shakings/10 s/15 min) for one hour by using an automatic shaker. The flasks were left for 72 hour at room temperature to continue the reaction and then filtered using a Buchner funnels. The precipitate were washed with the distilled water, and finally dried under vacuum at room temperature until constant weight.

2.6. Elemental and spectroscopic analysis

The elemental analysis of the prepared monomeric and polymeric surfactants were carried out in the micro analytical laboratory at Cairo University by using oxygen flask combustion and a dosimat E415 titrator (Switzerland).

The ultraviolet-visible absorption spectra of the prepared monomeric and polymeric surfactants were measured using Shimadzu UV spectrophotometer (M 160 PC) at room temperature in the range 200-400 nm using dimethylformamide as a solvent and reference.

Scanning electron microscopy and X-ray diffractometer (philip1976. model1390) was operated for the polymer samples under the following conditions which were kept constant for all of

the analysis processes Cu X-ray tube, scan speed =8/min, current=30mA, voltage =40kv and preset time=10

2.7. Critical micelle concentration and surface tension

Critical micelle concentration and surface tension were measured by using K100 Tensiometer (Kruss Type, Germany) for the hydrochloric form of synthesized monomeric and polymeric surfactants using different concentrations.

3. Results and discussion

3.1. The elemental analysis and spectroscopic analysis of the prepared monomeric surfactants and their polymers

The elemental analysis of the prepared monomeric and polymeric surfactants are summarized in Table (2). The data show that, there is a good agreement with the calculated one for the suggested structures present in scheme (3).

The UV-visible spectra of the prepared monomeric surfactants and their polymers are represented in figure (1); the spectra show the following absorption bands:

1. The two absorption bands appear at $\lambda_{\max} = 214$ and 227 nm In case of MC_6 , which may be attributed to $\pi-\pi^*$ transition (E_2 -band) of the benzene ring and the β -band for $\pi-\pi^*$ transition ($A_{1g} - B_{2u}$), appears at $\lambda_{\max} = 206$ and 210 nm in case of MC_{10} and at $\lambda_{\max} = 207$ and 211 nm in case of MC_{12} .
2. In case of PC_6 , two absorption bands appear at $\lambda_{\max} = 211$ and 225 nm which may be attributed to $\pi-\pi^*$ transition showing a bathochromic shift, appears at $\lambda_{\max} = 211$ and 253 nm in case of PC_{10} and appears at $\lambda_{\max} = 210$ and 240 nm in case of PC_{12} . Beside these bands, an absorption band appears in the visible region at $\lambda_{\max} = 352$, $\lambda_{\max} = 348$ and $\lambda_{\max} = 344$ nm in case of PC_6 , PC_{10} and PC_{12} respectively which may be due to the high conjugation of the aromatic polymeric chain.

The X-ray diffraction patterns of the three prepared polymers (PC_6 , PC_{10} and PC_{12}) are represented in figure (2). The figure shows that one of the prepared polymers (PC_{12}) is amorphous while the polymer PC_6 and PC_{10} give peak at 2-Theta equal to 19.835 degree with d-spacing (4.4726) and the peak intensity in case of PC_6 is higher than that of polymer PC_{10} has a small portion of crystallinity which are also confirmed by the electron microscopic picture represented in figure (3). In case of (PC_{12}) there is no characteristic peak in the X-ray diffraction patterns in the region of crystalline organic compounds indicating that the polymer is amorphous and from the electron microscopic picture it is clear that the amorphous grain particles of the polymers (PC_{12}) are ranged from spherical to elongated particles.

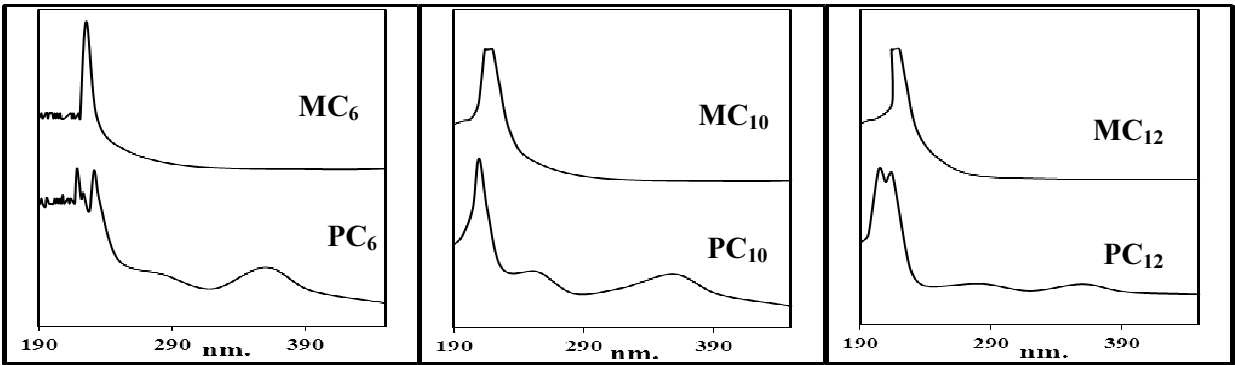


Figure 1. UV spectrum of the prepared monomeric and polymeric surfactants.

Name	C %		H %		Cl %		S %		N %	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
MC ₆	48.81	48.12	6.10	5.99	–	–	10.85	10.65	4.75	4.58
PC ₆	46.27	46.92	6.72	6.54	5.70	5.75	10.28	10.36	4.50	4.53
MC ₁₀	65.08	64.12	8.81	8.73	–	–	10.85	10.73	4.75	4.61
PC ₁₀	52.28	52.14	7.49	7.54	4.83	4.68	8.71	8.75	3.81	3.72
MC ₁₂	73.22	72.93	10.17	10.02	–	–	10.85	10.63	4.75	7.66
PC ₁₂	54.65	55.37	7.97	7.69	4.44	4.51	8.10	8.04	3.54	3.52

Table 2. Elemental analysis of the prepared monomeric and polymeric surfactants.

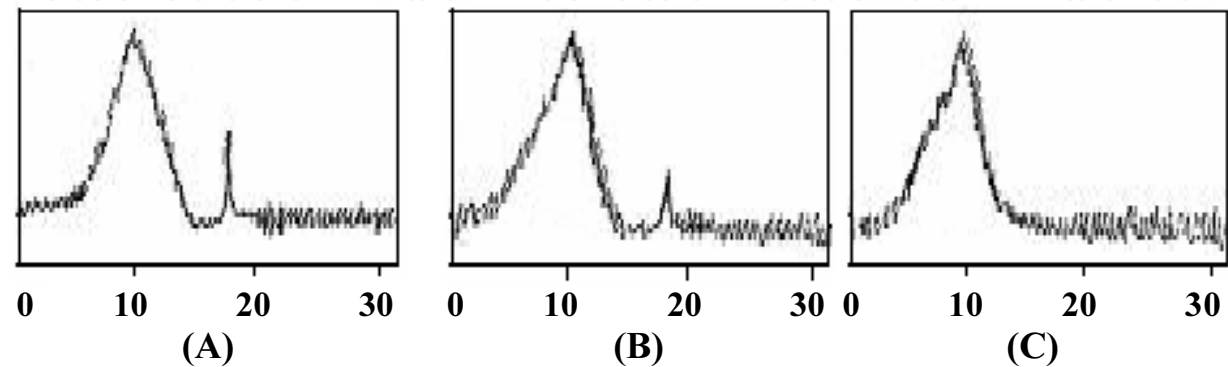


Figure 2. X-Ray of the prepared polymer samples PC₆ (A), PC₁₀ (B) and PC₁₂ (C).

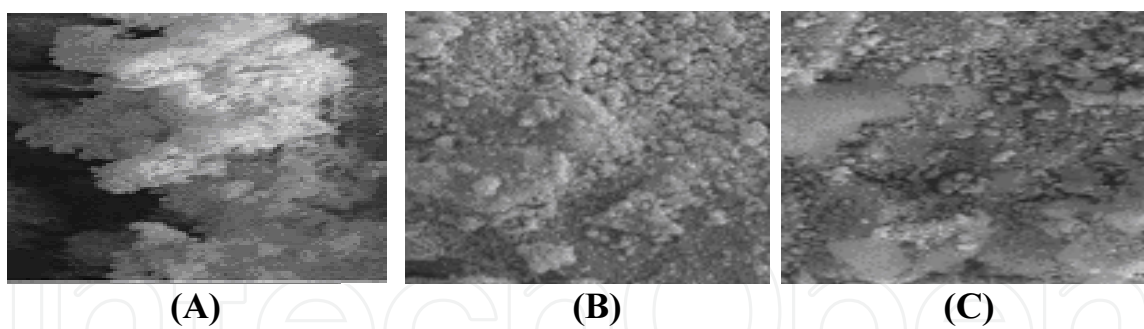
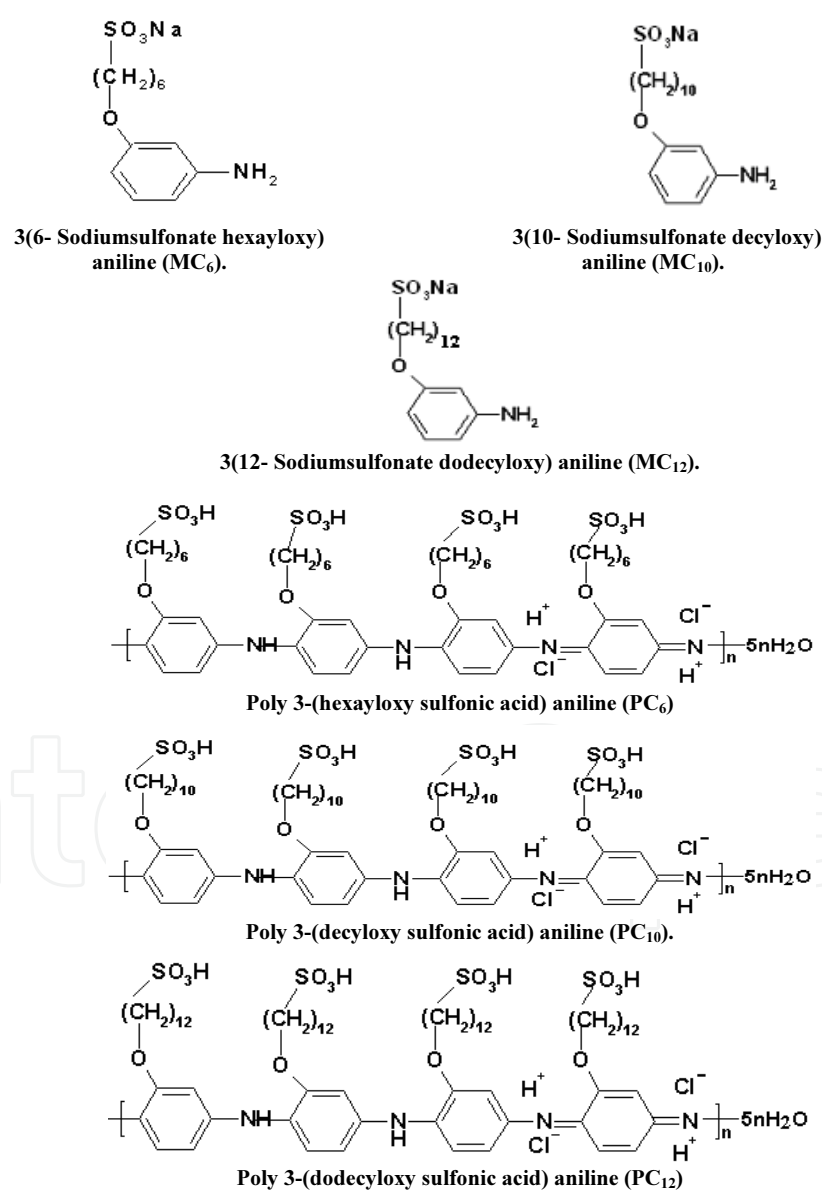


Figure 3. Electron microscope picture of the prepared polymer samples PC₆ (A), PC₁₀ (B) and PC₁₂ (C).



Scheme 3. Structure of monomeric surfactants and their polymers.

3.2. Critical micelle concentration and surface tension

3.2.1. Critical micelle concentration (CMC) of the prepared surfactants

The relations between the surface tension (γ) and the different concentrations of the prepared monomeric and their analogues polymeric surfactants at 25 °C are represented in figure (4). From figure (4), it is clear that the surface tension (γ) decreases with the increase of the prepared monomer and polymer concentrations which means also the increase of adsorption at air / water interface. The critical micelle concentration (CMC) of the prepared monomeric and their analogs polymeric surfactants was determined from the abrupt change in the slope of the corresponding plot of the surface tension (γ) versus concentration. The CMC results in Table (3) show that the CMC values decrease as the alkyl chain moiety increase from C₆-C₁₂ for all samples under investigation. The lower values of CMC for the prepared surfactants indicate the ability of these surfactants to dissolve in water solution which is due to the presence of the hydrophilic SO₃Na anionic group of the alkyl chain moiety, which increases the solvation of H₂O molecules surround it and increase the solubility of the surfactant molecule in solution. It was noticed that the CMC values of the prepared polymeric surfactants were lower than those of the prepared monomeric surfactants as shown in table (3). These results show that the polymeric surfactants have more hydrophilic and hydrophobic groups than those of the monomeric surfactants which enhance the solubility of the polymeric surfactants and lead to the decrease in CMC values.

Surfactant	T (°C)	CMC (mol/l)	$r_{\max} \times 10^{-11} (\text{mol.cm}^{-2})$	$A_{\min} \text{ nm}^2$	Π_{CMC}
MC ⁶	25	0.0005	4.85828	3.39548	7.80
MC ¹⁰		0.00025	8.46044	1.94980	17.80
MC ¹²		0.00025	2.82015	5.84941	25.80
PC ⁶		0.00025	2.82015	5.84941	8.80
PC ¹⁰		0.0001	2.82015	5.84941	18.80
PC ¹²		0.0001	8.46044	1.94980	26.80
MC ⁶	35	0.0025	2.96452	5.56454	4.00
MC ¹⁰		0.001	7.41131	2.22582	12.00
MC ¹²		0.0005	4.44678	3.70969	20.00
PC ⁶		0.001	4.44678	3.70969	4.00
PC ¹⁰		0.0005	5.92905	2.78227	13.00
PC ¹²		0.00025	2.96452	5.56454	21.00
MC ⁶	50	0.001	3.47450	4.74779	1.00
MC ¹⁰		0.00025	8.06754	2.04476	6.00
MC ¹²		0.00025	2.68918	6.13429	16.00
PC ⁶		0.00025	2.68918	6.13429	1.00
PC ¹⁰		0.0001	2.68918	6.13429	9.00
PC ¹²		0.0001	8.06754	2.04476	17.00

Table 3. Critical micelle concentration (CMC), effectiveness Π_{CMC} , Maximum surface Excess ($\Gamma_{\max}$) and Minimum area ($A_{\min}$) of monomeric surfactants (MC₆, MC₁₀ and MC₁₂) and their analogs polymeric surfactants.

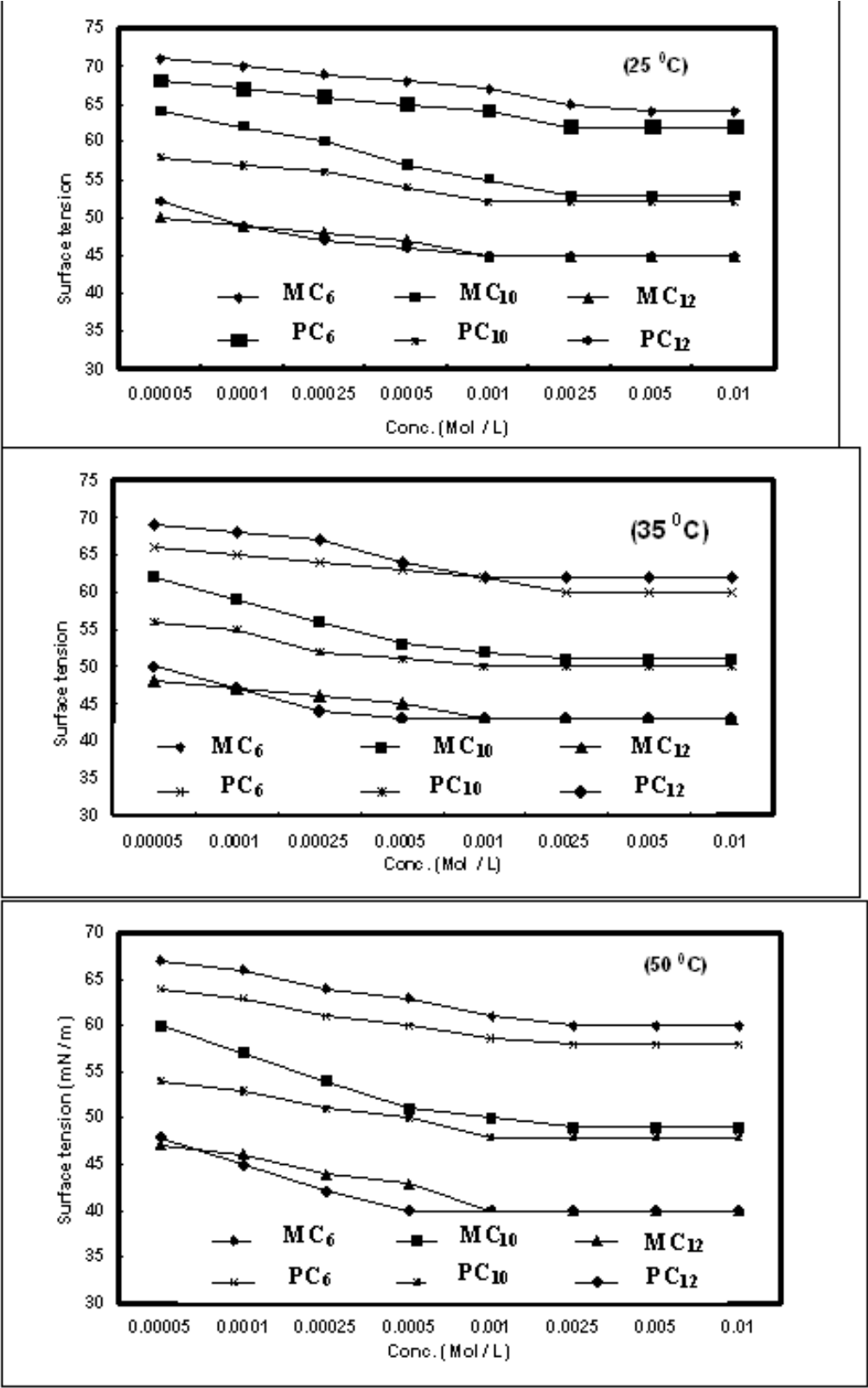


Figure 4. The relations between the surface tension (γ) and the different concentrations of the prepared monomeric and their analogues polymeric surfactants at 25, 35 and 50 °C

3.2.2. Surface parameters of the prepared surfactants

The surface parameters (effectiveness λ_{CMC}), maximum surface excess (Γ_{max}) and minimum area (A_{min}) of the surfactants were calculated according to Rosen et al. [90] and the data are summarized in table (3). These data show the good surface activity of the prepared surfactants and their ability for adsorption at air / water interface. The effectiveness values in table (3) show increasing with increasing of the alkyl chain moiety of the prepared monomeric and polymeric surfactants which give indication about the ability of these surfactants toward the adsorption at air / water interface and decrease the surface tension. Also, it is noticed that the effectiveness values of the prepared polymeric surfactants are higher than those of monomeric surfactants.

3.2.3. Thermodynamic parameters of micellization

Table (4) lists the free energies, ΔG_{mic} , enthalpies ΔH_{mic} and entropies, ΔS_{mic} of micellization for the prepared monomeric and polymeric surfactants in this study. These parameters were calculated using the following equations according to Rosen et al. [90].

$$\Delta G_{\text{mic}} = 2RT \ln \text{CMC} \quad (1)$$

$$d [\Delta G_{\text{mic}}] / dT = -\Delta S_{\text{mic}} \quad (2)$$

$$\Delta H_{\text{mic}} = \Delta G_{\text{mic}} + T\Delta S_{\text{mic}} \quad (3)$$

The ΔS_{mic} values in table (3) are all positive for the prepared surfactants, indicating increasing in randomness of the system upon transformation of the surfactant molecules into micelles. ΔH_{mic} in table (3) are significant factor in the process of micellization. The ΔH_{mic} values are positive for the prepared surfactants due to the endothermic solvation associated with micellization process. The data in table (4) show that the free energies ΔG_{mic} of micellization for the prepared monomeric and polymeric surfactants are always negative values, indicating that, micellization of such surfactants is a spontaneous process. It was noticed that the ΔG_{mic} values of the polymeric surfactants are higher than those of the monomeric surfactants which related to the more ability of the polymeric surfactants toward the micellization process than the monomeric surfactants.

3.2.4. Thermodynamic parameters of adsorption

The free energies ΔG_{ad} , enthalpies, ΔH_{ad} and entropies, ΔS_{ad} values of adsorption listed in table (4) were calculated by use of the following equations according to Rosen et al. [90].

$$\Delta G_{\text{ad}} = \Delta G_{\text{mic}} - (6.023 \times 10^{-1} \pi_{\text{cmc}} A_{\text{min}}) \quad (4)$$

$$\Delta S_{ad} = d \Delta G_{ad} / dT \tag{5}$$

$$\Delta H_{ad} = \Delta G_{ad} + T \Delta S_{ad} \tag{6}$$

According to the data given in table (5), the ΔG_{ad} values are negative, reflecting to the tendency of adsorption at liquid / air interface for the prepared surfactants. Comparing the data in table (5) it is noticed that the ΔG_{ad} values of the prepared monomeric and polymeric surfactants are higher than the G_{mic} values indicating that the prepared surfactants are favored the adsorption at air / water interface more than the micellization process. The ΔS_{ad} values are all positive this may reflect the greater freedom of motion of the hydrocarbon chains at the planar air / aqueous solution interface compared to that in the relatively cramped interior beneath the convex surface of the micelle. The most ΔH_{ad} values are less than ΔH_{mic} which indicates that less hydrogen bonds between the hydrophilic groups (SO_3Na) in the synthesized surfactants and water molecules are broken in the process of adsorption at the air/solution interface than in micellization process.

Name	T(°C)	$\Delta G^0_{mic} \text{ kJmol}^{-1}$	$\Delta S^0_{mic} \text{ kJmol}^{-1} \cdot K^{-1}$	$\Delta H^0_{mic} \text{ kJmol}^{-1}$	$\Delta G^0_{ad} \text{ kJmol}^{-1}$	$\Delta S^0_{ad} \text{ kJmol}^{-1} \cdot K^{-1}$	$\Delta H^0_{ad} \text{ kJmol}^{-1}$
MC ₆	25	-14.5788			-17.1930		
MC ₁₀		-16.8084			-19.1947		
MC ₁₂		-18.4950			-24.2596		
PC ₆		-16.8084			-18.7746		
PC ₁₀		-18.4950			-21.6455		
PC ₁₂		-20.1816			-29.1637		
MC ₆	35	-19.4419	0.06312		-20.2599		
MC ₁₀		-21.2148	0.06888		-22.6241		
MC ₁₂		-21.2148	0.06888		-28.9657		
PC ₆		-21.2148	0.06888		-22.6241		
PC ₁₀		-23.5586	0.07649		-28.1386		
PC ₁₂		-23.5586	0.07649		-26.0247		
MC ₆	50	-18.5294	0.13169	24.0051	-18.8154	0.05408	-1.3481
MC ₁₀		-22.2480	0.25564	60.3235	-22.9870	0.19313	39.3944
MC ₁₂		-22.2480	0.25564	60.3235	-28.1595	0.36555	89.9130
PC ₆		-22.2480	0.25564	60.3235	-22.6175	0.18082	35.7859
PC ₁₀		-24.7059	0.33757	84.3287	-28.0311	0.36127	88.6588
PC ₁₂		-24.7059	0.33757	84.3287	-26.7995	0.32022	76.6306

Table 4. Thermodynamic parameters of micellization and adsorption for the prepared monomeric surfactant and their analogs polymeric surfactants.

3.3. Corrosion inhibition of aluminium using monomeric and polymeric surfactant in 0.5 M HCl solution

Corrosion inhibitors play a very important role in protecting metals and alloys. Recently many new corrosion inhibitors have been developed. Some authors [91, 92] indicate that polymeric surfactants constitute an important class of corrosion inhibitor for this reason we investigated the inhibition properties of the three monomeric surfactants ;viz, 3-(6-sodium sulphonate hexayloxy) aniline (MC₆), 3-(10-sodium sulphonate decyloxy) aniline (MC₁₀), 3-(12-sodium sulphonate dodecyloxy) aniline (MC₁₂) and their analogues polymeric surfactants poly 3-(hexayloxy sulphonic acid) aniline (PC₆), poly 3-(decyloxy sulphonic acid) aniline (PC₁₀) and poly 3-(dodecyloxy sulphonic acid) aniline (PC₁₂) for the corrosion of aluminium in 0.5 M HCl solution by using weight loss (chemical) and potentiodynamic polarization (electrochemical) techniques under different experimental conditions. The conditions included the influence of the immersion time, structure, concentrations of the surfactants and the solution temperature on the rate of aluminium corrosion in 0.5M HCl solution.

In acid medium, the corrosion of aluminium proceeds via two possible reactions; the partial anodic reaction which can be represented by the dissolution of the metal, according to the following reaction:



and the partial cathodic reaction which can be represented by the overall hydrogen evolution reaction:



The monomeric surfactants have the same structure but differ in the terminal of alkyl chain length. In the aqueous acidic solution, each monomer is ionized to an amphiphilic anion and Na⁺ cation.

3.3.1. Weight loss technique

The weight loss (in mg cm⁻²) of aluminium in 0.5 M HCl solution with and without different concentrations of the monomeric surfactants (MC₆), (MC₁₀) and (MC₁₂) and their polymers (PC₆), (PC₁₀) and (PC₁₂) was plotted as a function of immersion time at 30 °C. The plots are shown in figure (5). It is clear from this figure that, the weight loss of aluminium in 0.5 M HCl solution increases linearly with the immersion time. The linear increase in the weight loss with time in the absence of additives have greater value than in the presence of the prepared monomeric and polymeric surfactants. The slope of each line (mg.cm⁻² min⁻¹) represents the corrosion rate of aluminium in these solutions. It is obvious that the rate of corrosion of aluminium decreases with increasing the immersion time under the prevailing conditions.

It follows from figure (6) that, the weight loss (i.e., the corrosion rate) is suppressed in the presence of the additives (the monomers and their corresponding polymers). These results reveal that the addition of each compound hinders the acid attack on the metal surface and prevent aluminium from dissolution, so these compounds act as corrosion inhibitors. The decrease in weight loss and hence the suppression in the rate of corrosion enhances with increasing the concentration of each additive. On the other hand, the weight loss and consequently the corrosion rate of aluminium in 0.5 M HCl solution in the absence and presence of surfactant increase with a rise in solution temperature.

The inhibition efficiency values (P %) of these surfactants at different inhibitor concentrations and temperatures were calculated using the following equation [93]:

$$P\% = 100 \times \left[1 - \left(W/W^0 \right) \right] \quad (9)$$

Where W^0 and W are the weight loss per unit time in the absence and presence of definite inhibitor concentration, respectively. The calculated values of (P%) are listed in table (5). It is noticed from the obtained data that:

1. At a given temperature, the inhibition efficiency (P %) of each inhibitor increases with increasing inhibitor concentration and reaches a maximum at certain critical concentration. The critical concentration is 8.47×10^{-5} mol/L for MC_6 , 1.43×10^{-5} mol/L for MC_{10} , 1.32×10^{-5} mol/L for MC_{12} and 4.11×10^{-6} mol/L for PC_6 , 3.44×10^{-6} mol/L for PC_{10} , 3.19×10^{-6} mol/L for PC_{12} . Beyond the critical concentration, the inhibition efficiency tends to decrease slightly and finally achieves steady state values [94].

At a given inhibitor concentration, the inhibition efficiency (P%) of each inhibitor decrease with the increasing of the temperature.

2. The inhibition efficiency (P %) increases with increasing the number of methylene group in the side terminal group, since the values of (P %) decrease in the following order: $MC_{12} < MC_{10} < MC_6$ for the monomers and also in case of polymers: $PC_{12} < PC_{10} < PC_6$. But, the inhibition efficiency of the monomers are lower than those of their analogues polymers.

The inhibition action of these surfactants is due to their adsorption and formation of barrier film on the metal surface which separates the metal from direct contact with corrosive medium and to protect the metal against corrosion. These monomers and their analogues polymers are characterized by the presence of several adsorption centers as N, S, and O atoms and aromatic rings in the molecule. Adsorption might arise via electrostatic interaction between the adsorption centers and the charged metal surface suggesting that the adsorption is of physical-type.

The increase in the inhibition efficiency observed with the increasing of each inhibitor concentration (before the critical concentration) indicating that more inhibitor species are adsorbed on the metal surface. This means the increase of the surface metal coverage.

It is found that under similar conditions the inhibition efficiency of the three monomers increases in the order: $MC_6 > MC_{10} > MC_{12}$. Since the three monomers have the same structure unit different number of carbon atoms in the alkyl chain, the increase of inhibition efficiency could be due to an increase in the number of carbon atoms in the alkyl chain. The obtained data are in good agreement with what found by Maitra. A., et.al [95] and Al-Sabagh et.al, [96]. The action of the long alkyl chain is to stabilize the adsorption of the ionic group cohesion on the metal surface through van-der Waal forces which allow a more closely packed layer at the metal solution interface [97]. Higher efficiency of the polymers than those of their corresponding monomers could be due to the large size of the polymers which cover wide area of the metal surface and also to the presence of more adsorption centers in the polymers than their respective monomers [98].

In order to get more insight on the inhibition properties of the tested surfactants, the contact angles between the adsorbed inhibitors and aluminium surface in 0.5M HCl solution were measured. It is known that the contact angle (C.A) varies from 0° (perfectly wetting) to 180° (completely nonwetting). The measured contact angles in 0.5 M HCl solution containing different concentrations of monomeric surfactant and their analogues polymers at 30°C are given in table (4). The obtained data proved the adsorption of these surfactants on the metal surface [99]. The data demonstrate that the inhibition efficiency of the inhibitors increases as their contact angles of the adsorption on aluminium surface decreases. Further more, it is clear that in all cases, the contact angles in the presence of polymers are lower than those in the presence of their respective monomers confirming the suggestion that the polymers used are more effective than their monomers for inhibition of aluminium corrosion in acid medium.

MC ₆				MC ₁₀				MC ₁₂			
C(M)	P % (WT)	P % (Pot)	C.A	C(M)	P % (WT)	P % (Pot)	C.A	C(M)	P % (WT)	P % (Pot)	C.A
3.38×10^{-6}	20.4	18.7	98.6	2.84×10^{-6}	26.2	26.6	29.07	2.64×10^{-6}	28.1	25.8	83.16
1.02×10^{-5}	24.5	25.5	93.2	8.54×10^{-5}	42.2	44.0	25.97	7.91×10^{-6}	43.5	42.0	50.12
1.69×10^{-5}	27.3	28.9	73.4	1.42×10^{-5}	48.1	49.9	8.52	1.31×10^{-5}	55.0	56.5	6.82
3.38×10^{-5}	31.1	32.2	68.6	2.84×10^{-5}	47.0	46.4	10.33	2.64×10^{-5}	49.0	50.0	12.34
PC ₆				PC ₁₀				PC ₁₂			
C(M)	P % (WT)	P % (Pot)	C.A	C(M)	P % (WT)	P % (Pot)	C.A	C(M)	P % (WT)	P % (Pot)	C.A
8.12×10^{-7}	30.4	25.8	91.5	6.87×10^{-7}	32.7	34.9	61.22	6.38×10^{-7}	35.5	36.2	76.91
2.43×10^{-6}	44.7	42.0	69.8	2.06×10^{-6}	46.7	50.8	48.01	1.91×10^{-6}	48.6	50.9	47.12
4.06×10^{-6}	56.1	56.5	0.0	3.43×10^{-6}	59.3	58.3	0.0	3.19×10^{-6}	71.3	69.0	10.78
8.12×10^{-6}	49.7	53.5	12.1	6.87×10^{-6}	53.0	54.0	22.9	6.38×10^{-6}	56.1	55.1	21.45
WT=Weight loss technique				Pot = Polarization technique				C.A= Contact angle			

Table 5. The variation of the inhibition efficiency(P%)and the contact angle (C.A) of aluminium with different inhibitor concentrations using weight loss and polarization measurements of the corrosion reaction at 30°C .

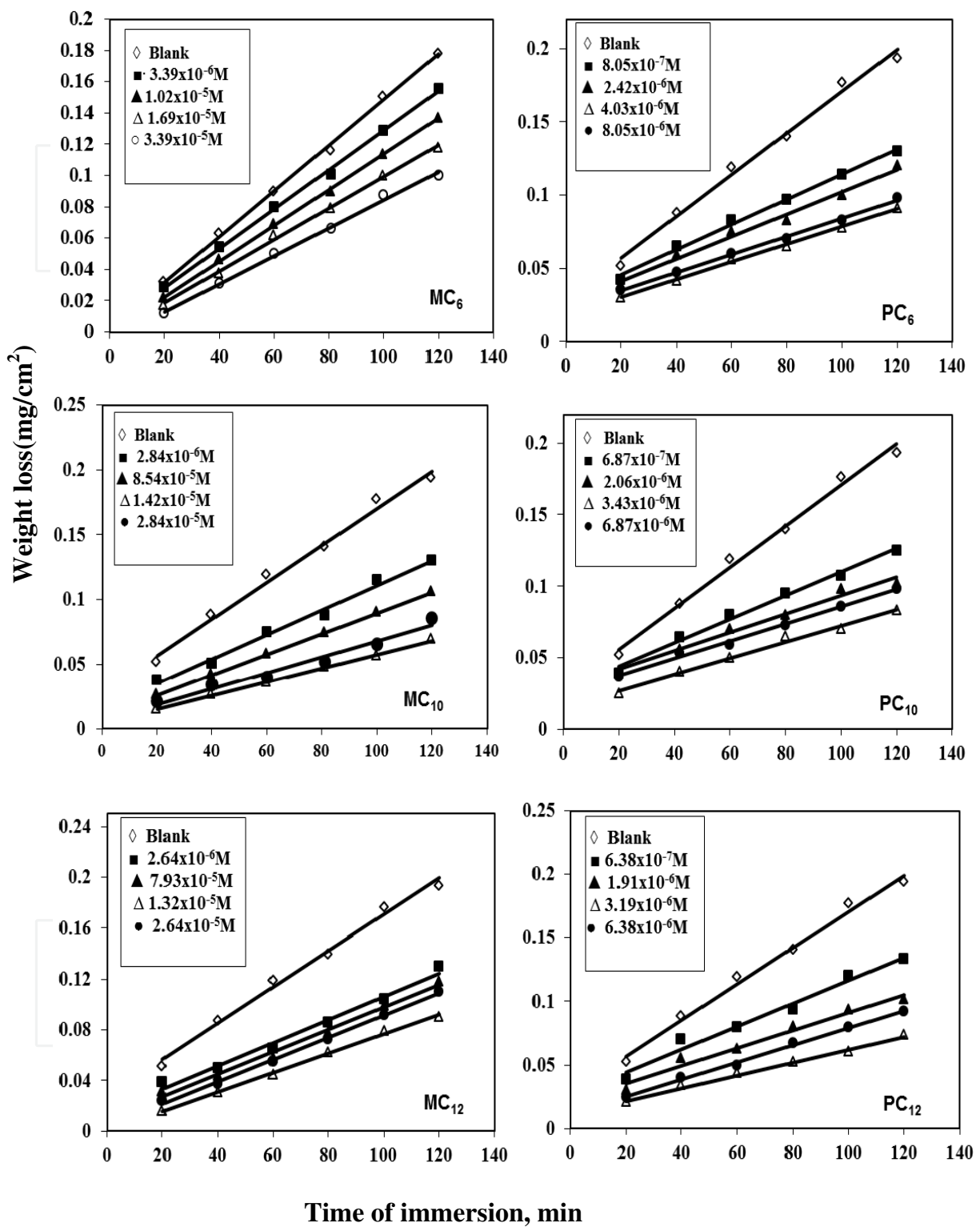


Figure 5. Weight loss vs. immersion time for Al in 0.5 M HCl solution with and without the addition of different concentrations of monomeric and polymeric surfactant at 30 °C.

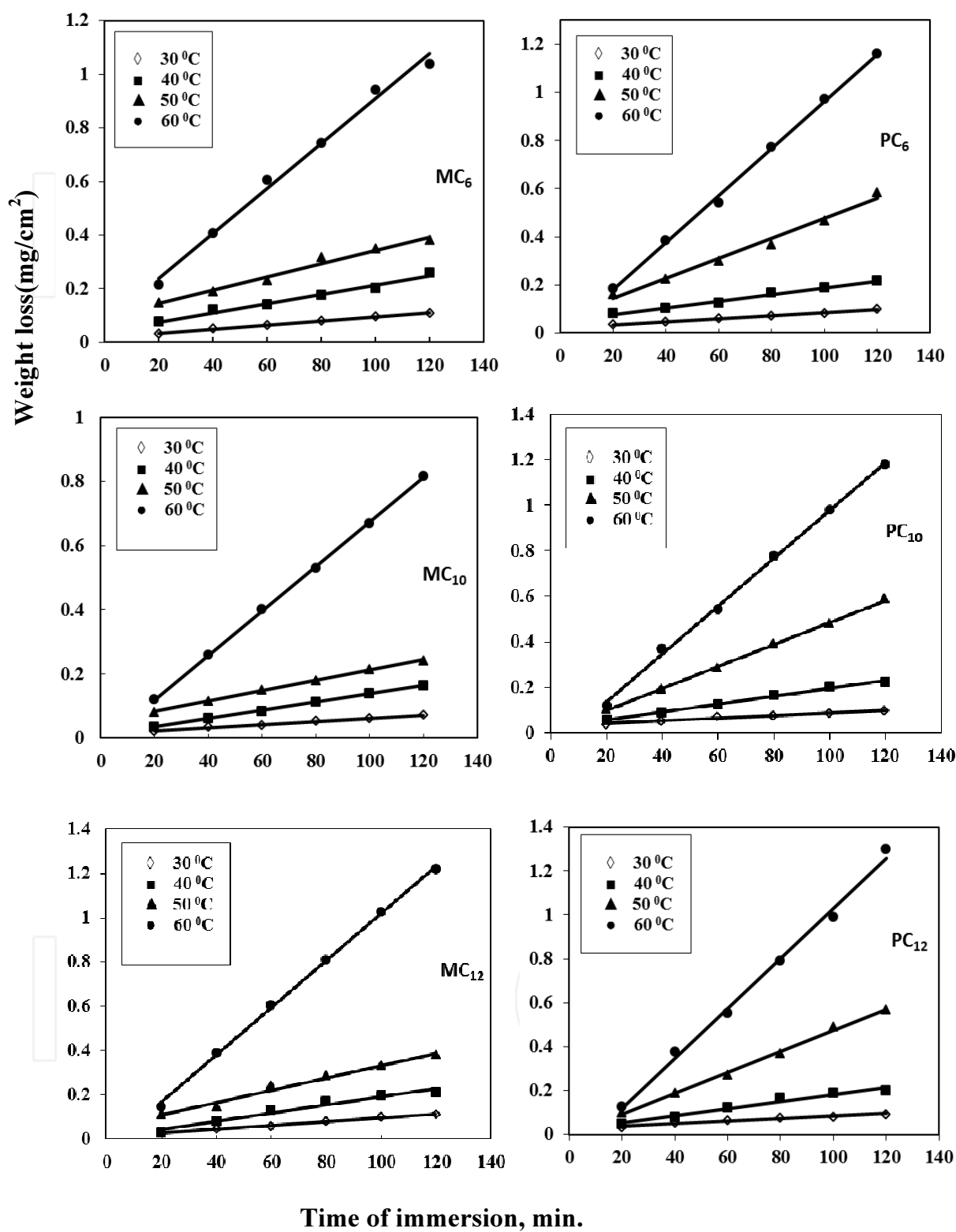


Figure 6. Weight loss vs. immersion time for Al in 0.5 M HCl solution containing 10 ppm of monomeric and polymeric surfactant at different temperatures.

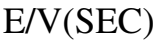
3.3.2. Potentiodynamic polarization measurements

Potentiodynamic cathodic and anodic polarization curves for aluminium in 0.5 M HCl solution in the absence and presence of various concentrations of the prepared monomeric surfactants and their analogues polymers at 30^o C are shown in figure (7). The curves were swept from -1.05 to 0.6 mV with scan rate 25 mVs⁻¹ at 30^oC. On the other hand, figure (8) illustrate the influence of temperature on the polarization curves of aluminium in 0.5 M HCl containing 3.39x10⁻⁵ ML⁻¹ MC₆, 2.84x10⁻⁵ ML⁻¹ of MC₁₀, 2.64x10⁻⁵ ML⁻¹ of MC₁₂, 8.05x10⁻⁶ ML⁻¹ of PC₆, 6.87x10⁻⁶ ML⁻¹ of PC₁₀ and 6.38x10⁻⁶ ML⁻¹ of PC₁₂. The figure display that the presence of inhibitor in 0.5 M HCl solution decreases both the cathodic and anodic overpotentials indicating that these surfactants inhibit both the partial hydrogen evolution and the partial dissolution of aluminium. The anodic curves are more polarized than the cathodic curves indicating that these inhibitors are considered as mixed-type inhibitors with anodic predominance. The inhibition action of the prepared monomeric surfactants and their analogues polymers are related to their physical adsorption on the metal surface. The adsorption of the inhibitors modifies the interface between the solution and metal surface, consequently both of the anodic, cathodic overpotential and the corresponding current densities decreases. These results reveal that the inhibitors act by simply blocking the available surface area [100]. In other words, the inhibitor decreases the surface area for corrosion without affecting the mechanism of the partial corrosion reactions and only causes inactivation of a part of surface area with respect to the corrosive medium. Moreover, it is observed that the value of (*i*_{corr}) in the absence and presence of inhibitor enhances with an increase of temperature. Such behavior indicates that the corrosion rate of aluminium in 0.5M HCl solution in all cases increases with raising temperature.

Since, the corrosion current density (*i*_{corr}) is directly proportional to the rate of corrosion, the inhibition efficiency (P %) of each inhibitor under the prevailing conditions was calculated using the following equation [101].

$$P\% = 100 \times \left[1 - \frac{(i_{\text{corr}})_I}{(i_{\text{corr}})_0} \right] \quad (10)$$

Where (*i*_{corr})₀ and (*i*_{corr})_I are the corrosion current densities in uninhibited and inhibited solution respectively. The calculated (P %) values are given in table (4). It follows from these data that at given temperature, the values of (P%) of monomers and their analogues polymers increase gradually with increasing their concentrations up to their critical concentrations. Beyond the critical concentrations, the values of (P%) decrease slightly and then tend to go to steady state values. The inhibition efficiency of the polymers are higher than those of respective monomers. Also, the inhibition efficiency increases with increasing the side chain length of the surfactants. By comparing the values of (P%) of the inhibitors obtained from weight loss measurements with those obtained from polarization measurements, it is seen that the data are comparable and in good agreements. The slight difference exist between these data may be attributed to the short time in case of polarization measurements.



in 0.5 M HCl solution with a scan rate of 25 mVs⁻¹ at 30 °C.

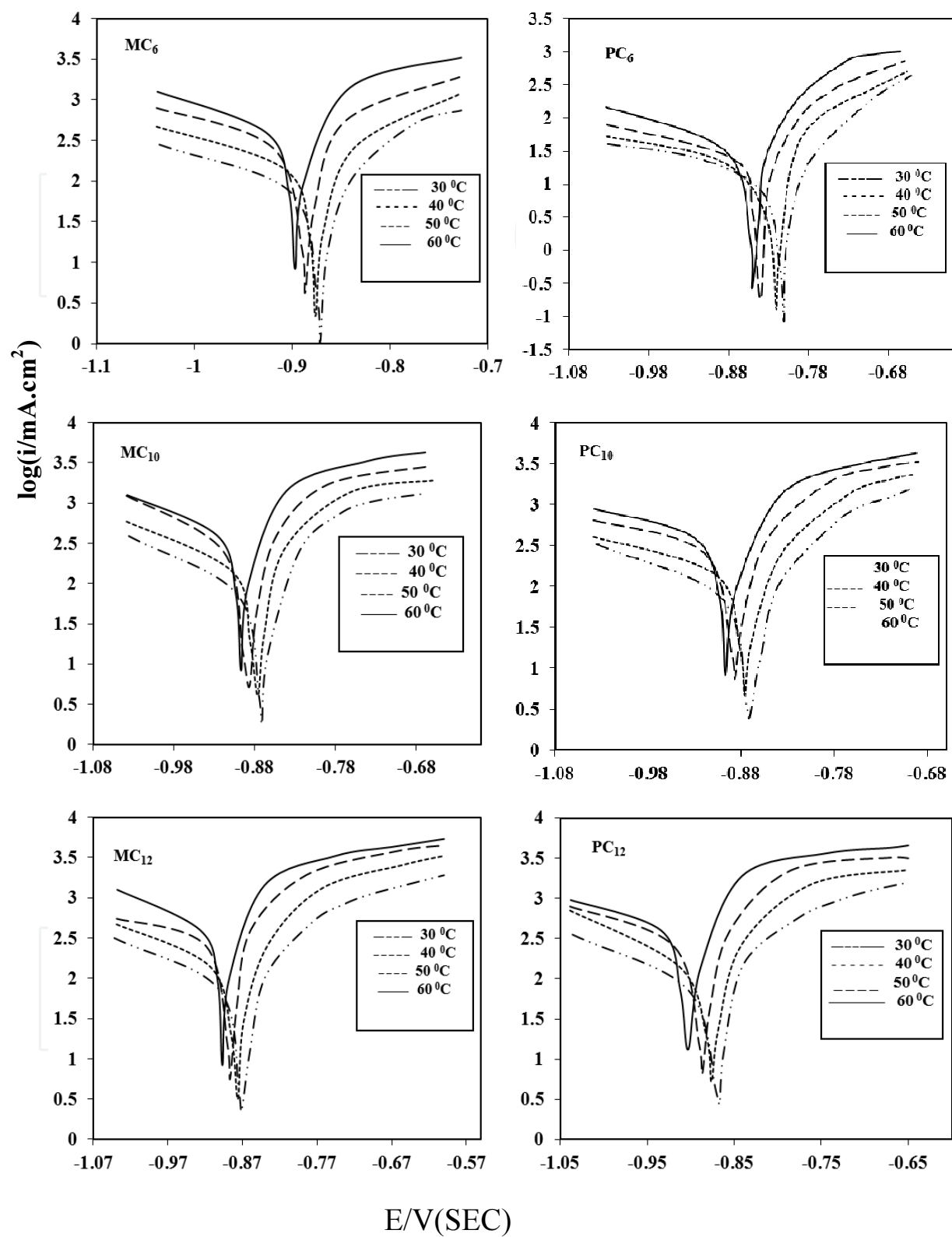


Figure 8. Effect of temperature on the cathodic and anodic polarization of Al in 0.5 M HCl in the presence of 10 ppm of monomeric surfactants and their polymers with a scan rate of 25 mVs⁻¹.

3.3.3. Activation parameters

The corrosion rate for each concentration of monomeric and polymeric surfactant 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 [102]:

$$\text{Logarithm of the corrosion rate} = -E_a / 2.303 RT + A \quad (11)$$

Where E_a is the apparent effective activation energy, R is the universal gas constant, and A is the Arrhenius pre-exponential factor. The values of E_a in the absence and presence of each concentration of both surfactants were calculated and are tabulated in tables (6,7).

An alternative formula of the Arrhenius equation is the transition state equation [102]:

$$\text{Rate} = RT/Nh \exp(\Delta S^0/R) \exp(-\Delta H^0/RT) \quad (12)$$

Where h is Planck's constant, N is Avogadro's number, ΔS^0 is the entropy of the activation, and ΔH^0 is the enthalpy of activation. The plot of the $\log(\text{corrosion rate}/T)$ versus $1/T$ gives a straight line with a slope of $(-\Delta H^0/2.303R)$, from which the values of ΔH^0 were calculated; and are listed in tables (6, 7). The data in tables (5, 7) reveal that the addition of both monomeric and polymeric surfactants inhibitors leads to increase of the values of both E_a and ΔH^0 . This enhancement may be due to the adsorption of surfactant inhibitors on the Al surface leading to an increase in the energy barrier of the corrosion reaction as the concentrations of the inhibitors increased. This means that the corrosion reactions will be further pushed to surface sites that are characterized by progressively higher values of E_a as the concentration of the inhibitor become larger [103]. Also the values of E_a in presence of the polymers are higher than those in presence of the monomers. The positive sign of the ΔH_a indicates that the corrosion process of aluminium in HCl solution is endothermic. Addition of inhibitor to the acid solution increases the values of ΔH_a to an extent depends on the type and concentration of inhibitor. It observed that the values of E_a and ΔH_a obtained from the two techniques are comparable.

MC ₆			MC ₁₀			MC ₁₂		
C(M)	E _a kJmol ⁻¹	ΔH _a kJmol ⁻¹	C(M)	E _a kJmol ⁻¹	ΔH _a kJmol ⁻¹	C(M)	E _a kJmol ⁻¹	ΔH _a kJmol ⁻¹
Blank	57.9	55.5	Blank	57.9	55.5	Blank	57.9	55.5
3.38 x 10 ⁻⁶	61.6	57.9	2.84 x 10 ⁻⁶	62.3	59.6	2.64 x 10 ⁻⁶	64.5	62.3
1.02 x 10 ⁻⁵	64.2	62.8	8.54 x 10 ⁻⁵	67.9	64.6	7.91 x 10 ⁻⁶	67.3	65.1
1.69 x 10 ⁻⁵	67.2	64.5	1.42 x 10 ⁻⁵	70.2	68.8	1.31 x 10 ⁻⁵	72.8	70.0
3.38 x 10 ⁻⁵	69.1	68.3	2.84 x 10 ⁻⁵	69.3	67.0	2.64 x 10 ⁻⁵	70.1	68.5
PC ₆			PC ₁₀			PC ₁₂		

C(M)	E _a kJmol ⁻¹	ΔH _a kJmol ⁻¹	C(M)	E _a kJmol ⁻¹	ΔH _a kJmol ⁻¹	C(M)	E _a kJmol ⁻¹	ΔH _a kJmol ⁻¹
Blank	57.9	55.5	Blank	57.9	55.5	Blank	57.9	55.5
8.12 x 10 ⁻⁷	63.5	62.10	6.87 x 10 ⁻⁷	66.7	63.51	6.38 x 10 ⁻⁷	66.63	64.10
2.43 x 10 ⁻⁶	69.4	69.30	2.06 x 10 ⁻⁶	70.9	68.95	1.91 x 10 ⁻⁶	73.73	70.50
4.06 x 10 ⁻⁶	80.6	77.60	3.43 x 10 ⁻⁶	81.4	78.90	3.19 x 10 ⁻⁶	82.5	80.15
8.12 x 10 ⁻⁶	77.7	75.80	6.87 x 10 ⁻⁶	78.6	77.00	6.38 x 10 ⁻⁶	80.11	78.60

Table 6. Effect of inhibitor concentrations on thermodynamic parameters for aluminium corrosion in 0.5 M HCl solution (obtained from Weight loss technique).

MC ₆			MC ₁₀			MC ₁₂		
C(M)	E _a kJmol ⁻¹	ΔH _a kJmol ⁻¹	C(M)	E _a kJmol ⁻¹	ΔH _a kJmol ⁻¹	C(M)	E _a kJmol ⁻¹	ΔH _a kJmol ⁻¹
Blank	57.3	54.7	Blank	57.3	54.7	Blank	57.3	54.7
3.38 x 10 ⁻⁶	63.2	60.6	2.84 x 10 ⁻⁶	61.7	59.2	2.64 x 10 ⁻⁶	62.6	59.9
1.02 x 10 ⁻⁵	65.7	63.2	8.54 x 10 ⁻⁵	68.7	66.1	7.91 x 10 ⁻⁶	66.4	64.3
1.69 x 10 ⁻⁵	66.8	64.1	1.42 x 10 ⁻⁵	70.1	65.4	1.31 x 10 ⁻⁵	72.0	68.9
3.38 x 10 ⁻⁵	68.2	65.5	2.84 x 10 ⁻⁵	68.9	67.4	2.64 x 10 ⁻⁵	69.8	67.6

PC ₆			PC ₁₀			PC ₁₂		
C(M)	E _a kJmol ⁻¹	ΔH _a kJmol ⁻¹	C(M)	E _a kJmol ⁻¹	ΔH _a kJmol ⁻¹	C(M)	E _a kJmol ⁻¹	ΔH _a kJmol ⁻¹
Blank	57.3	54.7	Blank	57.3	54.7	Blank	57.3	54.7
8.12 x 10 ⁻⁷	64.0	61.3	6.87 x 10 ⁻⁷	65.1	62.2	6.38 x 10 ⁻⁷	65.3	62.6
2.43 x 10 ⁻⁶	71.0	68.4	2.06 x 10 ⁻⁶	71.3	68.7	1.91 x 10 ⁻⁶	72.5	68.9
4.06 x 10 ⁻⁶	78.2	75.6	3.43 x 10 ⁻⁶	79.4	75.8	3.19 x 10 ⁻⁶	80.4	76.8
8.12 x 10 ⁻⁶	75.1	72.4	6.87 x 10 ⁻⁶	74.8	71.4	6.38 x 10 ⁻⁶	76.2	70.2

Table 7. Effect of inhibitor concentrations on thermodynamic parameters for aluminium corrosion in 0.5 M HCl solution (obtained from Polarization technique)

3.3.4. Adsorption isotherm

In order to gain more information about the mode of adsorption of the inhibitors on the metal surface at different concentrations and temperatures, the data obtained from weight loss and potentiodynamic polarization techniques have been tested with Frumkin adsorption isotherm [104]. Frumkin isotherm was found to fit well with our experimental data. The adsorption isotherm relationship of Frumkin isotherm is represented by the following equation:

$$\ln[\theta/C(1-\theta)] = \ln K_{\text{ads}} + 2a\theta \quad (13)$$

Where "a" the lateral interaction term describing the molecular interactions in the adsorption layer and the heterogeneity of the surface which reflect the steepness of the adsorption isotherm. Figure (9) represent curves fitting of monomeric and their analogues polymeric surfactants using weight loss, while figure (10) illustrate the data obtained from polarization measurements.

The average thermodynamic parameters viz; enthalpy and entropy of the adsorption process (ΔH_{ads} and ΔS_{ads}) of inhibitor adsorption on the aluminium surface in 0.5 M HCl solution at different temperatures were determined from the slopes and intercepts of the lines of $\log K_{\text{ads}}$ vs. $1/T$ according to the following equation [105]:

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

The free energy change ΔG_{ads} of adsorption process was calculated from the equation: $\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S_{\text{ads}}$.

Straight lines obtained when $\log K_{\text{ads}}$ were plotted against $1/T$ for weight loss and polarization data; with slopes of $(-\Delta H_{\text{ads}}/2.303R)$ and intercept $\Delta S_{\text{ads}}/2.303 R$. The calculated values of ΔH_{ads} , ΔS_{ads} and ΔG_{ads} from weight loss and polarization measurements are listed in tables (8) and (9) respectively. Inspection of these data reveal that, the values of ΔG_{ads} in all cases are negative and less than -40 kJmol^{-1} suggesting that the nature of inhibitor adsorption is mainly physisorption and spontaneous [106, 107]. The negative values of ΔH_{ads} imply that the adsorption process is an exothermic process [108]. The magnitude of the values of ΔH_{ads} , ΔS_{ads} are characteristic of the occurrence of replacement process during adsorption of surfactants on aluminium surface [109]. It is clear that the values of ΔH_{ads} , ΔS_{ads} and ΔG_{ads} obtained from weight loss measurements are in accordance with the respective values obtained from polarization measurements.

Surfactant	$-\Delta H_{\text{ads}} \text{ kJmol}^{-1}$	$-\Delta S_{\text{ads}} \text{ kJmol}^{-1}\text{K}^{-1}$	$-\Delta G_{\text{ads}} \text{ kJmol}^{-1}$
MC ₆	109.6	0.232	39.30
MC ₁₀	48.63	0.052	32.87
MC ₁₂	65.95	0.1105	32.47
PC ₆	45.11	0.0215	38.60
PC ₁₀	51.95	0.0491	37.08
PC ₁₂	46.32	0.0298	37.28

Table 8. The thermodynamic parameters of the adsorption process obtained by applying Frumkin isotherm from the weight loss data of Al in 0.5 M HCl.

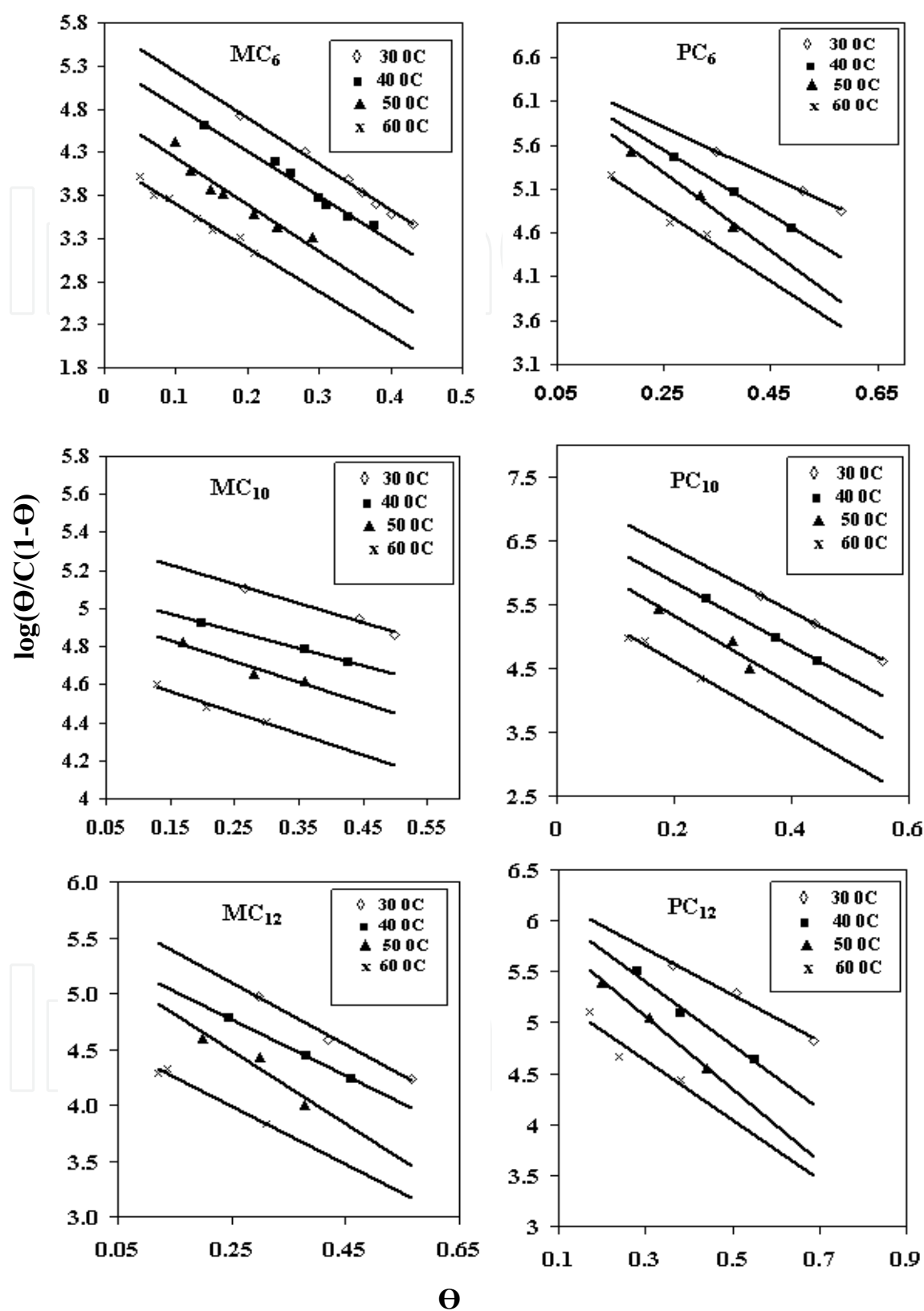


Figure 9. Curve fitting of weight loss data of Al in 0.5 M HCl solution containing various concentrations of monomeric and polymeric surfactant to Frumkin isotherm at different temperatures.

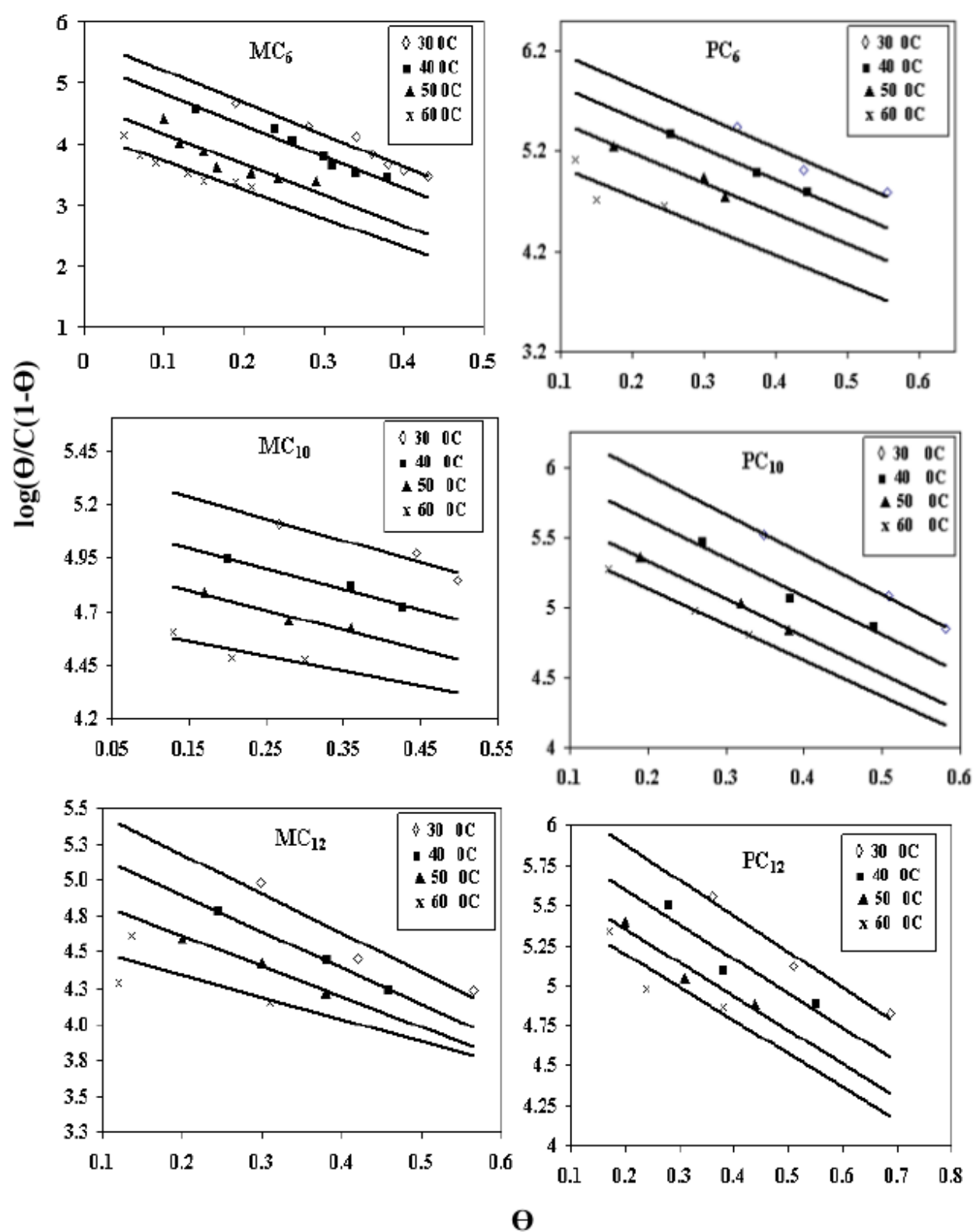


Figure 10. Curve fitting of polarization data of Al in 0.5 M HCl solution containing various concentrations of monomeric and polymeric surfactant to Frumkin isotherm at different temperatures.

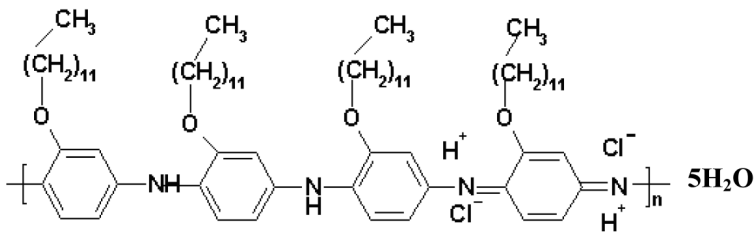
Surfactant	$-\Delta H_{\text{ads}} \text{ kJmol}^{-1}$	$-\Delta S_{\text{ads}} \text{ kJmol}^{-1}\text{K}^{-1}$	$-\Delta G_{\text{ads}} \text{ kJmol}^{-1}$
MC ₆	103.4	0.222	37.83
MC ₁₀	45.76	0.048	31.258
MC ₁₂	67.21	0.1128	33.01
PC ₆	44.03	0.0216	37.48
PC ₁₀	52.85	0.0504	37.59
PC ₁₂	45.57	0.0301	36.45

Table 9. The thermodynamic parameters of the adsorption process obtained by applying Frumkin isotherm from the polarization data of aluminum in 0.5 M HCl.

3.3.5. Effect of terminal side chain of polymeric surfactant on the inhibition efficiency of aluminium corrosion in 0.5M HCl solution

The previous results show that, the inhibition efficiency of the monomeric and polymeric surfactants increases in the order: MC₆> MC₁₀> MC₁₂>PC₆> PC₁₀> PC₁₂. The inhibition efficiency of PC₁₂ no more than (69%), however these surfactants are characterized by the presence of several adsorption centers as N, S, and O atoms and aromatic rings in the molecule. This may be due to the repulsion between the terminal side -SO₃H group and double layer exist on Al surface in 0.5 M HCl solution. To overcome this phenomenon, the -SO₃H group replaced by hydrogen atom as in poly 3-dodocyloxy aniline.

The suggested structure of poly 3-dodocyloxy aniline as mentioned by S. M. Sayyah et al [110], is given in scheme (4).



Scheme 4. Structure of poly 3-dodocyloxy aniline.

3.3.5.1. Potentiodynamic polarization measurements

Figure (11) shows the potentiodynamic cathodic and anodic polarization curves for Al in 0.5 M HCl in the absence and presence of different concentrations of PC₁₁R at 30°C. The curves were swept from -1.05 to 0.6 mV with scan rate 25 mVs⁻¹. The curves infer that the presence of PC₁₁R in acid solution increases both the cathodic and anodic overpotentials (mainly the anodic overpotential). The obtained results indicate that, this polymer inhibit both the partial cathodic hydrogen evolution and the partial anodic dissolution of aluminium reaction. The anodic curves are more polarized than the cathodic curves indicating that, this inhibitor is considered as mixed-type inhibitor with anodic predominance.

Figure (12) illustrates the potentiodynamic polarization curves for Al in 0.5M HCl solution containing 8.04×10^{-6} Mole $PC_{11}R$ at different temperatures. It is observed that the current corrosion density (i_{corr}) in the absence and presence of the inhibitor increased with raising the temperature.

Figure (12) shows the variation of inhibition efficiency (P%) with different concentrations of PC_{12} and $PC_{11}R$ at different temperatures. Inspection of these data reveal that:

1. At a given temperature, the inhibition efficiency (P%) of this polymer increases with increasing its concentration as a result of increasing the surface coverage, thus the Al surface is efficiently separated from the corrosion medium. The results also reveal that when the concentration of this polymeric surfactant reaches a certain critical value, the inhibition efficiency slightly increases with concentration and tend to reach a steady state value. Such behavior denoted that the amount of adsorption and coverage does not change and the corrosion of Al tends to achieve equilibrium. At high concentrations (Close to its CMC, the surfactant molecules tend to form micelles in solution rather than adsorbing on metal surface).
2. At given, inhibitor concentration, the inhibition efficiency of $PC_{11}R$ decreases with an increase in temperature. This could be due to the increase in the corrosivity of medium and /or desorption of some inhibitor molecules from Al surface. The desorption process leads to a decrease in the surface coverage indicating that the adsorption is of physical nature.
3. Under identical condition, it is found that the inhibition efficiency of $PC_{11}R$ is higher than that of PC_{12} . This may be assigned to the elimination of the terminal $-SO_3H$ groups in PC_{12} . The presence of terminal $-CH_3$ groups in polymer $PC_{11}R$ stabilizes the inhibition efficiency and may reduce repulsion between anionic head with similar charge as in PC_{12} . This allows a closed layer to form more easily and hence higher inhibition efficiency.

The apparent activation energy (E_a), enthalpy and entropy for corrosion of Al in the presence of $PC_{11}R$ was calculated using Arrhenius and alternative Arrhenius equations (11,12). The data of activation are calculated and tabulated in table (10), from which it is obvious that the values E_a , ΔH_a and ΔS_a of the corrosion of Al in the presence of the inhibitor are higher than those of uninhibited solution and increase with an increase in the inhibitor concentration indicating that more energy barrier for the corrosion reaction in the presence of inhibitor is attained.

Concentration ppm	E_a kJ.mol ⁻¹	ΔH kJmol ⁻¹	ΔS kJmol ⁻¹
Blank	57.30	54.70	0.381
1	71.61	68.97	0.267
3	71.99	69.36	0.268
5	99.37	96.88	0.039
10	109.31	106.65	0.016

Table 10. Effect of inhibitor ($PC_{11}CH_3$) concentrations on thermodynamic parameters for aluminium corrosion in 0.5 M HCl solution.

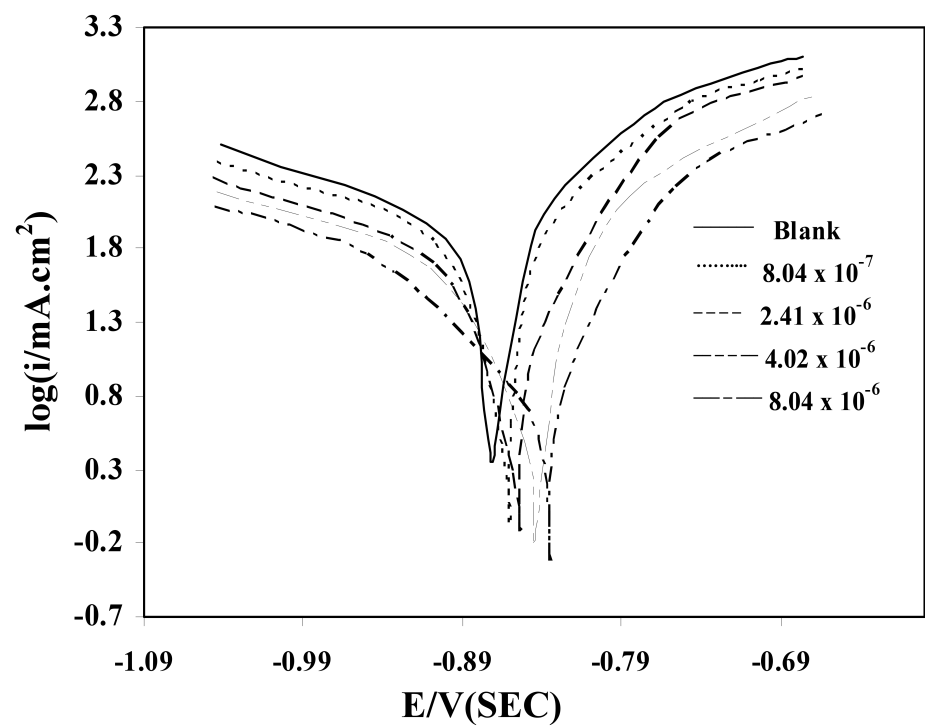


Figure 11. Effect of PC_{11}R concentration on the anodic and cathodic polarization of Al in 0.5 M HCl with a scan rate of 25 mVs^{-1} at 30°C

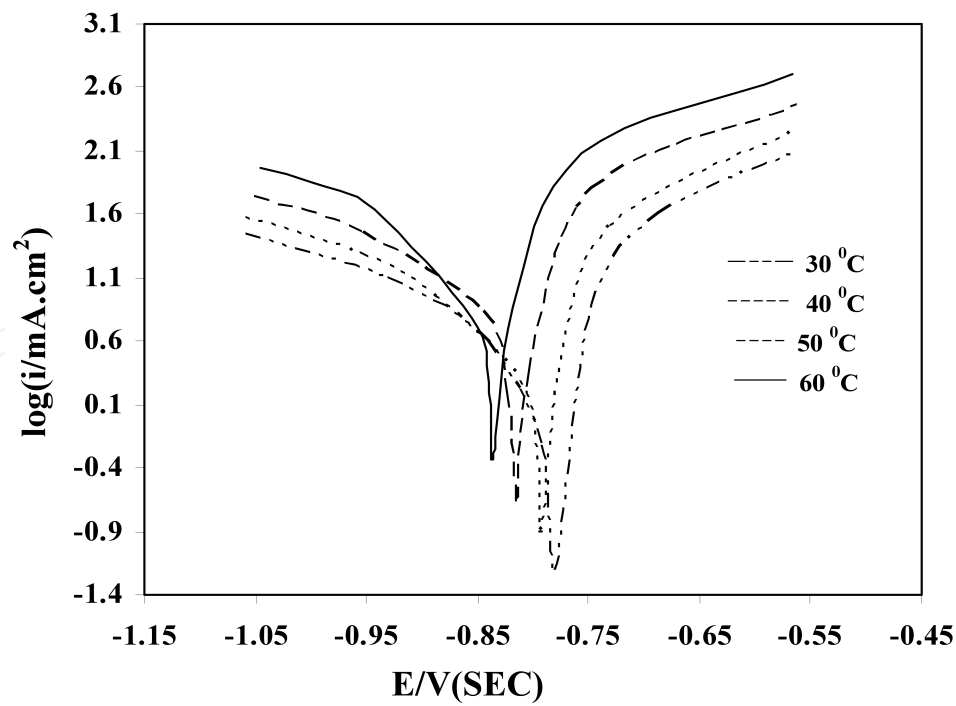


Figure 12. Effect of temperature on the anodic and cathodic polarization of aluminium in 0.5 M HCl in the absence and presence 8.04×10^{-6} Mole of PC_{11}R with a scan rate of 25 mVs^{-1} .

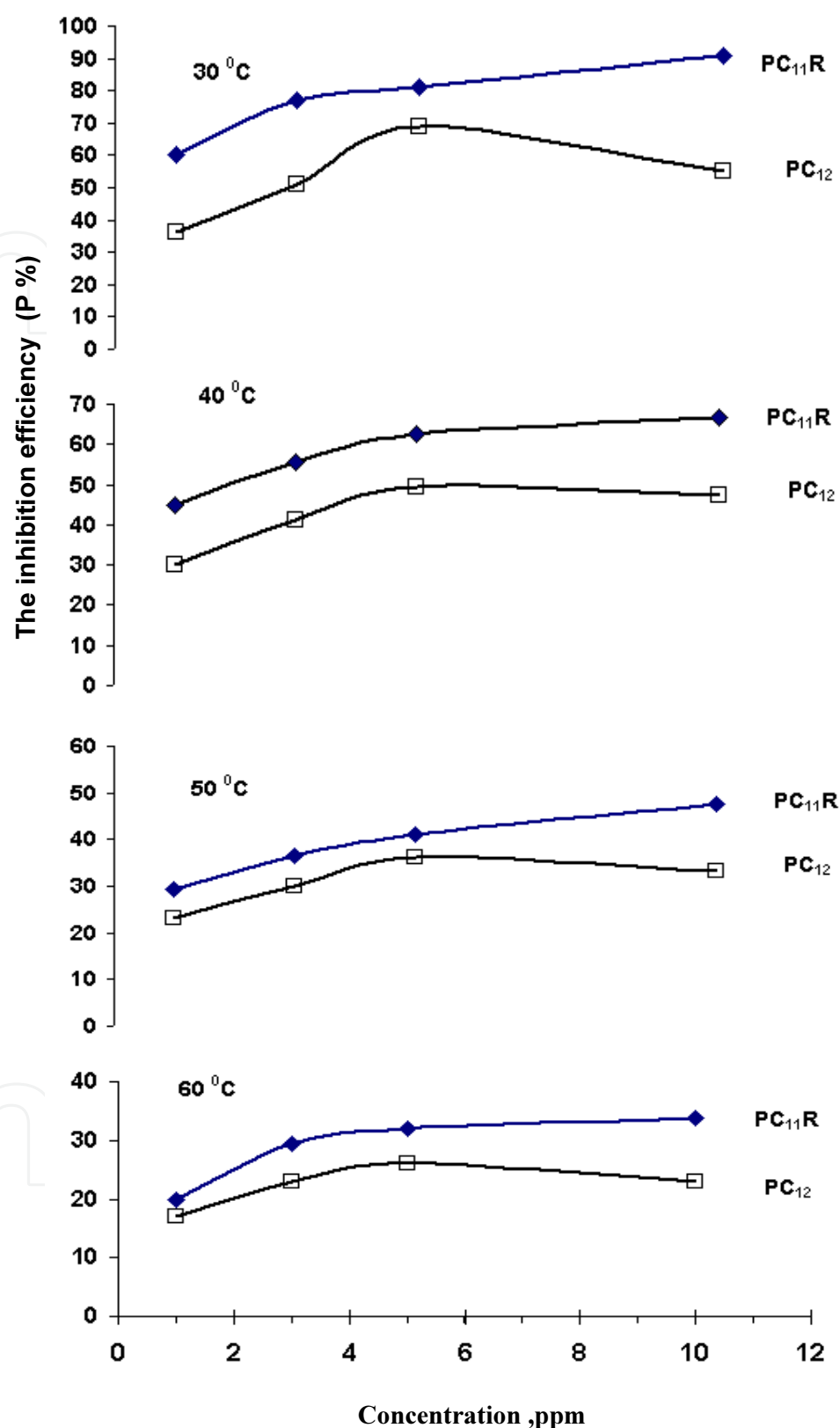


Figure 13. The variation of inhibition efficiency(P%) with different concentrations of PC₁₂ and PC₁₁R at different temperatures.

4. Conclusion

- Monomeric surfactants (MC_6), (MC_{10}) and (MC_{12}) and their analogues polymeric surfactants inhibit the corrosion of Al in a 0.5 M HCl solution.
- Weight loss measurements reveal that, the inhibition action of these surfactants is due to their adsorption and formation of barrier film on the Al surface which separates the Al from direct contact with corrosive medium and to protect the metal against corrosion.
- Corrosion tests display that, the presence of inhibitor in HCl solution decreases both the cathodic and anodic overpotentials indicating that, these surfactants inhibit both the partial hydrogen evolution and the partial dissolution of aluminium. The anodic curves are more polarized than the cathodic curves indicating that these inhibitors are considered as mixed-type inhibitors with anodic predominance.
- The inhibition efficiency of the polymeric surfactant was higher than that of the monomeric surfactant, and the inhibition efficiency increased with increasing inhibitor concentration but decreased with increasing temperature.
- Weight loss and potentiodynamic polarization techniques are in good agreements.
- The activation parameters for the corrosion of aluminium in 0.5M HCl solution of the monomers and their respective polymers were calculated from Arrhenius –type and alternatively, Arrhenius equations. The apparent activation energy (E_a), the enthalpy of activation (ΔH_a) of aluminium corrosion and the extent of the increase is proportional to the inhibitor concentration. Such trend indicates that the energy barrier for the corrosion process enhances with increasing of inhibitor concentrations.
- The inhibition efficiency of $PC_{11}R$ is higher than that of PC_{12} . This may be assigned to the elimination of the terminal $-SO_3H$ groups in PC_{12} . The presence of terminal $-CH_3$ groups stabilizes the inhibition efficiency. Also, the presence of terminal $-CH_3$ in the alkyl chain in $PC_{11}R$ molecules may reduce repulsion between anionic head with similar charge as in PC_{12} . This allows a closed layer to form more easily and hence higher inhibition efficiency.

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