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Effect of Surfactants on the Rate of Diffusion Controlled Anodic Dissolution of Copper in Orthophosphoric Acid

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The effect of Triton x-100 (non-ionic surfactant) , sodium dodecyl sulphate (anionic) and cetyl pyridinium chloride (cationic) on the corrosion rate of copper in 8 M H_3PO_4 was investigated using potentiodynamic polarization and surface tension measurements . The inhibition behavior of these surfactants was investigated. The surface parameters of each studied surfactant were calculated from its surface tension. The parameters studied include the critical micelle concentration (CMC), maximum surface excess (Γ_{max}), minimum surface area (A_{min}) and effectiveness (π_{CMC}).The thermodynamic parameters of micellization (ΔG_{mic}, ΔS_{mic}) for the studied surfactants were also calculated. The greatest reduction of surface tension (effectiveness, π_{cmc}) and higher minimum area (A_{min}) were achieved by Triton x-100 relative to the other two surfactants. This behavior agrees with the highest inhibition efficiency results achieved by Triton x- 100 obtained from potentiodynamic polarization method. The effect of temperature on the dissolution behavior of copper was studied at temperatures ranging from 25 to 40°C. A kinetic study of copper in uninhibited and inhibited acid was also discussed. The kinetic and activated parameters were calculated for the dissolution process .The adsorption of surfactants on copper surface in the acid solution was found to obey Kinetic-thermodynamic adsorption isotherm. The thermodynamic parameters were calculated.

Keywords: copper; corrosion inhibition; Surfactants; Surface parameters.

1. INTRODUCTION

The corrosion of copper and its alloy has received great attention and industrial concern. The corrosion of copper in acid media is important in the context of pickling, acid cleaning, acid descaling, etc. Because of the general aggressiveness of acid solutions, the use of inhibitors to control the destructive attack of acid environment finds widespread application in many industries. A variety of organic compounds with functional groups containing heteroatom (which can donate electron pairs) are found to be useful as inhibitors in various media [1].

The effect of sodium dodecyl sulphate and benzotriazoles on copper corrosion in sulphuric media has been studied [2]. The inhibition efficiency of imidizole derivatives on copper corrosion in sulphuric acid was investigated [3]. The corrosion inhibition of a copper electrode in 0.1 M H_2SO_4 was studied using azoles compounds [4]. Recently, the addition of high molecular weight organic compounds like surface active agents to hydrochloric and sulphuric acid solution, in order to reduce the rate of corrosion of copper, has been proved to be effective method [5-10]. Phosphoric acid (H_3PO_4) is widely used in surface treatment of steel such as chemical and electrolytic polishing or etching, removal of oxide film, phosphating, passivating, and surface cleaning [11].

However, little work appears to have been done on the corrosion inhibition of copper in H_3PO_4. The corrosion of copper in phosphoric acid was studied previously in the presence of alcohols [12], amines [13], aldehydes [14] and amino acids [15]. Hence, the aim of this work is to examine the corrosion behavior of copper in H_3PO_4 in presence of cheap, less toxic and easy produced surfactants. In the present study, potentiodynamic polarization method was performed to examine the acid corrosion inhibition of pure copper by a nonionic surfactant (Triton x-100), an anionic surfactant (sodium dodecyl sulphate ,SDS) and a cationic surfactant (cetyl pyridinium chloride ,CPC). The surface parameters of each studied surfactant (SAS) were calculated (from its surface tension profile) to correlate the inhibition efficiency of the inhibitors with their surface parameters.

2. MATERIAL & METHOD

2.1. Materials

Analar grade H_3PO_4 (98% w/w), supplied by BDH Chemicals Ltd., was used for the preparation of the electrolyte. The chosen surfactants were Fluka products of pure quality (>97%) and used without purification. Doubly distilled de-ionized water was used in the preparation of solutions.

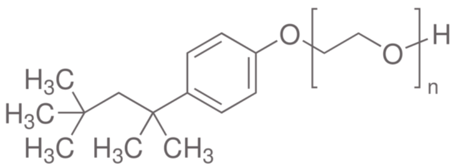
2.2. Perpration of solutions

Blank solution consists of 8M H_3PO_4 and different concentrations of surfactants. The concentrations of surfactants cover range from $5x10^{-7}$ to $1x\ 10^{-2}$M.

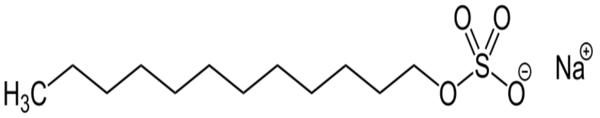
2.3. Potentiodynamic measurements

The cell used in the present work consists of rectangular container having the dimensions of 5×10 cm with electrodes fitting the whole cross section. The electrodes were rectangular copper sheets of 10 cm height and 5 cm width. Electrode separation was 5 cm; a porous PVC diaphragm was used to prevent the stirring effect due to H_2 bubbles evolved at the cathode interfering with the natural convection process at the anode. The electrical circuit consisted of a 6V D.C. power supply, a variable resistance and a multi range ammeter connected in a series with cell. A high impedance voltammeter was connected in parallel with the cell to measure its potential. The steady state anode potential was measured against reference electrode consisted of copper wire immersed in a cup of luggin tube filled with phosphoric acid-surfactants solution similar to that in the cell. The tip of the luggin tube was placed 0.5–1mm from anode wall. Polarization curves, from which the limiting current (I_L), was determined, were plotted by increasing the applied current stepwise and measuring the corresponding steady-state anode potential. Two minutes were allowed for reaching the steady state potential. Before each run, the back of anode was insulated with polystyrene lacquer and the active surface was polished with fine emery paper, degreased with trichloroethylene, washed with alcohol and finally rinsed in distilled water. The temperature was regulated by placing the cell in thermostatic water bath at different temperatures (25, 30, 35 and 40^{o}C). The copper used had the following chemical composition (Wt %): 0.0001 Cd, 0.001Ag , 0.003Ag , 0.003Pb , 0.005Sn and Cu is 99.98.

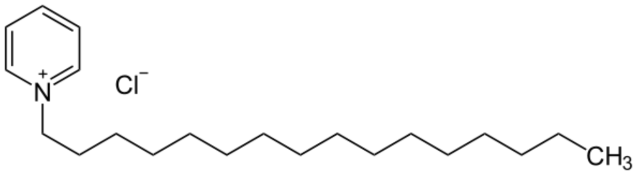
The structure of SAS is given below.



Triton x-100 (n = 10)



Sodium dodecyl sulphate (SDS)



Cetyl pyridinium chloride (CPC)

2.4. Surface tension measurements

The surface tension was measured at 25,35and 45 ^{0}C using a Du Nouy tensiometer .The temperature (±0.1^{o}C) was kept constant by circulating the thermostatted water through a jacketed vessel containing the solution. The concentration of the solution was varied by adding aliquots of stock solution of known concentration to the known volume of the solution in the vessel.

3. RESULTS & DISCUSSION

3.1. Surface active properties

3.1.1. Determination of the CMC of SAS in 8 M H_3PO_4

The main importance of the CMC consists of the fact, at this concentration, most of the physical and chemical properties of the surfactant solution present an abrupt variation [16].

Measured values of the surface tension were plotted as a function of the logarithm of the surfactant concentration in H_3PO_4at different temperatures. The CMC was estimated from the break point in the resulting curves. Representative plots of surface tension γ (mN/m) versus the logarithm to base ten of surfactant concentration $\log_{10}C$ are shown in Fig. 1.

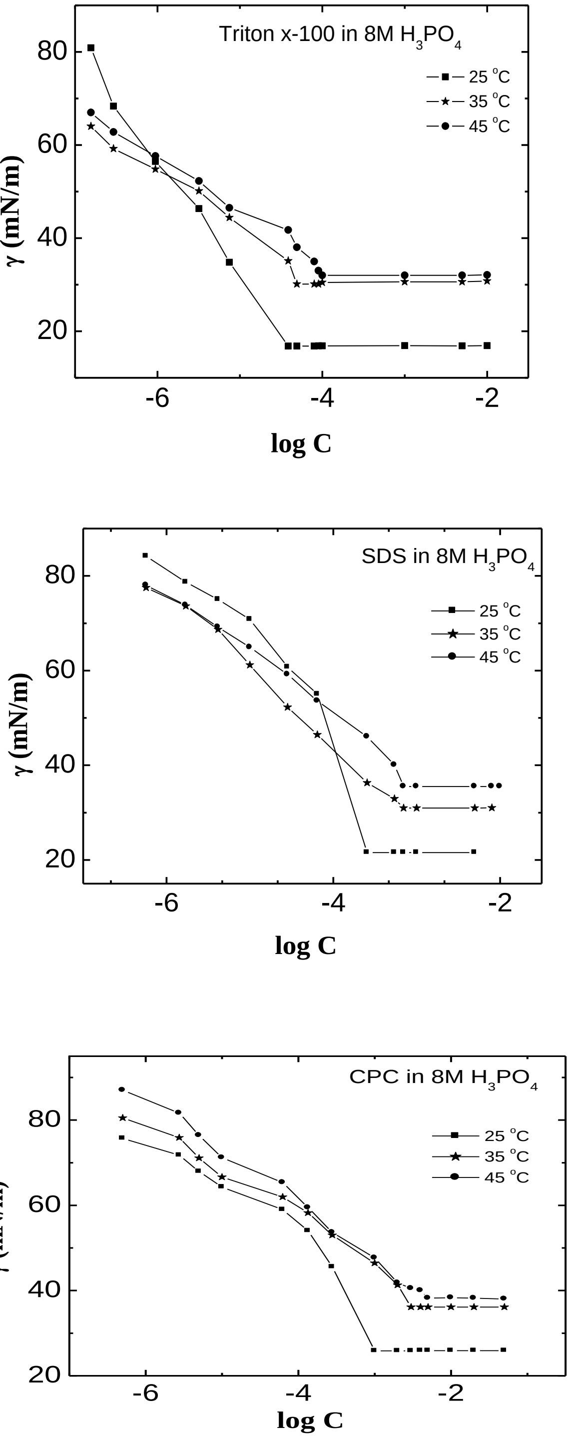


Figure 1. Variation in surface tension with concentration of Triton x-100, SDS and CPC in 8M H_3PO_4 at different temperatures.

The reproducibility of the surface tension versus concentration curve was checked by performing at least three separate experiments. CMCs for Triton x-100, SDS and CPC in H_2O are 3.0×10^{-4}, 8.0×10^{-3} and 1.24×10^{-3} [17,18] respectively and decrease in 8 M H_3PO_4 to 5.0×10^{-5} , 5.0×10^{-4} and 1.0×10^{-3}.

Generally, SDS and CPC, posses higher CMC than Triton x-100. This can be explained on the basis that, the free energy cost of bringing the polar heads together is much smaller when the head group is uncharged than when it is charged [19]. In the absence of a charged head group, the driving force of micellization is the hydrophobic force and Vander Waals attraction. The strong interaction between water molecules repels the hydrocarbon chain from the water bulk phase.

This drives the surfactants to form aggregates, where the hydrophilic head groups conceal the hydrocarbon chains. Micelle formation is therefore expected to take place at lower concentration for non-ionic surfactant vis-à-vis ionic surfactants. For ionic surfactants, high concentrations are necessary to overcome the electrostatic repulsion between ionic head groups during the aggregation process. So Triton x-100 exhibits lower CMC than SDS and CPC .

The CMC is influenced by a number of factors that are dependant on the nature of SAS and the aqueous environment. The presence of HPO_4^{2-} in the present study is one of the influential factors being responsible for the shift of the CMC values with respect to their primary values in pure water.

These phenomena are related to the famous Hofmeister series, which is an empirical measure of ions hydration degree. The Hofmeister series orders ions with increased salting in potency from left to right, and is as a follows:

SO_4^{2-}, HPO_4^{2-}, OH^-, F^-,$HCOO^-$,$CH3COO^-$,Cl^-,Br^-, NO_3^-,I^-,SCN^-,ClO_4^- ,

HPO_4^{2-} which is located to the left of chloride ion (Cl^- represents in some way, a borderline with the Hofmeister series) acts as water structure makers (salting out ions) or (cosmotropic ions). The salting out effect is produced when HPO_4^{2-} competing with surfactant for hydration water, reduces the amount of water available in the micelles for polar chain hydration. Thus micelle formation will be produced at lower surfactant concentration [20, 21]

Another explanation in case of Triton x-100 is it hydrogen bond formed with water molecules through the oxyethylene unit required higher energy to broke, in order to surfactant aggregation, so the micelles formed at higher concentration But in *8M* H_3PO_4, there is no hydrogen bond formed so tendency of Triton x-100 molecules to form micelle is greater and formed at lower concentration compared with water [22] .

While in case of SDS, a reduction in the electrostatic repulsion between anionic hydrophilic head group and, consequently, a smaller contribution of repulsion opposing micellization . Therefore, in 8M H_3PO_4, SDS starts forming micelles easier and causes CMC of SDS to be lower than that reported in distilled water[23].

3.1.2. Effect of temperature on CMC values

The obtained CMC values show an increasing trend with increasing temperature (Table 1). Rising temperature causes a decrease in the hydration of the hydrophilic group (which favour micellization) or causes disruption of the structured water surrounding the hydrophobic group (an effect that disfavors micellization). The relative magnitude of these two opposing effects, therefore, determines whether the CMC increases or decreases over a particular temperature range. From the data in Table 1, it is clear that CMC increases by rising temperature which implies that the magnitude of two factors is disfavouring micellization thus CMC increases [24, 25].

3.1.3. Surface active parameters

The surface active properties of pure surfactant, effectiveness (π_{cmc}), maximum surface excess (Γ_{max}) , minimum area per molecule (A_{min}) were calculated using the following equations [26] :

$$\pi_{cmc} = \gamma_o - \gamma_{cmc} \qquad (1)$$

$$\Gamma_{max} = \frac{1}{2.303RT}\frac{-\delta\gamma}{\delta \log C} \qquad (2)$$

$$A_{min} = 10^{16}/[\,\Gamma_{max}\,.N_A] \qquad (3)$$

where γ_o is the surface tension measured for pure water at the appropriate temperature and γ_{cmc} is the surface tension at CMC (mN/m). (Γ_{max}) is expressed as the concentration of surfactant molecules at the interface per unit area(mol cm^{-2}), T is the absolute temperature, R is the molar gas constant (R=8.314 J/mol.K) , C is the concentration of surfactant in mol/l . N_A is the Avogadros number (6.023×10^{23} molecule/mol)

The thermodynamic parameters of micellization expressed by standard free energy ΔG_{mic} and entropy of micellization ΔS_{mic} are calculated from the equations:

$$\Delta G_{mic} = RT\ln CMC \qquad (4)$$

$$\Delta S_{mic} = (-\delta\Delta G_{mic}/\,\delta T) \qquad (5)$$

$$\Delta G_{ads} = \Delta G_{mic} - [0.6022] \times [\pi_{cmc} \times A_{min}] \qquad (6)$$

$$\Delta S_{ads} = (-\delta\Delta G_{ads}/\delta T) \qquad (7)$$

From Table 1, it is clear that the lesser Γ_{max} , and the greater A_{min} recorded for Triton x-100 relative to SDS and CPC . Also it is evident that A_{min} increases with temperature. This is probably due to the increased thermal motion. The values of π_{cmc} indicate that Triton x-100 is the most effective surfactants which give large reduction in surface tension at CMC so that it act as effective inhibitor for dissolution process [27].

Analyzing thermodynamic parameters of micellization (Table 1), one may conclude that micellization process is spontaneous process ($\Delta G_{mic} < 0$) [28]. The ΔG_{mic} for Triton x-100 is more negative than SDS and CPC. This behavior shows that Triton x-100 form micelle more easily than SDS and CPC which confirm the values of CMC for each one, where CMC of Triton x-100 is less than SDS and CPC as mentioned above. Also, it is observed that ΔG_{mic} decreases with increasing temperature which confirmed that the values of CMC increase with increasing temperature [22].

We can observe that ΔS_{mic} are positive value (Table 1). Higher positive value recorded by Triton x-100 designates increasing in the randomness in the system upon transformation of surfactant molecules into micelle. Investigation of thermodynamic parameters of adsorption (Table 1) showed that; 1- ΔG_{ads} are negative values which are a sign of spontaneity the adsorption process.

2-the negative values of ΔG_{ads} are greater than ΔG_{mic} showing that surfactants favour adsorption rather than micellization.

3-adsorption at interface is associated with a decrease in the free energy of the system. These observations agree with the data reported before [29] which indicate that the steric factors inhibit the micellization more than they affect adsorption at the air/aqueous interface.

Also, an examination of ΔS_{ads} values , it is observed that the ΔS_{ads} values are all positive and greater than the ΔS_{mic} values reflecting the greater freedom of motion of the hydrocarbon chain at the planar /air aqueous solution interface compared to that in the relatively cramped interior beneath the convex surface of the micelle [22]. The relation between surface properties of the studied surfactants and dissolution inhibition were discussed in the next section (3.2.2)

Table 1. Surface active properties for the surfactant at different temperatures

Surfactant	Tritonx-100			SDS			CPC		
Temperature ° C	25	35	45	25	35	45	25	35	45
Parameters									
CMC (mol/l)	5×10^{-5}	8×10^{-5}	1×10^{-4}	5×10^{-4}	7×10^{-4}	1×10^{-3}	1×10^{-3}	3×10^{-3}	5×10^{-3}
$10^{10}\Gamma$(mol/cm^2)	1.80	1.67	1.52	2.57	2.04	1.90	2.95	2.50	1.95
π_{cmc}(mN/m)	55.15	40.28	36.00	50.43	39.46	32.5	46.14	34.30	29.78
A_{min}(A^2)	89.17	96.11	105.92	62.45	78.68	84.47	54.5	64.20	82.31
ΔG_{mic}(kJ/mol)	-24.53	-24.16	-24.35	-18.83	-18.60	-18.26	-17.11	-14.87	-14.00
ΔG_{ads}(kJ/mol)	-27.48	-26.48	-26.63	-20.72	-20.46	-19.91	-18.62	-16.19	-15.47
ΔS_{mic}(kJ/mol.K)	0.079			0.060			0.049		
ΔS_{ads}(kJ/mol.K)	0.087			0.066			0.054		

3.2 Effect of SAS concentrations

3.2.1. Potentiodynamic measurements

Fig.2. shows polarization curves for dissolution of copper in the presence of different concentrations of SAS, from which limiting current (I_L) was obtained.

The dissolution rate (I_L values) and inhibition efficiency percentage (IE %) for the studied SAS at concentration range from 5 $\times 10^{-7}$ to 1×10^{-2} mol/l and temperatures ranged from 25 to 40^{o}C are given in Table 2.

Table 2. Values of limiting current and inhibition efficiency % for dissolution of copper in 8M H_3PO_4 in absence and presence of SAS at different temperatures and activated parameters for process.

Conc. (mol/l)	SAS	25 °C		30 °C		35 °C		40 °C		Activated parameters			
		I_L(A)	IE%	I_L(A)	IE%	I_L(A)	IE%	I_L(A)	IE%	Ea kj.mol^{-1}	A*10^{3}	ΔHa kj.mol^{-1}	-ΔSa J.mol^{-1}.K^{-1}
0.0	Triton x-100	0.448	-	0.570	-	0.642	-	**0.744**	-	25.52	13.49	23.04	174.06
5.0E-07		0.281	37.28	0.365	35.96	0.436	32.09	0.512	31.18	30.76	69.56	28.28	160.40
1.0E-06		0.271	39.50	0.355	37.72	0.422	34.27	0.491	34.00	30.43	59.28	27.95	161.77
5.0E-06		0.262	41.52	0.345	39.47	0.400	37.69	0.480	35.48	30.55	59.87	28.07	161.67
1.0E-05		0.255	43.08	0.330	42.11	0.384	40.19	0.455	38.84	29.37	35.95	26.89	165.87
5.0E-05		0.290	35.27	0.380	33.33	0.442	31.15	0.515	30.78	29.16	37.79	26.68	165.45
1.0E-04		0.274	38.84	0.364	36.14	0.422	34.27	0.493	33.73	29.72	43.47	27.24	164.00
5.0E-04		0.262	41.52	0.349	38.77	0.412	35.82	0.478	35.75	28.17	50.01	28.17	161.24
1.0E-03		0.254	43.30	0.330	42.11	0.390	39.25	0.455	38.84	29.80	43.04	27.32	164.42
5.0E-03		0.242	45.98	0.310	45.61	0.362	43.61	0.432	41.94	29.43	36.68	26.96	166.11
1.0E-02		0.214	52.23	0.291	48.95	0.345	46.26	0.411	44.75	33.11	138.69	30.63	154.68
0.0	SDS	0.448	-	0.570	-	0.642	-	**0.744**	-	25.52	13.49	23.04	174.06
5.0E-07		0.310	30.28	0.404	29.12	0.470	26.79	0.572	23.12	30.92	81.63	28.44	159.07
1.0E-06		0.303	32.37	0.392	31.23	0.460	28.35	0.562	24.46	31.21	92.04	28.73	158.30
5.0E-06		0.292	34.82	0.380	33.33	0.442	31.15	0.543	27.02	31.27	88.43	28.79	158.41
1.0E-05		0.280	37.50	0.368	35.44	0.425	33.80	0.527	29.17	31.72	101.72	29.24	157.22
5.0E-05		0.270	39.73	0.353	38.07	0.413	35.67	0.490	34.14	30.25	54.72	27.77	162.43
1.0E-04		0.262	41.52	0.341	40.18	0.400	37.69	0.470	36.83	29.75	43.47	27.27	164.34
5.0E-04		0.250	44.20	0.320	43.86	0.380	40.81	0.463	37.77	31.40	79.22	28.92	159.32
1.0E-03		0.233	47.99	0.300	47.37	0.362	43.61	0.433	41.80	31.82	87.55	29.34	158.46
5.0E-03		0.215	52.00	0.282	50.53	0.333	48.13	0.402	45.97	31.77	80.01	29.29	159.23
1.0E-02		0.170	62.05	0.242	57.54	0.300	53.27	0.355	52.28	37.73	714.97	35.25	141.03
0.0	CPC	0.448	-	0.570	-	0.642	-	**0.744**	-	25.52	13.49	23.04	174.06
5.0E-07		0.338	24.55	0.462	18.95	0.530	17.44	0.630	15.32	31.21	101.72	28.73	157.22
1.0E-06		0.319	28.79	0.443	22.28	0.510	20.56	0.600	19.35	31.70	118.18	29.22	156.00
5.0E-06		0.310	30.80	0.427	25.09	0.495	22.90	0.584	21.51	31.87	123.00	29.39	155.68
1.0E-05		0.302	32.59	0.418	26.67	0.480	25.23	0.565	24.06	31.41	99.71	28.93	157.44
5.0E-05		0.296	33.93	0.406	28.77	0.471	26.64	0.555	25.40	31.66	108.01	29.18	156.78
1.0E-04		0.290	35.27	0.382	32.98	0.452	29.60	0.540	27.42	31.62	101.72	29.14	157.23
5.0E-04		0.282	37.05	0.366	35.79	0.422	34.27	0.500	32.80	28.93	33.52	26.45	166.48
1.0E-03		0.296	33.93	0.400	29.82	0.456	28.97	0.532	28.49	29.42	43.47	26.94	164.32
5.0E-03		0.313	30.13	0.418	26.67	0.478	25.55	0.560	24.73	29.25	42.61	26.77	164.46
1.0E-02		0.336	25.00	0.441	22.63	0.494	23.05	0.585	21.37	27.64	23.86	25.16	169.29

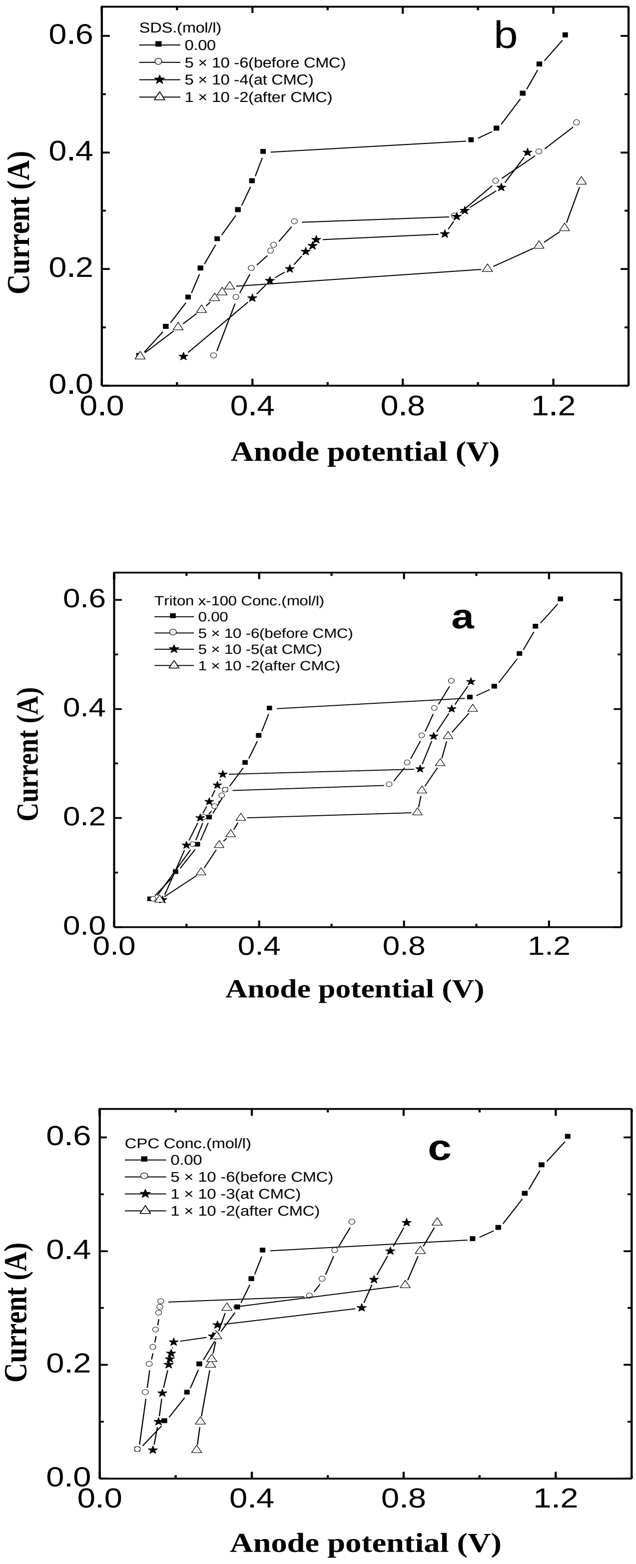


Figure 2. Typical polarization curves obtained for dissolution of vertical copper plate in 8 M H_3PO_4 in presence of different concentrations of: a) Triton x-100, b) SDS and c) CPC at 25°C.

It is clear (Table 2) that I_L decreases and IE % increases by increasing Triton x-100 concentration up to 1 $\times 10^{-5}$. At 5 $\times 10^{-5}$ (the CMC of Triton x-100), I_L increases. At higher concentrations of Triton x-100, I_L of copper dissolution and IE% increases. For low concentration of Triton x-100 (5 $\times 10^{-7}$ - 1 $\times 10^{-5}$ mol/l), the first adsorbed layer is composed of monomer units (surface is filling with adsorbed Triton x-100 from low coverage to mono layer coverage). At concentration 5 $\times 10^{-5}$ mol/l, an additional phenomenon was observed, I_L increases. This effect probably indicates the poor stability of the adsorbed layer. When the concentration of Triton x-100 exceeds the CMC value, I_L decreases, where increasing Triton x-100 concentration leads to saturation of the first adsorbed layer and consequently the formation of the second layer is in progress.

The molecular structure of Triton x-100 is composed of fairly polar hydrophilic head $(OCH_2CH_2)_{10}OH$ and hydrophobic part from C_8H_{17}-C_6H_4 , the structure of Triton x-100 suggests that it is able to adsorb on the copper surface through two lone pairs of electrons on the oxygen atom of the polar hydrophilic head group . On the other hand, IE% after CMC (Table 2) is higher than that before CMC. This may be due to change in orientation of Triton x-100 at the interface resulting from hydrophobic interaction between the chains. When $C_{\text{Triton x-100}}$ < CMC , the Triton x-100 is lying flat on the copper surface but when $C_{\text{Triton x-100}}$ > CMC , it is likely that surfactant molecules bind perpendicularly to the surface which lead to increase in the number of adsorbed molecules and this lead to increase in inhibition properties of Triton x-100 [30].

The inhibitive action of SDS results from the physical (electrostatic) adsorption of the $C_{12}H_{25}SO_4^-$ ion on the positively charged copper surface. It is obvious that I_L decreases and IE % increases at all studied concentration range (before and after CMC). This seems to be due to micelle formation; the micelles are highly charged and because of the higher electrostatic attraction, the adsorption of SDS increases and consequently reduces I_L of copper dissolution process. At higher concentration of SDS (1×10^{-2} mol/l) a double layer of adsorbed SDS may form [6], in this case IE % is maximum (62.05).

On further inspection of Table 2 , it is observed that addition of CPC leads to decrease in I_L of copper dissolution process and increase in the value of IE % up to 5 $\times 10^{-4}$ mol/l. Further increase in CPC concentration leads to increase in I_L and subsequent decrease in IE%. To understand the dual role of CPC as dissolution inhibitor and promoter, we must show the structure of CPC which consists of $C_{21}H_{38}N^+$ and counter chloride ion Cl^-. CPC as cationic surfactant exhibits retardation behavior for dissolution of positively charged copper electrode. This can be attributed to the adsorption of chloride ion firstly at the electrode solution interface through the electrostatic attraction and create excess negative charge toward the solution phase which favour more adsorption of positively charged cetyl pyridnium cation, so Cl^- anion acts as an adsorption mediator of an adsorption composite film in which Cl^- ions are sandwiched between copper anode and positively charged part of CPC [10, 31]. To explain this observation, Ma et al [32] suggest that the specific adsorption of catalytically active chloride counter ions from CPC molecules on the copper electrode promotes dissolution process at surfactant concentration above 5 $\times 10^{-4}$M, where CPC micelle formed carry concentrated positively charged heads with concentrated negatively charged chloride counter ions, the higher concentration of aggressive chloride ions lead to copper dissolution promotion [33].

Also another reason for inhibition behavior of the three studied surfactants is that the concentration of the SAS molecules at the electrode- solution interface may increase the interfacial viscosity with consequent decrease in the diffusivity of electroactive ions .This lead to hinder the flow of solution past the electrode surface and consequently decrease in the values of limiting current [34].

From the above discussion, we can conclude that the inhibitive behavior of SAS is a function of CMC. If the SAS are compared according to maximum inhibition efficiency, they are ranked as follow

Triton x-100 > SDS > CPC (Before CMC)

SDS > Triton x-100 > CPC (After CMC)

3.2.2 The relation between dissolution inhibition and surface properties of the studied surfactants.

The Gibbs equation (equation 2) was applied to calculate the area per surfactant molecule (A_{min}) at the air/liquid interface (section 3.1.3, Table 1). This value was used to calculate the monolayer coverage of surfactant at the copper/electrolyte interface. Assuming that the occupied area per surfactant molecule at the copper /electrolyte interface is the same as that at the air/liquid interface [35].

Surface active properties data of surfactants (Table 1) show that lower Γ_{max} , higher A_{min} and greatest reduction in surface tension, π_{cmc} were achieved by Triton x-100 compared to SDS and CPC. This is in harmony with maximum inhibition efficiency results achieved by Triton x-100 from potentiodynamic measurements (Table 2) .Increasing A_{min} leads to increasing the area of metal surface covered by surfactant molecule,as a result increasing the IE % [36,37]. The greatest reduction of surface tension (effectiveness, π_{cmc}) was achieved by Triton x-100 compared to that obtained by other two surfactants. This is in good agreement with the inhibition efficiency results achieved by Triton x-100 [27, 38]. (Table 2)

3.3. Effect of temperature and activation parameters of dissolution process

To verify the effect of temperature on the dissolution process for copper metal in 8M H_3PO_4 acid in the absence and presence of different concentrations of the studied surfactants, potentiodynamic measurements were undertaken in this study in the temperature range of (25-40^{o}C). Results obtained indicate that the dissolution rate (I_L) increases with increasing temperature both in the absence and presence of surfactants, while IE % decreases with temperature rise (Table 2). This increase could be explained on the basis that increasing temperature enhances the transfer rate of the PO_4^{-3} ions and increases the conductivity. So the dissolution rate may be affected by the transfer of the aggressive ions in solution. Also the increase in temperature reduces solution viscosity with a consequent increase in Cu^{2+} diffusivity which leads to increase in the dissolution rate [9].

If $(I_L)_{\text{blank}}$ is the limiting current in absence of surfactant and $(I_L)_{\text{SAS}}$ in the presence of surfactant, then IE % can be calculated from the following equation

$$IE\% = \frac{I_{L(blank)} - I_{L(SAS)}}{I_{L(blank)}} \quad \text{X100} \qquad (8)$$

Table 2 shows that IE% caused by surfactants ranged from 62.05 % to 15.32 % depending on their type and concentration. The decrease in IE% is due to the desorption of surfactant molecules from Cu surface by increasing temperature. The decrease in inhibition efficiency (IE %) with increasing temperature is suggestive of physical adsorption of the used surfactants on copper surface [39].

The thermodynamic activated functions were obtained by applying the Arrhenius and the transition-state equations

$$\ln I_L = - (Ea/RT) + \ln A \qquad (9)$$

$$I_L = (RT/Nh) \exp (\Delta S_a/R) \exp (-\Delta H_a/RT) \qquad (10)$$

where I_L is the limiting current , Ea is the apparent activation energy , R is the molar gas constant, T is the absolute temperature ,A is the frequency factor, ΔH_a is the enthalpy of activation , ΔS_a is the entropy of activation and N is the Avogadro's number.

Arrhenius and Transition state plots obtained from the electrochemical measurements were constructed for copper in8 M H_3PO_4 solutions containing various concentrations of the three tested surfactants in the range of temperature (25-40^{o}C). Fig.3 and 4 represent the Arrhenius and Transition state plots, obtained from electrochemical measurements of Cu in *8 M* H_3PO_4 solutions containing1 $\times 10^{-2}$ mol/l Triton x-100, SDS or CPC (as an example). Similar trend was obtained for the other tested concentrations of the inhibitors. The values of thermodynamic activation functions were calculated from these plots and listed in Table 2 as a function of each inhibitor concentration.

From Table 2, it is clear that the values of Ea in presence of SAS are higher than that of 8M H_3PO_4 free solution indicating that the dissolution reaction of copper is inhibited by the three studied surfactants molecules hence supports the phenomena of physical adsorption. Higher values of Ea in the presence SAS can be correlated with increasing thickness of the double layer which enhances the Ea of the dissolution process. [40-42].

It is also noticed that higher values of ΔH_a in presence of Triton x-100, SDS and CPC comparing to value of ΔH_a for free acids solution (Table 2). This implies that the addition of these three surfactants increases the height of energy barrier of the dissolution reaction to an extent depend on the type and concentration of surfactants [40].

The values of ΔS_a are large and negative both in the absence and presence of SAS which implies that the activated complex in the rate determining step represents an association rather than dissociation step meaning that a decrease in disorder takes place on going from reactants to the activated complex . Thus a greater degree of order appears during its transformation from reactants to activated complex [41, 43].

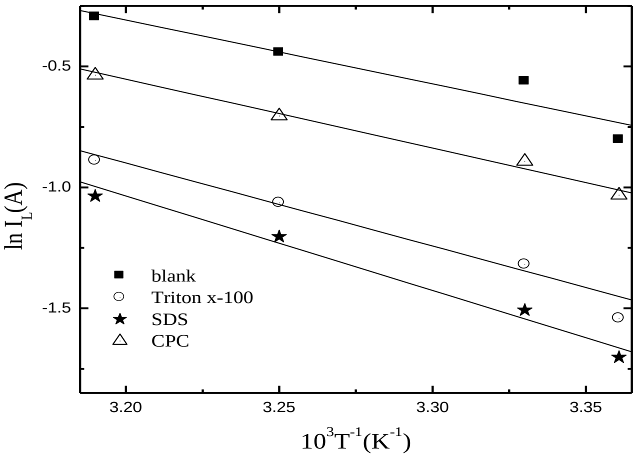


Figure 3. Arrhenius plot of the dissolution process recorded for copper in 8 M H_3PO_4 solution containing 1× 10^{-2} mol/l Triton x-100, SDS and CPC.

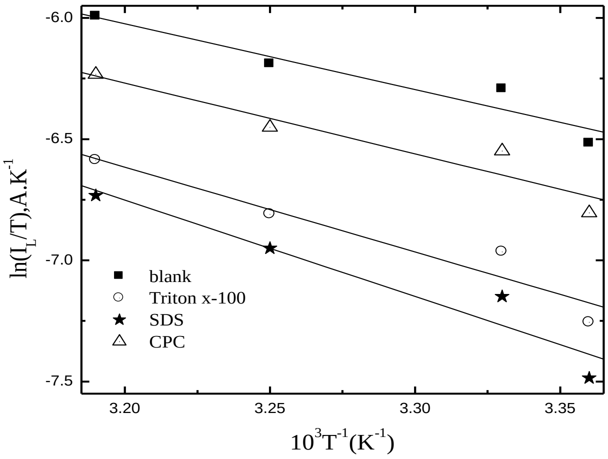


Figure 4. Transition state plot of the dissolution process recorded for copper in 8M H_3PO_4 solution containing 1× 10^{-2} mol/l Triton x-100, SDS and CPC

The pre-exponential factor in the Arrhenius equation (A), for heterogeneous reaction is related to the number of active centers. The adsorbed inhibitor's molecules block an essential part of the active sites, i.e., those with the lowest Ea value, on the metal surface. On the other hand these active centers have different energies, if energetic surface heterogeneity is assumed. There are two possibilities: in the first case ($E_{a,additives} > E_{a,\text{ free acid}}$) which observed in the three studied SAS , where the values of A in case of SAS is greater than that of blank (Table 2). The surfactants molecules are adsorbed on the most active adsorption sites (having the lowest energy) and the dissolution process takes place predominantly on the active sites of higher energy. In the second case ($E_{a,additives} < E_{a,\text{ free acid}}$) , the values of A in presence of additives lower than in pure acid . i.e. a smaller number of more active sites remain uncovered which take part in the dissolution process . [9, 42]

3.4. Adsorption isotherm

In order to gain more information about the mode of adsorption of surfactants on the copper surface at different temperatures, the experimental data have been tested with two adsorption isotherms (Langmuir, and Kinetic-thermodynamic model).

The adsorption isotherm relationships of Langmuir and Kinetic-thermodynamic model are represented by equations 11 and 12 [44, 45]

$$C/\theta=1/K_{ads}+C \tag{11}$$

$$\log(\theta/1-\theta)=\log K'+y\log C \tag{12}$$

where θ is the surface coverage , $\theta=\frac{I_{L(blank)}-I_{L(SAS)}}{I_{L(blank)}}$ (13)

K_{ads} is the equilibrium constant of adsorption process, C is the surfactant concentration in the bulk solution. y is the number of inhibitor molecules occupying one active site. Values of y greater than one imply the formation of multilayers of the inhibitor on the metal surface; however, values of y less than one indicate that the given inhibitor will occupy more than one active site. K′ is a constant related to the binding constant of adsorption process K by the following relationship [46].

$$K=K'^{(1/Y)} \tag{14}$$

where 1/y represents ,the number of active sites of the surface occupied by one molecule of the inhibitor [46].

Langmuir isotherm considers uniform activity over the surface for adsorption to takes place and no interaction among adsorbed molecules. But this is not true in the case of large organic compounds (such as surfactanst) having polar atoms or groups which can adsorbed on the active sites of the metal surface. Such adsorbed species interact by mutual repulsion or attraction [41, 47].

Experimental results obtained in this study were fitted into the modified form of Langmuir isotherm known as El-Awady kinetic thermodynamic adsorption model which can appropriately represent the adsorption behavior of the studied surfactants onto copper surface. Curves fitting the experimental data to the kinetic thermodynamic are shown in Fig.5. Straight lines were obtained suggesting the validity of this model for the three studied surfactants. The calculated values of K, Y and 1/Y are given in Table 3

The data (Table 3) reveals that values of y are less than one .This indicate that surfactants will occupy more than one active site [15]. The high value of K for Triton x-100 compared to the other surfactants (CPC, SDS) indicates stronger adsorption of Triton x-100 on copper surface. The higher the K is, the stronger and more stable adsorbed layer is forming, which increase the inhibition efficiency of Triton x-100 [48]. K is related to the free energy of adsorption ΔG_{ads} by the equation

$$\Delta G_{ads} = -RT \ln (55.5\ K) \qquad (15)$$

where R is the universal gas constant , T is the absolute temperature and the value of 55.5 is the concentration of water in the solution .

The negative values of ΔG_{ads} (Table 3) calculated from equation (15) are consistent with the spontaneity of the adsorption process and the stability of the adsorbed layer on the copper surface. Generally, the energy values of -20 kJ/mol or less negative are consistent with an electrostatic interaction between the charged molecules and the charged metal surface physisorption; those of 40 kJ/mol or more negative are associated with chemisorptions which results of a charge sharing or transfer of electrons from the additives molecules to metal surface to from a coordinate covalent bond [49].

Table 3. Adsorption parameters, calculated values of free energy of adsorption $-\Delta G_{ads}$ (kJ mol $^{-1}$) at different temperatures and thermodynamic functions for adsorption process.

Surfactant	Kinetic adsorption isotherm			$-\Delta G_{ads}$ (kJ mol $^{-1}$)				ΔH^{o} (kJ mol $^{-1}$)	ΔS^{o} (J.mol^{-1}.K^{-1})
	y	1/y	K	25 ^{o}C	30 ^{o}C	35 ^{o}C	40 ^{o}C		
Triton x-100	0.070	14.28	3767.0	30.3	29.9	28.6	27.4	-90.4	-234.1
SDS	0.111	9.010	827.38	26.6	25.1	22.4	22.0	-87.4	-363.3
CPC	0.076	13.06	27.93	18.2	17.2	15.3	15.0	-85.4	-259.1

In present study (Table 3), - ΔG_{ads} values obtained for CPC are ranging between -15.0 and -18.2 which are lower than -20 kJ/mol. This indicates that the adsorption is physical [41]. While the calculated values of - ΔG_{ads} in case of Triton x-100 and SDS are ranging between -30.3 and -26.6 kJ/mol .This indicates that the adsorption mechanism of Triton x-100 and SDS on copper surface is neither typical physical adsorption nor typical chemisorptions but it involves both electrostatic adsorption and chemisorptions (where Triton x-100 and SDS posses unpaired electron pairs on oxygen atoms which can interact with d-orbital of copper) and physisorption is predominant mode of adsorption [50] . This assumption is supported by data obtained from temperature dependence of inhibition process (Table 2).

3.5. Thermodynamic parameters of the adsorption process

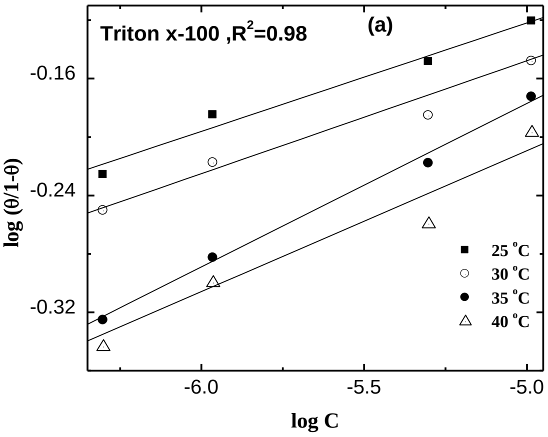
In studying the mechanism of copper dissolution inhibition, thermodynamic parameters are important. The heat of adsorption (ΔH^o) and entropy of adsorption (ΔS^o) are calculated using the Van't Hoff equation [48]

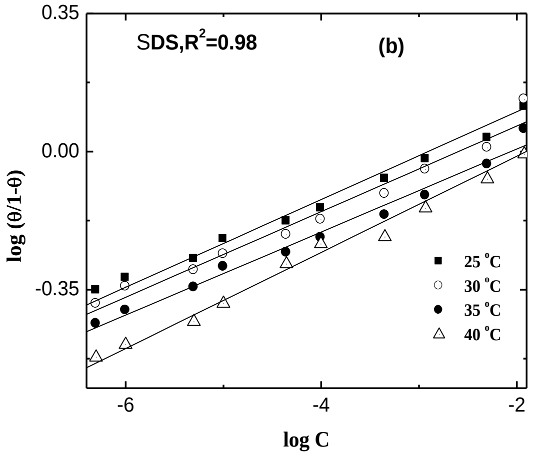
$$\ln K = - \Delta H^o_{ads} /R .1/T+ \Delta S^o_{ads} /R \quad (16)$$

ΔH^o is calculated by linear regression between ln K and 1/T,(Fig. 6) shows the straight lines of ln K verses 1/T having slope of these straight lines is equal to $- \Delta H^o_{ads} /R$ and intercept equal $\Delta S^o_{ads} /R$,

All the calculated thermodynamic parameters are listed in Table 3. Adsorption is generally accompanied by release of energy, that is, most adsorption process is exothermic in nature. An endothermic adsorption process ($\Delta H^o >0$) signifies unequivocally chemisorption , while an exothermic adsorption process ($\Delta H^o < 0$) may involve either physisorption or chemisorption or a mixture of both the process. [51]

The obtained ΔH^o values are -90.4,-87.4 and -85.4 kJ/mol for Triton x-100, SDS and CPC respectively. The ΔH^o values in presence of SAS onto metal surface are large and negative indicating that the adsorption of SAS onto metal surface is an exothermic process, physisorption is distinguished from chemisorptions by considering the absolute value of ΔH^o, for the chemisorptions process ΔH^o approach 100 kJ/mol while for the physisorption process, it is less than 40 kJ/mol [52]. In the present study, the ΔH^o value is larger than the expected physical adsorption but smaller than the one for chemical adsorption. This result suggests that the adsorption mechanism of three studied SAS on copper surface at the studied temperatures could involve both physisorption and chemisorptions. Chemisorptions of the SAS molecules could occur due to the formation of links between the d orbital of copper atoms, involving the displacement of water molecules from the metal surface, and lone SP^2 electron pair present on N or O atoms of SAS





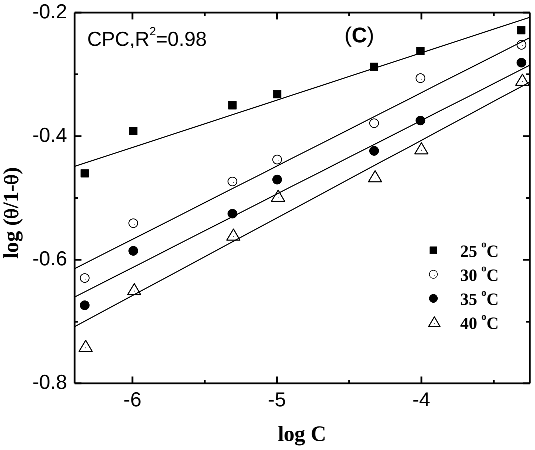


Figure 5. Kinetic-thermodynamic adsorption isotherm for a) Triton x-100 b) SDS and c) CPC at different temperatures

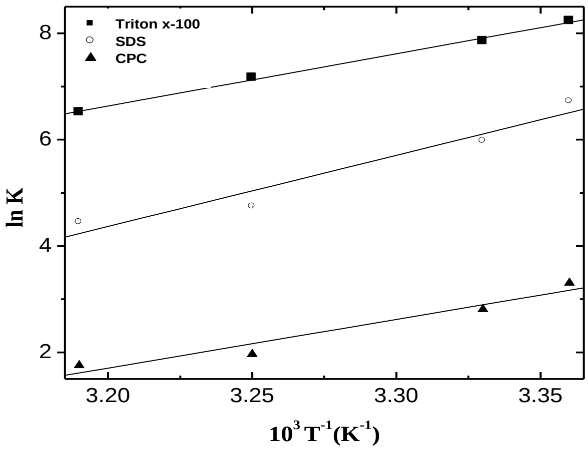


Figure 6. The relation between ln (binding constant) and 1/T for the surfactants on copper surface obtained by applying Kinetic adsorption model data

The obtained large negative value of ΔS^o indicates a reduction of translational degree of freedom. This means that an increase of order takes place in going from the free SAS molecules to the more orderly inhibitor molecule on the metal surface [51].

4. CONCLUSIONS

- For each surfactant studied the dissolution rate of copper decreases with the increase of concentration and inhibition efficiency is a function of SAS concentration.
- The critical micelle concentration considers a key factor in determining the effectiveness of SAS as corrosion inhibitors.
- Surfactant compounds increase the value of activation energy of dissolution process and consequently decrease the rate of dissolution of copper in H_3PO_4 solution.
- The adsorption of surfactants on copper surface does not obey Langmuir adsorption isotherm but obey Kinetic –thermodynamic model. The adsorption process is spontaneous and exothermic accompanied by a decrease in entropy.
- The inhibition mechanism is attributed to the strong adsorption ability of the selected surfactants on copper surface, forming a good protective layer , which isolate the surface from the aggressive environment.

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