Potentiostatic Study for the effect Of LAS on the Corrosion Of pure Zinc in 0.01 M HCl solutions

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Abstract

A potentiostatic study for the corrosion of pure zinc in 0.01 M HCl was achieved in absence and presence of (linear alkylbenzene solfonate LAS) detergents in a range of concentrations (0-50) mg/L. The electrochemical studies included anodic, cathodic polarization by using potentiostat over temperature rang (293- 323) K.   The mechanism of corrosion rate of pure zinc was suggested by evaluating of α_a , α_c , b_a , b_c , i_0 , R_p and the kinetic parameters also calculated (E_a , A) at the above temperature rang, The thermodynamic of corrosion, corrosion accelerating and corrosion protecting were investigated by calculating (ΔG, ΔH and Δs) values.

Keyword: zinc corrosion, potentiostat, linear alkylbenzene solfonate LAS.

Introduction

" corrosion is the deterioration of substance or its properties because of the reaction with its environment. In the water works industry, the "substance" that deteriorates may be metal pipe or fixture, the cement in a pipe lining or an asbestos-cement (A-C) pipe" (AWWA 1990, Aly et at 1998). This normal and natural process may result in failure of component and can seldom be totally prevented. The effect of corrotion is important in water utility industry[1]. Electrochemical theory is one way to understand the structure of metals on the basic of particles by imagining an array of positively charged ions sitting in negatively- charged "yas" of free electrons, coulombic attraction holds these oppositely-charged particles together, but the positively-charged ions are attracted to negatively charged particles outside the metal as well, such as the negative ions (anions) in an electrolyte. For a given ion at the surface of a metal, there is a certain amount of energy to be gained or lost by dissolving into the electrolyte or becoming a part of the metal, which reflects an atom scale tug-of-war between the electron gas and dissolved anions. The quantity of energy then strongly depends on a host of variables, including the types of ions in a solution and their concentrations, and the number of electrons present at the metals surface[2].

Zinc is a metal with numerous industrial applications and is mainly used for the corrosion protection of steel. Zinc is an industrially important metal and is corroded by many agents, of which aqueous acids are the most dangerous[3].

Surfactants are the active cleaning ingredients in synthetic detergents used for all kinds of washing. They consist of a water-soluble (hydrophilic) and a water-insoluble (hydrophobic) component. As a result of this structure, the molecules of surfactants align themselves to form micelles able to separate dirt and oily stains[4].
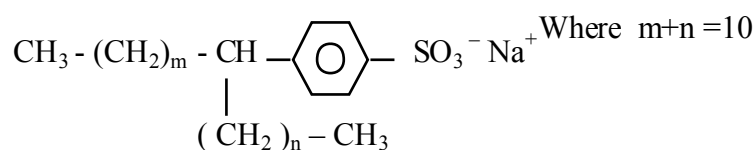
Organic substances as well as inorganic ones affect the corrosion rate. It is claimed that if organic molecules have groups like -OH, -CHO, -COOH, -CN, -SCN, -CO, $-NH_2$, $-SO_3$, double or triple bonds or unpaired electrons, the substance and the metals interact easily, and charging the zero charge potential, an effective protection is provided [5].

In this study, the effects of the organic molecules like linear alkylbenzene solfonate LAS (which is a raw material of detergents and has surface active properties) on zinc were investigated.

Experimental procedure

A pure zinc (99.99%) pieces of 1cm² were served in the corrosion cell as a working electrode. Platinum was served as the counter electrode while saturated calomel electrode (SCE) was used as a reference electrode. The corrosion cell were conducted with advanced potentiostat winking M Lab-200(2007) [Bank Elektronik – Intelligent controls GmbH with all accessories] Cell + Electrode + working electrode holder (Germany).

The open circuit potential (OCP) was measured and the polarization curves were scanned between   (-1.1 to - 0.2) V. The 0.01M HCl solutions were prepared by using HCl (37% Aldrich) and diluted with DI water (with a measure conductivity less than 2 μs /cm). LAS, Fw=362.498 g.mole^{-1}.

$$CH_3 - (CH_2)_m - CH -\!\!\left\langle\bigcirc\right\rangle\!\!- SO_3^- Na^+ \quad \text{Where } m+n =10$$
$$\underset{(CH_2)_n - CH_3}{|}$$

A dilute solution (500 ppm) of LAS (98% pure) was prepared using DI water and then used for preparation of all acid electrolytes solutions (by addition of the desired amount of LAS solution (500 mg/L)) in the concentration ranges of study (0-50) mg/L.

Results and Discussion

(I) Polarization curve

Figs (1– 4) show typical polarization curves for Zn in 0.01M HCl in presence and absent of different concentration of LAS ranging between (2.5-50) mg/L, at temperature range (293-323) K.

Table 1. shows the resulting data (the corrosion potential E_c and corrosion current densities(i_c) which have been derived from the polarization curves.

The data of table 1 show that the corrosion current density (i_c) increased while the corrosion potential E_c generally decreased with the increase of temperature in absence and presence of LAS.

The corrosion current densities (i_c) and corrosion potential (E_c) have been obtained by extrapolation of the linear logarithmic sections of cathodic and anodic Tafel lines to the point of intersection.

The rate of an electrochemical reaction is limited by various physical and chemical factors. The behavior of electrochemical system depends on the charge transfer reactions which occur at the interface. The basic law of charge –transfer reaction has been expressed through the Butler-Volmer electrodic equation [6] as

$$i = i_0 \left[e^{(1-\beta)\, \eta F/RT} - e^{-\beta\, \eta F/RT} \right] \text{------- (1)}$$

In which, i_0, is the equilibrium exchange current density, β, is the symmetry factor, the term $\eta = E - E_c$ measures how much the potential E has departed from the equilibrium value E_c.

The following equation provides a simple way of understanding non-polarizable and polarizable interface [7]:-

$$i = i_0\, F\eta\, /\, RT \text{-------------- (2)}$$

where η is about 0.01V or less for one electron transfer reaction. By rearrangement of this equation, one obtains [5].

$$\eta / I = RT/ i_0F = R_p \text{---------------- (3)}$$

so the term η / i corresponding to the resistance R_p of interface at an electrode to the charge transfer reaction and is termed the polarization resistance.

The higher the value of i_0, the less does the potential difference across an interface depart from the equilibrium value on passage of a current [6].

(II) The Tafel slopes and Transfer coefficients

The cathodic (b_c) and anodic (b_a) Tafel slopes which were obtained from the slopes of cathodic and anodic Tafel regions of the polarization curves are given in table 1. The data of the table show that the cathodic and anodic Tafel slopes shifted slightly with increasing temperature at all LAS concentration.

Values of transfer coefficients for the cathodic (α_c) and anodic (α_a), processes have been calculated from the corresponding cathodic (b_c) and anodi (ba) Tafel slopes using the relationship [6]:

$$\alpha_c = 2.303RT / b_cF \text{--------------- (4)}$$

$$\alpha_a = 2.303RT /b_aF \text{--------------- (5)}$$

Where R is the gas constant and F is the faraday constant. The results obtained are given in table 2.

A values of α_c of ~ 0.5 could be diagnostic of a proton discharge-chemical desorption mechanism in which the proton discharge is the rate-determining step (r.d.s). Values of α_a are shown in table 2, and in most cases α_a were close to 0.5 in absence of LAS at the temperature range (303-323)K, indicating the metal dissolution reaction to be the rate-determining step for the reactions taking place at the anode.

The variation of α_a could be interpreted in terms of the variation of the rate-determining step from charge transfer process to either chemical-desorption or to electrochemical desorption, in presence of LAS and in absent LAS at 293K.

The variation of (b_a) and (α_a) may be attributed to the variation of the rate-determining step in the metal dissolution reaction. A change in mechanism as well as in the rate-determining step cannot be ignored throughout the anodic processes.

(iii) The exchange current desities and polarization resistances.

The polarization resistance (R_p) was determined from Stern-Geary equation [6]:

$$R_p = [d(\Delta E)/di]_{\Delta E \to 0} = b_ab_c / 2.303(b_a + b_c)i_c \text{--- (6)}$$

Values of R_p are presented in table 2. Values of exchange current density were calculated from equation (3) and the i_0 values presented in table 2. The i_0 for a metal electrode determines the extent of the polarization of the interface adjacent to the electrode; a nonpolarizable interface corresponds to one at which the potential difference does not change easily with the passage of current. The higher the value of i_0 is, the less does the potential difference across an interface depart from the equilibrium value on the passage of a current. Similarly, the case of $i_0 \to 0$ or $R_p \to \infty$ means that the potential departs from the equilibrium values even with a very small current density leaking across the interface. The value of $i_0 \to 0$ is the idealized extreme of a polarizable interface; $i_0 \to \infty$ is idealized extreme of a non-polarized interface.

Values of i_0 in absence of LAS are higher than corresponding i_0 values in presence of LAS at all temperature and LAS concentrations, indicating the variation of interface polarization, that means LAS led to increase the interface polarization. The maximum LAS concentration effect i_0 was at 323K by using 5 mg/L LAS.

(iv) The protection efficiency (P%)

The protection efficiency (P%) of an inhibitor or of a protection mean was calculated by [7,8]:

$$P\% = 100[1- (i_c)_2 / (i_c)_1] \text{ ------------- (7)}$$

where $(i_c)_1$ and $(i_c)_2$ are respectively the corrosion current densities of the Zn in the absence and presence of the LAS at the same temperature; $(i_c)_1$ and $(i_c)_2$ refer also the corrosion rate of unprotected and protected metal by any protection methods.

Values of protection efficiency which were calculated for various concentration of LAS at temperature range (293-323) K are given in table 2.

LAS concentration led to accelerate the corrosion rate of Zn in 0.01 M HCl at (293 – 303)K while at 313 and 323 K it lead to protect the zinc from corrosion where LAS used in concentrations (5 and 25) mg/L. Using 50 ppm LAS led to inhibit the zinc corrosion at the four temperatures above, but using 2.5 ppm LAS at 313 accelerate corrosion of Zinc.

Fig. 5 shows the variation of P% with temperatures for the different LAS concentration, while Fig. 6 shows the variation of P% with LAS concentrations for the different temperatures.

Fig.7 shows the variation of corrosion rate (i_c) against temperature for different LAS concentrations, while Fig.8 shows the variation of corrosion rate against LAS concentrations at different temperatures.

(v) Kinetics of corrosion

The effect of temperature on the rate of corrosion has been studied over the temperature range from 293 to 323K. The rate(r) of corrosion may be expressed as [9].

$$r = 0.13 (e / \rho) i_{corr} \text{ --------------- (8)}$$

where (e) is the best chemical equivalent of the metal, (ρ) its density and i_{corr} is the corrosion current density, the value of i_{corr} may b taken to be proportional with the rate of corrosion (r). Fig.9 shows log i_{corr} plotted against the reciprocal of the absolute temperature (1/T) for the Zn in 0.01HCl.

The result is shown to be almost a linear dependence on the corrosion rate (log i_{corr}) on (1/T) which can be expressed as [10]:

$$\text{Log } i_{corr} = \log A – Ea /2.303RT \text{ ----------- (9)}$$

Which is similar to the well-known Arrhenius equation with:

$$r = A \exp (-Ea / RT) \text{ ----------- (10)}$$

Ea represents the activation energy of the corrosion and A is the pre-exponential factor in the rate equation. Values of Ea and A are then derived from the slop and the intercept of log i_{corr} versus 1/T plot. Table 3 presents the values of Ea and log A for pure zinc in 0.01M HCl.

Fig.10 shows the resulting values of Ea as a function of LAS concentration in 0.01M HCl.

There was non-linear decrease in E_a values on increasing LAS concentration, up to 25 mg/L and then increased reaching to 50 mg/L thus, the presence of LAS in the acidic media probably lowering the energy barrier for the metal corrosion through the decrease of the apparent energy of activation resulting in the consequent increase of the surface tendency for corrosion, but a value reaches to 7.48×10^{10} in absence of LAS and by adding LAS the A value be so lower that means LAS led to decrease the number of anodic corrosion sites.

A liner relationship is frequently observed between the energy of activation (E_a) and the pre-exponential factor (A) for a given reaction over a different LAS concentrations Fig.11. It is usually of the form [11].

$$Log A = m Ea + C \text{ ----------- (11)}$$

This relation is referred to as a "compensation effect" or the "Theta Rule". The former name is meaningful, since an increase in Log A at constant Ea implies a higher rates while an increase in Ea at a constant Log A therefore tend to compensate from the standpoint of the rate. When such a compensation operates, it is possible for striking variations in Ea and LogA through a surface series to yield only relatively small change in activity; alternatively when the effect does not operate (that is, when either Ea or LogA alone changes) striking variation in activity results. The high LogA values are due to the greater concentration of corroding sites on zinc.

The comparatively lower Ea values combined with greater values of LogA for corrosion of the metals make the corrosion much easier [15].

Although that Ea with using 50 mg/L LAS is equal to 37.19 KJ.mol^{-1} and the Ea with absence of LAS is equal to 50.34 KJ.mol^{-1} but values of LogA for the first is 8.28 and for the second is equal 10.87, that means the 50 mg/L LAS led to decrease the energy barrier but in the same time it led to decrease the number of the active corrosion sites (anodic sites) and overall process is reached to protect the corrosion of zinc.

vi) Thermodynamic of corrosion

Values of E_c for various LAS concentration and at different experimental temperatures reflect the variation in the Gibbs free energy (ΔG) values of the corrosion, and reflect the tendency of metal for corrosion on thermodynamic grounds [12,13].

Table (1) shows the decreasing of E_c with temperature increasing in absence and presence of LAS.

In each temperature the addition of LAS let to increase E_c in active direction and $- \Delta G$ increased according to the following equation [14]:

$$\Delta G = - nFE_c \text{ -------------- (12)}$$

$$\Delta G = \Delta H - T\Delta S \text{ -------------- (13)}$$

Where n is number of electron, and F is the Faraday constant.

Fig.12 shows the variation of ΔG with temperature at the different LAS concentration.

Table 4: shows ΔH (intercept) and ΔS (from slope) for the corrosion of Zn in HCl 0.01 M solution at different LAS concentrations.

Conclusion

LAS led to protect Zn from corrosion in 0.01M HCl solution and the best LAS concentration was 50 mg/L (P% close to 64-25 %) at 313K.

The uses of 50 mg/L LAS led to lowest ΔS values for the corrosion which is due to the decreasing of the zinc ions effluence as a result of LAS layer adsorbed on zinc surface.

The presence of low concentration of LAS at low temperature, led to accelerate the corrosion of zinc because LAS act as an oxidation agent react with electrons in the cathodic regions and on increasing temperature the LAS particles go far from cathodic regions and act as a protected layer of anodic regions preventing the effluence of zinc ions to the solution.

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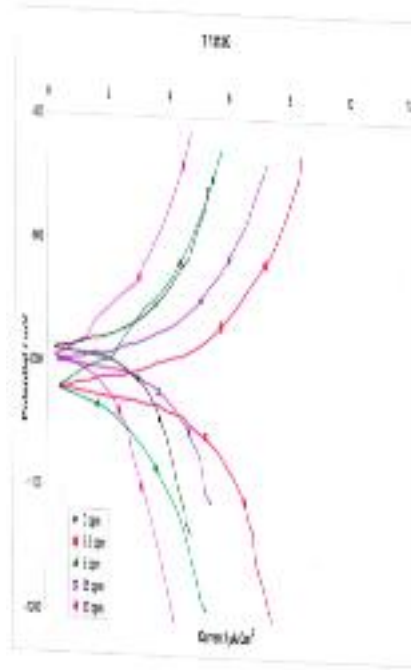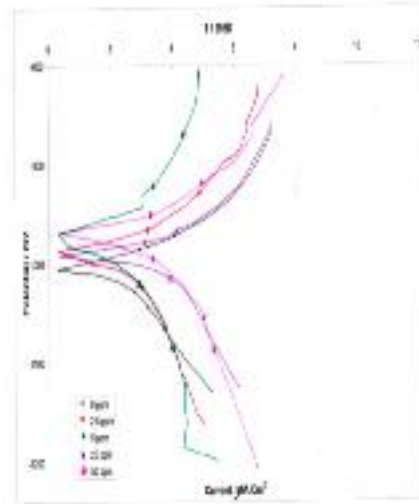
Fig.(1): Effect of LAS (0-50) mg/L on polarization curve for Zn in 0.01 M HCl at 293 K.
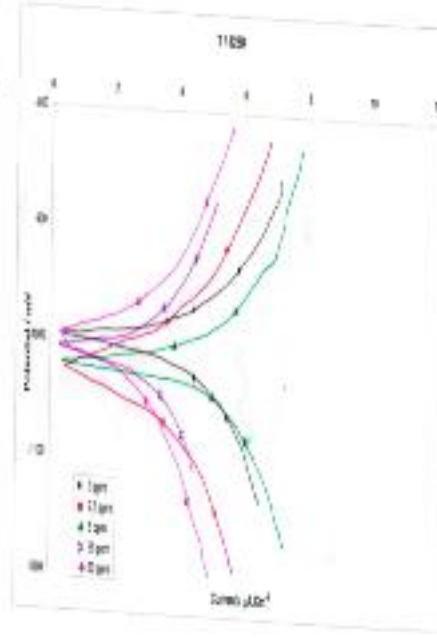
Fig.(2): Effect of LAS (0-50) mg/L on Polarization curve for Zn in 0.01 M HCl at 303 K.
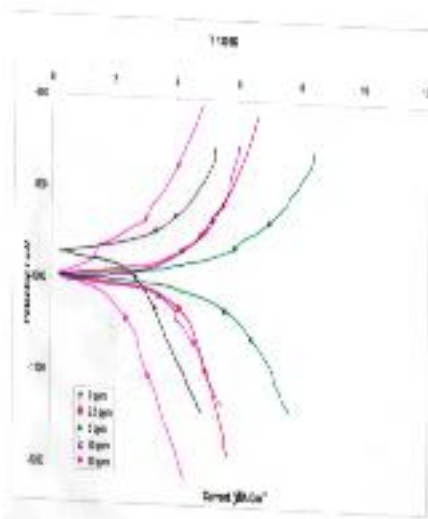
Fig.(3): Effect of LAS (0-50) mg/L on polarization curve for Zn in 0.01 M HCl at 313 K.

Fig.(4): Effect of LAS (0-50) mg/L on polarization curve for Zn in 0.01 M HCl at 323 K.

Table (1): Variation of corrosion potential (E$_c$), corrosion current densities (i$_c$), cathodic (b$_c$) and anodic (b$_a$) Tafel slopes for Zn in 0.01M HCl in absence and presence of LAS.

Solution C/mg. L^{-1}	T/K	- Ec /v	i$_c$ x 10^{-6} A.cm^{-2}	-b$_c$ x 10^{-3} v/decade	b$_a$ x 10^{-3} v/decade
0 mg/L	293	1.0082	59.60	138.7	62.90
	303	0.9694	239.16	156.2	80.10
	313	0.9886	316.70	136.7	106.80
	323	0.9955	449.55	138.3	107.20
2.5 mg/L	293	0.9855	158.39	182.3	68.50
	303	0.9974	264.19	178.8	101.70
	313	1.0154	436.28	121.6	108.90
	323	1.0157	498.11	134.0	106.40
5 mg/L	293	0.9778	165.09	146.4	105.10
	303	0.9954	284.15	135.6	109.30
	313	1.0156	296.80	83.60	101.70
	323	1.0144	359.79	91.80	90.00
25 mg/L	293	0.9890	213.85	147.1	99.40
	303	0.9991	252.02	152.2	96.80
	313	0.9985	246.08	130.2	99.50
	323	1.0091	428.87	152.3	123.80
50 mg/L	293	0.9766	36.99	124.5	64.80
	303	0.9960	106.25	162.8	105.70
	313	0.9972	113.2	129.0	95.80
	323	0.9951	173.07	142.2	85.50

Table (2): Variation of activation energy ΔG, protection efficiencies P% and polarization resistances (R_p), corresponding transfer coefficients (α_a and αc) and exchange current densities (i_0) for Zn at 0.01M HCl.
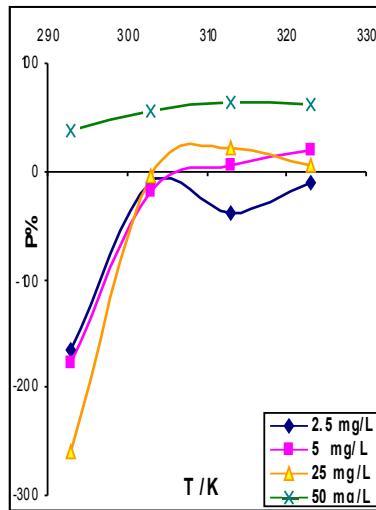
Solution c/ mg. L^{-1}	T/K	$-\Delta G/$ kJ.mol^{-1}	P%	$R_p \times 10^3$ Ω.cm²	$i_0 \times 10^7$ A.cm^{-2}	$-\alpha_c \times 10^{-4}$	$\alpha_a \times 10^{-4}$
0 mg/L	293	185.63	---	315.27	0.800	4191	9242
	303	187.09	---	96.13	2.715	3848	7505
	313	190.79	---	82.19	3.281	4543	3874
	323	192.13	---	58.33	4.770	4634	5978
2.5 mg/L	293	190.20	-165.75	136.49	1.849	3189	8487
	303	192.49	-10.46	106.54	2.450	3362	5911
	313	195.97	-37.73	57.17	4.716	5107	5702
	323	199.60	-10.80	51.70	5.382	4782	6023
5 mg/L	293	188.71	-176.99	160.91	1.568	3971	5531
	303	192.11	-18.81	92.48	2.822	4454	5500
	313	196.01	+6.29	67.12	4.017	7428	6106
	323	1.95.77	+19.96	54.84	5.073	6981	7120
25 mg/L	293	190.87	-258.8	120.44	2.095	3952	5848
	303	192.82	-5.37	101.94	2.560	3950	6210
	313	192.71	+22.31	99.51	2.709	4769	6241
	323	194.75	+4.60	69.12	4.026	4210	5176
50 mg/L	293	188.48	+37.93	500.28	0.504	4669	8971
	303	192.22	+55.57	261.91	0.996	3692	5687
	313	192.45	+64.26	210.87	1.278	4814	6482
	323	192.05	+61.50	133.96	2.077	4506	7495

Table(3):Values Ea, log A and A at different LAS concentration

C/mg. L^{-1}	Ea/kJ.mol^{-1}	Log A/ molecule.cm^{-2}	A / molecule.cm^{-2}
0	50.337	10.8740	7.48×10^{10}
2.5	31.1504	7.7750	5.95×10^7
5	18.8788	5.6296	4.26×10^5
25	16.0290	5.1597	1.44×10^5
50	37.1875	8.2841	1.92×10^8

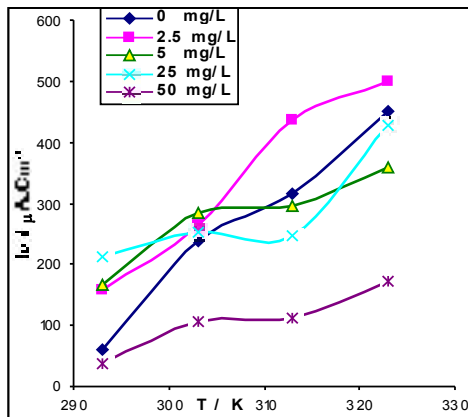**Table(4):Values ∆H, and ∆S at different LAS concentration**

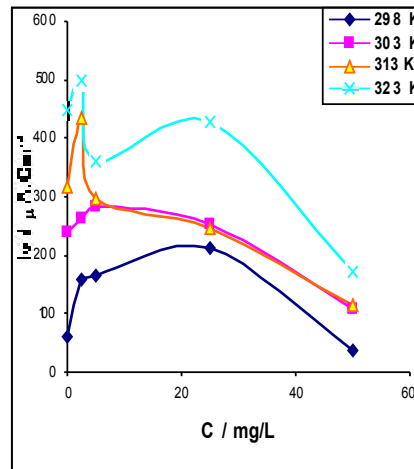| $C/mg.L^{-1}$	$- \Delta H / kJ.mol^{-1}$	$\Delta S / J.K^{-1}.mol^{-1}$
0	202.39	360
2.5	129.08	21
5	115.90	25
25	157.28	12
50	157.6	11

Fig.(5): Variation of p% with temperatures for different LAS concentration.
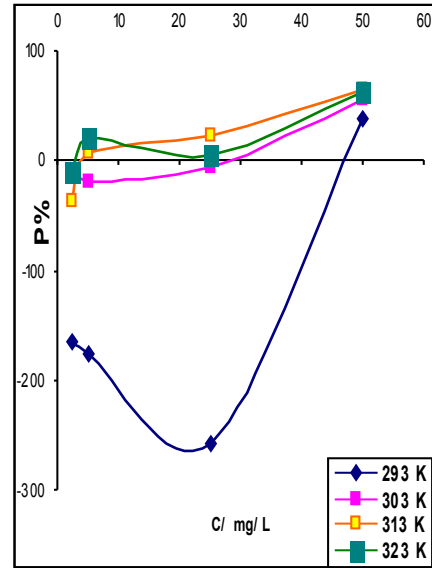
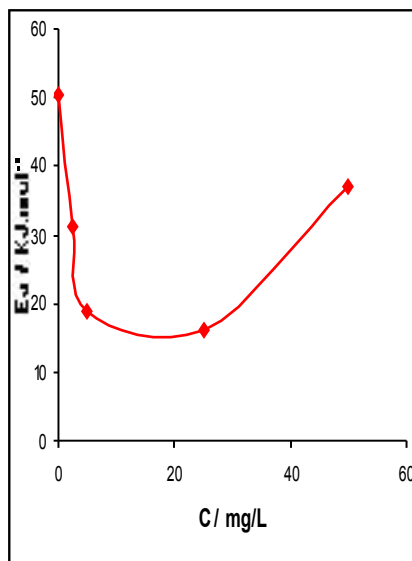**Fig.(6): Variation of p% with LAS concentration at different temperatures.**

Fig.(7): Variation of corrosion rate with temperatures for different LAS concentration

Fig.(8): Variation of corrosion rate with LAS concentration at different temperatures
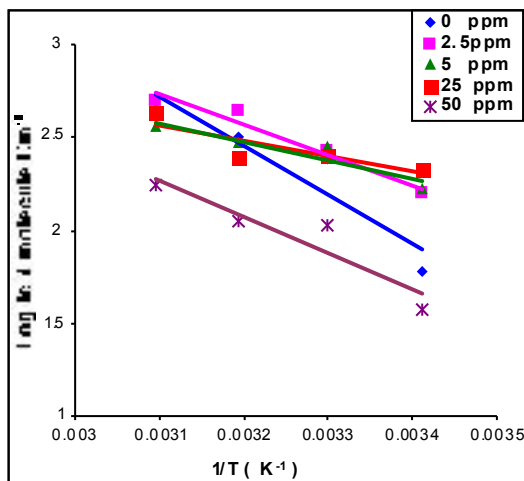
Fig.(9): Variation log i$_{corr}$ against 1/T for the corrosion of Zn in absence and presence of LAS in 0.01 M HCl
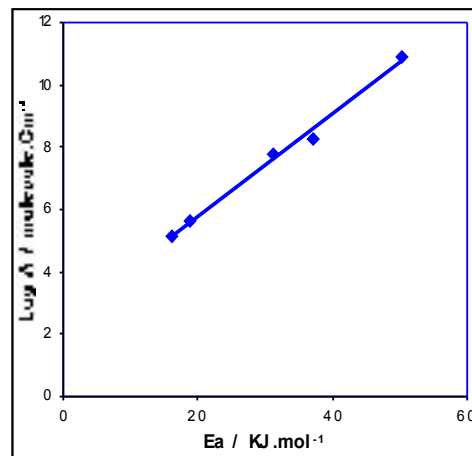

Fig.(10): Variation of E$_a$ against LAS concentration

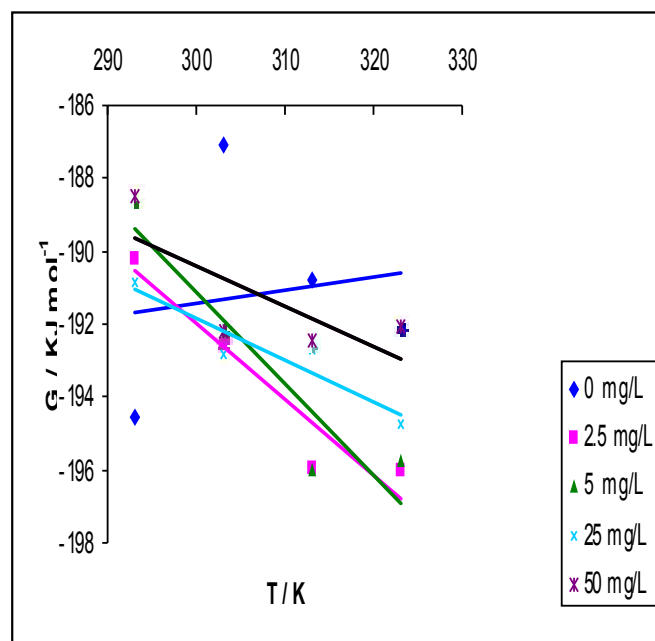**Fig.(11): Variation of E_a against Log A**

**Fig.(12): Variation of ΔG against temperature
at the different LAS concentration.**

إستخدام المجهاد الساكن لدراسة تأثير مادة الـ LAS في تآكل الزنك النقي في وسط حامض الهيدروكلوريك ذي تركيز 0.01 M

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الخلاصة :

تمت دراسة السلوك الكهروكيميائي لتاكل الزنك في محلول حامض الهيدروكلوريك 0.01 M بوجود وغياب المنظف سلفونات الكيل البنزين الخطيـة (LAS). ،اذ درس تأثير وجود المنظف (LAS) في مدى من التراكيز mg/L (0 – 50).

تضمنت الدراسة الكهروكيميائية متابعة الأستقطاب الكاثودي والأنودي باستخدام المجهاد الساكن في مدى حراري يتراوح K (293 – 323). اقترحت ميكانيكية لسرعة تآكل الزنك من خلال تقدير قيم (R_p , i_0 , b_c , b_a , α_c , α_a) والقيم الحركية (A , E_a) عند المدى الحراري أعلاه. كمـا عينت القيم الثرموديناميكية (Δs , ΔH , ΔG) لتآكل الزنك وتأثير الـ LAS بوصفها مادة مثبطة أو معجلة للتآكل.

الكلمات المفتاحية: تآكل الزنك، المجهاد الساكن، سلفونات الكيل البنزين الخطية