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CORROSION INHIBITION OF ZINC IN HYDROCHLORIC ACID MEDIUM USING UREA INHIBITOR

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Abstract

The corrosion behavior of Zn in 1 M HCl solution containing various concentration of Urea range ($10^{-3} \rightarrow 5x\ 10^{-3}$) M at temperature range (285-328) K was investigated. The corrosion inhibitive action of Urea on Zinc metal was studied using weight loss measurement and analytical titration of the amounts of dissolved Zinc in acidic solution in presence and absence of Urea , the results showed that Urea caused to protection efficiency reached to 88% when (50)mM Urea concentration was used . The coverage (θ) of metal surface by Urea could be obtained from the rate of corrosion in the presence and absence of Urea in the acid solution. A linear relationship was found to exist between the value of (C/ θ) and the corresponding Urea concentration (C) indicating that the inhibition action to occur via adsorption mechanism. Changes in the free energy, enthalpy and entropy associated with Urea adsorption have been determined. Apparent energies of activation have been calculated for the corrosion process of Zinc in the acid from corrosion rates and Arrhenius Plots.

Introduction

The dissolution behavior of Zinc in acidic and nearly neutral media known to be inhibited by nitrogen and sulfur containing organic compounds(1-4) such compounds contain electron–donating groups that decrease the corrosion rate by increasing the hydrogen over voltage on the corroding metal (5). Pyridine derivatives act as corrosion inhibitors and show a high inhibitive action for Zinc in a high concentration range of onium ions(6). The inhibitive action was attributed to the adsorption of the onium ions on the metallic Zinc surface. The corrosion inhibition of some β-diketo amino compounds was studied by a thermometric method(7). It was claimed that the adsorption process occur over the electrode surface through their carbonyl and nitrogen atom in two-step adsorption processes. The mechanism of a mixture of orgain compounds and metal ions was also examined(8). In the present investigation , the effect of Urea on the corrosion behavior of Zinc in 1M HCl solution was studied by weight losses(loss) and titration measurement(tit.). Inhibitors are widely used to control the corrosion of metallic materials and function by one or more of the following mechanisms(9):

(1) by adsorption on the surface of a corroding material.
(2) bychanging the corrosion characteristics of the environment.
(3) by inducing the function of a protective layer of corrosion product.

Experimental

The Zinc specimen had the following composition as revealed by emission spectroscopic analysis: (Fe,0.001%, Pb, 0.01%, Cd,0.001%) were used for the measurement of the corrosion rate. All test pieces (1.5 x 2.5 x 0.0027)cm. Were first degreased with hot trichloroethylene for 8h , and then treated for (30)s at (353-358)K in an alkaline bath of [(15g/L).

Na_2CO_3 + (15g/L) Na_2PO_4]. This was followed by rinsing distilled water and drying between filter paper(10). Each experiment was carried out with 100 ml of the corroding solution and with a fresh test piece. The temperature was measured to (± 0.1) C°. All chemical used were of A.R quality and were employed without further purification. HCl solution of 1M was prepared by analytical dilution from stock solution. EDTA solution of (0.01) M was prepared to determine the Zn^{+2} in acidic solution using Eriochrome BlakT (E.B.T) as indicator(11).

Results

The corrosion of Zinc in 1M HCl solution containing various Urea concentrations studied by weight loss measurements at various temperature (285-328)K at immersion period of 2h. The corrosion rate of Zinc is determined by using the relation(17):

$R_{(W)Loss} = \Delta m / \Delta t$ .... (1)

$R(w)tit = \Delta m / \Delta t$ .... (2)

Where Δ m is the mass loss or mass of Zn^{+2} in acidic solution and Δt is the immersion period. The corrosion rate result was shown in Table (1). The percentage protection efficiency (P%) is calculating using the relationship(17).

$P\% = ((1 - R_{(Winh)}) / R_{(Wo)}) \times 100$ .... (3)

where $R_{(Winh)}, R_{(Wo)}$ are the corrosion rate of Zinc in presence and absence of Urea . Table 2 shows the percent protection efficiency (P%) using the weight–loss and titiration measurements. The protection efficiency increase with temperature increase with different Urea concentration ranging (1-50) mM except with (1) mm Urea over (300) K as shown in Fig.(1a). The P% calculated from weight-loss and titration varied with Urea concentration at temperature varing (285-328)K as shown in Fig. (2).

The degree of coverage ϴinh can be obtained using the equation(12):

$\Theta inh = (R_{(Wo)} - R_{(Winh)}) / R_{(Wo)}$ .... (4)

The ϴinh values shown in Table (2). The adsorption behavior of Urea on the Zinc surface, can be described as indicated in Fig.(3a, 3b) where a linear relationship is shown to exist between the values of (C/ϴ) and the corresponding Urea concentration (C) .Such relationships suggest that Urea acts as corrosion inhibitor via adsorption on Zinc surface. The type of adsorbate-adsorbent interaction fallows Langmuir adsorption isotherm which may be represented as(13) :

$C/\Theta = (1/b) + C$ .... (5)

Where (1/b) is the intercept of each line on the (C/ϴ) axis when Urea concentration (C) approaches Zero .The constant b in equation (5) may be considered as an equilibrium constant which could be defined by the following equation (14) :

$b = a \times \exp(q / RT)$ .... (6)

where q is the heat of Urea adsorption on Zinc surface .A plot of logb against (1/T) (eq.6) should produce a straight line provided (q) and (a) remained independent of temperature over the mesurment temperature as indicated in Fig (4). The term b, defined by equation (6), is the equilibrium constant of the adsorption-desorption processes for Urea-Zinc system which may be represented as (17,18):

$b = \exp(-\Delta Ga/RT)$

$= \exp(\Delta Sa/R)\exp(-\Delta Ha/RT$ .... (7)

where ΔGa, ΔSa , ΔHa are respectively the changes in the free energy ,entropy and enthalpy of adsorption of Urea on Zinc specimen . Table (3)gives the b, ΔGa, ΔSa , ΔHa for the adsorption of urea on Zinc surface .The rate (R) of corrosion of Zinc in HCl solution ,in the absence and presence of Urea ,increased with temperature over the range (285-328)K .This is reflected in the variation of (log R) values with the reciprocal of temperature (1/T) in the manner depicted in Fig.(5). The linear relationship observed between the values of logR and (1/T) conform to an Arrhenius type equation(18,19) :

$R = A \exp(-Ea/ RT)$ .... (8)

where Ea is the apparent energy of activation for the corrosion process and A is the per-exponential factor ; values of Ea could thus be derived from the slopes of Fig.(5) . Fig.(6) shows the resulting values of Ea as a function of Urea concentration in 1M HCl solution . There was an initial sharp increase in Fig.(6) at Urea additions 1mM decreasing thereafter steadily with increasing Urea concentration to 50 mM . Thus, the presence of Urea in acid medium probably alters the energy barrier for the metal corrosion through enhancing the apparent of activation resulting in the consequent decrease of the surface tending for corrosion.

A linear relationship was found to exist between the experimental values of log A and the corresponding values of Ea as in Fig.(7) which could be expressed as (15) :

$\text{Log } A = I + (m \times Ea)$ .... (9)

where m and I respectively the slope and the intercept of the plots in Fig.(7). Such a relationship is termed a (compensation effect) which is frequently found to describe the kinetics of catalytic reactions on alloys (16). Equation (9) shows that simultaneous increase or decreases in Ea and Log A for a particular system tend to compensate from the standpoint of the reaction rate.

Discussion

The overall reaction during the corrosion of Zinc in acidic solution is as follows:

$$Zn + 2H^{+} \rightarrow Zn^{+2} + H_2$$

Which is the sum of galvanic reactions :

Anodic : $Zn \rightarrow Zn+ + e$

$Zn^{+} \rightarrow Zn^{+2} + e$

Cathodic : $H^{+} + e \rightarrow Hads$

$Hads + Hads \rightarrow H_2$

rds = rate determining step

Most inhibitors contain at least one polar group with an atom of Nitrogen, Sulfur or Oxygen, Sulfur or Oxygen, and each of them is considered an adsorption center. The protective properties of such compounds depend on the electron densities around the adsorption center. The higher the electron density at the center, the more effective the inhibitor. The corrosion rate values (at low temperatures) in the presence of 1mm of Urea in acidic medium cause to increase the active sites on the Zinc surface by reducing the activation energy of rds of the anodic or cathodic corrosion reaction. The reduction in the dissolution of Zinc in the presence of Urea may be attributed to Nitrogen and Oxygen atoms present in the functional group. These groups electroactive and interact with the metals surface to a greater extent. Adsorption can be electrostatic or chemisorptive or the inhibitor can act simply by physically blocking the active sites. An adsorption isotherm gives the relationship between the coverage of an interface with the adsorbed species ϴ and the concentration of species in the solution C.

A linear relationship between (C/ϴ) and C suggesting that the (inhibitor undergo adsorption according to the Langmuir adsorption isotherm. The low ΔHa values which reach to 26 kg mol^{-1} in titration way and reach to (1) k$_J$.mol^{-1} in weight–loss way indicated to the physically blocking for the active sites of Zinc surface, and indicate to the changing of the corrosion characteristic of the environment near surface. The temperature effect was significant in the presence of high concentration of Urea, and the P% increased with temperature increase generally, with simultaneous decrease in Ea and thus indicates the adsorption of Urea. This result may be related to the modification of metal dissolution mechanism interpreted by many authors(17) for the following reason. Temperature is a predominant factor in the formation of a protective layer at the metallic surface formed by metal inhibitor interaction, Based on this reason, the present inhibitor form a protective layer, and interaction between metal and inhibitor increase with temperature. This cause more surface coverage by the inhibitor and thus decrease the dissolution of Zinc.

Conclusion

Urea is a good corrosion inhibitor of Zinc in aqueous HCl medium. The highest protection efficiency reach to(88.2%) at (382) k by using 10 mm of Urea in HCl solution . This concentration (10 mm) causes to coverage equal to (0 - 88.2) of Zinc surface , and the corrosion process have ΔGa = -5.5 kJ mol-1, Urea can be synthesized easily , are readily soluable in water, and can be used as effective corrosion inhibitor for zinc in acid medium.

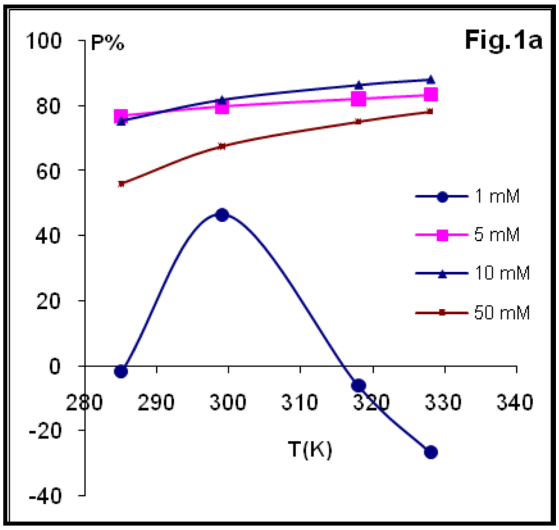


Fig.1a

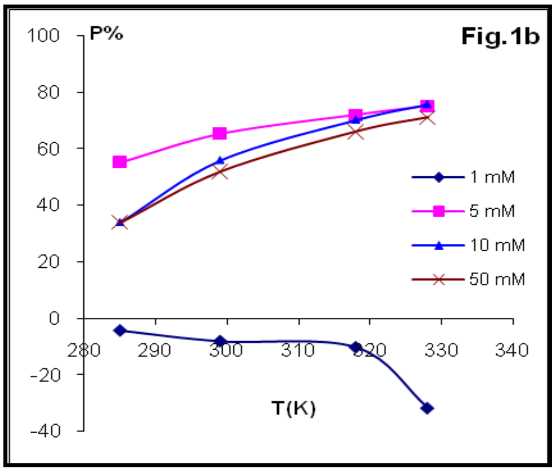
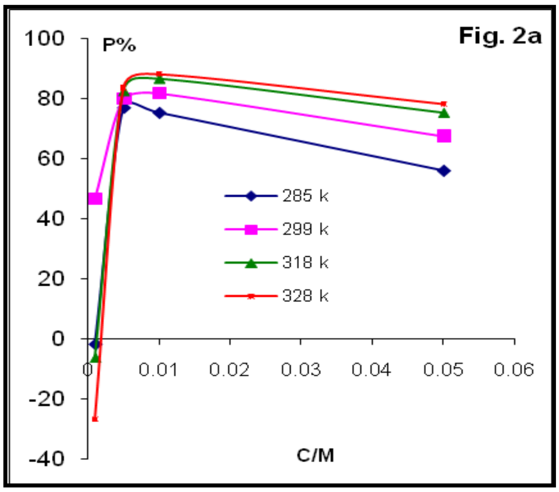


Fig. (1) : The relationship between P% and T(K) with different Urea concentration (a) by using weight-loss measurement (b) by using titration EDTA.



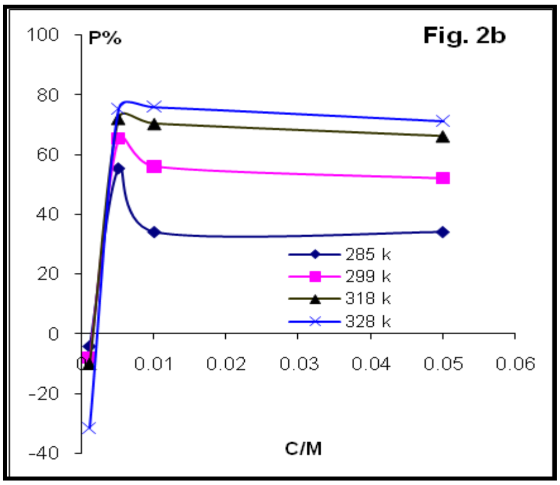
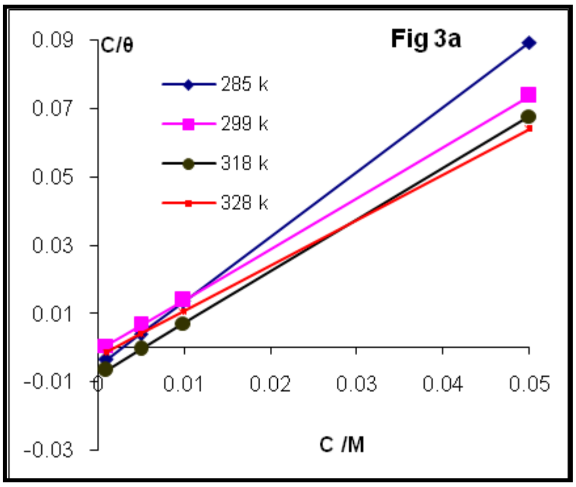


Fig. (2) : P% against Urea concentration temperature ranges (285-328). (a) by using weight-loss measurement (b) by using titration EDTA.



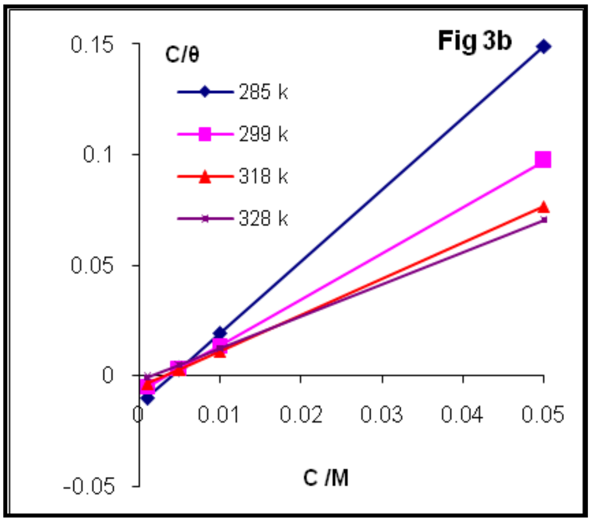


Fig. (3) : Langmuir adsorption of Urea on Zinc in 1 M HCl plotted as (C/θ) versus Urea concentration. (a) by using weight-loss measurement (b) by using titration EDTA.

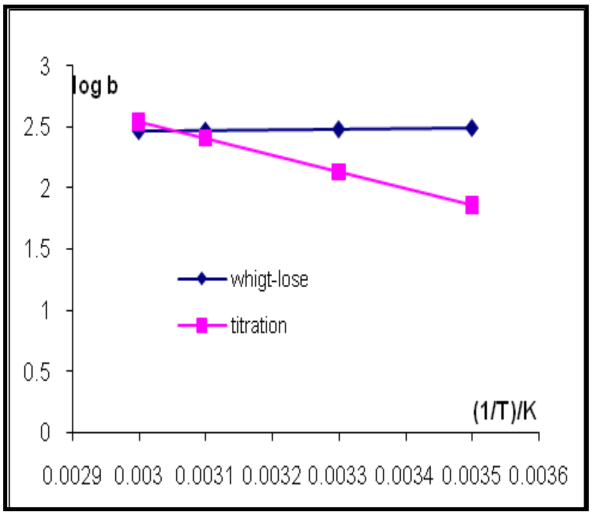


Fig.(4) : (log b) versus (1/T).

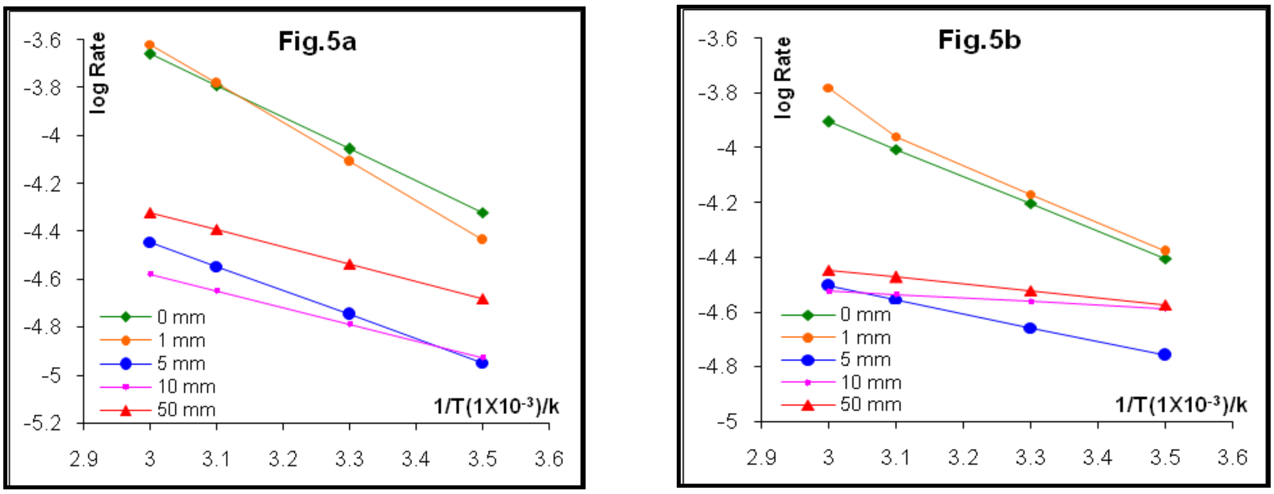


Fig.(5) : Arrhenius plot for the corrosion of Zinc in 1 M HCl at versus concentration
(a) by using weight-loss measurement
(b) by using titration EDTA.

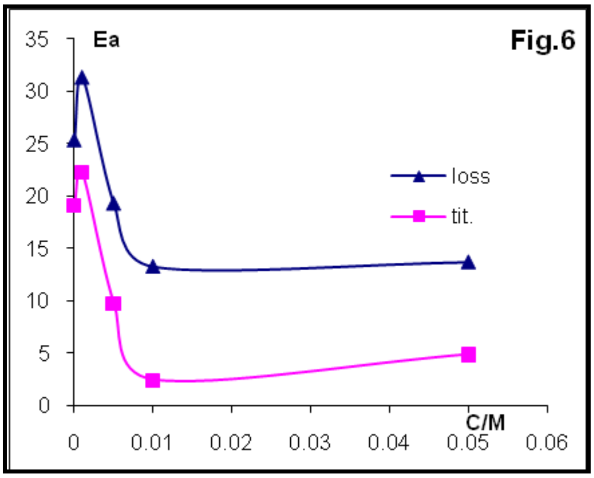


Fig. (6) : Values of apperent energy of activation (Ea) for the corrosion of Zinc in 1 M MCl solution as a function of Urea concentration (C/M).

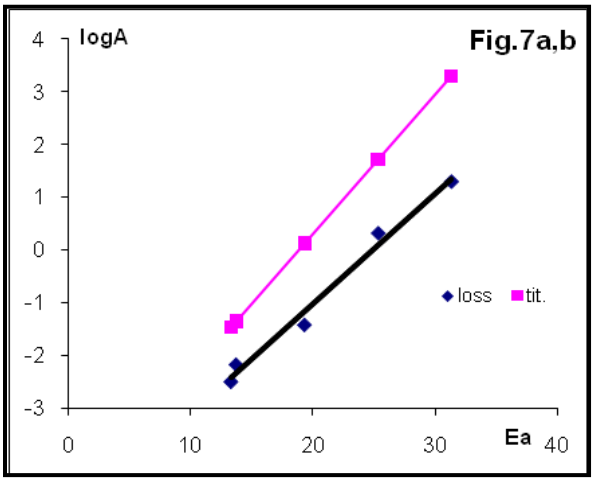


Fig. (7) : Ea values plotted versus log A for the corrosion of zinc in 1 M HCl with different Urea concentration.
(a) by using weight-loss measurement
(b) by using titration EDTA.

Table (1)
Corrosion rate (g/min) at different temperatures using different Urea concentration.

Tc^o	T_K	1/T	Con.$_{mm}$	$\Delta\, \omega t_{lose}$	Rate x 10^{-5}	Log (Rate) x -1	$\Delta\, \omega t_{tit}$	Rate x 10^{-5}	Log (Rate) x -1
12	285	0.0035	0	0.0057	4.7	4.321	0.0047	3.9	4.404
26	299	0.0033	0	0.0105	8.7	4.056	0.0075	6.2	4.204
45	318	0.0031	0	0.0194	16.1	3.791	0.0118	9.8	4.005
55	328	0.003	0	0.0263	21.9	3.659	0.0149	1.2	3.905
12	285	0.0035	1	0.0058	4.8	4.31	0.0049	4	4.38
26	299	0.0033	1	0.0056	4.6	4.33	0.0081	6.7	4.17
45	318	0.0031	1	0.0206	17.1	3.76	0.013	10.8	3.96
55	328	0.003	1	0.0333	27.7	3.55	0.0196	16.3	3.78
12	285	0.0035	5	0.0013	1.1	4.949	0.0021	1.7	4.75
26	299	0.0033	5	0.0021	1.7	4.748	0.0026	2.2	4.65
45	318	0.0031	5	0.0034	2.8	4.546	0.0033	2.8	4.55
55	328	0.003	5	0.0043	3.5	4.445	0.0037	3.1	4.5
12	285	0.0035	10	0.0014	1.1	4.926	0.0031	2.6	4.58
26	299	0.0033	10	0.0019	1.6	4.787	0.0033	2.7	4.56
45	318	0.0031	10	0.0026	2.2	4.648	0.0035	2.9	4.53
55	328	0.003	10	0.0031	2.6	4.578	0.0036	3	4.52
12	285	0.0035	50	0.0025	2	4.679	0.0031	2.6	4.57
26	299	0.0033	50	0.0034	2.9	4.536	0.0036	3	4.52
45	318	0.0031	50	0.0048	4	4.392	0.004	3.3	4.47
55	328	0.003	50	0.0057	4.7	4.321	0.0043	3.6	4.44

Table (2)
Protection efficiency, the degree of coverage at different temperature.

Con. mm	T_K	1/T	ω loss	θ	p%	ω tit.	θ	p%
0	285	0.0035	0.0057	-	-	0.0047	-	-
0	299	0.0033	0.0105	-	-	0.0075	-	-
0	318	0.0031	0.0194	-	-	0.0118	-	-
0	328	0.003	0.0263	-	-	0.0149	-	-
1	285	0.0035	0.0058	-0.0175	-1.754	0.0049	-0.042	-4.255
1	299	0.0033	0.0056	0.466	46.6	0.0081	-0.08	-8
1	318	0.0031	0.0206	-0.0618	-6.18	0.013	-0.101	-10.16
1	328	0.003	0.0333	-0.2661	-26.61	0.0196	-0.315	-31.54
5	285	0.0035	0.0013	0.771	77.1	0.0021	0.553	55.3
5	299	0.0033	0.0021	0.8	80	0.0026	0.653	65.3
5	318	0.0031	0.0034	0.824	82.4	0.0033	0.72	72
5	328	0.003	0.0043	0.836	83.6	0.0037	0.751	75.1
10	285	0.0035	0.0014	0.754	75.4	0.0031	0.34	34
10	299	0.0033	0.0019	0.819	81.9	0.0033	0.56	56
10	318	0.0031	0.0026	0.865	86.5	0.0035	0.703	70.3
10	328	0.003	0.0031	0.882	88.2	0.0036	0.758	75.8
50	285	0.0035	0.0025	0.561	56.1	0.0031	0.34	34
50	299	0.0033	0.0034	0.676	67.6	0.0036	0.52	52
50	318	0.0031	0.0048	0.752	75.2	0.004	0.661	66.1
50	328	0.003	0.0057	0.783	78.3	0.0043	0.711	71.1

Table (3)
Values of b, ΔH, ΔS, ΔG from the adsotption of Urea on

$T_{(K)}$	b		$-\Delta G$ kJ	
	loss	tit.	loss	tit.
285	181.81	75.187	13.6	37.575
299	1000	138.88	14.22	39.353
318	123.45	188.67	50.65	41.767
328	370.37	434.78	55.09	43.038

[redacted]

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الخلاصة

تم دراسة السلوك التاكلي للزنك في الوسط الحامضي لحامض الهيدروكلوريك (1مولاري) الحاوي على مدى من التراكيز المختلفة لليوريا تتراوح بين $(10^{-3}-5\times10^{-3})$ ملي مولار وبمدى من درجات الحرارة الذي يتراوح مابين (285−328) كلفن .وقد تمت هذه الدراسة باستخدام تقنيتين هما : 1. تقدير الوزن المفقود للزنك نتيجة التاكل و 2.تقدير الزنك الذائب في محلول الحامض بالتسحيح. وقد أظهرت النتائج ان اليوريا خفضت عملية التاكل الى 88 % اذا استخدمت بتركيز (50) ملي مولار ، كما تم الحصول على عامل التغطية (θ) لليوريا على سطح الزنك من سرعة التاكل بوجود وغياب اليوريا في الوسط الحامضي .وقد أظهرت الدراسة في هذا البحث أن هناك علاقة خطية مابين تركيز اليوريا وقيمة (C/θ) وهذا يدل على حدوث التثبيط بالأمتزاز،كما وتم دراسة التغير في قيمة الطاقة الحرة والأنثالبي والأنتروبي نتيجة لأمتزاز اليوريا على سطح الزنك .وأخيرا حسبت طاقة التنشيط لعملية التاكل من سرعة تاكل الزنك في الوسط الحامضي وعلاقة أرينوس.