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Corrosion *inhibition of Zinc by Imidazol in Acidic* Media

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Abstract :

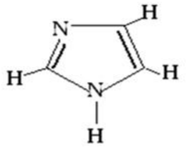
The inhibitive effect of imidazol on the dissolution of Zn in (1M) HCl has been studied. The inhibion effect of imidazol ,protection efficiency and the corrosion rate of Zn in (1M) HCl were investigated at various concentrations (1x 10^{-3} – 5x10^{-3}) M and tempearture range (285-328) K. The corrosion inhibitive of Zn by imidazol was studied using weight loss measurement and analytical titration of the amounts of dissolved zinc in acidic solution in presence and absent of imidazol. It was observed that imidazol led to protection efficiency reached to (88.93)% when (10)mM imidazol concentration was used. A linear relationship came true between (C/θ) and (C); where (θ) is the coverage of Zn surface by imidazol which could be obtained from the rate of corrosion in the presence and absent of inhibitor in the acid solution and (C) is the concentration of imidazol. This linear relationship indicate that the inhibition action occure via Langmiur adsorption mechanism. Eventually, the corrosion rates, activated energy ,Arrhenius constant, changes in free energy, enthalpy and entropy accompanying with imidazol adsorption on Zn surface were calculated.

Key word: zinc imidazol corrosion

Introduction

Zinc is a metal with numerous industrial applications and is mainly used for the corrosion protection of steel, it is corroded by many agents, of which aqueous acids are the most dangerous.[1] The problem is the acid solutions which are widely used in industry. The most important fields of application being acid pickling, industrial acid cleaning, acid descaling and oil well acidizing, and because of the general aggressively of acid solutions the practice inhibition is comonly used to reduce the corrosive attack on metallic materials.[2] The corrosion of zinc in acid media could be inhibited by nitrogen and sulfur containing organic compounds which they have electron- donating groups that make the hydrogen over-voltage on the corroding surface is faint and that will decrease the dissolution rate of the metal.[3] Methods for comparing the inhibition efficiencies of surfactants are numerous such as polarization measurements, weight loss determination, electrode potential measurement, construction of electrocapillary curves, depression of polarographic maxim, determination of electrode reaction parameters and determination of elements dissolved by ultraviolet – absorption spectroscopy.[4]

The present work has been planned to investigate the corrosion behaviour of Zn speciman in presence and absent of imidazol as inhibitor agent, which is an organic compound having a formula $C_3H_4N_2$ as shown in the following scheme[5,7] :



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Imidazol structure (M. Wt.=68.08g /mol, m.p.=90 °C, b.p.=257).

Two methods used for this purpose weight losses (loss) and titration measurements (tit). Inhibitors are widely used to control the corrosion of metallic materials and function by one or more of the following mechanisms:[5,8]

1- Adsorption on the surface of corroding material.
2- Changing the corrosion characteristics of the environment.
3- Inducing the function of a protective layer of corrosion product.

Materials and Methods:

In this study five samples of zinc pieces (1.5 x 2.5 x 0.0027) cm (which were first degreased with hot trichloroethylene for 8 h, 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], then rinsed with distilled water and drying by filter paper.[9]) were immersed in five beakers, each one containing 100 ml of (1M) hydrochloric acid and a certain concentration of imidazol as an inhibitor, these beakers putted in a water bath (fixing on a certine temperature electrically to ± 0.1C° by A.Gallenkamp thermometer) four 2 hr. Then the weight loss of zinc (resulting by corrosion) have been determined by two methods first by weighting the sample before and after corrosion(using sensitive ($\pm 10^{-4}$) balance type mettler HL 32 from Switzerland), and second by chemical titration, using ethelendiamine (EDTA) and Eriochrome Black T (EBT) as indicator in a solution of pH=10.[10] Both of methodes shown a good approximation values in final results. The spectroscopic analysis of the zinc specimen demonstrate the following composition: (Fe, 0.001% , Pb, 0.01%, Cd, 0.001%).

Results

In this study the rate of zinc corrosion in (1M) HCl solution containing various imidazol concentrations ranging (1-50) mM at various temperature ranging between (285-328) K at immersion period of 2 hr, were determined by weight loss measurements (table1).The corrosion rates(R) determined by using the relation:[11]

$R_{w(loss)} = \Delta m / t$ .... (1)

$R_{w(tit)} = \Delta m / t$ .... (2)

Where Δm is the mass loss or mass of Zn^{2+} in acidic solution and t is the imersion period(2hr). The rate of zinc corrosion (R) decreases extremely with increasing the imidazol concentration especially at the range of (5-50)m M as shown in table (1).

The degree of coverage θ_{inh} determined by using the following equation of:[12]

$\theta_{inh} = (R_{(wo)} - R_{(winh)}) / R_{(wo)}$ ....(3)

Where $R_{(wo)}$, $R_{(winh)}$ are the corrosion rate of zinc in absence and present of imidazol respectively. Where θ_{inh} multiplying by 100%, the percentage protection efficiency (P%) will obtained by an equation of:[13]

$P\% = [1-(R_{(winh)} / R_{(wo)})] \times 100$..(4)

Table (2) shows θ_{inh} and (P%) values which calculated by using the weight loss and titration measurements, at various concentration of Imidazol ranging (1-50)mM at range temperature (285-328) K with immersion period of 2h. The percent protection efficiency (P%) increase with temperature increasing at different imidazol concentration ranging (1-50)m M except with (1)mM imidazol as shown in fig(1):

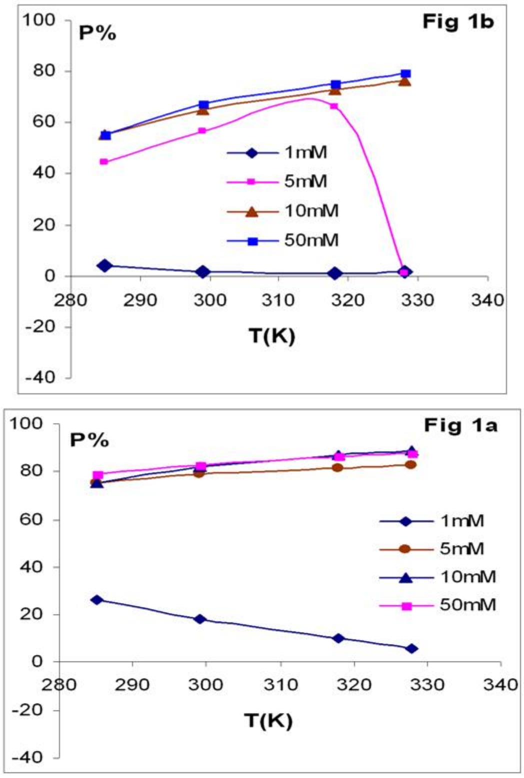


Fig. 1 :The relationship between P% and T(k) at different Imidazol concentration
(a) by using weight - loss measurement .
(b) by using titration with EDTA

and p% increase with concentration increasing at different temperature as shown in fig. (2) :

Table (1): Corrosion rate (g/min) at different temperatures using different imidazol concentration for the corrosion of Zn in (1M HCl)

Tc°	T_K	$(1/T)/K^{-1}$	C/mM	$\Delta \omega t_{lose}$ g	Rate(10^{-5}) g/min	Log (Rate) (10^{-1})	$\Delta\omega_g\ t_{tit}$	Rate(10^{-5}) g/min	Log (Rate) (10^{-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	0.0074	6.2	4.204
45	318	0.0031	0	0.0193	16.1	3.791	0.0118	9.8	4.005
55	328	0.003	0	0.0262	21.1	3.659	0.0149	12.4	3.905
12	285	0.0035	1	0.0042	3.5	4.449	0.0045	3.8	4.419
26	299	0.0033	1	0.0086	7.1	4.144	0.0073	6.1	4.21

45	318	0.0031	1	0.0173	14.4	3.839	0.0119	9.9	4.002
55	328	0.003	1	0.0246	20.5	3.686	0.0151	12.6	3.898
12	285	0.0035	5	0.0014	1.2	4.918	0.0026	2.1	4.658
26	299	0.0033	5	0.0022	1.9	4.719	0.0032	2.7	4.566
45	318	0.0031	5	0.0036	3	4.52	0.004	3.3	4.475
55	328	0.003	5	0.0045	3.7	4.421	0.0044	3.7	4.429
12	285	0.0035	10	0.0014	1.2	4.913	0.0012	1.7	4.745
26	299	0.0033	10	0.0019	1.6	4.789	0.0026	2.1	4.659
45	318	0.0031	10	0.0025	2.1	4.664	0.0032	2.6	4.573
55	328	0.003	10	0.0029	2.4	4.602	0.0035	2.9	4.531
12	285	0.0035	50	0.0012	1	4.972	0.0021	1.7	4.747
26	299	0.0033	50	0.0018	1.5	4.812	0.0024	2	4.681
45	318	0.0031	50	0.0026	2.2	4.652	0.0029	2.4	4.616
55	328	0.003	50	0.0032	2.6	4.572	0.0031	2.6	4.583

Table (2): Protection efficiency, the degree of coverage at different temperature for the corrosion of Zn in (1M)HCl by using different imidazol concentration

Con.(C) M	T_K	1/T	W_{loss} g	θ	C/ θ	p%	W_{tit} g	θ	C/ θ	p%
0	285	0.0035	0.0057	-	-	-	0.0047	-	-	-
0	299	0.0033	0.0105	-	-	-	0.0074	-	-	-
0	318	0.0031	0.0193	-	-	-	0.0118	-	-	-
0	328	0.003	0.0262	-	-	-	0.0149	-	-	-
1	285	0.0035	0.0042	0.2631	.0038	26.31	0.0045	0.0425	.0235	4.25
1	299	0.0033	0.0086	0.1809	.0055	18.09	0.0073	0.0135	.0740	1.35
1	318	0.0031	0.0173	0.1036	.0096	10.36	0.0119	0.0084	.1190	0.84
1	328	0.003	0.0246	0.061	.0163	6.1	0.0151	0.0134	.0746	1.34
5	285	0.0035	0.0014	0.7543	.0066	75.43	0.0026	0.4468	.0111	44.68
5	299	0.0033	0.0022	0.7904	.0063	79.04	0.0032	0.5675	.0088	56.75
5	318	0.0031	0.0036	0.8134	.0061	81.34	0.004	0.661	.0075	66.1
5	328	0.003	0.0045	0.8282	.006	82.82	0.0044	0.0105	.4761	1.05
10	285	0.0035	0.0014	0.7543	.0132	75.43	0.0021	0.5531	.018	55.31
10	299	0.0033	0.0019	0.819	.0122	81.9	0.0026	0.6486	.0154	64.86
10	318	0.0031	0.0025	0.8704	.0114	87.04	0.0032	0.7288	.0137	72.88
10	328	0.003	0.0029	0.8893	.0112	88.93	0.0035	0.7651	.0130	76.51
50	285	0.0035	0.0012	0.7894	.0633	78.94	0.0021	0.5531	.0903	55.31
50	299	0.0033	0.0018	0.8285	.0603	82.85	0.0024	0.6756	.0740	76.56
50	318	0.0031	0.0026	0.8652	.0577	86.52	0.0029	0.7542	.0662	75.42
50	328	0.003	0.0032	0.8778	.0569	87.78	0.0031	0.7919	.0631	79.19

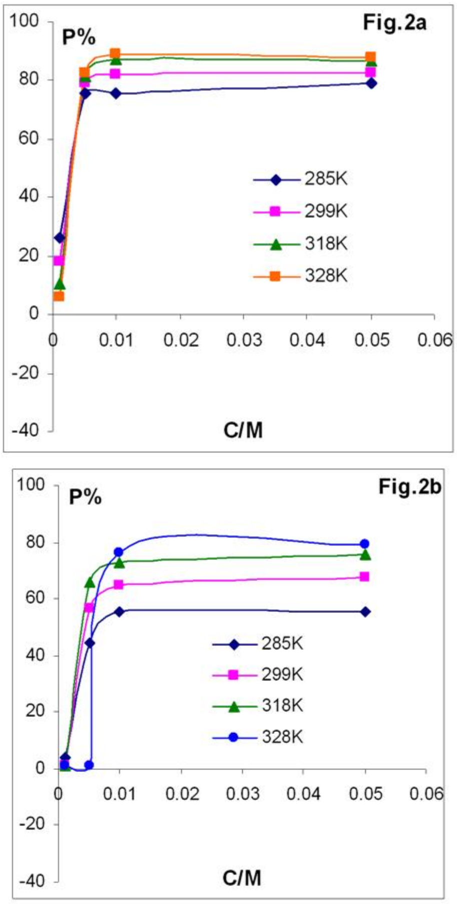
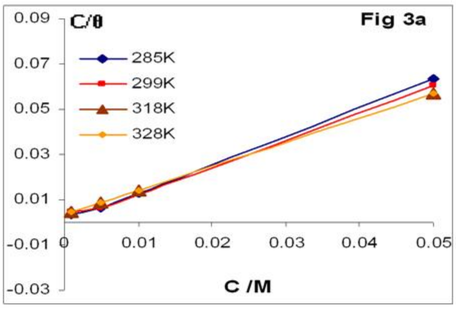


Fig.2: P% against Imidazol concentration at temperature ranges (285-328) K .
(a) by using weight - loss mesurement .
(b) by using titration with EDTA .

The adsorption behavior of Imidazol on zinc surface shown in fig. (3) where a linear relationship is shown to exist between the values of (C/θ) and the corresponding imidazol concentration (C), which is means that imidazol acts as corrosion inhibitor by adsorption on zinc surface:



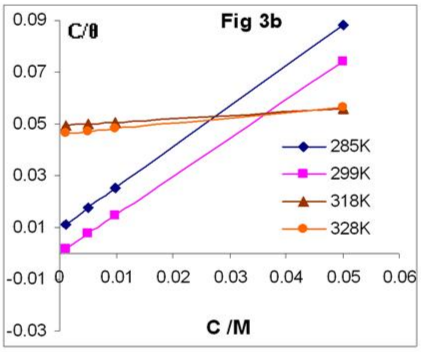


Fig. 3 : Langmuir adsorption of Imidazol on zinc in 1M HCl plotted as (C/θ) versus concentration of Imidazol.
(a) by using weight - loss mesurement .
(b) by using titration with EDTA .

This type of adsorbate –adsorbent interaction follows Langmuir adsorption isotherm[14,15] :

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

Where (1/b) is the intercept of each line on the (C/θ) axis when Imidazol concentration (C) approaches zero. Thermodynamic parameters (ΔG, ΔH and ΔS) for zinc adsorption can be calculated by the following equations:[16]

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

$a = \exp(\Delta S/R)$ ....(7)

$b = \exp(-\Delta H/RT)\ .\ \exp(\Delta S/R)$....(8)

$\text{Log}b = -\Delta H/2.303x(1/T) + (\Delta S/2.303)xR$ ..(9)

$\Delta G = \Delta H - T\Delta S$ ....(10)

Where q in equation (6) is the heat of imidazol adsorption on zinc surface which can be obtained from the plote of log b against (1/T) as shown in fig. (4) :

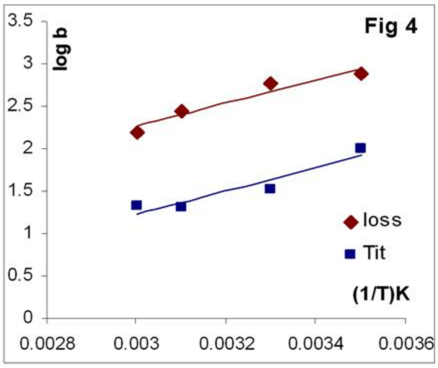
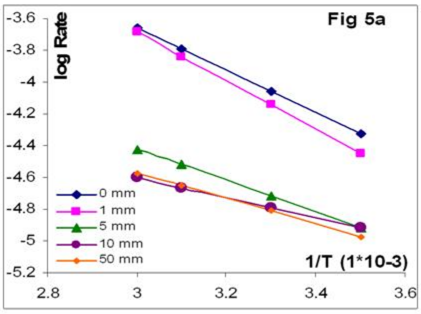


fig.(4) :a plot of (log b) versus (1/T) to fined the heat of Imidazol adsorption on Zn surface in 1M HCl solution.

Changes in free energy, entropy enthalpy (ΔG_a, ΔS_a, ΔH_a and b) of adsorption of imidazol on zinc specimen are given in table (3). The rate (R) of zinc corrosion in HCl solution in the absence and present of imidazol, increased with temperature increased from (285to 328)K, this reflected in the variation of (log R) values with the reciprocal of temperature (1/T) in the manner depicted in fig. (5) :



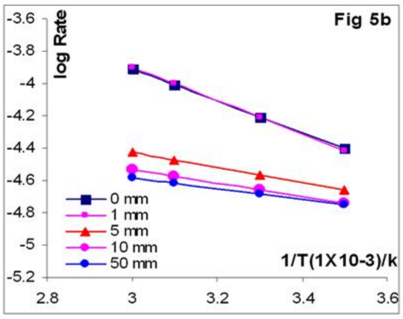


Fig.5 :Arrhenius plot for the corrosion of zinc in 1M HCl at versus Imidazol concentration.

(a) by using weight - loss mesurement .

(b) by using titration with EDTA .

The linear relationship observed between the values of log R and (1/T) conform to an Arrhenius type equation[17,18]:

$K= A \exp (-E_a/RT)$ ...... (11)

Where E_a is the apparent energy of activation for the corrosion process q and A is the per- exponential factor (table 4); values of E_a could be obtained from the slopes of fig.(5)and A from intercept. Fig. (6) is a diagram of resulting values of E_a against imidazol concentration (C) in 1M HCl solution.

Table 3 : Values of b , Δ H, Δ S, Δ G obtained from the adsorption of imidazol **on Zn surface.**

$T_{(K)}$	b		- Δ G J		**Δ H and Δ S at the range of temperature of (285-328)K**
	loss	tit.	loss	tit.	
285	769.23	102.04	16.66	10.52	**Δ H loss = -26291 J**
299	588.23	32.36	15.66	9.754	**Δ H tit = -26186 J**
318	277.77	20.2	14.99	8.71	**Δ S loss = -35.52 J**
328	156.25	21.69	14.63	8.161	**Δ S tit = -54.95 J**

Table 4 : Ea and log A Values for the corrosion of Zn in 1M HCl solution with different Imidazol concentration by using weight - loss measurements and titration with EDTA.

Con. mM	Log A		Ea /J.mol-1	
	Loss	Tit	Loss	tit
0	0.3114	-0.9158	25.33	19.07
1	0.8896	-0.7707	29.19	19.95
5	-1.4419	-3.0515	19.00	8.789
10	-2.7364	-3.2444	11.90	8.207
50	-2.1783	-3.6001	15.27	6.274

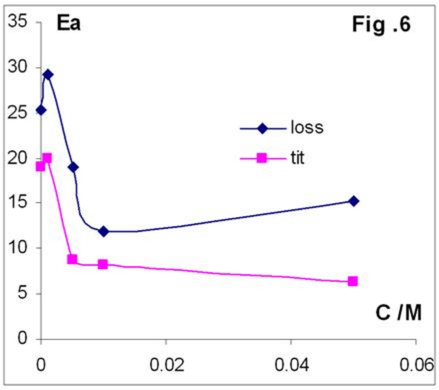


Fig. 6 : Values of apperent energy of activation (E_a) for the corrosion of zinc in 1M HCl solution as function of imidazol concentration (C/M).

It is easily realize an initial elevated sharp concentration of (1 M) imidazol ,but it will be decrease steadily with increasing Imidazol concentration to (50) mM .Thus the presence of imidazol in acid medium decresed the energy level for zinc corrosion by changing the activation energy (E_a) through decreasing the surface tendency for corrosion ,so the relationship above is found to explain this truth .

Fig.(7) shows a diagram of experimental values of log A against corresponding values of E_a which obtained from the equation[19]

Log A = I + (m x E_a) ......(12)

Where I and m respectively the intercept and slope of the plots in fig.(7):

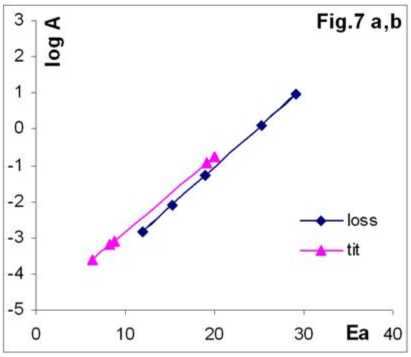


Fig. 7 :Ea values plotted versus log A for the corrosion of zinc in 1M HCl with different Imidazol concentration.
(a) by using weight - loss mesurement .
(b) by using titration with EDTA.

Such relationship is termed a (compensation effect) which is often found for description the kinetics of catalytic reaction on alloys. Equation (12) shows that simultaneous increase or decrease in E_a and log A for a particular system tend to compensate from the standpoint of the reaction rate.[8]

Discussion

The expectation galvanic reaction are :

Anodic : $Zn \longrightarrow Zn^{+} + e$

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

Cathodic : $H^{+} + e \longrightarrow Hrds$

$H\,rds + H\,rds \longrightarrow H_2$

rds = rate determining step

thus the sum of overall reaction occurrence during the corrosion of zinc in acidic solution is :

$$Zn + 2H^{+} \longrightarrow Zn^{2+} + H_2 \uparrow$$

The mechanism of corrosion inhibition depend on the truth of hydrogen reduction, which is the principle of the cathodic reaction during the corrosion of zinc in HCl solution. In acid solution the used inhibitors found as protonated type, which can adsorb on the cathodic sites of zinc and decrease the evolution of hydrogen, the rate of cathodic reaction is thus reduced in presence of inhibitors. The corrosion rate values at low temperatures in the presence of (1)mM of imidazols 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 functional group presence imidazol which is contain nitrogen may be cause the reducion in the dissolution of zinc metal due to the high density of electrons around the adsorption center, such groups electro active and interact with metals surface or species to a greater extent, thus a physical blocking formed for the active sites of zinc surface, so that ΔH decrease and reach to 26186 J. mol^{-1} and 26291 J. mol^{-1} in titration way and weight - loss way respectively. Adsorption of imidazol on zinc surface occur according to Langmuir adsorption. Isotherm such conclusion infer from relationship between (C/θ) and C. The protection efficiency P% and the surface coverage increase with high values of temperature due to the interaction between zinc and imidazol which owing to form a protective layer at the metallic surface.

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Fig. 3 :
Langmuir
adsorption
of Imidazol
on Zinc in

تثبيط تاكل الزنك في الوسط الحامضي بأستخدام الأميدازول

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خلاصة البحث:

تمت دراسة التاثير التثبيطي للأميدازول في تاكل الزنك في وسط محلول حامض الهيدروكلوريك (1M) باستخدام مدى من تراكيز المثبط (الاميدازول) تتراوح ما بين ($1x10^{-3}$ -$5x10^{-3}$) ملي مولاري وبمدى من درجات الحرارة تراوح بين (285 – 328) كلفن , وقد تم متابعة تلك العملية بطريقتين , الأولى قياس الوزن المفقود لسبيكة الزنك المستخدمة قبل وبعد التثبيط والثانية هي تقدير الزنك في محلول الحامض بتسحيحه ضد محلول الـ EDTA وقد أظهرت النتائج أن الأميدازول قد ثبط فعلا عملية التاكل وبنسبة تصل الى (88.93%) عند استخدام تركيز 10 ملي مولاري من المثبط. تم الحصول على علاقة مستقيمة بين (C/θ) و (C) حيث θ هو مدى التغطية لسطح الزنك بالمثبط و C هو تركيز المثبط هذه العلاقة المستقيمة تشير لحدوث ميكانيكية الامتزاز نوع لانكماير. كما وتم حساب تغيرات الطاقة الحرة لكبس والانثالبي والانتروبي المصاحبة لامتزاز الاميدازول على سطح الزنك وكذلك تم حساب قيم طاقة التنشيط E_a وثابت ارينوس.

الكلمات المفتاحية: زنك، اميدازول.