CORROSION INHIBITION OF ZINC IN HYDROCHLORIC ACID MEDIUM BY THIOUREA AND GUANIDIN.

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Abstract

The inhibition action of thiourea and guanidine on the corrosion behavior of zinc in 1M HCl was investigated using weight loss measurement and by following the zinc ions concentration in solution after several times by atomic absorption spectroscopy (AAS). The two inhibitors reduced the corrosion rate of zinc and the protection efficiency ranging between(10.6-59.8) at low temperature (285, 299) K and the two inhibitors get to a similar protection at (318, 328) K almost. Adsorption isotherm was like the Langmuir adsorption isotherm. The two organic compounds reduced the rate of the hydrogen evolution reaction.

تثبيط تأكل الزنك في حامض الهيدروكلوريك بأستخدام, الثايويوريا والگواندين

الخلاصة

تمت دراسة الفعل التثبيطي للثايويوريا والگواندين على تأكل الزنك في محيط حامض الهيدروكلوريك (1مولاري). أستخدمت طريقة فرق الوزن وطريقة متابعة تركيز ايونات الخارصين في المحلول بعد أوقات مختلفة باستخدام مطيافية الامتصاص الذري. بينت الدراسة أن المادتين أدت الى تقليل سرعة تأكل الزنك وبكفاءة حماية تراوحت بين (10.6 – 59.8) في الدرجات الحرارية الواطئة(285و299) كلفن. كلا المثبطين اعطيا حماية متشابهة عند االدرجات(328و318) كلفن غالباً.آيزوثيرم الأمتزاز كان من نوع ايزوثيرم لنكماير. سبب المثبطين العضويين تقليل سرعة تحرر غاز الهيدروجين الناتج من التفاعل الكاثودي ضمن عملية التآكل.

Introduction

The use of various types of organic inhibitor in acid solution is very common, particularly in view of the rate of corrosion shown by metallic materials in such media. Recently it was shown [1] that most metals have poor corrosion resistance in acids, but that several compounds inhibit their corrosion. Nitrogen or sulfur containing organic compounds like thiourea generally effective corrosion inhibitors for many metals like steels in acidic media, because sulfur is a better electron donor than nitrogen and thus such compounds adsorb well on the metal surface [2].

As part of programme of evaluation of various organic compounds as corrosion inhibitors to many metals like zinc, the present work determin the effectiveness of two compounds thiourea: $(NH_2)_2C{=}S$ and guanidine: $(NH_2)_2C{=}NH$ on zinc corrosion rate. In other words, this study investigated the protection changing when C=O group is converted to C=S and C=NH and how theses groups affected the mechanism of inhibitors adsorption on the zinc surface at different temperature.

Experimental Method

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 (1.5X2.5X0.0027) cm, were first degreased with hot trichloroethylene for 8 hours, and then

treated for 30 seconds at (80-85) ^{o}C in an alkaline bath of [(15g/L) Na_2CO_3 + (15g/L) Na_3PO_4].This was followed by rinsing with distilled water and drying between filter paper [3]. Each experiment was carried out with 100mL of the corroding solution and with a fresh test piece. The temperature was measured to (± 0.1) ^{o}C. All chemicals used were of A.R quality. HCl solution of 1M was prepared by analytical dilution from stock solution (3M).
Atomic absorption spectrophotometer type GBC 933 plus was used to determine the concentrations of zinc ions in the corrosion solution.

Results and Discussion

The corrosion of zinc in 1M HCl solution containing various urea concentrate was studied before [4], and the (U) inhibition effect was compared with the inhibition effect of TU, and G.
Table 1 gives the corrosion rate (C.R) of zinc in 1M HCl with inhibitor concentrations (0,1,5,10,50) mM of thiourea (TU) and guanidine (G) at different temperature (285-328) K by using weight loss relation [4]. Table 1 also involved protection percentage (p%) and C/θ values, where θ equal to the coverage ratio. There is a good agreement between weight loss result and AAS results. Fig.1, 2 show the variation of p% with temperature for TU and G, while fig. 3, 4 show the variation of P% with TU and G concentration at different temperatures.

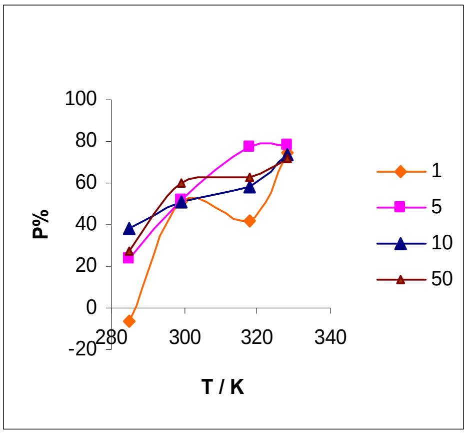

Figure (1): P% against T at different concentrations of thiourea

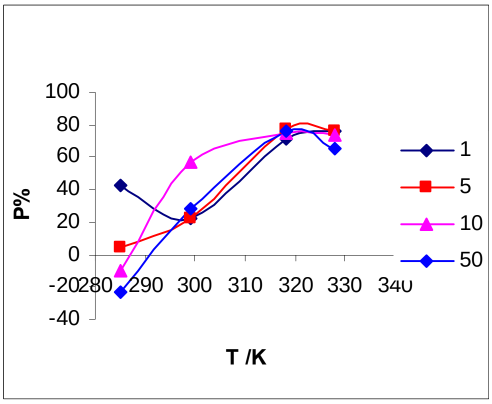

Figure (2): P% against T at different concentrations of guanidine

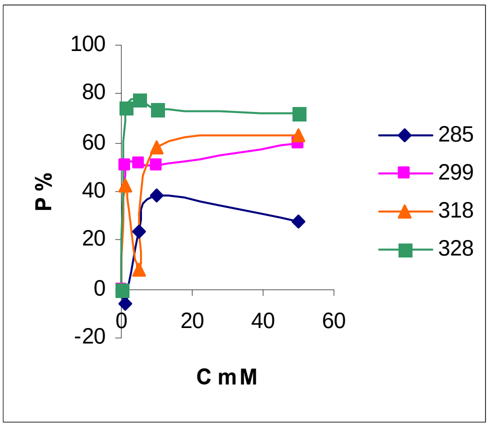

Figure (3): P% against concentration for thiourea at different temperatures.

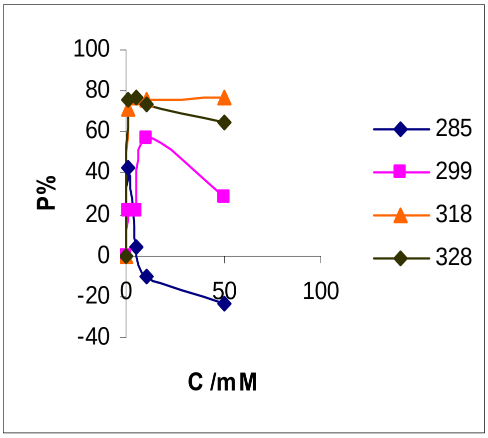

Figure (4): P% against concentration for guanidin at different temperatures.

Table (1): Values of corrosion rate (g / min), C/ θ and P% for the corrosion of zinc in 1M HCl with two inhibitors over temperature range (285-328) K.

		$CS(NH_2)_2$ (TU)					$CNH(NH_2)_2$ (G)				
T/K	Conc./ mmol. L^{-1}	rateX10^{-5}	P%	-log Rate	1/TX 10^{-3}	C/ θ	Rate X 10^{-5}	P%	-log rate	1/TX 10^{-3}	C/ θ
285	0	4.7	-	4.32	3.5	-	4.7	-	4.32	3.5	-
	1	5	-6.4	4.3	3.5	-0.0156	2.7	42.6	4.57	3.5	0.00235
	5	3.6	23.4	4.44	3.5	0.0212	4.5	4.3	4.35	3.5	0.11628
	10	2.9	38.3	4.45	3.5	0.0261	5.2	-10.6	4.28	3.5	-0.0943
	50	3.4	27.7	4.47	3.5	0.1805	5.8	-23.4	4.24	3.5	-0.2137
299	0	8.7	-	4.06	3.3	-	8.7	-	4.06	3.3	-
	1	4.3	50.6	4.37	3.3	0.00198	6.8	21.8	4.17	3.3	0.00459
	5	4.2	51.7	4.38	3.3	0.00967	6.8	21.8	4.17	3.3	0.02294
	10	4.3	50.6	4.37	3.3	0.0198	3.7	57.5	4.43	3.3	0.01739
	50	3.5	59.8	4.46	3.3	0.0836	6.2	28.7	4.21	3.3	0.17422
318	0	16.9	-	3.79	3.1	-	60.1	-	3.79	3.1	-
	1	9.3	42.2	4.03	3.1	0.00237	4.6	71.4	4.34	3.1	0.0014
	5	3.7	77	4.43	3.1	0.00649	3.7	77	4.43	3.1	0.00649
	10	6.7	58.4	4.17	3.1	0.01712	4	75.2	4.4	3.1	0.0133
	50	6	62.7	4.22	3.1	0.0798	3.8	76.4	4.42	3.1	0.0655
328	0	21.9	-	3.66	3	-	21.9	-	3.66	3	-
	1	5.5	74.9	4.26	3	0.00134	5.3	75.8	4.28	3	0.00132
	5	4.8	78.1	4.32	3	0.0064	5.2	76.3	4.28	3	0.00655
	10	5.8	73.5	4.24	3	0.01361	5.8	73.5	4.24	3	0.01361
	50	6.2	71.7	4.21	3	0.0697	17.7	64.8	4.11	3	0.07716

The corrosion rate of zinc is determined by using the relation [9]:

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

Where Δ m is the mass loss or mass of Zn^{+2} in acidic solutions and Δ t is the immersion period. The corrosion rate (C.R) result was shown in table (1) .The percentage protection efficiency P% is calculating using the relationship:

$$P\% = ((1 - R_{(Winh)}) / R_{(Wo)}) x100 \qquad (2)$$

where $R_{(Winh)}$, $R_{(Wo)}$ are the corrosion rate of zinc in presence and absence of inhibitor

$$\Theta inh = (R_{(Wo)} - R_{(Winh)}) / R_{(Wo)} \qquad (3)$$

Where Θ is the degree of coverage.
Fig. 5, 6 show plots of (C/θ) against concentration (C) for TU and G, the data fit straight lines indicating that these inhibitors adsorb according to the Langmuir adsorption isotherm. The Langmuir rearranging equation is:

$$C/\theta = 1/b + C \qquad (4)$$

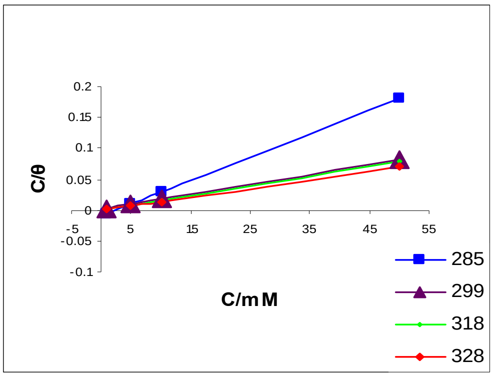

Figure (5): C/θ against C for thiourea at different temperatures.

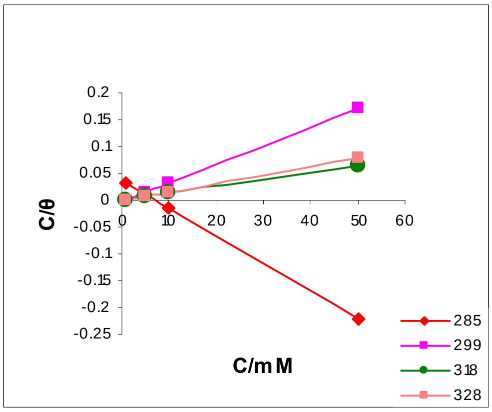

Figure (6): C/θ against C for guanidin at different temperatures.

The constant b in equation above may be considered as an equilibrium constant which could be defined by the following equation [6]:

$$b = \exp(\Delta S_a / R) \exp(-\Delta H_a / RT) \qquad (5)$$

The rate of corrosion (C.R)or R follows Arrhenius equation:

$$R = A \exp(-Ea/RT) \qquad (6)$$

Where Ea is the apparent energy of activation for corrosion process and A is the pre-exponential factor; values of Ea could thus be derived from the slopes of fig.7,8 (R against 1/T for TU and G).

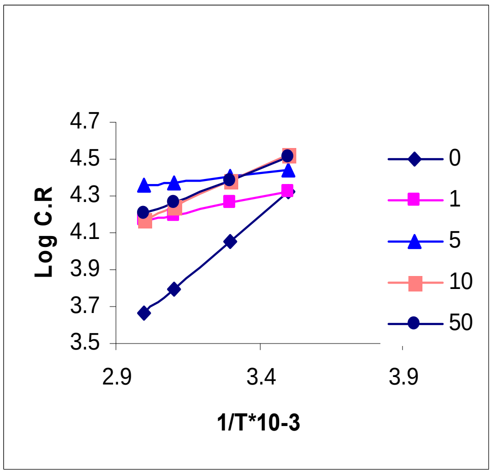

Figure (7): log C.R against 1/T for different concentrations of thiourea.

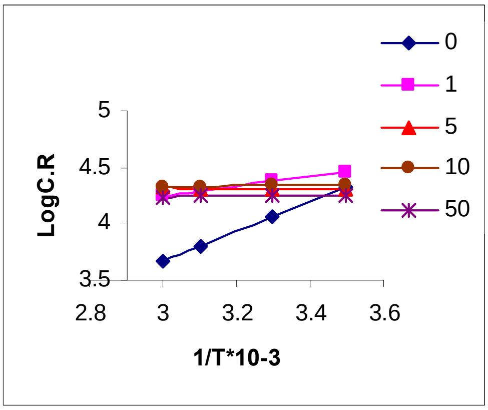

Figure (8): log C.R against 1/T for different concentrations of guanidin.

The variation of Ea with inhibitors concentrations were shown in fig.9.

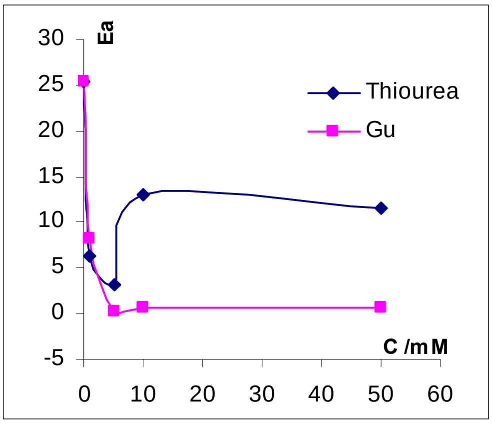

Figure (9): Ea against C for the two inhibitors.

A linear relationship was found to exist between experimental log A values and the corresponding values of Ea as shown in fig.10 and table 2, which could be expressed as [7]:

$$\log A = I + m \, . \, Ea \qquad (7)$$

where m and I respectively the slope and the intercept of all the plots in fig.10. such a relation is termed a (compensation effect) which is frequently found to describe the kinetics of catalytic reactions on alloys [8].

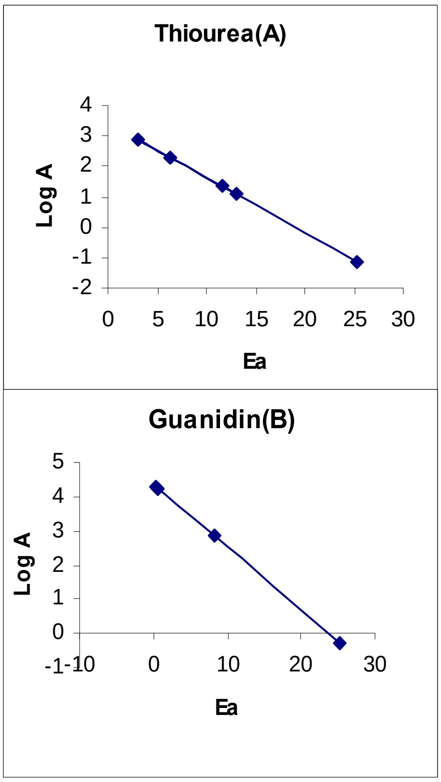

Figure (10): (A,B)- log A against Ea for the two inhibitors

Table (2): values of Ea ,Log A for thiourea and guanidin

Thiourea		Guanidin	
Ea Kj.mol-1	Log A	Ea Kj.mol-1	Log A
25.345	-1.14044	25.345	-0.2811
6.23	2.313639	8.308	2.840074
3.083	2.882302	0.29295	4.308432
13.11	1.070423	0.6816	4.237231
11.554	1.351592	0.584	4.255111

Equation (7) shows that simultaneous increase or decrease in Ea and log A for a particular system tend to compensate from the standpoint of the reaction rate.

Conclusion

In the light of the present study the following points were concluded:

1. Generally, TU, and G protection percentage (P%) increased with temperature rising from (285-328) K (for the same inhibiter concentration). The maximum P% by U was 75.8% by using $10X10^{-3}$ M at 328 K[(4)], and the maximum P% by TU reach to 78.1 by using $5X10^{-3}$ M at 328 K while the maximum P% by using G reach to 77 by using $5X10^{-3}$ M at 318 K and reach to76.3 when $5X10^{-3}$ M of G was used at 328 K.
2. The negative (p%) values occur with low inhibitor concentration $1X10^{-3}$M which is due to displacement of protonated species instead of hydrogen ions. In recent years attempts have been made to understand the nature of the interaction between the additives and the metal surface in terms of adsorption isotherms [12,13].
3. The mechanism of inhibited corrosion of zinc in HCl solution by the two compounds suppress the hydrogen evolution by adsorption and blocking of active sites, and the adsorption isotherms obey Langmuir isotherm.
4. The corrosion rate of zinc in HCl solution with and without the two inhibitors followed Arrhenius equation and the activation energy increased generally in the order:U> TU>G. The different of the center adsorbed atoms O,S,N may be the reason for this effect as well as the molecular weight variation.

The activation energies indicate to the interaction nature between the inhibitors and the metal surface.

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