THE EFFECT OF ORGANIC COMPOUNDS ON THE CORROSION OF ZINC IN AQUEOUS SOULTIONS

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ABSTRACT

The effect of benzotriazole (BTA), tolytriazole (TTA), benzo (c) cinnoline (E1), benzo (c) cinnoline 5-oxy (E2), 2,2-dinitro benzidyn (E4) and 2-Aminobenzo (c) cinnoline (E5), were investigated on the corrosion of pure zinc metal in four different aqueous solutions. The corrosion rates of the species were determined by electrochemical current density-potential curves. Primary studies have shown that BTA and TTA have inhibitory effect on copper, and compounds containing nitrogen and sulphur reduce the corrosion rate of zinc. The inhibition efficiencies were studied at different pH values in order to clarify the effect of organic compounds. The results revealed that BTA and TTA act as effective inhibitors on zinc in HCl, NaOH and NaCl solutions. Cinnolines were only effective in NaOH solution.

KEYWORDS: Corrosion, Zinc, Inhibition

INTRODUCTION

Zinc is most commonly used for cathodic protection of metals. Since zinc has a sufficiently negative standard electrode potential (-0.764 V), it is highly reactive and acts as sacrifial anode in cathodic protection [1]. Despite its highly negative electrode potential, a protective layer, either as zinc oxide or zinc hydroxide, forms on the metal surface in near- neutral aqueous solutions under normal atmosphere conditions which prevents its further reaction. This layer provides a better corrosion resistance for zinc, thus zinc is used as a galvanizing element for iron and steel. However, the oxide layer formed on the galvanized surface is not stable at all pH ranges, and corrosion is a critical problem when galvanized metal surface is exposed to acidic solutions or to an atmosphere polluted by SO_2.

In order to improve the corrosion resistance, surface pretreatments, coatings and additives are applied to the corrosive media[2-8]. Nitrogen and sulphur containing organic compounds have been found to prevent corrosion of zinc in acidic and near-neutral solutions by inhibiting reduction of hydrogen [9-11].

The present study investigates the inhibiting effects of the triazolic compounds benzotriazole (BTA), tolytriazole (TTA), benzo (c) cinnoline (E1), benzo (c)

cinnoline 5-oxy (E2), 2,2-dinitro benzidyn (E4) and 2-aminobenzo (c) cinnoline (E5) in NaCl, HCl, NaOH and NaCl/NaOH solutions.

2. EXPERIMENTAL DETAILS

The working electrode was prepared from cylindirical zinc rod (99.99 % purity, 2 mm diameter) embedded in a teflon tube using adhesive. The electrode was polished with 1200 grid emery paper prior to each experiment and rinsed with double distilled water. A platinum electrode and saturated calomel electrode were used as counter and reference electrodes, respectively. The electrolytes were prepared using Merck grade chemicals with double-distilled water.

The electrochemical measurements were performed in 1N HCl (pH=0.5), 1N NaCl (pH=6.8), 0.1N NaOH (pH=13) and 0.9N NaCl+0.1N NaOH (pH=11) for various concentrations of BTA, TTA, E1, E2, E4 and E5. The current-potential curves were obtained via a system of a Wenking potentiostat, a Tacussel EDI rotating disc electrode and a Heto Hetofring CB IIe termostat at 25 °C. All potentials were measured against SCE. The molecular structures of the organic compounds BTA, TTA, E1, E2, E4 and E5 are shown in Figure 1.

3. RESULTS AND DISCUSSION

The corrosion characteristics of zinc metal were obtained by electrochemical current-potential curves. The corrosion potential E_{corr}, corrosion current densities i_{corr}, polarization resistance R_p and inhibition efficiencies % η were listed for each experiment in Tables 1-11. Each experiment was performed at least three times and the results were reported as the average. Inhibition efficiencies were calculated from Stern-Geary equation given below.

$$\%\eta = \left[\frac{i_{cor} - i_{cor}(inh.)}{i_{cor}} \right] \times 100 \qquad (1)$$

$$\%\eta = \left[\frac{R(inh.) - R}{R(inh.)} \right] \times 100 \qquad (2)$$

The metal surface is probably covered with ZnO in aerated acidic solution and shows a high corrosion resistance. The corrosion current densities of the blank solutions follow the descending order: 0.9N NaCl + 0.1N NaOH>0.1N NaOH>1N NaCl>1N HCl. The lowest corrosion rate is observed at low pH, the rate increases as the pH goes from neutral to basic. The corrosion product formed on the metal in neutral solution is probably $Zn(OH)_2$, which is more porous compared to ZnO. Thus, the corrosion rate in $Zn(OH)_2$ is higher than that in ZnO. when the solution pH is increased to 11, the metal suface is left uncoated by $Zn(OH)_2$ dissolves as complex ions $Zn(OH)_4^{-2}$ in the solution.

BTA and TTA were widely used as corrosion inhibitors for copper, copper alloys and carbon steel [12, 13, 14]. Reduced corrosion current densities and the inhibition efficiencies indicate that BTA and TTA are effective corrosion inhibitors for zinc in aqueous solutions. The inhibition efficiencies of BTA and TTA follow the order 1N NaCl>0.9N NaCl+ 0.1N NaOH>0.1N NaOH>1N HCl. The inhibition efficiencies of both are pH-dependent, solution pH is increased in acidic media but decreased in neutral and basic medium with addition of inhibitors. The decrease in corrosion rate with increasing inhibitor concentration shows that the adsorption obeys Langmuir adsorption isoterm (Figures 2-3). The changes surface coverages and concentration of inhibitors are given by the following (3-5) equations. The slope of equations are aproximately same in acidic and neutral solution for BTA and TTA. It shows that action mechanism is same in both solution.

$$\log \frac{\theta}{1-\theta} = 0.60 + 0.27 \log c_{BTA} \qquad \text{(HCl)} \qquad (3)$$

$$\log \frac{\theta}{1-\theta} = 0.62 + 0.24 \log c_{BTA} \qquad \text{(NaOH)} \qquad (4)$$

$$\log \frac{\theta}{1-\theta} = 0.55 + 0.20 \log c_{TTA} \qquad \text{(HCl)} \qquad (5)$$

$$\log \frac{\theta}{1-\theta} = 0.63 + 0.17 \log c_{TTA} \qquad \text{(NaOH)} \qquad (6)$$

Triazoles in aqueous solutions hold a partial negative charge and the charge distribution may change depending on pH of the solution. For example, TTA takes the form of $TTAH_2^+$ in acidic solution, TTAH in neutral solution and TTA^- in basic solution. In acidic medium, the adsorption rate of $TTAH_2^+$ is less compared to H^+ [12], therefore, the inhibition efficiency of TTA is low at pH=0.5(Table 2). Increasing the pH to 11 results in a better adsorption of TTA depending on its changed structure with pH although the electrode potential shifted to a more

negative side. The increase in adsorption is not very high beacuse OH⁻ ions compete with TTA⁻ in this case.

The corrosion potentials shift to more negative values as the pH is increased. In general, a negative shift of 60 mV per pH in electrode potential potential is observed for the reactions occurring by hydrogen reduction. Likewise, a negative shift of approximately 500 V was observed when the pH changed from 0.5 to 11.

The corrosion potential changes firstly on the negative side, secondly on the positive side and then again on the negative side with a sum of negative change (Tables 1-11). Thus, TTA and BTA act as cathodic inhibitors on zinc. Since the adsorption of TTA and BTA molecules on the metal surface compete with adsorption of H^+ ions in acidic solution and OH⁻ ions in basic solution, the adsorption of these molecules is insufficient in both cases. H^+ ions are adsorbed more on the surface than OH⁻ ions leading to a lower inhibition effect in acidic medium. TTA exhibits a bit higher inhibition effect than BTA due to formation of a more stable complex between zinc cations and TTA. The electron releasing -CH_3 group destabilise TTA by increasing the negative charge density (Figure 1). In acidic media (HCl), solution's pH increased with addition of BTA, TTA and cinnolines, but solution's pH decreased in neutral and basic studied solution with addition of studied compounds to the solution (NaCl and NaOH).

When the slopes calculated from Tafel curves are considered, it may be claimed that the corrosion reduction reactions is as follows:

$$2H^+ + 2e^- \rightarrow H_2$$
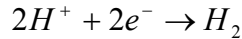
The cathodic Tafel slope b_c should be around 120 mV for this reaction. The slopes of the reactions in 1N HCl are around this value (Tables 1-2). As the pH increases, the slope increases due to decreased H^+ concentration. Nevertheless, a lower polarization resistance (R_p) is observed on the metal surface when the pH is increased. This shows that b_c depends on R_p value and b_a value is decreased more.

In addition to BTA and TTA, the inhibition effect of four cinnoline derivatives on corrosion of zinc were investigated in this study. The corrosion rates and the other corrosion parameters were obtained for each concentration at three different pH's using current-potential curves (Tables 9-11). The cinnolines form with Zn^{+2} ion soluble compounds in acidic and neutral solutions, therefore, they accelerated the corrosion of Zn^{2+} ions in these two media. They showed an inhibiting effect to a low extent in basic solution. This may be explained by decreased dissolution of the corrosion products of Zn^{+2} ion with cinnolines in basic solution.
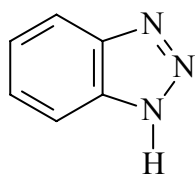
Benzotriazole (BTA)
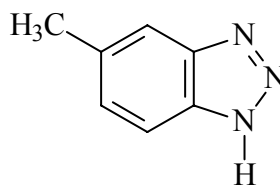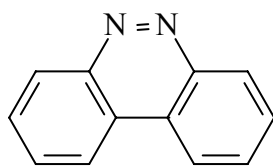
Tolytriazole (TTA)

Benzo(c)cinnolin (E1)

Benzo(c)cinnolin 5-oxide (E2)
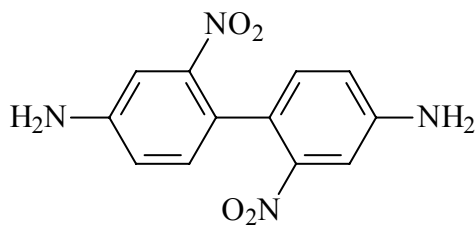
2,2-Dinitrobenzidin (E4)
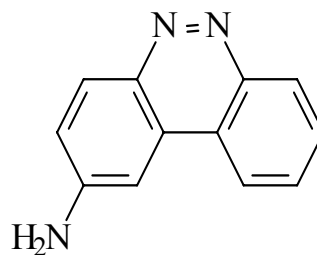
2-Aminobenzo(c)cinnolin (E5)
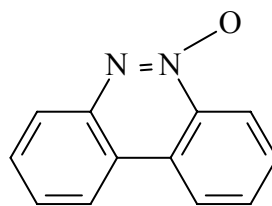
Fig.1. Molecular structure of 1, 2, 3-benzotriazole (BTA), tolytriazole (TTA), benzo (c) cinnoline (E1), benzo (c) cinnoline 5-oxy (E2), 2,2-dinitro benzidyn (E4) and 2-aminobenzo (c) cinnoline (E5).
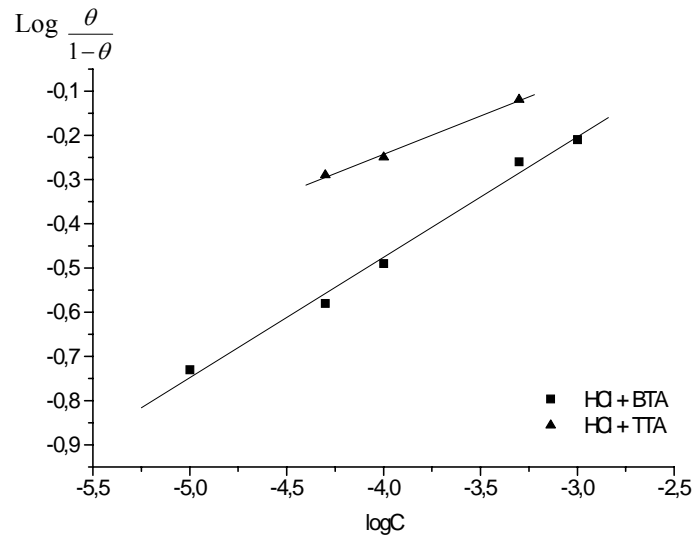
Fig.2. Langmuir adsorption isoterm of zinc in 1 N HCl solution.
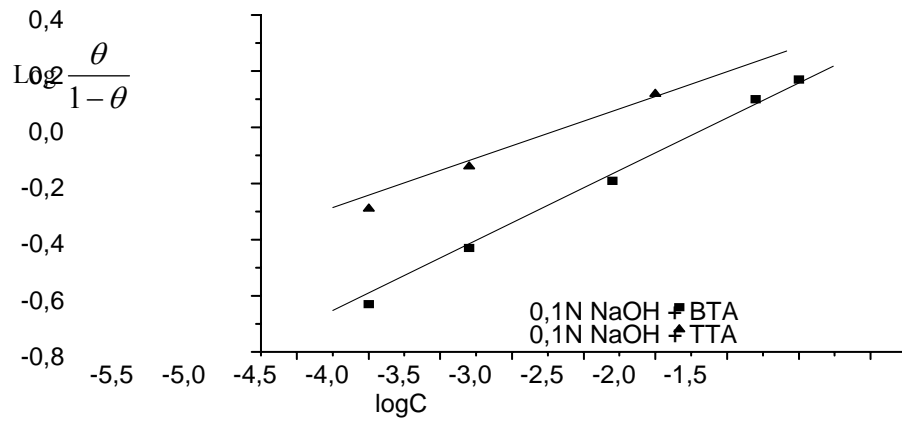
Fig.3. Langmuir adsorption isoterm of zinc in 0.1 N NaOH

Table1. The corrosion parameters of zinc in the presence of BTA

inhibitorin acidic (HCl) solution at 25°C

1N HCl	E_{cor} vs.SCE V	pH	$-b_c$ mV/dec.	b_a mV/dec.	R Ohm.cm^2	i_{cor} µA/cm^2	%η i_{cor}	%η R	%η Average
Blank m M, BTA	1060	0.45	182	84	1057	22			
0.01	1070	0.52	193	175	1250	20	12	15	13.5
0.05	1080	0.51	183	115	1320	18	15	19	17.0
0.1	1074	0.51	211	137	1360	17	22	23	22.5
0.5	991	0.48	270	157	1430	16	26	26	26.0
1.0	1083	0.52	209	128	1453	15	30	27	29.0

Table2. The corrosion parameters of zinc in the presence of TTA inhibitor

in acidic (HCl) solution at 25°C

1N HCl	E_{cor} vs.SCE V	pH	$-b_c$ mV/dec.	b_a mV/dec.	R Ohm.cm^2	i_{cor} µA/cm^2	%η i_{cor}	%η R	%η Average
Blank m M, TTA	1190	0.40	183	194	1770	23			
0.01	1080	0.42	223	150	1888	22	4.4	6.6	5.5
0.05	1078	0.44	225	125	2380	17	24	34	29.0
0.1	1195	0.47	222	181	2440	17	28	37	32.5
0.5	1165	0.57	150	173	2500	13	45	41	43.0

Table 3. The corrosion parameters of zinc in the presence of BTA inhibitor
in neutral (NaCl) solution at 25°C

1N NaCl	E_{cor} vs.SCE V	pH	$-b_c$ mV/dec.	b_a mV/dec.	R Ohm.cm^2	i_{cor} μA/cm^2	%η i_{cor}	%η R	%η Aver-age
Blank	1030	6.8	616	300	566	65			
m M, BTA									
0.01	1150	6.7	134	160	637	33	48	11	29.5
0.05	1160	6.9	110	112	676	31	52	16	34.0
0.1	1153	6.8	111	96	767	29	56	26	41.0
0.5	1152	6.8	83	92	793	28	57	29	43.0

Table 4. The corrosion parameters of zinc in the presence of TTA inhibitor
in neutral (NaCl) solution at 25°C

1N NaCl	E_{cor} vs.SCE V	pH	$-b_c$ mV/dec.	b_a mV/dec.	R Ohm.cm^2	i_{cor} μA/cm^2	%η i_{cor}	%η R	%η Aver-age
Blank	1030	6.8	616	300	566	65			
m M, TTA									
0.01	1000	6.5	527	545	1175	38	42	51	46.5
0.05	975	6.4	546	194	1562	30	53	63	58.0
0.1	1030	6.3	510	203	1590	26	60	64	62.0
0.5	1035	6.1	572	184	2142	25	61	73	67.0

Table 5. The corrosion parameters of zinc in the presence of BTA inhibitor in basic (NaOH) solution at 25°C

0.1N NaOH	E_{cor} vs.SCE V	pH	$-b_c$ mV/dec.	b_a mV/dec.	R Ohm.cm^2	i_{cor} µA/cm^2	%η i_{cor}	%η R	%η Average
Blank mM, BTA	1438	13.00	310	164	42	1044			
0.01	1418	13.01	148	54	46	855	18	23	20.5
0.05	1393	13.01	264	119	48	725	30	28	29.0
0.1	1440	13.02	415	93	51	660	36	18	27.0
0.5	1425	13.06	250	92	58	625	40	34	37.0
1.0	1450	13.04	203	88	58	640	38	34	36.0
5.0	1457	12.90	180	100	62	460	56	44	50.0
10	1460	12.80	178	137	69	450	57	60	58.5

Table 6. The corrosion parameters of zinc in the presence of TTA inhibitor in basic (NaOH) solution at 25°C

0.1N NaOH	E_{cor} vs.SCE V	pH	$-b_c$ mV/dec.	b_a mV/dec.	R Ohm.cm^2	i_{cor} µA/cm^2	%η i_{cor}	%η R	%η Average
Blank mM, TTA	1438	13.00	310	164	42	1044			
0.01	1474	13.04	178	182	51	617	40	30	35.0
0.05	1512	13.05	181	150	56	585	43	33	38.0
0.1	1493	13.07	200	115	60	502	51	42	46.5
0.5	1500	13.02	143	124	66	501	52	57	54.5
1.0	1499	12.96	165	112	65	475	54	55	54.5
5.0	1506	12.51	154	127	67	465	55	59	57

Table 7. The corrosion parameters of zinc in the presence of BTA inhibitor

     in basic (0.9 N NaCl + 0.1 NaOH) solution at 25°C.

0.1N NaOH+ 0.9NaCl	E_{cor} vs.SCE V	pH	$-b_c$ mV/dec.	b_a mV/dec.	R Ohmcm^2	i_{cor} μA/cm^2	%η i_{cor}	%η R	%η Average
Blank	1425	11	286	193	45	1400			
m M, BTA									
0.01	1412	13.07	300	120	58	820	41	30	35.5
0.05	1388	13.05	310	100	63	800	43	55	49.0
0.1	1425	12.9	172	104	71	720	49	57	53.0
0.5	1370	12.9	126	113	73	660	53	63	58.0
1.0	1430	12.8	191	96	76	650	54	41	67.0

Table 8. The corrosion parameters of zinc in the presence of TTA inhibitor

     in alkaline (0.9 N NaCl + 0.1 NaOH) solution at 25°C

0.1N NaOH+ 0.9N NaCl	E_{cor} vs.SCE V	pH	$-b_c$ mV/dec.	b_a mV/dec.	R Ohm.cm^2	i_{cor} μA/cm^2	%η i_{cor}	%η R	%η Average
Blank	1425	11	286	194	45	1400			
m M, TTA									
0.01	1438	11.04	185	132	63	830	41	36	38.5
0.05	1445	11.12	213	103	60	810	42	34	37.5
0.1	1425	11.21	200	99	62	700	50	38	44.5
0.5	1475	11.23	150	132	66	690	51	47	49.0
1.0	1430	11.24	157	68	65	600	54	49	51.5
5.0	1470	11.27	175	148	77	400	71	72	71.5

Table 9. The corrosion parameters of zinc in the presence of E1, E2, E4 ve

E5 cinnolines in asidic (1 N HCl) solution at 25°C

1N HCl	E_{cor} vs.SCE V	pH	$-b_c$ mV/dec.	b_a mV/dec.	R Ohm.cm²	i_{cor} µA/cm²
Blank	1125	0.42	183	139	413	23
0.1m M						
E1	1114	0.54	207	92	6	4650
E2	1106	0.51	297	252	6	12000
E4	1125	0.50	140	241	11	5500
E5	1097	0.53	176	108	9	3800

Table 10. The corrosion parameters of zinc in the presence of E1, E2, E4 ve

E5 cinnolines in neutral (1 N NaCl) solution at 25°C

1N NaCl	E_{cor} vs.SCE V	pH	$-b_c$ mV/dec.	b_a mV/dec.	R Ohm.cm²	i_{cor} µA/cm²
Blank	1030	6.8	616	300	566	65
0.1m M						
E1	1076	6.2	416	77	22	2600
E2	1115	6.5	198	320	19	2650
E4	1080	6.3	213	70	10	2100
E5	1081	6.4	70	64	13	1250

4. CONCLUSIONS

• Benzotriazole and tolytriazole decelerated the corrosion of pure zinc in 1N HCl, 1N NaCl, 0.1N NaOH and 0.9N NaCl+ 0.1N NaOH solutions at 25 °C.

• The inhibition effect of tolytriazole was more significant than the inhibition effect of benzotriazole in all solutions. The effect of inhibitors depend on the functional groups.

• The highest inhibition effect was observed in 1N NaCl 0.1 N NaOH solutions for tolytriazole and benzotriazole.

• Tolytriazole, benzotriazole and cinnolines act as cathodic inhibitors for pure zinc metal in studied solutions, the corrosion potentials changed to the negative direction.

• Cinnolines act as inhibitor in 0.9N NaCl+ 0.1N NaOH solution.

• There is a significant change in pH of solutions with addition of BTA, TTA and cinnolines.

ÖZET: Bu çalışmada, çinkonun HCl, NaOH ve NaCl ortamlarındaki korozyonuna BTA, TTA, Benzo (c) Sinnolin, Benzo (c) Sinnolin 5-oksit, 2,2′-Dinitro Benzidin ve 2-Aminobenzo (c) Sinnolin organik maddelerin etkisi araştırılmıştır. Bu konunun belirlenmesinde amaç daha önceki çalışmada bakırın triazollerle inhibitör etkinliğini olumlu yönde etkilemesidir. Ayrıca azot ve kükürt bileşiklerinin çinkonun korozyonunu azaltıcı etkisi olabileceği ileri sürülmüştür. Bu nedenle bu etkiyi net olarak belirlemek için değişik pH'daki sulu çözeltilerine inhibisyon etkinliği belirlenmiştir. Bu amaçla inhibitör içeren ve içermeyen sulu çözeltilerindeki akım yoğunluğu-potansiyel eğrilerinden yararlanılarak korozyon hızları elektrokimyasal yolla belirlenmiştir. Belirlenen bu korozyon hızlarından da inhibitör etkinliği hesaplanmıştır. Bulunan sonuçlardan benzotriazol ve tolitriazolün HCl, NaOH ve nötr ortamlarındaki çinko metaline korozyonunda inhibitör olarak kullanılabileceği ve sinnolinler ise sadece NaOH ortamda inhibitör etkisi gösterdiği bulunmuştur.

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