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# Amidopoly Ethylamines as Corrosion Inhibitors for Zinc Dissolution in Different Acidic Electrolytes

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### **Abstract**

The effect of some amidopoly ethylamine, with different numbers of ethylamine units, on the corrosion of zinc electrode in ZnCl<sub>2</sub>, NH<sub>4</sub>Cl and (ZnCl<sub>2</sub> + NH<sub>4</sub>Cl) electrolytes has been studied using galvanostatic polarization measurements. The inhibition efficiency was found to increase with increasing concentration, number of ethylamine units per molecule and with decreasing the temperature. Inhibition is explained on the basis of adsorption of amidopoly ethylamine molecules on the zinc electrode surface through their ethylamine groups. The inhibitors are adsorbed on the zinc electrode surface according to Langmuir adsorption isotherm. Some thermodynamic parameters are calculated and explained for the tested systems from the data obtained at different temperatures.

*Keywords*: zinc, corrosion inhibitors, amidopoly ethylamine, ZnCl<sub>2</sub>, NH<sub>4</sub>Cl, adsorption.

### Introduction

Zinc metal is used in many practical applications such as a favorable anode for primary dry batteries [1], a coating for carbon steel and alloying element in electrical contacts [2]. Due to relatively low price, high discharge efficiency and high safety features associated with its manufacturing processes and use, its protection against corrosion has attracted much attention. Mercury is widely used as inhibitor for corrosion of zinc electrode in zinc-manganese batteries [3], but it causes severe pollution because of its high toxicity. With increasing concern about pollution control, the use of mercury in batteries is to be replaced. The use of inhibitors is one of the most practical method for protection against corrosion especially in acidic media [4-12]. Most of well-known corrosion inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms [13-18]. Such compounds contain electron-donating groups, which decrease the corrosion rate

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by increasing the hydrogen overpotential on the corroding metal [19]. The effectiveness of such compounds as inhibitors generally increases with increasing chain length [20-22].

The present work aims to study the effect of four compounds of amidopoly ethylamine, which have surface active properties, as inhibitors for the corrosion of zinc used in zinc-manganese battery electrolytes ZnCl<sub>2</sub>, NH<sub>4</sub>Cl and (ZnCl<sub>2</sub> + NH<sub>4</sub>Cl). The effect of increasing of the ethylamine units contained in the chemical structure of the used compounds on the inhibition efficiency is studied. Moreover, the effect of temperature on the dissolution of zinc electrode as well as on the inhibition efficiency of the used compounds is also investigated.

### **Experimental method**

Zinc electrodes are fabricated from battery grade zinc disk sealed in araldite resin with an exposed surface area of 0.385 cm<sup>2</sup>. The electrode which is composed of Zn (99.35 %), Pb (0.5 %), Cd (0.003 %) and Fe (0.002 %), was supplied by Kaha company for chemical industries (Egypt). The electrode surface was polished with different grades of emery papers 600 and 1200, degreased with acetone and rinsed with distilled water. AR grade zinc chloride and ammonium chloride were used for preparing the test solutions.

The four amidopoly ethylamine compounds are prepared using a simple method described elsewhere [23]. They have the general formula:

### R-CONH-[-CH<sub>2</sub>CH<sub>2</sub>NH-]<sub>n</sub>-H

where, R is  $C_{16}H_{33}$  and n is the number of ethylamine units (EA). The numbers of (EA) per molecule of amide are 2, 3, 4, and 5 for compounds I, II, III and IV, respectively. The used surfactant compounds in the present work are cationic, which form positive charges at their heads when dissolved in water.

Anodic and cathodic Tafel polarization experiments are preformed using economical potentiostat Voltalab 21, PGP 201. The electrolytic cell was a three-necked glass bottle fitted with a platinum counter electrode, a saturated calomel electrode (SCE) as reference electrode, and the working zinc electrode.

# Results and discussion Galvanostatic polarization measurements

The effect of addition of amidopoly ethylamine on the anodic and cathodic polarization curves of zinc electrode in 0.1 M ZnCl<sub>2</sub>, 0.1 M NH<sub>4</sub>Cl and (0.1 M ZnCl<sub>2</sub> + 0.1 M NH<sub>4</sub>Cl) solutions at 25 °C is studied. The effect of increased concentration of compound IV in 0.1 M ZnCl<sub>2</sub> is represented in Fig. 1 as an example. However, similar curves for other solutions were also obtained (not shown).

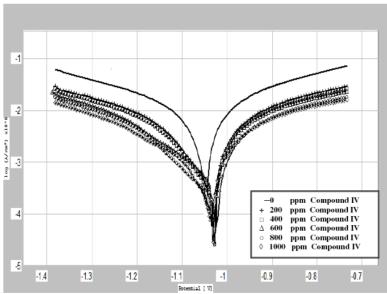
An inspection of the curves in Fig. 1 reveals that the presence of increasing concentration of the inhibitor shifted the anodic current/potential curves in the anodic direction and cathodic curves in the cathodic direction.

Tables 1-3 present the corrosion parameters of zinc electrode in 0.1 M ZnCl<sub>2</sub>, 0.1

M NH<sub>4</sub>Cl and (0.1 M ZnCl<sub>2</sub> + 0.1 M NH<sub>4</sub>Cl) solutions, respectively. These parameters are anodic Tafel slope ( $b_a$ ), cathodic Tafel slope ( $b_c$ ), corrosion potential ( $E_{corr}$ ), corrosion current ( $i_{corr}$ ) and inhibition efficiency (I.E.). The corrosion current density ( $i_{corr}$ ) is calculated by the extrapolation of anodic and cathodic Tafel lines with the steady state (corrosion) potential ( $E_{corr.}$ ). The inhibition efficiency was calculated using the following equation:

$$IE = 100[1 - (i_{add}/i_{free})]$$
 (1)

where,  $i_{add}$  and  $i_{free}$  are the corrosion current of zinc electrode in the presence and in the absence of inhibitors, respectively.



**Figure 1**. Anodic and cathodic polarization curves of Zn electrode in 0.1 M ZnCl<sub>2</sub> solution containing different concentrations of compound IV at 25 °C.

Inspection of Tables 1-3 reveals that: the value of  $i_{corr.}$  in case of  $(ZnCl_2 + NH_4Cl)$  was higher than that obtained in  $NH_4Cl$  and less than that obtained in  $ZnCl_2$  of the same concentration. This indicates that, both  $ZnCl_2$  and  $NH_4Cl$  accelerate the corrosion of zinc electrode. The combined effect of  $ZnCl_2$  and  $NH_4Cl$  on the corrosion of zinc electrode is greater than that caused by  $NH_4Cl$  and less than that caused by  $ZnCl_2$ .

The corrosion potential shifted to less negative values and  $i_{corr}$  decreased when the concentration of amidopoly ethylamine was increased, indicating the inhibiting effect of these compounds.

The IE increased with increasing concentration of additives and number of ethylamine units per molecule of the additive. The inhibition efficiencies of the four tested compounds measured by the galvanostatic polarization measurements decreased in the following order:

Compound IV > Compound III > Compound I

Furthermore both anodic and the cathodic Tafel slopes increase upon addition of the inhibitors. This result suggests that the used surfactant compounds act as mixed inhibitors.

**Table 1.** Corrosion parameters of Zn electrode in  $0.1~M~ZnCl_2$  solution containing different concentrations of inhibitors.

3.6 T	$b_a \times 10^{-2}$	$b_c \times 10^{-2}$	- $\mathbf{E}_{\mathbf{corr.}}$	i <sub>corr.</sub> x 10 <sup>-1</sup>	I.E.
Medium	(mV/decade)	(mV/decade)	mV (S.C.E.)	(mA)	(%)
$0.1 \text{ M ZnCl}_2 + \text{compound I}$					
0.0 ppm compound I	153	280	1046	33.5	
200 pp	397	289	1039	24.7	26.3
400 ppm compound I	425	305	1039	19.1	42.9
600 ppm compound I	434	307	1039	15.3	54.3
800 ppm compound I	442	322	1039	13.9	58.5
1000 ppm compound I	443	323	1039	12.3	63.3
0.1 M ZnCl <sub>2</sub> + compound II					
0.0 ppm compound II	153	280	1046	33.5	
200 ppm compound II	410	291	1033	21.0	37.3
400 ppm compound II	430	310	1033	14.5	56.8
600 ppm compound II	520	320	1033	12.8	61.7
800 ppm compound II	521	322	1033	10.5	68.6
1000 ppm compound II	571	324	1033	8.9	73.4
0.1 M ZnCl <sub>2</sub> + compound III					
0.0 ppm compound III	153	280	1046	33.5	
200 ppm compound III	416	288	1031	17.7	47.1
400 ppm compound III	476	305	1031	11.1	66.8
600 ppm compound III	526	319	1031	9.5	71.6
800 ppm compound III	571	328	1031	8.3	75.2
1000 ppm compound III	590	354	1031	7.1	78.9
0.1 M ZnCl <sub>2</sub> + compound IV					
0.0 ppm compound IV	153	280	1046	33.5	
200 ppm compound IV	666	366	1027	13.6	59.5
400 ppm compound IV	666	407	1027	9.9	70.3
600 ppm compound IV	790	418	1027	7.5	77.5
800 ppm compound IV	782	427	1027	6.4	80.8
1000 ppm compound IV	792	427	1027	5.4	84.0

**Table 2**. Corrosion parameters of Zn electrode in 0.1 M NH<sub>4</sub>Cl solution containing different concentrations of inhibitors.

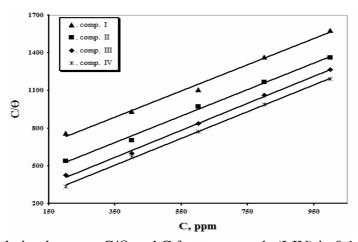
Modium	b <sub>a</sub> x 10 <sup>-2</sup>	b <sub>c</sub> x 10 <sup>-2</sup>	-E <sub>corr.</sub>	i <sub>corr.</sub> x 10 <sup>-3</sup>	I.E.
Medium	(mV/decade)	(mV/decade)	mV (S.C.E.)	(mA)	(%)
0.1 M NH <sub>4</sub> Cl + compound I					
0.0 ppm compound I	824.2	402.9	1145	39.9	
200 ppm compound I	1201.3	402.9	1145	32.0	19.7
400 ppm compound I	1201.3	458.3	1130	26.1	34.5
600 ppm compound I	1195.2	350.3	1130	22.2	44.3
800 ppm compound I	1176.1	364.0	1127	19.6	50.8
1000 ppm compound I	1176.1	385.0	1123	17.7	55.6
1000 ppiii compound 1	1113.4	363.0	1122	17.7	33.0
0.1 M NH <sub>4</sub> Cl + compound II					
0.0 ppm compound II	824.2	402.9	1145	39.9	
200 ppm compound II	994.4	376.7	1134	30.6	23.3
400 ppm compound II	1081.0	334.1	1133	24.2	39.3
600 ppm compound II	1113.8	339.7	1130	20.2	49.3
800 ppm compound II	1235.5	343.9	1130	17.9	55.1
1000 ppm compound II	1193.6	347.4	1130	16.1	59.6
0.1 M NH <sub>4</sub> Cl + compound III					
0.0 ppm compound III	824.2	402.9	1145	39.9	
200 ppm compound III	1753.7	196.3	1123	29.1	27.1
400 ppm compound III	1762.1	498.2	1123	22.1	44.6
600 ppm compound III	1932.3	498.2	1123	18.4	53.8
800 ppm compound III	1917.1	477.0	1123	16.0	59.8
1000 ppm compound III	1195.5	456.6	1123	14.6	63.4
0.1 M NH <sub>4</sub> Cl + compound IV					
0.0 ppm compound IV	824.2	402.9	1145	39.9	
200 ppm compound IV	1899.2	430.0	1129	26.6	33.3
400 ppm compound IV	1977.5	457.8	1125	19.8	50.3
600 ppm compound IV	2010.8	454.0	1125	16.4	58.8
800 ppm compound IV	2011.8	455.0	1125	13.9	65.1
1000 ppm compound IV	2013.6	448.8	1125	12.6	68.4

**Table 3.** Corrosion parameters of Zn electrode in  $(0.1 \text{ M ZnCl}_2 + 0.1 \text{ M NH}_4\text{Cl})$  solution containing different concentrations of inhibitors.

Madama	b <sub>a</sub> x 10 <sup>-2</sup>	b <sub>c</sub> x 10 <sup>-2</sup>	-E <sub>corr.</sub>	i <sub>corr.</sub> x 10 <sup>-1</sup>	I.E.
Medium	(mV/decade)	(mV/decade)	mV (S.C.E.)	(mA)	(%)
$(0.1 \text{ M ZnCl}_2 + 0.1 \text{ M NH}_4)$	Cl) + compound I				
0.0 ppm compound I	384	211	1045	30.2	
200 ppm compound I	366	226	1045	21.8	27.8
400 ppm compound I	419	237	1044	17.9	40.7
600 ppm compound I	437	247	1044	14.7	51.3
800 ppm compound I	467	260	1044	13.6	54.9
1000 ppm compound I	485	278	1040	11.8	60.9
(0.1 M ZnCl <sub>2</sub> + 0.1 M NH <sub>4</sub>	Cl) + compound II				
0.0 ppm compound II	384	211	1045	30.2	
200 ppm compound II	366	226	1045	20.9	30.7
400 ppm compound II	419	237	1045	16.2	46.3
600 ppm compound II	437	247	1043	13.5	55.2
800 ppm compound II	467	260	1043	11.5	61.9
1000 ppm compound II	485	278	1043	10.3	65.8
(0.1 M ZnCl <sub>2</sub> + 0.1 M NH <sub>4</sub>	Cl) + compound III				
0.0 ppm compound III	384	211	1045	30.2	
200 ppm compound III	377	231	1040	17.3	42.7
400 ppm compound III	403	250	1040	13.3	55.9
600 ppm compound III	456	252	1040	11.4	62.2
800 ppm compound III	541	291	1039	9.9	67.2
1000 ppm compound III	493	277	1039	8.8	70.8
proceeding in	.,,,		1007	0.0	, 0.0
(0.1 M ZnCl <sub>2</sub> + 0.1 M NH <sub>4</sub>	Cl) + compound IV				
0.0 ppm compound IV	384	211	1045	30.2	
200 ppm compound IV	533	265	1040	16.4	45.5
400 ppm compound IV	631	276	1040	11.3	62.5
600 ppm compound IV	679	293	1039	8.9	70.5
800 ppm compound IV	746	343	1039	7.5	75.1
1000 ppm compound IV	761	329	1039	6.1	79.8

### Mechanism of inhibition

The possible explanation of the inhibition is due to adsorption process which is considered as the key of the mechanism of inhibition action. It might be suggested that the inhibitor molecules adhere to the zinc electrode surface. This leads to a decrease of the surface area at which cathodic and anodic reactions take place. At one and the same inhibitor concentration, the values of inhibition efficiency decreased in the following order: Compound IV > Compound III > Compound II > Compound. This order reflects the increased tendency of these compounds to act as corrosion inhibitors by increasing the ethylamine units per molecule. The adsorption of the surfactant molecules takes place through their hydrophilic parts which usually contain the active groups. As a result of this behavior, the hydrocarbon tail, which is hydrophobic, is forced towards the aqueous solution side. These tails repel the water and aggressive molecules out from the surface and thus decrease their corrosion effects. As a fact, the surfactant compounds used in the present study are cationic. Thus, a positive charge is created at their heads upon dissolved in water. The presence of this positive charge may leading to increase the strength of adsorption of the head part at the anode surface. At the same time the repulsion force between water molecules and hydrocarbon chain tends to push the latter towards the metal surface. These two effects lead to one possible orientation of the surfactant molecules on the metal surface which is horizontal. So, one may expect that the used cationic surfactants adsorbed horizontally on the zinc electrode surface. In this case the effect of ethylamine becomes more important as seen from the obtained sequence. Thus, the inhibition efficiency increases as the number of ethylamine unit is increased.



**Figure 2**. The relation between  $C/\Theta$  and C for compounds (I-IV) in 0.1 M ZnCl<sub>2</sub>.

### Adsorption isotherm

The degree of surface coverage  $(\Theta)$  of zinc surface by the adsorbed of amidopoly ethylamine compounds is calculated at constant potential using the following equation [25]:

$$\Theta = 1 - (i_{add}/i_{free}) \tag{2}$$

where,  $i_{free}$  and  $i_{add}$  are the corrosion current densities in absence and presence of the additive compounds, respectively. The degree of surface coverage  $\Theta$  is found to increase with increasing concentration of the additives. Plotting of  $C/\Theta$  against concentration of inhibitor (C) gives straight lines with unit slopes. [Figs (2-4)], This indicates that the adsorption of the inhibitors takes place following Langmuir adsorption isotherm. This isotherm postulates that there is no interaction between the adsorbed molecules and the adsorption free energy is independent of  $\Theta$  value.

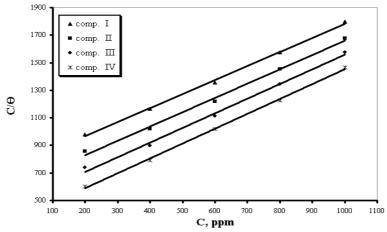
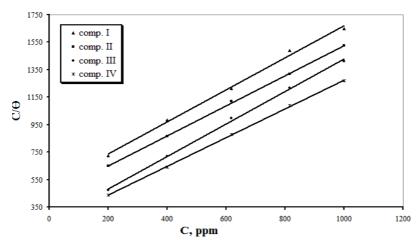


Figure 3. The relation between  $C/\Theta$  and C for compounds (I-IV) in 0.1 M NH<sub>4</sub>Cl.



**Figure 4**. The relation between C/ $\Theta$  and C for compounds (I-IV) in (0.1 M NH<sub>4</sub>Cl + 0.1 M ZnCl<sub>2</sub>).

# Effect of temperature

The effect of temperature on the corrosion parameters such as  $i_{corr}$ ,  $E_{corr}$  and IE was studied in 0.1 M ZnCl<sub>2</sub>, 0.1 M NH<sub>4</sub>Cl and (0.1 M ZnCl<sub>2</sub> + 0.1 M NH<sub>4</sub>Cl) solutions, devoid and containing 1000 ppm of inhibitors over the temperature ranges of 25 - 65 °C. The results showed that the variation of temperature had almost no effect on the shape of the polarization curves. The data listed in Tables 4-6 show that,  $E_{corr}$  shifted to less negative values whereas the values of  $i_{corr}$  increased with the increase in temperature. This indicates the accelerating effect

of rising temperature on the corrosion reaction. On the other hand, the increase in temperature led to a decrease in the inhibition efficiencies of all the tested compounds. It is clear from Tables 4-6 that the best inhibition efficiencies are obtained at 25  $^{\circ}$ C.

**Table 4**. Effect of temperature on the corrosion parameters of Zn electrode in 0.1 M ZnCl<sub>2</sub> and 0.1 M ZnCl<sub>2</sub> + 1000 ppm of inhibitors.

T (K)	-E <sub>corr</sub> .	i <sub>corr.</sub> x 10 <sup>-1</sup>	I.E.
T (K)	mV (SCE)	(mA)	(%)
0.1 M ZnCl <sub>2</sub>			
298	1046	33.5	
308	1040	40.7	
318	1038	56.2	
328	1035	70.2	
338	1021	103.9	
0.1 M ZnCl <sub>2</sub> + compound I			
298	1039	12.3	63.2
308	1044	20.2	50.3
318	1038	27.8	50.5
328	1025	42.6	39.3
338	1021	66.3	36.1
0.1 M ZnCl <sub>2</sub> + compound II			
298	1033	8.9	73.4
308	1045	16.6	59.2
318	1039	24.5	56.4
328	1027	39.0	44.4
338	1021	57.6	44.5
0.1 M ZnCl <sub>2</sub> + compound III			
298	1031	7.1	78.8
308	1034	11.6	71.4
318	1033	20.3	63.8
328	1027	29.9	57.4
338	1021	49.5	52.3
0.1 M ZnCl <sub>2</sub> + compound IV			
298	1017	5.4	84.0
308	1033	8.4	79.3
318	1032	14.3	74.5
328	1027	25.2	64.1
338	1026	41.6	59.5

**Table 5**. Effect of temperature on the corrosion parameters of Zn electrode in 0.1 M NH<sub>4</sub>Cl and 0.1 M NH<sub>4</sub>Cl + 1000 ppm of inhibitors.

T (K)	-E <sub>corr</sub> .	i <sub>corr.</sub> x 10 <sup>-3</sup>	I.E.
T (K)	mV (SCE)	(mA)	(%)
0.1 M NH <sub>4</sub> Cl			
298	1145	39.9	
308	1131	50.7	
318	1117	64.7	
328	1106	81.7	
338	1085	95.1	
0.1 M NH <sub>4</sub> Cl + compound I			
298	1122	17.7	55.6
308	1108	22.7	55.2
318	1104	31.0	52.0
328	1102	39.9	51.1
338	1093	47.2	50.3
0.1 M NH <sub>4</sub> Cl + compound II			
298	1130	16.1	59.6
308	1113	20.6	59.3
318	1102	26.4	59.1
328	1099	34.4	57.9
338	1089	43.2	54.5
0.1 M NH <sub>4</sub> Cl + compound III			
298	1123	14.6	63.4
308	1092	18.6	63.3
318	1085	24.7	61.7
328	1076	32.4	60.3
338	1071	40.9	56.9
0.1 M NH <sub>4</sub> Cl + compound IV			
298	1125	12.6	68.4
308	1089	17.5	65.4
318	1086	22.5	65.2
328	1078	29.4	64.0
338	1072	39.1	58.8

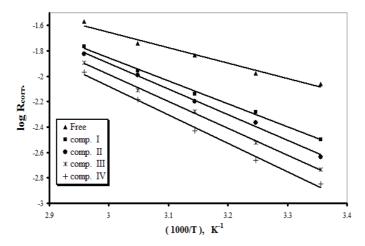
**Table 6**. Effect of temperature on the corrosion parameters of Zn electrode in (0.1 M  $ZnCl_2 + 0.1$  M  $NH_4Cl$ ) and (0.1 M  $ZnCl_2 + 0.1$  M  $NH_4Cl$ ) + 1000 ppm of inhibitors.

T (V)	-E <sub>corr.</sub>	i <sub>corr.</sub> x 10 <sup>-1</sup>	I.E.
T (K)	mV (SCE)	(mA)	(%)
0.1 M ZnCl <sub>2</sub> + 0.1 M NH <sub>4</sub> Cl			
298	1045	30.2	
308	1057	37.8	
318	1054	44.0	
328	1045	52.3	
338	1039	60.0	
0.1 M ZnCl <sub>2</sub> + 0.1 M NH <sub>4</sub> Cl +	compound I		
298	1039	11.8	60.9
308	1051	15.0	60.3
318	1049	17.5	60.2
328	1045	21.0	59.8
338	1033	24.2	59.6
0.1 M ZnCl <sub>2</sub> + 0.1 M NH <sub>4</sub> Cl +	compound II		
298	1045	10.3	65.8
308	1043	13.0	65.6
318	1040	15.2	65.4
328	1037	18.1	65.3
338	1033	22.3	62.8
0.1 M ZnCl <sub>2</sub> + 0.1M NH <sub>4</sub> Cl +	compound III		
298	1039	8.8	70.8
308	1048	11.1	70.6
318	1040	13.5	69.3
328	1040	16.5	68.4
338	1039	20.6	65.6
0.1 M ZnCl <sub>2</sub> + 0.1 M NH <sub>4</sub> Cl +	compound IV		
298	1039	6.1	79.8
308	1048	8.5	77.5
318	1040	11.4	74.0
328	1040	14.9	71.5
338	1039	18.2	69.6

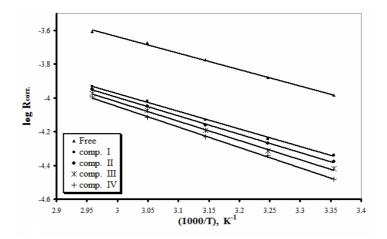
The corrosion reaction is regarded as a rate process which is given by Arrehenius equation [6]

$$\log R_{\text{corr.}} = \log A - E_a/2.303RT \tag{3}$$

where  $R_{corr.}$  is the rate constant of the metal dissolution reaction which is directly related to corrosion current density,  $i_{corr.}$  [26], A is the frequency factor, T is the absolute temperature and  $E_a$  is the activation energy. By plotting log  $R_{corr.}$  versus (1/T), the values of  $E_a$  can be calculated from the slope of the obtained straight lines [Figs. 5-7].



**Figure 5**. Arrhenius plots of zinc corrosion rate in 0.1 M ZnCl<sub>2</sub> in absence and presence of 1000 ppm of compounds (I-IV).

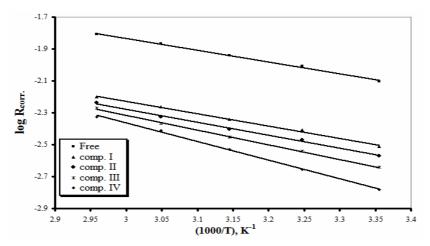


**Figure 6**. Arrhenius plots of zinc corrosion rate in 0.1 M NH<sub>4</sub>Cl in absence and presence of 1000 ppm of compounds (I-IV).

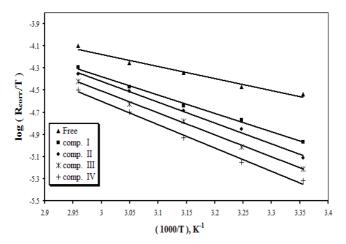
An alternative formulation of the Arrehenius equation is the transition state equation [6]

$$\log (R_{corr.}/T) = [\log (R/Nh) + (\Delta S^*/2.303R)] - \Delta H^*/2.303RT$$
 (4)

where h is Planck's constant, N is Avogadro's number,  $\Delta S^*$  is the entropy of activation and  $\Delta H^*$  is the enthalpy of activation.

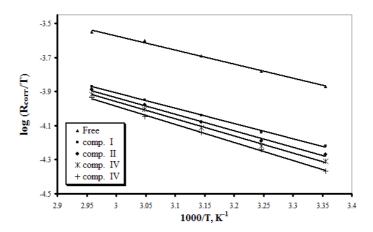


**Figure 7**. Arrhenius plots of zinc corrosion rate in a solution of  $(0.1 \text{ M NH}_4\text{Cl} + 0.1 \text{ M} \text{ ZnCl}_2)$  in absence and presence of 1000 ppm of compounds (I-IV).

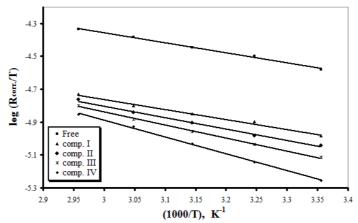


**Figure 8**. The relation between  $log (R_{corr}/T)$  and (1/T) for zinc electrode in 0.1 M ZnCl<sub>2</sub>, in absence and presence of 1000 ppm of compounds (I-IV).

Figs. 8-10 show a plot of  $\log (R_{corr}/T)$  against (1/T). Straight lines are obtained with a slope of  $(-\Delta H^*/2.303R)$ , and an intercept of  $(\log [R/Nh] + \Delta S^*/2.303R)$ from which the values of  $\Delta H^*$  and  $\Delta S^*$  were calculated are listed in Table 7. The data show that the activation parameters  $(E_a, \Delta H^*, \Delta S^*)$  of the dissolution of zinc electrode in all solutions in the presence of 1000 ppm of the four studied compounds increased more than those of the uninhibited solution. The presence of the tested compounds increased the activation energy values and consequently decreased the corrosion rate of the zinc electrode. Furthermore, E<sub>a</sub> increases with the increased in ethylamine units per the inhibitor molecule. These findings indicate that amidopoly ethylamine compounds acted as inhibitors through increasing the activation energy of zinc electrode dissolution by making a barrier to mass and charge transfer by their adsorption on zinc electrode surface. The positive values of  $\Delta H^*$  reflect a strong chemisorptions of the inhibitor on the zinc electrode surface. The values of entropy of activation  $\Delta S^*$  in the absence and in the presence of the studied compounds are negative. This implies that the activated complex in the rate determining step represents an association rather than a dissociation step [25]. This means that the activated molecules are in higher order state than that at the initial stage.



**Figure 9**. The relation between  $\log (R_{corr}/T)$  and (1/T) for zinc electrode in 0.1 M NH<sub>4</sub>Cl, in absence and presence of 1000 ppm of compounds (I-IV).



**Figure 10**. The relation between log ( $R_{corr}/T$ ) and (1/T) for zinc electrode in a solution (0.1 M NH<sub>4</sub>Cl + 0.1 M ZnCl<sub>2</sub>), in absence and presence of 1000 ppm of compounds (I-IV).

## **Conclusions**

- 1. The value of i<sub>corr.</sub> in case of (ZnCl<sub>2</sub> + NH<sub>4</sub>Cl) is higher than that obtained in NH<sub>4</sub>Cl and less than that obtained in ZnCl<sub>2</sub> of the same concentration. This indicates that, both ZnCl<sub>2</sub> and NH<sub>4</sub>Cl accelerate the corrosion of zinc electrode. The combined effect of ZnCl<sub>2</sub> and NH<sub>4</sub>Cl on the corrosion of zinc electrode is greater than that caused by NH<sub>4</sub>Cl and less than that caused by ZnCl<sub>2</sub>.
- 2. The amidopoly ethylamines are considered as inhibitors for zinc electrode corrosion in 0.1 M ZnCl<sub>2</sub>, 0.1 M NH<sub>4</sub>Cl and (0.1 M ZnCl<sub>2</sub> + 0.1 M NH<sub>4</sub>Cl)

solutions. The inhibition efficiency is found to increase by increasing the inhibitor concentrations, number of ethylamine unit and/or decreasing of the temperature.

- 3. The inhibitive action of these compounds takes place through the adsorption of their molecules on the zinc electrode surface.
- 4. The adsorption of these compounds on a zinc electrode surface obeyed the Langmuir adsorption isotherm.

**Table 7**. Activation parameters of the dissolution reaction of zinc electrode in 0.1 M ZnCl<sub>2</sub>, 0.1 M NH<sub>4</sub>Cl and (0.1 M ZnCl<sub>2</sub> + 0.1 M NH<sub>4</sub>Cl) solutions in absence and presence of 1000 ppm of the amidopoly ethylamine compounds.

aanaantuutian	$\mathbf{E_a}$	$\Delta \mathbf{H}^*$	-∆S*
concentration	$(kJ.mol^{-1})$	$(kJ.mol^{-1})$	$(J.mol^{-1}.K^{-1})$
0.1 M ZnCl <sub>2</sub>	23.8	20.5	141.3
0.1 M ZnCl <sub>2</sub> + 1000 ppm compound I	35.6	31.2	143.9
0.1 M ZnCl <sub>2</sub> + 1000 ppm compound II	39.6	34.6	144.4
0.1 M ZnCl <sub>2</sub> + 1000 ppm compound III	42.4	37.1	145.9
0.1 M ZnCl <sub>2</sub> + 1000 ppm compound IV	46.1	39.7	147.3
0.1 M NH₄Cl	18.9	15.4	130.3
0.1 M NH₄Cl + 1000 ppm compound I	20.5	17.1	136.6
0.1 M NH <sub>4</sub> Cl + 1000 ppm compound II	21.3	18.5	137.0
0.1 M NH <sub>4</sub> Cl + 1000 ppm compound III	22.3	18.8	137.4
0.1 M NH <sub>4</sub> Cl + 1000 ppm compound IV	23.7	20.2	137.8
$(0.1 \text{ M ZnCl}_2 + 0.1 \text{ M NH}_4\text{Cl})$	14.7	11.2	145.9
$(0.1 \text{ M ZnCl}_2 + 0.1 \text{ M NH}_4\text{Cl}) + 1000 \text{ ppm compound I}$	16.4	11.5	153.5
$(0.1 \text{ M ZnCl}_2 + 0.1 \text{ M NH}_4\text{Cl}) + 1000 \text{ ppm compound II}$	16.9	12.8	154.1
$(0.1 \text{ M ZnCl}_2 + 0.1 \text{ M NH}_4\text{Cl}) + 1000 \text{ ppm compound III}$	18.6	14.4	154.7
$(0.1 \text{ M ZnCl}_2 + 0.1 \text{ M NH}_4\text{Cl}) + 1000 \text{ ppm compound IV}$	22.8	19.0	155.2

### References

- 1. Y. Ein-Eli, M. Auinat, D. Straosvetsky, J. Power Sources 114 (2003) 330.
- 2. Q. Qu, L. Li, W. Bai, C. Yan, C. Cao, Corr. Sci. 47 (2005) 2832.
- 3. D. Zhang, L. Lidong, L. Cao, N. Yang, C. Huang, *Corr. Sci.* 43 (2001) 1627.
- 4. K. Orubite Okorosaye, N.C. Oforka, *J. Appl. Sci. Environ. Mgt.* 8 (2004) 57.

- 5. Y.K. Agrawal, J.D. Talati, M.D. Shah, M.N. Desai, N.K. Shah, *Corr. Sci.* 46 (2004) 633.
- 6. M. Abdallah, Corr. Sci. 45 (2003) 2705.
- 7. A.Y. El-Etre, M. Abdallah, Z.E. El-Tantawy, *Corr. Sci.* 47 (2005) 385.
- 8. E.E. Foad El-Sherbini, S.M. Abdel Wahaab, M. Deyab, *Mater. Chem. Phys.* 89 (2005) 183.
- 9. L. Wang, J. Pu, H. Luo, Corr. Sci. 45 (2003) 677.
- 10. S.K. Rajappa, T.V. Venkatesha, *Turk. J. Chem.* 27 (2003) 189.
- 11. J.D. Talati, M.N. Desai, N.K. Shah, *Mater. Chem. Phys.* 93 (2005) 54.
- 12. S. Magaino, M. Soga, K. Sobue, A. Kawaguchi, N. Ishida, H. Imai, *Electrochim. Acta* 44 (1999) 4307.
- 13. M.S. Morad, *J. Appl. Electrochem.* 29 (1999) 619.
- 14. A.M. Gad Allah, M.M. Hefiny, S.A. Salim, M.S. El-Basiouny, *Corr.* 45 (1989) 574.
- 15. B. Muller, G. Inblo, Corr. Sci. 38 (1996) 293.
- 16. A.A. Abdel Fattah, E.M. Mabrouk, R.M. Abd El Gulil, M.M. Ghoneim, *Bull. Soc. Chim. Fr.* 127 (1991) 98.
- 17. R. Sethumodbavan, S. Manavlan, S. Subramanian, H.D. Christopher, *Bull. Electrochem.* 8 (1992) 101.
- 18. M.S. Abdel Aal, Z.A. Ahmed, M.S. Hassan, *J. Appl. Electrochem.* 22 (1992) 1104.
- 19. F. Basio, R.G. Poarson, Mechanism of Inorganic Reaction, 2<sup>nd</sup> ed., John Wiley, London, 1967.
- 20. L.L. Shreir (Ed.), Corrosion, 2<sup>nd</sup> ed., vol. 2, Newnes–Butterworth, London, 1977, pp. 18.2–18.3.
- 21. Y. Kumar, D. Dhirandra, B. Sanyal, G.N. Pandey, Met. Finish. 45 (1983)
- 22. R.L. Every, O.L. Riggs, *Mater. Prot.* 3 (1964) 46.
- 23. W.I.A. El Dougdoug, *Grasas Y. Aceites* (Spain) 50(5) 385 (1999).
- 24. F. Hanna, G.M. Sherbini, Y. Barakat, Br. Corr. J. 17 (1982) 131.
- 25. I.A. Ammer, S. Darwish, Corr. Sci. 7 (1967) 679.
- 26. K.J. Laider, Chemical Kinetics, Mc-Graw-Hill Publishing.