SYNERGISTIC EFFECT OF AMINO ACIDS AND CHLORIDE ION ON ADSORPTION ON COPPER METAL

By

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تأثيـر الأحماض الأمينية وأيون الكلوريد

على الادمصاص على فلز النحاس

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تمت دراسة تأثيـر إدمصاص α – الأنـين، B – الأنـين، DL ، الأنـين – أسـبـارتيك ، L –
جلوتامين، أيسو – ليوسين ، L – ليسين على تآكل النحاس في محلول مولاري من حمض
الهيدروكلوريك باستخدام التقنية البوتنشيوكيناتيكية .

وقـد وجـد أن الأحماض الأمينية التي تمت دراستها تثبط تآكل النحاس بينما يزيد –
L – ليسين من سرعة التآكل .

وقد تمت دراسة معدلات التآكل كدالة لدرجة الحرارة كما حسبت درجة تغطية السطح
من معدلات التآكل .

وقـد نوقش تأثيـر الأحـمـاض الأمـينيـة وأيونات الكلوريد من وجـهـة نظر نماذج
الإدمصاص كما تم تعيين أيزوثرمات الإدمصاص لمثبطات عملية التآكل .

Key Words:: Corrosion inhibition, amino acids, steel, acid medium.

ABSTRACT

The effect of adsorption of α- alanine, β-alanine, DL-aspartic, L-glutamine, iso-leucine and L-lysine in 1 M HC1 solution on the corrosion of copper has been studied using the potentiokinetic technique. The examined amino acids inhibited the corrosion of copper at all examined concentrations, but L-lysine accelerated the corrosion rate. The corrosion rates of copper were measured as a function of concentrations. The degree of surface coverage as calculated from the corrosion rate is used to calculate the free energy of adsorption of the amino acids. The variation of the free energy of adsorption with surface coverage is interpreted in terms of change in the mechanism of inhibition of amino acids with concentration. The synergistic effect of amino acids and chloride ions is discussed from the viewpoint of adsorption models. The inhibitive action requires a knowledge of inhibitor at the electrode-solution interface. Adsorption isotherm of the inhibitors for the corrosion process have been discussed.

INTRODUCTION

The inhibitive action during corrosion requires a knowledge of inhibitor at the electrode-solution interface [1]. Adsorption isotherms of the inhibitors for the corrosion process have been discussed [2-4]. The surface morphology of metallic electrodes was found to be one of the important factors affecting the inhibiting action of organic corrosion inhibitors [5]. The inhibition characteristics of organic compound containing amino group during acid corrosion of copper have been reported from this laboratory [6].

The main goal of the present investigation was taken up to find out the inhibitive actions of different amino acids in acidic chloride solution of HC1.

EXPERIMENTAL

The copper electrode (0.029 Pb; 0.001 Fe; 0.015 Zn %) was donated by Bohler (V. E. Austria). The specimens were machined in the cylindrical form, 2 cm in length and 0.2 cm in diameter. They were inserted in Teflon in such a way that only the flat surface was in contact with the solution.

Reagent grade chemicals were used and solutions were made up with bi-distilled water. A stock solution of the amino acids were prepared and diluted to the appropriate concentration 10^{-5}, 5×10^{-5}, 10^{-4}, 5×10^{-4}, and 10^{-3}M with 1 M HC1 solution as required., and were deaerated by passing O_2- free nitrogen through the solutions for at least 6 Hrs. before the electrode was introduced into the cell.

The details of the cell used in the present investigation was described earlier [7]. A conventional three electrodes system was used. Platinum sheet was used for the auxiliary electrode, the working electrode was copper bar, and the reference electrode was a saturated calomel electrode (SCE) with a Lugging capillary.

Potentiodynamic studies were performed using a corrosion measurement system, a model (273 A soft corr)

corrosion software potentiostat/galvanostat. The anodic and cathodic polarisation measurements were obtained at a scan rate of 1 mV/s in the potential range of -200 to +100 mV. The corrosion rate was obtained by linear polarisation and Tafel extrapolation methods at 30°C.

RESULTS AND DISCUSSION

Copper dissolved in acidic solution containing various concentrations of tested amino acids at 30°C. The corrosion rates were calculated. Amino acids were found to have an effect on the corrosion rates of copper except for lysine which accelerated the corrosion rates, The corrosion rates decreased gradually with the increase in concentration of amino acids to 10^{-3} M (Table 1). At each concentration of the amino acids, inhibition efficiency was calculated using Eq. (1).

Table 1
Effect of additive concentration on corrosion behaviour of copper in chloride ion - containing I M HC1.

Additive	Concentration mole/L		0.0	1×10^{-5}	5×10^{-5}	1×10^{-4}	5×10^{-4}	1×10^{-3}
α–Alanine	Corrosion rate	MPY	288	101	50	35	21	18
		$\mu A/cm^2$	277	97	48	34	20	17
	% P		-	65	83	88	93	94
β–Alanine	Corrosion rate	MPY	288	283	280	277	245	243
		$\mu A/cm^2$	277	273	270	266	238	234
	% P		-	1	3	4	12	16
DL-Aspartic	Corrosion rate	MPY	288	233	219	195	160	141
		$\mu A/cm^2$	277	240	187	178	157	100
	% P		-	19	24	32	44	51
L-Glutamine	Corrosion rate	MPY	288	187	168	160	146	146
		$\mu A/cm^2$	277	203	175	157	148	148
	% P		-	35	42	44	49	49
Iso- Leucine	Corrosion rate	MPY	288	252	249	242	233	234
		$\mu A/cm^2$	277	275	250	222	222	222
	% P		-	13	20	16	19	12
L-Lysine	Corrosion rate	MPY	288	81	213	273	235	247
		$\mu A/cm^2$	277	88	213	273	356	379
	% P		-	72	26	0.5	---	---

where P% is the inhibition efficiency, W_1 is the uninhibited and W_2 the inhibited corrosion rate. The higher inhibitor efficiency (94 %) was observed at 10^{-3} M of α-alanine. The variation of inhibition efficiency, with concentration of amino acids is shown in Fig. 1.

The corrosion potential values were always less negative in the presence of the tested amino acids than in HCl solution.

An increase in the concentration of the tested amino acids reduce the corrosion rate and corrosion current (Table 1).

The surface coverage (θ) of the amino acids at different concentrations was calculated using the Eq. (2).

$$\%P = \frac{W_1 - W_2}{W_1} \times 100 \qquad (1)$$

$$\theta = 1 - W_2 / W_1 \qquad (2)$$

The apparent free energy of adsorption (ΔG^o_a) of the amino acids were calculated from θ - values using the Eq. (3) [8].

$$\Delta G^o_a = -2.303 \, RT \log \left[\frac{55.4}{C_o(1-\theta)} \right] \left[\frac{\theta + (1-\theta)n^{n-1}}{n^n} \right] \qquad (3)$$

where C_o is the concentration of the tested amino acids in the bulk of the solution and (n) is the size factor. A plot of the left hand side of Eq. (3) against the concentration of the amino acids was made to evaluate the exact value of n. A straight line obtained by using n=3 passes through the origin indicating that 3 is the most probable value for the amino acids. (Figs. are not shown). Using Eq. (3) with (n) = 3, the apparent free energies of adsorption (ΔG^o_a) were calculated. Table 2 shows the variation of ΔG^o_a of amino acids with q. The negative ΔG^o_a decreased with the increase of θ. However , the same trend in the variation of ΔG^o_a with θ is noticed for different amino acids.

The dissolution of copper in acidic chloride solution at constant concentration (10^{-3} M of the tested amino acids at different temperatures was done. At each temperature, for a constant concentration of the amino acids (10^{-3} M) , ΔS^o_a was evaluated from the relation between ΔG^o_a and T (Fig. 2). From the values of ΔG^o_a and ΔS^o_a, the heat of adsorption ΔH^o_a was calculated. Table a gives the values of ΔH^o_a, ΔS^o_a and ΔG^o_a at different temperatures of (10^{-3} M) amino acids. The values of ΔH^o_a and ΔS^o_a are positive and increase with increasing the temperatures.

The anodic dissolution reaction of copper in acidic chloride solution is as follows [9].

$$Cu \rightarrow Cu^+ + e$$

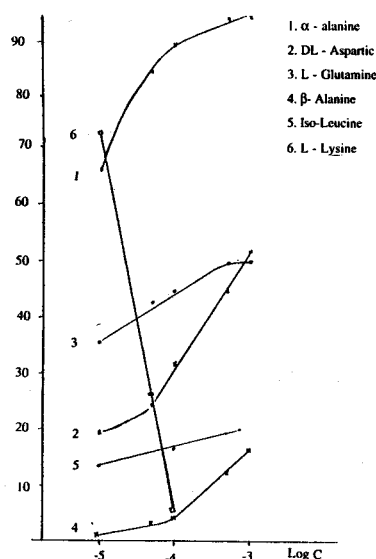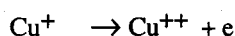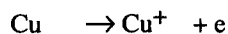$$Cu^+ \rightarrow Cu^{++} + e$$

Fig. 1. Variation of dissolution rate and P% with different concentrations of amino acids.
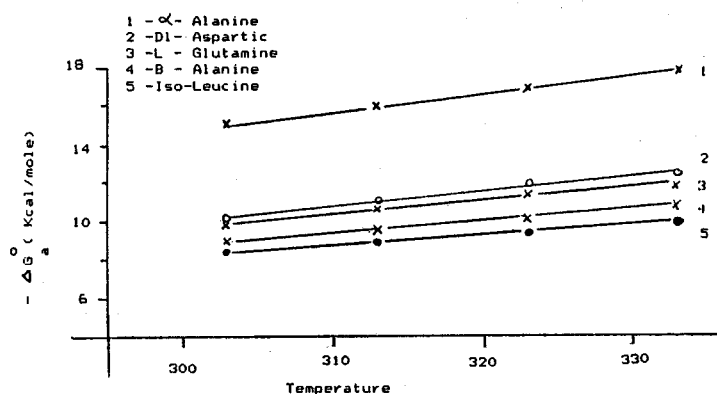

Fig. 2. Variation of dissolution rate and P % with different concentrations of amino acids.

The dissolution reaction initiates on the surface of the metal at the reaction sites (surface defects). Due to the adsorption, amino acids may prevent the removal of copper ions from the reaction sites of the surface. This is observed by the decrease of the corrosion potential [10] which depends on the concentration of the amino acids. This is in accordance with the observed results that the dissolution potential increases with θ. Chloride ions are known to adsorb on the electrode surface [11]. Amines are able to adsorb on the metal surface even at a high concentration of chloride ions [12]. Chloride ion has slight effect on the corrosion of copper in acidic solution [9]. The synergistic effect is a complex phenomena and no single mechanism accounts for all observations. The synergistic effect of Cl⁻ ions and decylamine in acid corrosion inhibition of steel has been reported. The variation of ΔG^o_a with θ (Table 2) indicates the change in the mechanism of inhibitor action with the amino acids concentrations. From Fig. 1, it is clear that the amino acids are not a film-forming inhibitor on the copper surface. On the base of the results in references [12-14), and our results, the following models for amino acids adsorption are proposed.

Table 2

Effect of additive concentration on surface coverage θ and

free energy of adsorption - DG_a^o (n=3)

Additive	Concentration mole/L	1×10^{-5}	5×10^{-5}	1×10^{-4}	5×10^{-4}	1×10^{-3}
α–Alanine	θ	0.65	0.83	0.88	0.93	0.94
	$-\Delta G_a^o$ (KJ mole^{-1})	63.2	62.2	57.9	55.5	54.7
β–Alanine	θ	0.01	0.03	0.04	0.12	0.16
	$-\Delta G_a^o$ (KJ mole^{-1})	52	51.44	44	39.2	37
DL-Aspartic	θ	0.19	0. 24	0.32	0.44	0.51
	$-\Delta G_a^o$ (KJ mole^{-1})	54.2	49	44	42	41
L-Glutamine	θ	0.35	0.42	0.44	0.49	0.49
	$-\Delta G_a^o$ (KJ mole^{-1})	56.5	52	49.8	45	42.6
Iso-Leucine	θ	0.125	0.135	0.16	0.19	0. 20
	$-\Delta G_a^o$ (KJ mole^{-1})	53	48.5	45.5	40	36.7
L-Lysine	θ	0.72	0. 26	0.05	---	----
	$-\Delta G_a^o$ (KJ mole-1)	65.6	69.3	75.14	—	----

Table 3

Effect of Temperature on standard free energy (- DG_a^o) of additivies (10^{-3} M)

Additive		Temperature (°K)			
		303	313	323	333
α-Alanine	$-\Delta G_a^o$ (KJ mole^{-1})	54.7	68.97	72.31	74.86
β–Alanine		37	39.71	43.0	46.40
D1-Aspartic		41	46	39.32	52.30
L-Glutamine		42.6	45.14	48	50.60
Iso-Leucine		36.7	38.	39.3	41.80
L-Lysine		acceleration			

Table 4

Effect of additives (10^{-3} M) on heat of adsorption DH_a^o

and entropy of adsorption DS_a^o

Additive 10^{-3} M	(ΔH_a^o) (KJ mole^{-1})	(ΔS_a^o) (KJ mole^{-1})
α-Alanine	56	392.92
β–Alanine	51.7	292.6
DL-Aspartic	54.88	321.86
L-Glutamine	53.62	317.68
Iso-Leucine	36.78	242.44

Adsorption from solution is influenced by several interactions between the metal and the components both on the surface and in the bulk of the solution. At low concentration $(10 \ M^{-5})$, amino acids cations (R^+) from solution gathered around the chloride ions, previously adsorbed on the copper surface, and as a result tend to be weakly bound to the chloride ions (Model 1). In the case of rather weak adsorption of chloride ions, R^+ at higher concentration tends to displace the chloride ions, on the surface into the solution [13]. On increasing the concentration of amino acids from 10^{-5} to 10^{-4} M, co-adsorption of cations and chloride ions is possible (Model II).

The extent of adsorption of chloride ions from the surface depends on the extend of adsorption of (R^+), which is a function of the concentration of amino acids. When the concentration of amino acids were increased to 10^{-3}M, the chloride ions on the surface provide a better electrostatic condition, which promotes a direct adsorption of cations on the surface through its polar group.

This is also in accordance with increase in negative ΔG°_a with θ above 10^{-4}M amino acids, which is the characteristic feature of lateral interaction between adsorbed amino acids molecules on the surface [6]. The positive values of ΔG°_a and ΔS°_a can be explained as a result of the occurrence of the replacement process during adsorption of amino acids on the surface [15,16].

The corrosion rate is some what low which is probably due to the existence of copper (I) oxide layer which impedes a direct interaction between copper and amino acids. The high cathodic Tafel slopes may be attributed to a mixed activation diffusion control of the electrochemical reaction through some surface (oxide) layer. As this layer is removed by cathodic polarization, hydrogen evolution occurs, and the Tafel slope become a kinetic one. The acceleration of corrosion in the presence of L-lysine is probably due to the non-contribution of lysine to the cathodic reactions, also the increase in both anodic and cathodic Tafel slopes in 1 M HCl by the presence of lysine shows the interference of anodic and cathodic partial reactions of the corrosion process compounds and thus acting as mixed inhibitor.

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