

THE EFFECT OF HYDROXYCARBOXYLIC ACIDS AND AMINO ACIDS ON THE CORROSION OF ALUMINIUM BASE ALLOYS IN 0.1 M NaCl SOLUTION

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ABSTRACT

The effects of several hydroxycarboxylic acids, such as glycolic acid, lactic acid, mandelic acid, benzilic acid and several amino acids, such as glycine, alanine, valine, phenyl glycine, phenyl alanine and aspartic acid on the corrosion behaviour of aluminum-base alloys have been investigated in 0.1 M sodium chloride by the potentiodynamic-polarization technique.

Hydroxy carboxylic acids accelerated the corrosion rate of aluminum and aluminum base alloys. The accelerating effects were explained by the formation of soluble complex ions.

Corrosion currents found in amino acids containing sodium chloride solutions, were lower than corrosion currents found in hydroxycarboxylic acid containing sodium chloride solutions. This was explained by the adsorption of amino acids.

It was found that some amino acids behaved as cathodic inhibitors and the inhibiting characteristics of amino acids were closely related to the electron densities of the functional groups at which adsorption occurred.

INTRODUCTION

Corrosion behaviour of aluminum-base alloys in saline solution is important in aerospace industry and in choosing suitable material that is going to be used in living organism (A.S. Saraç et al., 1990; Rachel L. 1988; R.C. Salvarezza et al., 1985; Herbert 1987). Carboxylic acids, hydroxy compounds and some amino acids have been long recognized as

important corrosion inhibitors since these compounds are quite cheap and nontoxic (C. Chakrabary et al., 1983; A.S. Fonda El-Semongy., 1982). On the other hand use of inorganic electrolytes such as saline solution for the study of corrosion behaviour of metals-which is the major process that cause problem when metals are used in the body-neglects the role of physiological organic species in the corrosion of implant materials. Organic components such as serum proteins may interact with alloy constituents and passive film on implant alloys thus alter the corrosion behaviour of these alloys. In this respect effects of amino acids on the corrosion behaviour on aluminum-base alloys in saline solutions must be consider.

EXPERIMENTAL

Pure aluminum, aluminum 1100, aluminum 2024, aluminum 6061, aluminum 7075 alloys which were supplied by Turkish Air Force in Eskişehir have been used in this investigation.

Composition of the alloys are as follows: Aluminum 1100 (99% Al), Aluminum 2024 (4.5% Cu, 1.5% Mg, 0.6% Mn, Al to 100). Aluminum 7075 (5.5% Zn, 2.5% Mg, 1.5% Cu, 0.3% Cr Al to 100). Aluminum 6061 (1% Mg, 0.6% Si, 0.25% Cu, 0.25% Cr, Al to 100).

Cathodic polarization of these alloys were obtained in air saturated 0.1 M NaCl with and without 1 mM hydroxycarboxylic acids or with and without 1 mM amino acids.

The polarization experiments were carried out in conventional three electrode system by using Pt-counter and saturated calomel reference electrode, with Tacussel PRG-5 polarographic analyzer. The scanning rates were 1 mV/sec and after attaining steady-state potential, the potential was scanned over 300 mV range in cathodic direction.

RESULTS AND DISCUSSIONS

Cathodic polarization curves of aluminum and aluminum alloys type 1100, 2024, 6061 and 7075 in 0.1 M NaCl with and without hydroxy carboxylic acids or with and without amino acids were obtained. Typical curves for pure aluminum and for 2024 type aluminum alloy are given in Figure 1 and 2 respectively. Results obtained from these polarization curves are summarized in Table 1 and 2. E_{corr} values of 2024 type

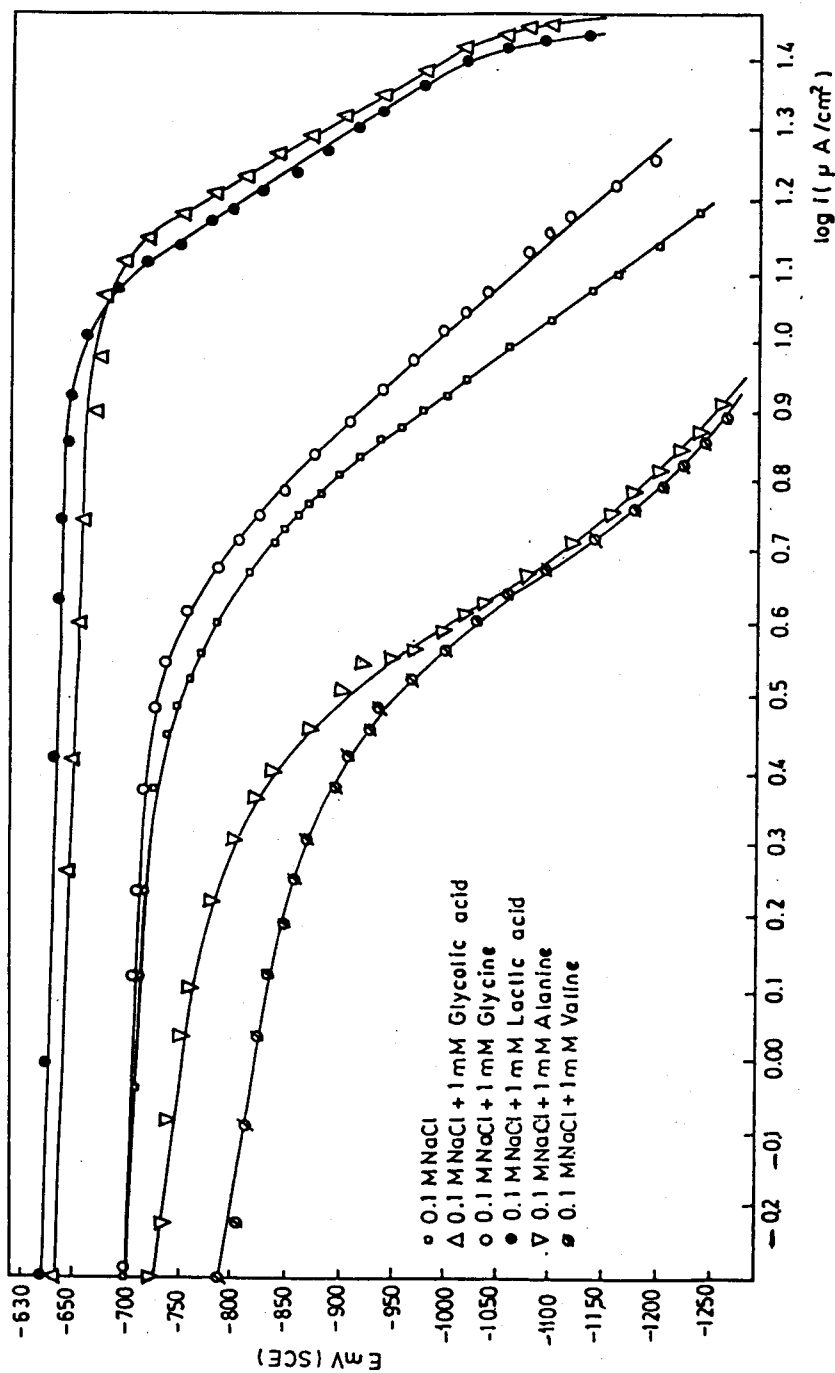


Fig. 1. Polarization curves of pure Al in 0.1 M NaCl in the presence and absence 1 mM of each glycolic acid, glycine, lactic acid, alanine, valine.

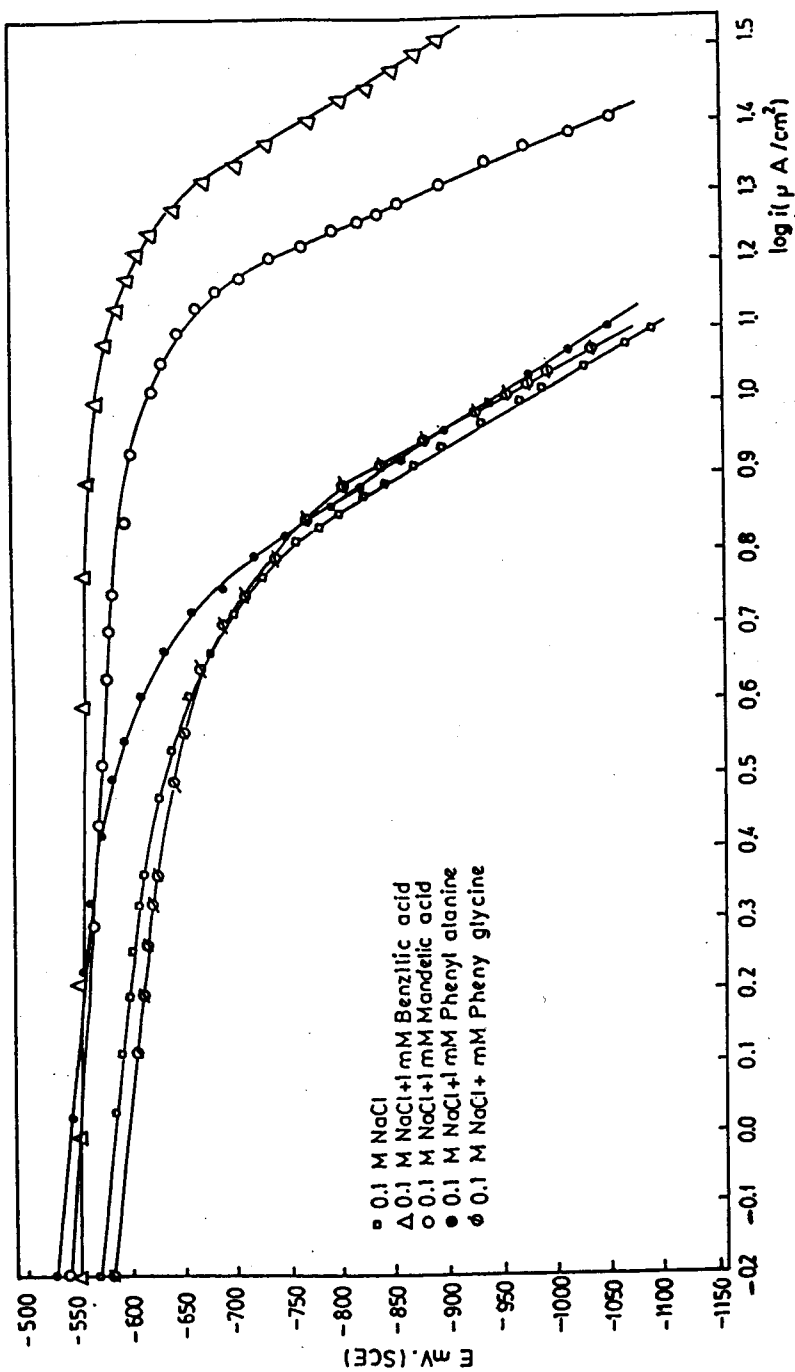


Fig. 2. Polarization curves of 2024 Al in 0.1 M NaCl in the presence and absence 1 mM of each benzilic acid, mandelic acid, phenyl alanine, phenyl glycine.

Table 1. Effect of Hydroxycarboxylic Acids and Amino Acids on Corrosion Behaviour of Pure Al and Al-1100 in 0.1 M NaCl.

Solution	Organik Compound	Pure Al			Al-1100		
		E _{corr} (mV)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	$\frac{i_0 - i_1}{i_0} \times 100$	E _{corr} (mV)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	$\frac{i_0 - i_1}{i_0} \times 100$
0.1 M NaCl	—	-700	3.9		-690	4.7	
0.1 M NaCl + 1mM glycolic acid	<chem>OC(=O)CO</chem>	-630	11.6	-197	-688	10.23	-117
0.1 M NaCl + 1 mM glycine	<chem>NC(=O)CO</chem>	-700	3.8	2.5	-680	6.9	-46.2
0.1 M NaCl + 1 mM lactic acid	<chem>CC(O)C(=O)O</chem>	-620	10.2	-161.5	-690	10	-111.4
0.1 M NaCl + 1 mM alanine	<chem>CC(N)C(=O)O</chem>	-725	2.1	46.1	-685	3.5	25.53
0.1 M NaCl + 1 mM valine	<chem>CC(N)C(C)C(=O)O</chem>	-790	1.9	51.2	-705	1.6	65.9
0.1 M NaCl + 1 mM mandelic acid	<chem>OC(O)Cc1ccccc1</chem>	-700	10.1	-158.9	-690	9.4	-100
0.1 M NaCl + 1 mM phenyl glycine	<chem>NC(=O)Cc1ccccc1</chem>	-725	3.6	7.6	-700	3	36.1
0.1 M NaCl + 1 mM phenyl alanine	<chem>NC(=O)Cc1ccc(cc1)C(O)C(=O)O</chem>	-785	1.8	53.8	-690	3.8	19.1
0.1 M NaCl + 1 mM benilic acid	<chem>OC(O)C(O)Cc1ccccc1</chem>	-635	6.6	-69.2	-695	8.5	-80
0.1 M NaCl + 1 mM malic acid	<chem>OC(O)C(O)C(=O)O</chem>	-695	7.2	-84.6	-690	11.8	-151
0.1 M NaCl + 1 mM aspartic acid	<chem>OC(O)C(O)C(N)C(=O)O</chem>	-695	7.5	92.3	-695	9.22	-96

Table 2. Effect of Hydroxycarboxylic Acids and Amino Acids on Corrosion Behaviour of Al-2024, Al-6061 and Al-7075 in 0.1 M NaCl.

Solution	Al-2024			Al-6061			Al-7075		
	E _{corr} (mV)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	$\frac{i_0 - i_1}{i_0} \times 100$	E _{corr} (mV)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	$\frac{i_0 - i_1}{i_0} \times 100$	E _{corr} (mV)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	$\frac{i_0 - i_1}{i_0} \times 100$
0.1 M NaCl	-570	4.2		-820	3.9		-750	16.6	
0.1 M NaCl + 1 mM glycolic acid	-585	5.5	-30.9	-660	7.5	-85.7	-750	16.6	0
0.1 M NaCl + 1 mM glycine	-545	4.8	14.2	-715	7.1	-82	-750	15.3	7.3
0.1 M NaCl + 1 mM lactic acid	-550	8.9	-271.4	-670	10.4	166.6	-755	17.8	-7.3
0.1 M NaCl + 1 mM alanine	-540	4.7	-11.9	-670	6.7	-71.7	-758	11.8	28.9
0.1 M NaCl + 1 mM valine	-600	2.9	30.9	-830	1.7	56.4	-780	4.1	75.3
0.1 M NaCl + 1 mM mandelic acid	-540	11.9	-183	-665	8.2	-110.2	-750	18.2	-9.6
0.1 M NaCl + 1 mM phenyl glycine	-580	5.2	-23.8	-780	4.9	-25.6	-760	14.2	14.4
0.1 M NaCl + 1 mM phenyl alanine	-524	4.1	2.3	-740	5.7	-46.1	-765	10.2	38.5
0.1 M NaCl + 1 mM benzoic acid	-550	16	-280	-670	7.5	-92.3	-760	15	9.6
0.1 M NaCl + 1 mM malic acid	-550	13.9	-230	-660	10	-156.4	-755	13.5	18.6
0.1 M NaCl + 1 mM aspartic acid	-580	8.6	-104.7	-665	8.4	-115.3	-760	9.6	42

aluminum alloy is in the range of -550 mV -600 mV while the E_{corr} values of the other alloys are in the range of -700 mV -750 mV. By comparison with the other alloys for 2024 shifting of the corrosion potential to anodic direction might be due to presence of highest Cu content (4.5%). E_{corr} values of 7075 is about of -750 mV, presence of highest Zn (5.5%) and Mg (2.5%) is responsible of shifting the corrosion potential to cathodic direction. Among the aluminum alloys highest corrosion rate in 0.1 M NaCl was observed for Al-7075. Presence of hydroxycarboxylic acids in sodium chloride solutions was found to increase the corrosion rate of all aluminum alloys. This can be explained by the possible complex formation of hydroxycarboxylic acids with the aluminum cation in the oxide film and with the alloying element.

For comparison, in the presence of -OH and -NH₂ groups, in carboxylic acids such as lactic acid and alanine in pure Al, -NH₂ group reduced the corrosion rate from 10.2 $\mu\text{A}/\text{cm}^2$ to 2.3 $\mu\text{A}/\text{cm}^2$. But this is not much pronounced in the case of alloy 7075.

Shifting of corrosion potentials to cathodic direction in amino acids compare to sodium chloride solutions shows that amino acids are of cathodic type inhibitors.

Lower corrosion current densities in amino acid containing solutions compare to current densities in hydroxycarboxylic acids containing solutions might be due to fact that besides complex formation of amino acids with metals, adsorption of amino acids on metal surface via -NH₂ groups takes place.

Presence of -OH or -NH₂ group in dicarboxylic acid case does not much effect for pure Al and alloy 1100. But in the case of 6061 and 2024 alloys because of presence of other alloying metals I_{corr} values in malic acid increases indicating dissolution of such metals.

But in the case of 7075 alloy malic acid and asparatic acid both acts as inhibitor. Inhibitory character of malic acid in this case might be due to accumulation of soluble malic acid complex of alloying metal (Zn) nearest to electrode surface. Inhibition by soluble metal complex have been reported in the case of nickel by nitrilotrisacetate (NTA) (Yu, I. Kazetsov, 1990).

P.S. Increase of corrosion rate in Al-2024, 6061, 7075 shows a parralelism with each other, on the other hand which also shows a reverse relation with log of first formation constant (Cu-ligand) (L.G. Sillen et al., 1971). Since this decrease is an indication instability of these ligands with one of the alloying element.

Ligand	log K_1	Al-2024 i_{corr}	Al-6061 i_{corr}	Al-7075 i_{corr}
Alanine	8.8	4.7	6.7	11.8
Aspartic acid	8.6	8.6	8.4	9.5
Malic acid	3.3	13.6	10.0	13.5
Lactic acid	3.2	15.7	10.5	17.8

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