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Inhibitory effect of amino acids on Al pitting corrosion in 0.1 M NaCl

A. A. EL-SHAFEI*, M. N. H. MOUSSA, A. A. EL-FAR

Department of Chemistry, Faculty of Science, El-Mansoura University, ET-35516 El-Mansoura, Egypt

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The effect of some α-amino acids on the inhibition of pitting corrosion of Al in 0.1 M NaCl solution was studied by the potentiodynamic technique. All inhibitors used shift the pitting potential (E_p) and the protection potential (E_{pp}) towards more noble values. The order of effectiveness of the inhibitors was arginine > histidine > glutamine > asparagine > alanine > glycine. The adsorption of amino acids on platinum was investigated by cyclic voltammetry using a flow cell technique. The results confirm that the inhibition efficiency of the amino acids studied is due to their adsorption on the metal surface. Variation in inhibition efficiency with the structure of the compounds was interpreted in terms of the number of adsorption active centres in the molecule, the molecular size and the mode of adsorption.

1. Introduction

Due to the various industrial applications and the remarkable economic importance of aluminium and its alloys, its protection against pitting corrosion has attracted much attention [1–8]. One of the available methods is the use of soluble inhibitors. Unfortunately, many of the inhibitors used are inorganic salts [9–12] and organic compounds [10, 13–16] with toxic properties or limited solubility. Increasing awareness of the health and ecological risks has drawn attention to finding more suitable inhibitors, which are non-toxic. Amino acid inhibitors fall into this category since they are cheap, completely soluble in aqueous media and easy to produce at high purity. In this work the efficiency of six α-amino acids as inhibitors for pitting corrosion of aluminium in Cl^- ion containing solution has been studied by the potentiodynamic technique and adsorption properties have been checked by cyclic voltammetry using a flow cell technique.

2. Experimental details

All experiments were carried out using a combined wave generator and potentiostat (Oxford electrodes) and *X–Y* recorder (Philips model PM 8043). The temperature was kept constant at 25 ± 0.1 °C using an ultrathermostat (Julabo HC). The potential was measured against a Ag/AgCl/sat. KNO_3 electrode and all values reported here were referenced to this electrode.

All solutions were prepared from distilled water obtained with a Megapure system (MP-A6 corning) and analytical grade chemicals: H_2SO_4 (BDH), NaCl (BDH) and amino acids (Merck).

2.1. *Corrosion studies*

Potentiodynamic measurements were done in a double-wall one compartment cell with Pt wire as a counter electrode. The working electrode was a 1 cm long cylindrical Al wire (99.999% Aldrich) having a thickness of 1 mm and sealed to a glass tube with a suitable adhesive (Araldite). Electrical contact was made via a small mercury pool on the enclosed end of the aluminium electrode. The electrode was polished with G400 grit emery paper, cleaned with distilled water, degreased in (Na_2CO_3 + Na_3PO_4) mixture [17], washed thoroughly with distilled water and finally dried with filter paper. In all experiments, the potential was scanned at a rate of 1 mV s^{-1} starting from the open circuit potential (0.7 V) in the more noble direction. At constant current (0.4 mA) the scan was reversed in the more negative direction until zero current was reached. Both the pitting potential (E_p, at the first initial increase of current) and the protection potential (E_{pp}) at which pits were repassivated (at zero current) were recorded.

2.2. *Adsorption measurements*

For adsorption measurements, Pt sheet was used as a working electrode. The experiments were performed using a flow cell technique [18] according to the following procedure:

(i) Activation of Pt electrode in 0.1 M H_2SO_4 by repetitive triangular sweep while changing the electrolyte repeatedly until the voltammogram acquired its usual shape (Fig. 1).
(ii) The potential was stopped at −0.325 V during the negative sweep and the electrolyte was replaced by 0.1 M NaCl and the voltammogram was recorded (Fig. 2).

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* Author to whom correspondence should be addressed.

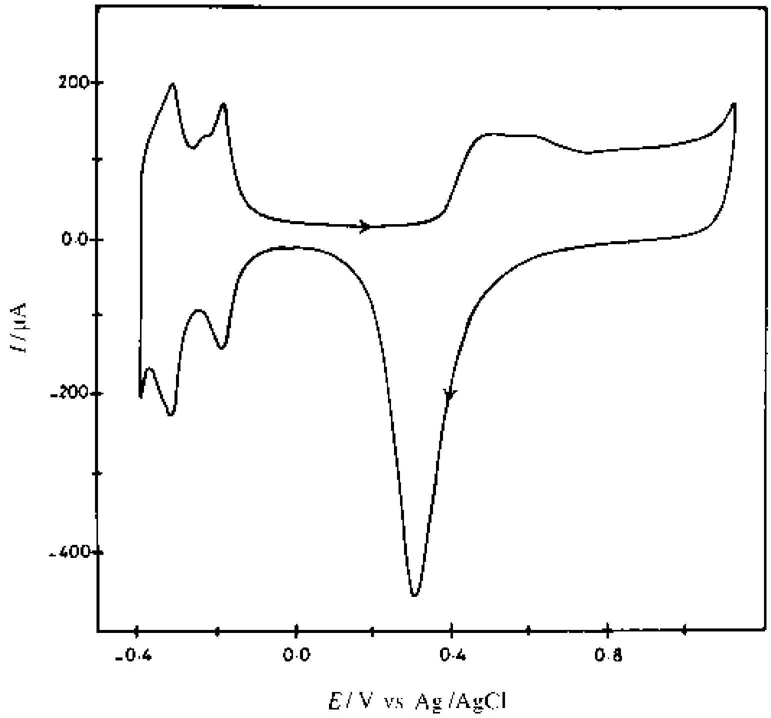


Fig. 1. Cyclic voltammogram of Pt electrode in 0.1 M H_2SO_4 at room temperature (v = 100 mV s^{-1}).

(iii) The potential was stopped again at −0.325 V during the negative sweep and the electrolyte was replaced by 10^{-5} M amino acid +0.1 M NaCl solution where amino acids were left to be adsorbed on the Pt electrode for 3 min.

(iv) After replacing the solution (0.1 M NaCl), the potential sweep started in the negative direction (v = 100 mV s^{-1}, Fig. 2).

The degree of coverage of the Pt electrode with adsorbed amino acids, θ, was estimated from the hydrogen adsorption region according to the following equation:

$$\theta = (Q^{H}_{Pt} - Q^{H}_{Pt,ads})/Q^{H}_{Pt} = \Delta Q^{H}_{Pt}/Q^{H}_{Pt} \qquad (1)$$

where Q^{H}_{Pt} and $Q^{H}_{Pt,ads}$ are the charges for hydrogen adsorption in the absence and the presence of adsorbed species.

3. Results and discussion

Figure 3 shows the potentiodynamic polarization curves of aluminium in 0.1 M NaCl solution in the

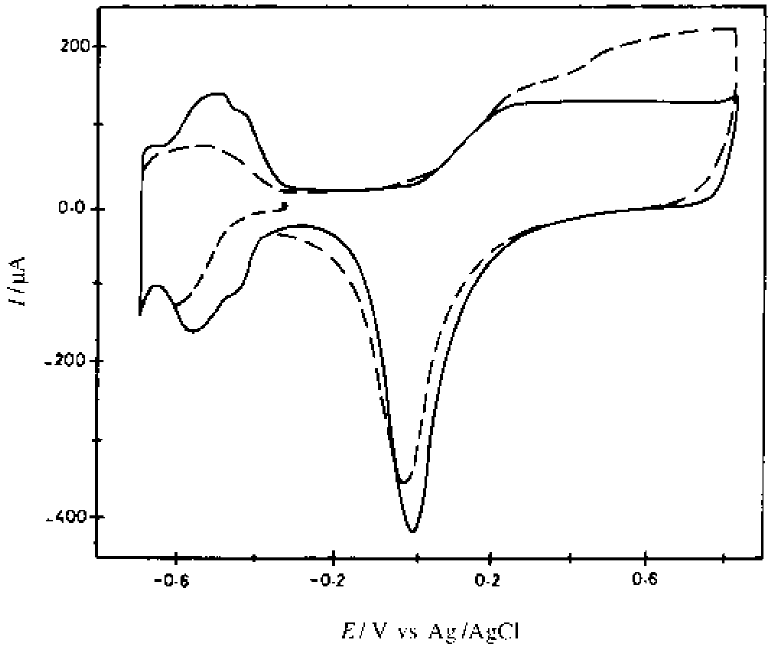


Fig. 2. Cyclic voltammogram of Pt electrode in 0.1 M NaCl at room temperature (v = 100 mV s^{-1}). Key: (——) bare Pt, (- - -) $\theta^{Pt}_{arginine}$ = 0.59.

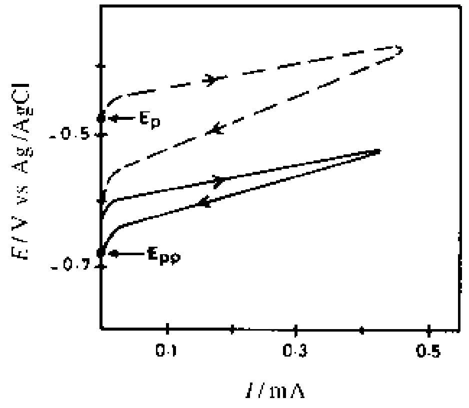


Fig. 3. Potentiodynamic polarization curves of aluminium in 0.1 M NaCl in absence (——) and presence (- - - -) of 5×10^{-2} M arginine ($v = 1\ \mathrm{mVs^{-1}}$).

Table 1. The effect of amino acids on the pitting and protection potentials of aluminium in 0.1 M NaCl. Scan rate 1 mV s⁻¹

Amino acid /5 × 10^{-2} M	E_p /V vs Ag/AgCl	E_{pp} /V vs Ag/AgCl
Arginine	−0.49	−0.620
Histidine	−0.52	−0.635
Glutamine	−0.53	−0.650
Asparagine	−0.55	−0.630
Alanine	−0.57	−0.645
Glycine	−0.58	−0.640

Table 2. Amino acid surface coverage at Pt electrode in 0.1 M NaCl

Amino acid /10^{-5} M	θ
Arginine	0.591
Histidine	0.560
Glutamine	0.530
Asparagine	0.504
Alanine	0.480
Glycine	0.367

absence and the presence of arginine. The presence of arginine shifts both E_p and E_{pp} to more noble values, thus increasing the resistance to pitting. The effect of varying concentration of added amino acid on E_p is shown in Fig. 4. A linear relationship between E_p and log inhibitor concentration was obtained in agreement with Bohni and Uhing [9]. The linearity between E_p and $\log C_{inh}$ can be represented by the following equation

$$E_p = A + B \log C_{inh}$$

where A and B are constants that depend on both the type of inhibitor and aggressive anions, as well as on the metal under test. All the other studied amino acids exhibit a similar effect (Table 1). From these results, the inhibition action of amino acids under examination decreases in the order: arginine > histidine > glutamine > asparagine > alanine > glycine.

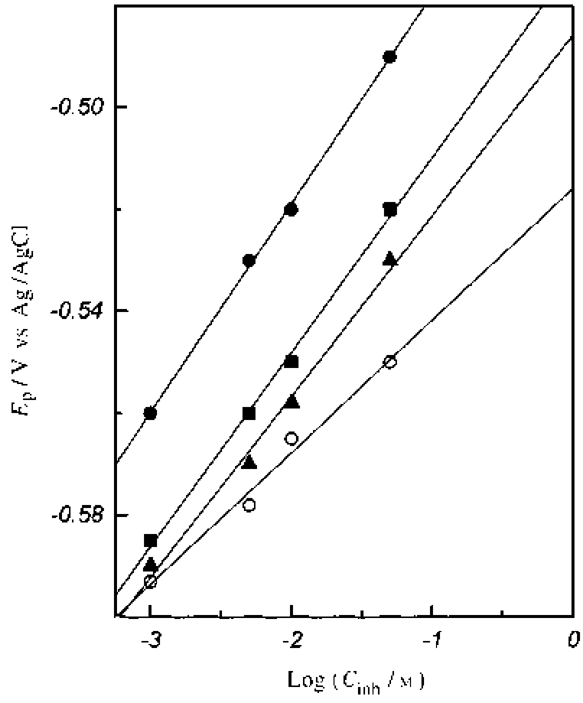
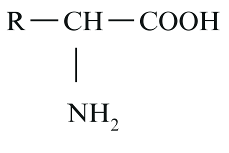


Fig. 4. Effect of inhibitors concentration on E_p in 0.1 M NaCl. Key: (●) arginine, (■) histidine, (▲) glutamine and (○) asparagine.

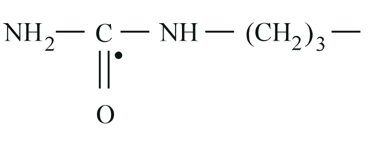
The effect of preadsorbed arginine at a Pt surface on the voltammogram recorded in 0.1 M NaCl is shown in Fig. 2. The preadsorbed amino acid blocked the Pt sites towards hydrogen adsorption, leading to a decrease in the amount of adsorbed hydrogen. This reduction in the hydrogen adsorption–desorption region was used to evaluate the amino acid coverage according to Equation 1. The data obtained for all amino acids studied are listed in Table 2. The adsorption ability of amino acids decreases in the order: arginine > histidine > glutamine > asparagine > alanine > glycine.

This agreement between the results obtained from both techniques indicates that inhibiting efficiency of amino acids for the pitting corrosion of Al in 0.1 M NaCl is due to their protection of aluminium surface from aggressive ions through adsorption. As previously reported [15, 19–23] inhibition efficiency depends on the number of adsorption sites in the molecule and their charge density, molecular size and mode of interaction with the metal surface. A general formula for amino acids can be written as

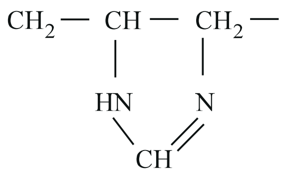


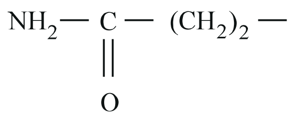
$$\underset{\displaystyle \mathrm{NH_2}}{\mathrm{R{-}\underset{|}{CH}{-}COOH}}$$

where the radical, R, is

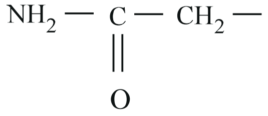


$$\mathrm{NH_2{-}\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}{-}NH{-}(CH_2)_3{-}}$$

or 

or 

$\mathrm{NH_2-\underset{\overset{\|}{O}}{C}-(CH_2)_2-}$

or 

$\mathrm{NH_2-\underset{\overset{\|}{O}}{C}-CH_2-}$

or CH_3-

or $H-$

The R radical differs in size and the number of adsorption active sites from one compound to another. The skeletal structures of compounds I, II and III are shown in Fig. 5. Arginine is the most efficient inhibitor for the pitting corrosion of aluminium in 0.1 M NaCl solutions. This is most probably due to its adsorption through the two N atoms of the primary and secondary amine groups in R radical (I, Fig. 5) and its high molecular size. Histidine (II, Fig. 5) comes next to arginine due to its adsorption through only one N atom in the secondary amine group in the R radical and its lower molecular size. Moreover, the R radical in histidine is cyclic, giving a smaller surface coverage than the straight chain structure of R in arginine, which is a better inhibitor than histidine. Glutamine (III, Fig. 5) is less effective than histidine due to a still lower molecular size, although it is adsorbed through one N active centre of the primary amine group. Asparagine comes after glutamine despite its adsorption through the N atom of primary amine group in R radical because its molecular size is lower than that of glutamine. For alanine and glycine no adsorption active sites in R radical exist. Therefore, alanine and glycine come after asparagine but glycine has the lowest inhibition efficiency due to lower molecular size than alanine.

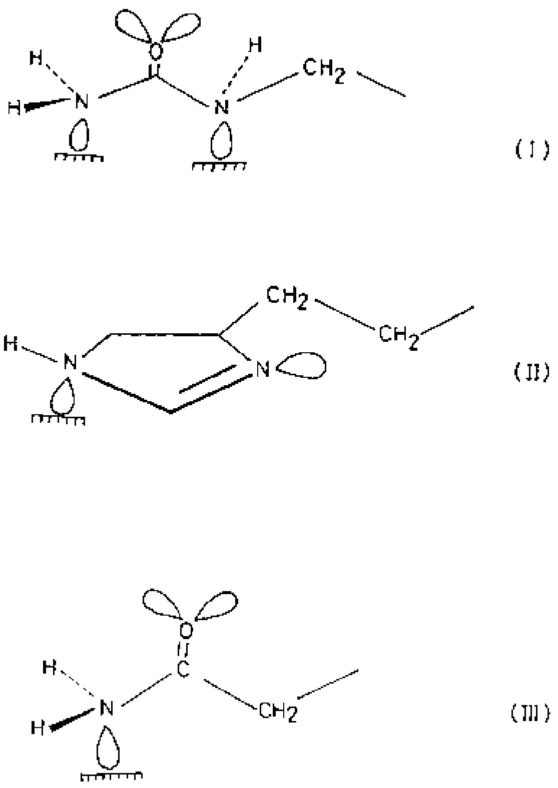


Fig. 5. Skeletal structures of amino acids I, II and III.

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