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PITTING CORROSION OF ALUMINIUM IN HALIDE SOLUTIONS CONTAINING SOME ANIONIC SURFACTANTS

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ABSTRACT

The pitting corrosion of Aluminium was studied in 0.1 M halide solutions in various concentrations of decyl and dodecyl sodium sulphate. The results obtained from the potentiodynamic measurement show that the pitting corrosion is inhibited by the presence of organic compounds in this medium. The percentage inhibition was found to increase with increasing the concentration of the organic compounds in the medium at constant halide concentration.

For solutions of constant halide concentration, the pitting potential varies with the logarithm of the inhibitor concentration according to a linear relationship. These results are interpreted in terms of competitive adsorption between halide ions and organic anions at the passive metal-solution interface. It was found that the efficiency of inhibition for a given halide concentration decreases in the order of dodecyl sodium sulphate > decyl sodium sulphate. At constant inhibitor concentration, the pitting corrosion was found to decrease in the order: $Cl^- > Br^- > I^-$.

Key words: Pitting corrosion, Aluminium, Potentiodynamic, Passivation, Surfactants.

INTRODUCTION

Pitting corrosion is an extremely localized attack, which result in deep, localized cavities in the metal. Two basic conditions must be fulfilled for the initiation and propagation of pitting corrosion. First, the metal surface should be covered with a passive film. Second, the medium should contain an aggressive species. Pitting potential can be readily evaluated in the laboratory with such techniques as potentiostatic, potentiodynamic anodic polarization and cyclic voltammetry[1,2]. The pitting potential depends on the concentration of aggressive ions, pH of the solution, temperature, metal composition and heat treatment [3-7].

Many authors [2,8-13] have studied the effect of aggressive anions on pit initiation. The linear relationship between the pitting potential and the logarithmic of aggressive ion concentration is expressed according to the equation [14]:

$$E_p = a_1 - b_1 \log [Cl^-] \qquad (1)$$

Where $E_p =$ is the pitting potential, [Cl⁻] is the activity of the chloride ion and a_1 and b_1 are experimentally determined constants, they are depend on both nature and type of aggressive anion as well as the electrode material.

Organic inhibitors have been widely used in the past in acidic media. Recently, however, they began being used in neutral [15,16] and alkaline [17,18] electrolytes as alternative to toxic inorganic inhibitors. Many early papers deal with the breakdown of passive film by aggressive anions in different buffers such as borate [19-23], acetate [24] and phosphate [25].

There is a little information about the application of decyl and dodecyl sodium sulphate to localized corrosion in neutral media [26]. In addition to that the investigated molecules are water soluble compounds, having a large molecular size and finally contains a hydrophobic and hydrophilic parts which lead to the increase of the effectiveness of the adsorption [27]. In the present paper, the pitting of aluminium in chloride, bromide and iodide solutions and the role of decyl and dodecyl sodium sulphate in the inhbitive process are discussed.

EXPERIMENTAL

The working electrode consists of aluminium wires containing 0.15% Si, 0.19% Fe, 0.05% Mn, 0.1% Mg and 0.02% Cu. They were inserted in Araldite holders to obtain a circular exposure area of 0.25 cm² prior to each experiment these specimens were polished with emery paper and degreased in alkaline solution (carbonate + phosphate solution)[28], washed with distilled water and dried between filter papers.

The electrochemical equipment consists of a three electrode polarization cell, platinum was used as a counter electrode and saturated calomel electrode as reference electrode. The solutions were prepared with bidistilled water. All experiments were repeated to verify their reproducibility at room temperature (25°C). NaCl, NaI and NaBr used were Analar BDH grade while decyl and dodecyl sodium sulphate of Analar Kodak grade.

The polarization curves were determined potentiodynamically at a rate of 1 mVs⁻¹. by using a Wenking Potentio-Galvano-Scan (PGS 95) and a Cole Parmer recorder (LY 14100 II).

RESULTS AND DISCUSSION

I) Variation of pitting potential with the concentration of chloride ions

Fig.1 shows the potntiodynamic anodic polarization curves of an aluminium electrode in different concentrations of NaCl solution as a pitting agent. Curves of Fig.1 reveal that upon the addition of Cl⁻ ions:

I) A sudden and marked increase of current at a given potential (pitting potential, E_P) and initiation of visible pits[29].

II) By increasing the Cl⁻ ion concentrations, the general shape of the curves does not changed, while E_P shifted to the lowervalues.
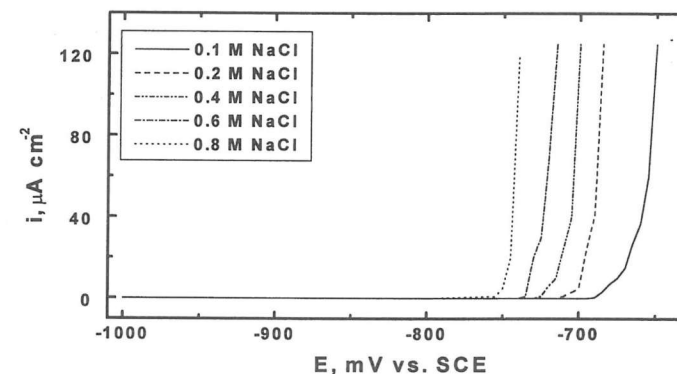

Fig.1 Potentiodynamic anodic polarization curves of aluminium in different concentrations of NaCl solutions.

Fig.2 displays the pitting potentials as function of the logarithm of Cl⁻ ion concentration. A linear relationship was obtained and this verifies equation (1) is obtained. This behaviour may be attributed to the destruction of the passive film formed on aluminium surface and the pits formed continuously propagate and cannot undergo repassivation [30].
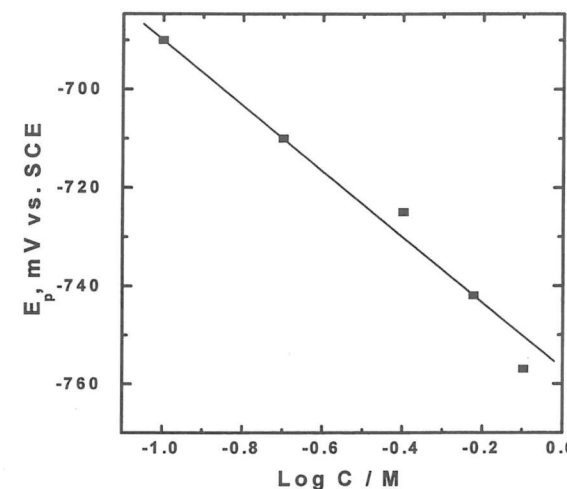

Fig.2 The pitting potential against log [Cl⁻]

II) **Inhibition of pitting corrosion by decyl and dodecyl sod. sulphate:**

Fig.3 represents the potentiodynamic anodic polarization curves of aluminium in 0.1 M NaCl at different concentration of decyl sodium sulphate at 25°C.. As shown from the figure, the pitting potentials were shifted to more noble direction as the concentration of decyl sodium sulphate increases and hence, the inhibiting effect increases. Similar behaviour was observed for dodecyl sodium sulphate.
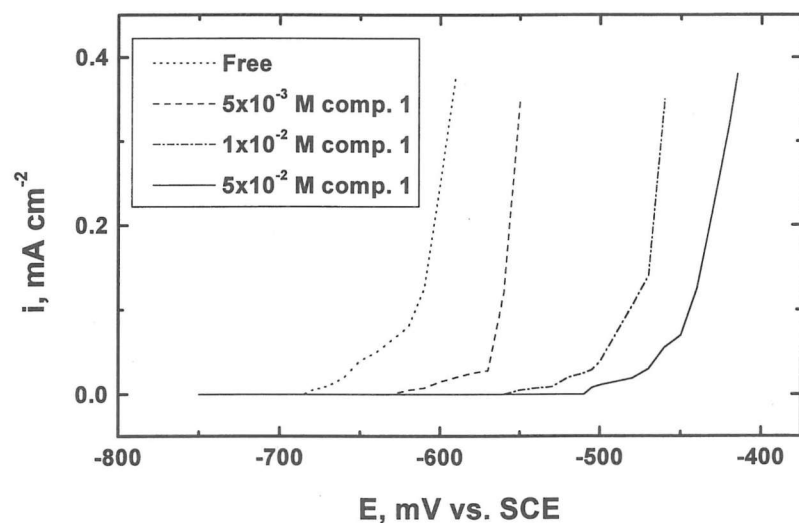

Fig.3 Potentiodynamic anodic polarization curves of aluminium in 0.1M NaCl at different concentrations of decyl sodium sulphate at 25°C.

Fig.4 shows the potentiodynamic curves of aluminium in presence and in absence of $5x10^{-3}$ M decyl and dodecyl sodium sulphate at 25°C. The figure shows that the pitting potentials shift to more noble direction in the order: $E_p(Cl^-) < E_p(decyl) < E_p(dodecyl)$

From this order, one can suggest that the efficiency of inhibition decreases in the order: dodecyl sodium sulphate > decyl sodium sulphate.
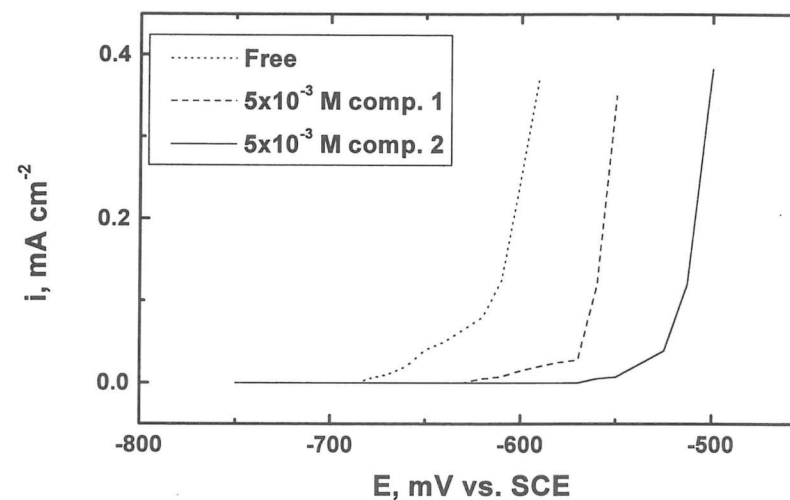
Fig.4 Potentiodynamic anodic polarization curves of aluminium in presence and absence of $5x10^{-3}$ M decyl and doecyl sodium sulphates at 25°C.

The nature of inhibitor interaction on the corroding surface during corrosion inhibition of metals and alloys has been deduced in terms of adsorption characteristics [31-33] of the inhibitor interface.

The mechanism of inhibition depends upon the competitive adsorption phenomenon between the two counteracting species for the active sites on the passive aluminium surface. The protective characteristics of the surface film depends upon the aliphatic chain length, following the sequence $C_{12}H_{25} > C_{10}H_{21}$.

The present results, therefore, support the mechanism of pitting proposed by Uhlig and co-workers for the inhibition of pitting in stainless steel [34].

Fig.5 represents the linear relationship between E_p and logarithm of molar concentration of decyl sodium sulphate at constant aggressive ion concentration (0.1 M). The results of this figure show that by increasing the concentration of the inhibitor, the pitting potentials are shifted to more noble direction according to the following equation:

$$E_p = a_2 + b_2 \log C_{inh.}$$

Where a_2 and b_2 are constants depending upon the type of both inhibitive and aggressive ions in solution. The value of the constant b_2 (Table 1) decreases in the order $Cl^- > Br^- > I^-$ which is the same order of decrease of their aggressive towards pitting corrosion [35-38].
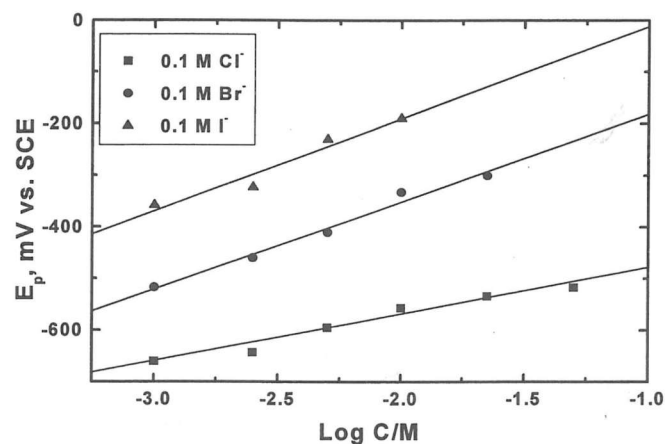
Fig.5 E_P as a function of log [concentrations] of decyl sodium sulphate.

As known iodide I^- have more inductive effect than Br^- and Cl^-. So, the iodide ions are highly displaced by the inhibitor molecules, hence, the inhibition efficiency increases due to the increase in the surface coverage. On the other hand Cl^- ions are more attached to the metal surface, thus its displacement process is more difficult than I^- ions by the inhibitor molecules. This causes a reduction in the value of inhibition efficiency. Br^- ions have an intermediate effect between the I^- and Cl^- ions, so, it has an intermediate effect on the inhibition efficiency.

Table 1 shows the values of a_1, b_1, a_2, b_2 for various systems studied containing decyl sodium sulphate.

System	a_1	b_1	a_2	b_2
0.1MCl+decyl sod.sulph.	-682	7.35	-633	67.6
0.1MBr+decyl sod.sulph.	-533	7.41	-562	167.6
0.1MI+decyl sod.sulph.	-332	13.63	-415	173.3

CONCLUSIONS

1- The pitting corrosion behaviour of Al metal has been investigated in neutral NaCl, NaBr and NaI solutions using potentiodynamic technique.

2- The susceptibility of Al anode to pitting corrosion enhances with increasing the halide concentration.

3- The aggressiveness of the halide ions decreases in the order $Cl^- > Br^- > I^-$.

4- The presence of decyl and dodecyl sodium sulphates shift the pitting potential to more noble direction and their efficiency increases as their concentrations increase.

5- Dodecyl sodium sulphate was found to be more efficient inhibitor than decyl sodium sulphate towards Al pitting corrosion.

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