Effect of Some Macromolecular Compounds and Amino Acids On The Pitting Corrosion of Zinc in CrO_4^{2-}/Cl^- Medium

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Summary: The anodic polarization technique was used to study the behaviour of Zn electrode in CrO_4^{2-} and CrO_4^{2-}/Cl^- solutions. The results revealed that in CrO_4^{2-} solutions two different types of behaviour were recorded. The addition of halides e.g. Cl^-, Br^-, I^- to CrO_4^{2-} solutions was also studied. The aggressivness of the three halides were in the following order $Cl^- > Br^- > I^-$. A linear relation was obtained according to the following equation: $E_p = a - b \log C_{agg.}$ where: E_p the pitting potential, a and b are constant. $C_{agg.}$ is the concentration of the aggressive anion. The effect of starch, gelatine, poly (vinyl alcohol), glycine, L-alanine and L-valine was studied to elucidate which of these additives can inhibit or promote the corrosion process of Zn electrode in CrO_4^{2-}/Cl^- solutions. The results revealed that glycine and L-alanine retarded the corrosion of zinc in CrO_4^{2-}/Cl^- solution. This was indicated by the decrease of the critical current with increasing concentration while L-valine was found to be of no effect. On the other hand, two effects were obtained when macromolecular compounds were used, whereas gelatine retards the corrosion, starch and poly (vinyl alcohol) (P.V.OH) accelerate the process.

Introduction

Break down of passivity by halogen ions occurs locally rather than generally. Fine anodes of active metal are formed surrounded by large cathodic areas of passive metal, the potential difference between the anodic and cathodic areas of such a passive-active cell amounting in some cases to about 0.5 V or more [1]. High current densities at the anode cause high rates of metal penetration, accompanied by cathodic protection of the metal area immediately surrounding the anode. This fixes the position of the anode and results in pitting type corrosion.

Potentiostatic or potentiodynamic polarization techniques have been usually applied to the study of pitting corrosion [2-16]. In presence of anions enabling pitting corrosion, the potential does not reach oxygen evolution, and the current increases steadily at lower potential, dependent

on a number of factors [2-9]. This increase in current does not occur directly after the addition of the aggressive ion, but a certain time elapses. This time is referred to as the "induction time" and is related to the penetration [17-19] or adsorption [20-22] of the anion on the passive surface.

In the present work, the metal electrode was made passive by CrO_4^{2-} solution, pitting was initiated by addition of different concentrations of Cl^-, Br^-, and I^- and critical current densities were determined. The critical current is taken as the point of intersection of the extrapolated lines from the bottom of the dissolution region with that obtained from the rising part of the curves.

The anodic polarization technique was used. Thus when a metal is anodically polarized in neutral solution, the primary oxidation process is the dissolution of the metal itself. If the current is raised in steps, a value is reached at which the electrode process is changed to the electrolysis of water, and O_2 gas evolves at the anode surface. This value is referred to as the critical current density for passivation. It is a good measure for the nobility of the metal [23-25]. Thus in one and the same environment, the nobler the metal, the smaller will be the current at which the mechanism of electrode process changes. On the other hand when the same metal is anodically polarized in a number of electrolytes of varying anions, the higher this current the more aggressive the anion solution and vice versa. The results revealed that Cl^- ion is the most aggressive anion. Consequently the inhibition of the attack of Cl^- by gelatine, soluble starch, poly vinyl alcohol, glycine, L-alanine and L-valine was studied as well. These compounds were expected to possess a high inhibition efficiency because:

a) their relatively large molecular size would ensure high surface coverage,

b) the presence of amino, carboxylic and alcoholic groups would add new active sites for adsorption on the metal surface.

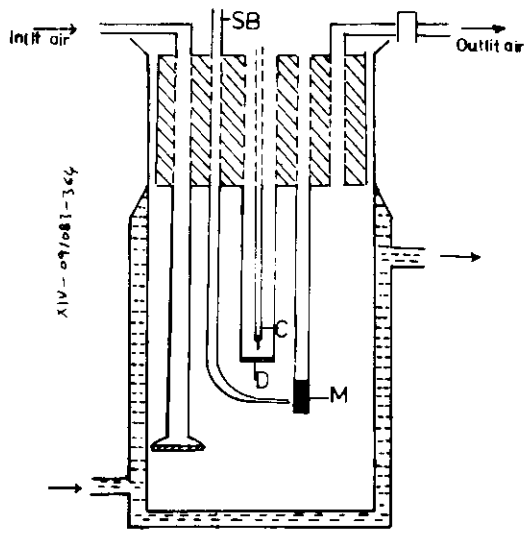

Fig. 1: Polarization Cell

Experimental

The simple electrolytic cell which was used is shown diagramatically in Fig. (1). it consists of a tall unlipped pyrex-glass beaker of about 200 ml capacity fitted with a rubber stopper carying 5 openings: Two of these were for the metal electorde "M" while the other was for the cathodic compartment which is separated from the main bulk of the electrolyte by means

of G_4 sintered glass disc, "D". The cathode was a platinum wire, C, (0.5 mm in diameter and 3 cm in length). The potential of the working electrode, was measured relative to a S.C.E. over a salt bridge "SB", whose tip was drawn to almost touching proximity to the working electrode. The other two openings were used for inlet and outlet dry air. The side openings were utilized for thermostating the cell by running water at 25 ± 1°C.

Spectroscopically pure Zn rods of ca 4.23 mm diameter were worked out in a manner that 2.5 cm^2 area of the electorde can be made in contact with the cell solution.

The metal electrode was abraded to the finest grade, degreased with acetone, cleaned with running distilled water, inserted in the test solution and left until the steady-state potential was established. Then the electrode was anodically polarized with successively increasing current intensities as described by Uhligh and Woodside [23]. A small anodic current was then imposed on the electrode and the corresponding potential was measured after 4 mins of polarization, to ± 5 m V. The current was disconnected and the open circuit potential was awaited for. The anodic polarization was again started with a higher current. The process of connecting and disconnecting of the current were repeated until oxygen evolution. Each experiment was done with freshly prepared electrode and with new portion of the solution. All chemicals are of A.R. grade and were

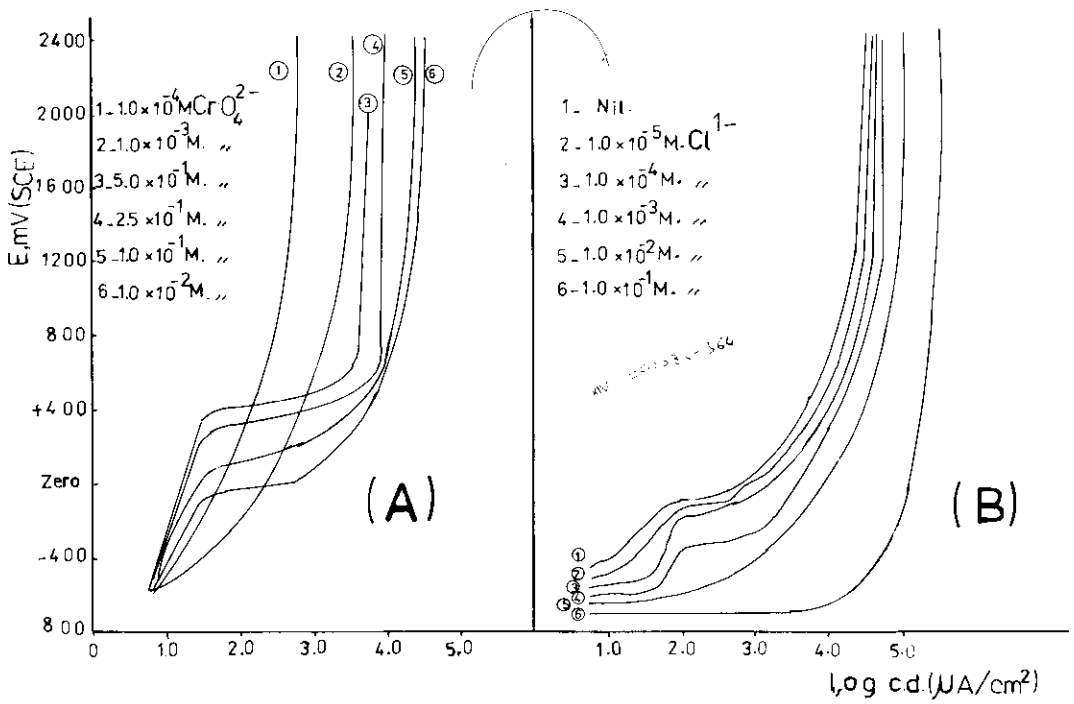

Fig.2: Anodic Polarization Curves for Zn-Electorde Curves (A) different concentrations of CrO_4^{2-} Curves (B) 10^{-2} CrO_4 containing different concentrations fo Cl^-.

used without further purification. These were supplied from BDH, Merck and Hoechst Company.

Results and Discussion

Fig.(2) curves (A) represents the variation of potential of Zn-electrode with increasing the polarizing current, in CrO_4^{2-} solutions of different concentrations varying between 10^{-4} to 5 x 10^{-1} M. Inspection of these curves reveals that two different types of behaviour can be distinguished. The first one is represented by the polarization curves recorded in the more dilute solutions (10^{-4} and 10^{-3}M) while the other is noted in the higher concentrated medium (10^{-2} to 5 x 10^{-1} M). In the more dilute solutions the potential increases moderately with the increase of the polarizing current and then a slight increase of current results in a sharp increase in the potential of the electrode denoting O_2 evolution. This may be explained assuming that in such dilute solutions the air formed preimmersion oxide film on the metal electrode does not interfere with the active disolution of the metal when anodically polarized. A similar behaviour for the same metal in dilute KOH solution was reported by Abd El-Haleem [26].

By increasing the electrolyte bulk concentration a plateau on the polarization curves was recorded. Along this plateau the potential of the Zn-electrode is independent on the polarizing current. This may be attributed to the formation of a passive film which is not sufficient to impart passivity at low current densities. Thickening of this passive film takes place with increasing the polarizing current. O2 is evolved after this film reaches a thickness sufficient for passivation. The length of this plateau decreases with increasing the concentration of CrO_4^{2-} solution. This may be due to high rate of formation of this film in concentrated solutions. This conclusion was substantiated by the noticeable ennoblement of the potential at this plateau with increasing the concentration of the solution. Further support for the same conclusion is provided from the opencircuit potentials of Zn-electrode in the same electrolyte reported by Shams El-Din and Khedr [27]. The authors recorded that as the concentration of the CrO_4^{2-} solution increased the potential of the electorde shifted to more nobler values.

Effect of halide additions of the behaviour of Zn-electrode in Chromate solutions

Fig. (2) curves (B) shows the anodic polarization curves E vs. Log c.d. for Zn-electrode in 10^{-2}M CrO_4^{2-} containing various concentrations of Cl^- similar curves were recorded using Br^- and I^-. The shape of curves obtained with the addition of the aggressive anions is more or less similar to that obtained in CrO_4^{2-} solution, Fig. (2) curves (A). However, it is remarkable that as the halide ion concentration increased the plateau diminished until it disappears in high concentrations of the halide. This behaviour is more pronounced with I^- solution, which may be due to the effect of small amounts of free I_2 or by the possible formation

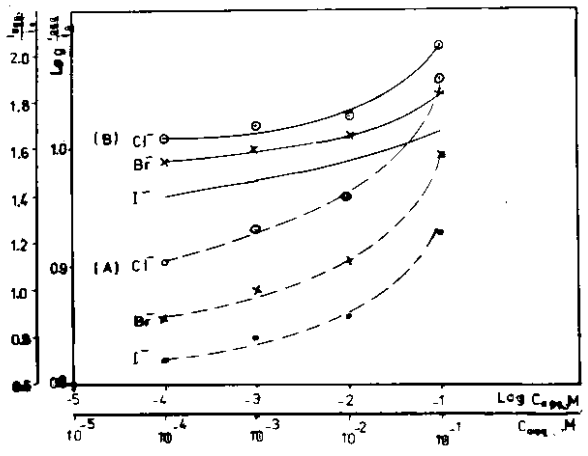

Fig.3: Variation of (A) $i_{agg.}/i_o$ vs. $C_{agg.}$ and (B) log $i_{agg.}/i_o$ vs. log C_{agg} for Cl^-, Br^- and I^- ions in 10^{-2} M CrO_4^{2-}.

of iodo-Zn^{2+} complexes. It is also noted that the exchange current becomes higher, the higher the aggressive anion concentration.

In the presence of the three aggressive anions Cl^-, Br^-, and I^- in 10^{-2} M CrO_4^{2-} solution, the potential of Zn electrode at the same polarizing current is displaced to more negative values as the aggressive anion concentration is increased. These changes are attributed to the effect of adsorption of the halide on the metal surface [28,29], leading to the destruction of the passive film.

In the present investigation it was found that the relations $i_{agg.}/i_o$ vs. $C_{agg.}$ & log i_{agg}/i_o vs log C_{agg}, Fig (3), are not linear especially in the presence of high concentrations of the aggressive anions, in which $i_{agg.}$ and i_o are the critical current for passivation in the presence and absence of aggressive anion respectively. This deviation from linearity is accounted for by the assumption that the attack is not only due to the aggressive anion. Consequently it was thought that the relation between log $(i_{agg.}-i_o)$ vs. log $C_{agg.}$ could be more reasonable. Fig. (4) represents this relation for the three aggressive anions. From these curves it is concluded that the aggressivness of the three anions can be ordered as follow $Cl^- > Br^-, > I^-$.

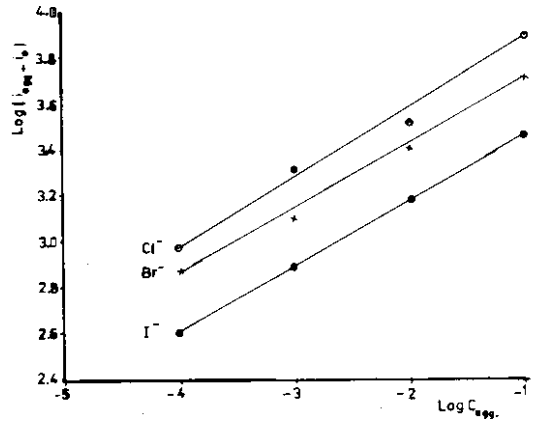

Fig.4: Variation of log $(i_{agg.}-i_o)$ with log $C_{agg.}$ for Cl^-, Br^- and I^- ions in 10^{-2} CrO_4^{2-}.

The potential which is not independent of current changes is taken as the pitting potential E_p. E_p vs log $C_{agg.}$ plots, Fig. (5) give straight line relations according to the equation:

$$E_p = a - b \log C_{agg} \quad (1)$$

Where "a" and "b" are constants depend on the nature of the aggressive anion. Relation of a similar form

was obtained for Zn [26], stainless steel [5,7,11], Fe [30] and Al [13,31].

Two different explanations were reported to account for pitting corrosion. Hoar, Mears and Rothwell [32] attributed the initiation of the pitting corrosion on stainless steel to the adsorption of the halogen ions on the passivating oxide film, followed by penetration through the film under the influence of an electrostatic field across the film solution interface. When the strength of the field reaches a certain definite value correspoding to the pitting potential, pitting corrosion occurs. It was suggested that the oxide film is undermined either by vacancy consideration at the metal interface or that the rapid release of cations at the electrolyte interface causes pitting attack. If this is the mechanism, then the induction period for pitting to occur is related to the time required to the anions to penetrate through the oxide film.

Lackie and Uhlig [2] on the other hand, proposed a model based on reversible competitive adsorption between the aggressive ions and oxygen for sites on the metal surface, assuming here that adsorbed O_2 rather than metal oxide is the cause of passive film formation on the metal surface [33]. Oxygen normally has a higher affinity than Cl^- ions for adsorption sites on the stainless steel, surface, but as the potential of the working electrode is shifted to the noble direction, more Cl^- ions move into the double layer. When the concentration of the Cl^- ions reaches a certain value, corresponding to the pitting potential, the Cl^- destroy passivity by displacing the O^{2-} ions.

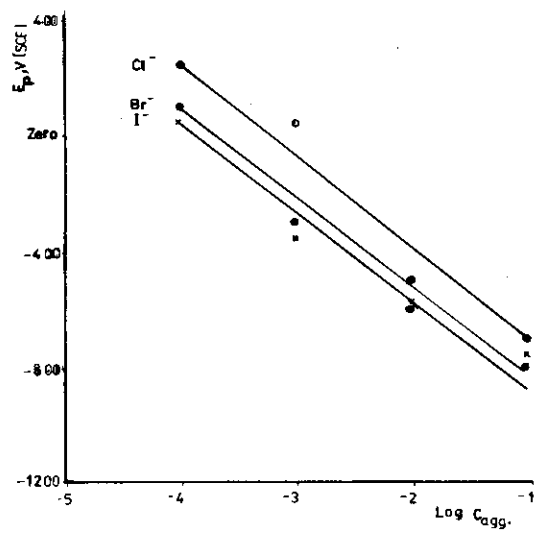

Fig.5: Varation of the critical pitting potential E_p, with log $C_{agg.}$ for Cl^-, Br^- and I^- ions respectively in 10^{-2}M CrO_4^{2-} solutions.

The induction time for pitting is attributed by Lackie and Uhlig [2] to the slow process of competitive adsorption. Similar views has been reported by Kolotyrkin [7,34], Rosenfeld and Maximtschuk [8] and Brauns and Schwenk [35].

Pitting corrosion of Zn-electrode in the prevailing conditions is assumed to be due to changing the physical and/or electrical properties of the passivating film originally present and repaired by CrO_4^{2-} solution. This may occur either by penetration or by being incorporated in it, as an impurity.

Effect of Some Macromolecular Compounds and Amino Acids on the Behaviour of Zn-Electrode in CrO_4^{2-}/Cl^- solutions

The inhibiting action exersised by organic compounds on the dissolution

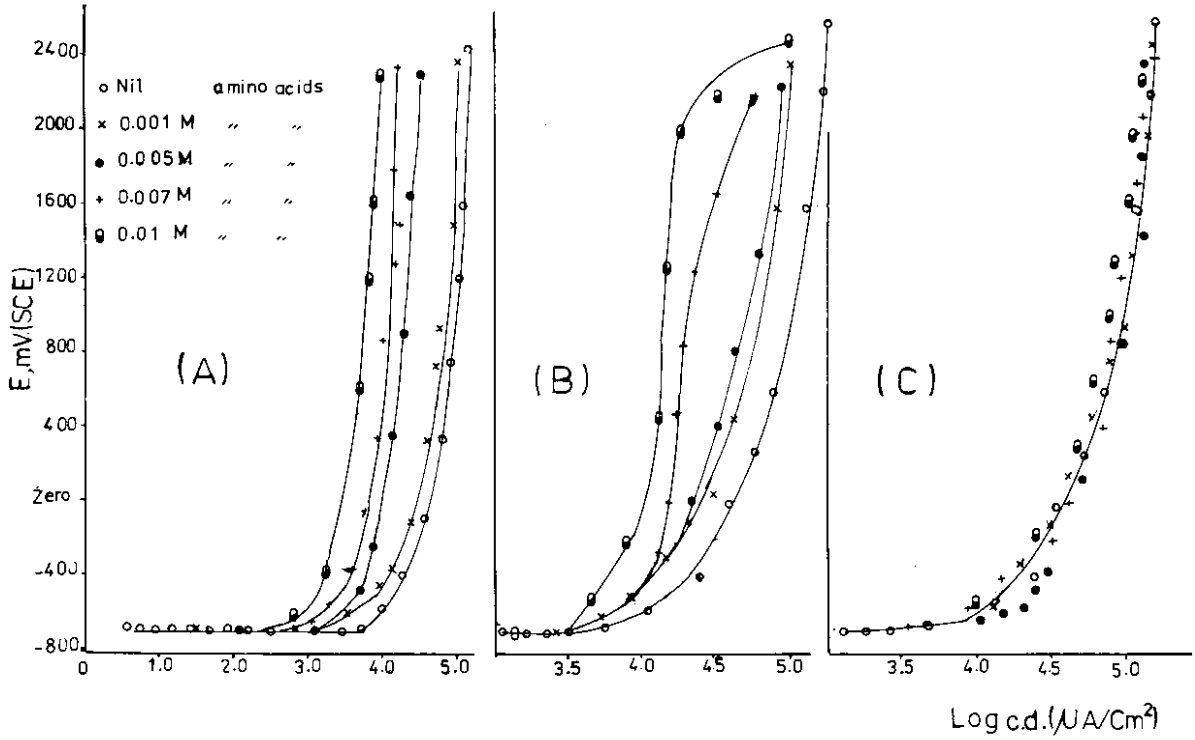

Fig. 6: Anodic polarization curves for Zn - Electode in (10^{-2} M CrO_4^{2-} + 10^{-1}M Cl^-) with different concentrations of Glycine (A), L-Alanine (B) and L-Valine (C).

of metallic materials is normally related to interactions by adsorption between the inhibitor and the metal surface. The species that are physically adsorbed interact rapidly with the metal but are easily removed from the surface, e.g. by immersion of the metal in an inhibitor-free solution. The chemisorption process involving sharing or transfer of charges takes place more slowly and with high heat of adsorption. In this case the adsorption is specific for certain metals and is not completely reversible [36]. Thus organic compounds containing atoms with free electron pairs and/or multiple bonds are usually effective inhibitors.

Many authors, on the other hand, have postulated an action of the inhibitor based on an increase of the over potential of the proton discharge process forming the cathodic reaction [37,38], on an increase in the ohmic resistance due to the formation of an inhibitor film at the metal-solution interface [39-41], or on nonspecific adsorption phenomena [42]. The type of interaction involved may be characterized through the study of the electrochemical behaviour of metallic species in environments containing inhibitors and by evaluating of the potential dependence of the adsorption phenomena.

As reported before, Cl^- ion is the most aggressive halide on the oxide film originally present on the metal surface and repaired by CrO_4^{2-} ions. This proxides an excuse for restric-

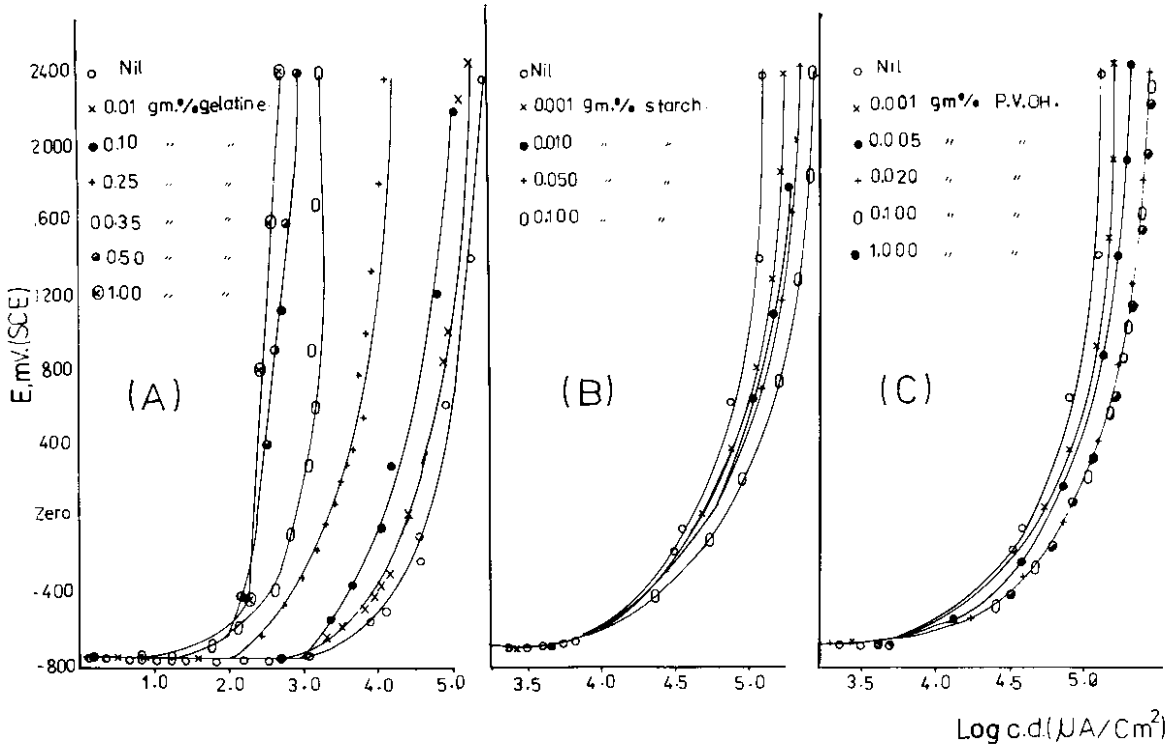

Fig. 7: Anodic polarization curves for Zn-Electrode in (10^{-2}M $CrO4^{2-}$ + 10 10^{-1} M Cl^{-1}) with different amount of Gelatine (A), Starch (B) and P.V. OH (C).

ting the study of the effect of amino acids and macromolecular compounds only in CrO_4^{2-}/Cl^- environment.

Figs. (6-7) represent the anodic polarization curves of Zn electrode in solutions containing 10^{-2} M CrO_4^{2-}, 10^{-1} M Cl^- and an increasing amounts of glycine, L-alanine, L-valine, gelatine, soluble starch and P.V.OH respectively. The concentration of macromolecular compounds is expressed in weight percent due to their uncertain molecular weights. Glycine and L-alanine retard the corrosion process of Zn electrode in CrO_4^{2-}/Cl solution. This was indicated from the progressive decrease in the critical current for passivation hand in hand with the increase of their concentrations, (Fig. (6) curves A & B). However, addition of L-valine was found to be of no effect. This was signified from the results recorded in Fig. (6) curves C which show that the anodic polarization curves are similar in presence and absence of the additive. The inhibition efficiency of the studied amino acids decreases as the molecular size increase. This may be accounted for assuming lateral repulsive interactions between zwietterion which lead to weaker adsorption [1]. On the other hand, two effects were observed when macromolecular compounds were used. Thus whereas gelatine retards the corrosion, starch and poly (vinyl) alcohol accelerate the process (Fig. (7)). This was manifested from the variation of the critical current density for passivation with the additive concentration (Fig. (8)).

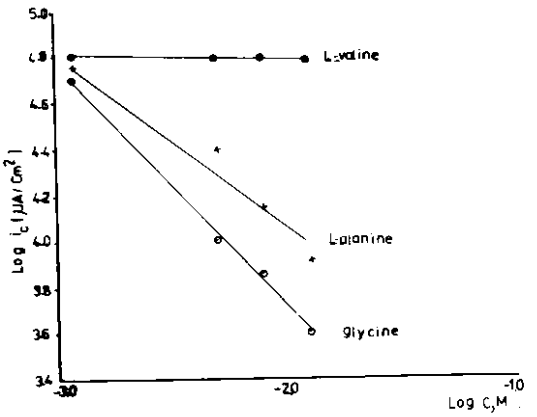

Fig. 8: Variation of critical current density for Passivation with the concentration of additive.

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