

POTENTIOSTATIC POLARIZATION OF MO ELECTRODE IN  
VARIOUS OXY AND HALOGEN ACID SOLUTIONS

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ABSTRACT

The potentiostatic polarization measurements on molybdenum electrodes has been examined in unstirred, aerated ( $10^{-2}$ -3 N) solutions of  $H_3PO_4$ ,  $HClO_4$ ,  $H_2SO_4$ ,  $HNO_3$ ,  $HCl$ ,  $HBr$  and  $HI$ . The anodic curves showed an active-passive transition, which lies in the region from (0.200-0.390 V) which may probably be due to the dissolution process and the formation of molybdenic acid  $H_2MoO_4$  which passes into solution as a dark gray colour. Upon increasing the potential to more positive values, the film formed becomes thicker and the thickness of the film depends on the type of the electrolyte and also on concentration.

INTRODUCTION

Although numerous publications and reviews (1965, 1967 and 1970) are available on the fundamentals of electrode process and their applications, only few features of the theoretical analysis of the kinetics of electrode processes are given. The electrochemical reaction rate can be

expressed as current density which depends on the potential across the electrode/electrolyte interphase, the nature of the electrode and the concentration of the reacting species. The analysis of electrode process in which two or more independent electrochemical reactions take place at an electrode (e.g. corroding electrode) can be made by the mixed potential theory (1938). The application of electrochemical principles to corrosive systems is reviewed by Stern (1958), and Others (1959 and 1962).

Stern work was particularly helpful in the interpretation of polarization curves of corroding systems. According to Tomashov et al. (1967), passivity can be defined as the state of improved corrosion resistance of a metal or an alloy at conditions where the metals or alloys are thermodynamically unstable. There are a number of theories on passivity e.g. Evan's (1946) oxide film theory and Uhlig's (1962) chemisorbed film theory are two of the more prominent theories. By potentiostatic polarization of metals much information can be obtained on the passivation behaviour of metals.

#### EXPERIMENTAL

Mechanically polished electrodes were abraded with finest grade emery paper, degreased with ethanol and

finally washing with bidistilled water, then it was dipped in aerated acid solution of different concentrations ( $10^{-2}$  - 3N). Potentiostatic polarization of Mo-electrode was performed anodically using an electronic potentiostat (Wenking LB 75H). The potential of working electrode was shifted to more noble direction in steps of 10 mV/min. The current was measured after each 10 mV setting.

All test solutions were used of Analar grade quality.

### RESULTS AND DISCUSSION

Figs. (1,2) give examples of the potentiostatic polarization curves for Mo in  $1N H_2SO_4$ ,  $HClO_4$ ,  $HNO_3$ ,  $H_3PO_4$ ,  $HCl$ ,  $HBr$  and  $HI$  solutions. As indicated by the shape of these curves, it can be seen that the corrosion current attained its maximum leading to a stabilized value by shifting the corrosion potential in the positive direction. Generally, the results showed a marked dependence of corrosion current and corrosion potential of molybdenum electrode on both concentration and nature of the acid used. The corrosion potential  $E_{corr}$ , and the corrosion current,  $i_{corr}$  for all acids studied are tabulated in table (1).

Table (1). Comparison between  $E_{corr}$  and  $I_{corr}$  for Oxy and Halogen Acid Solutions

Concentrations gm eq/L	Oxy Acid Solutions						Halogen Acid Solutions							
	$H_2SO_4$		$HClO_4$		$H_3PO_4$		$HNO_3$		$HCl$		$HBr$		$HI$	
	$E_{corr}$	$I_{corr}$	$E_{corr}$	$I_{corr}$	$E_{corr}$	$I_{corr}$	$E_{corr}$	$I_{corr}$	$E_{corr}$	$I_{corr}$	$E_{corr}$	$I_{corr}$	$E_{corr}$	$I_{corr}$
0.01 N	265	160	250	133	248	128	250	138	250	133	250	155	262	140
0.10 N	295	165	265	140	250	136	265	146	270	135	285	158	270	163
0.50 N	365	167	300	141	260	137	265	147	330	136	370	135	325	132
1.00 N	410	165	330	142	265	138	280	150	370	137	425	140	380	165
2.00 N	490	166	350	143	275	138	298	151	420	138	505	141	390	158
3.00 N	540	160	370	144	295	139	310	153	450	139	540	143	340	157

From the data presented in table (1) it can be concluded that :

- 1- In all acids studied the corrosion potential  $E_{corr}$  increase with increasing concentration (i.e. shifted to more noble values).
- 2- The corrosion potential for oxy acids are in the order (e.g. at 3N solution).  $H_2SO_4 > HClO_4 > H_3PO_4 > HNO_3$ , and for halogen acids  $HBr > HCl > HI$ .
- 3- Molybdenum electrode in aerated acid solutions has a rest (corrosion) potential ranging from 250-240 mV upon increasing the concentration from 0.01-3N solutions.
- 4- The corrosion current  $i_{corr}$  increases regularly by increasing the potential leading to more or less stabilized value. These results are in agreement with those obtained by previous authors (1952, and 1954).

The results obtained indicate that the surface of Mo is always covered in aqueous solution with an oxide(or oxides) film either before immersion or immediately thereafter. Thus, when one studies a redox reaction on a metal covered with an oxide film, like the present case, one may have to consider the nature of the oxide film and how this film affects the reaction taking place at the surface. The

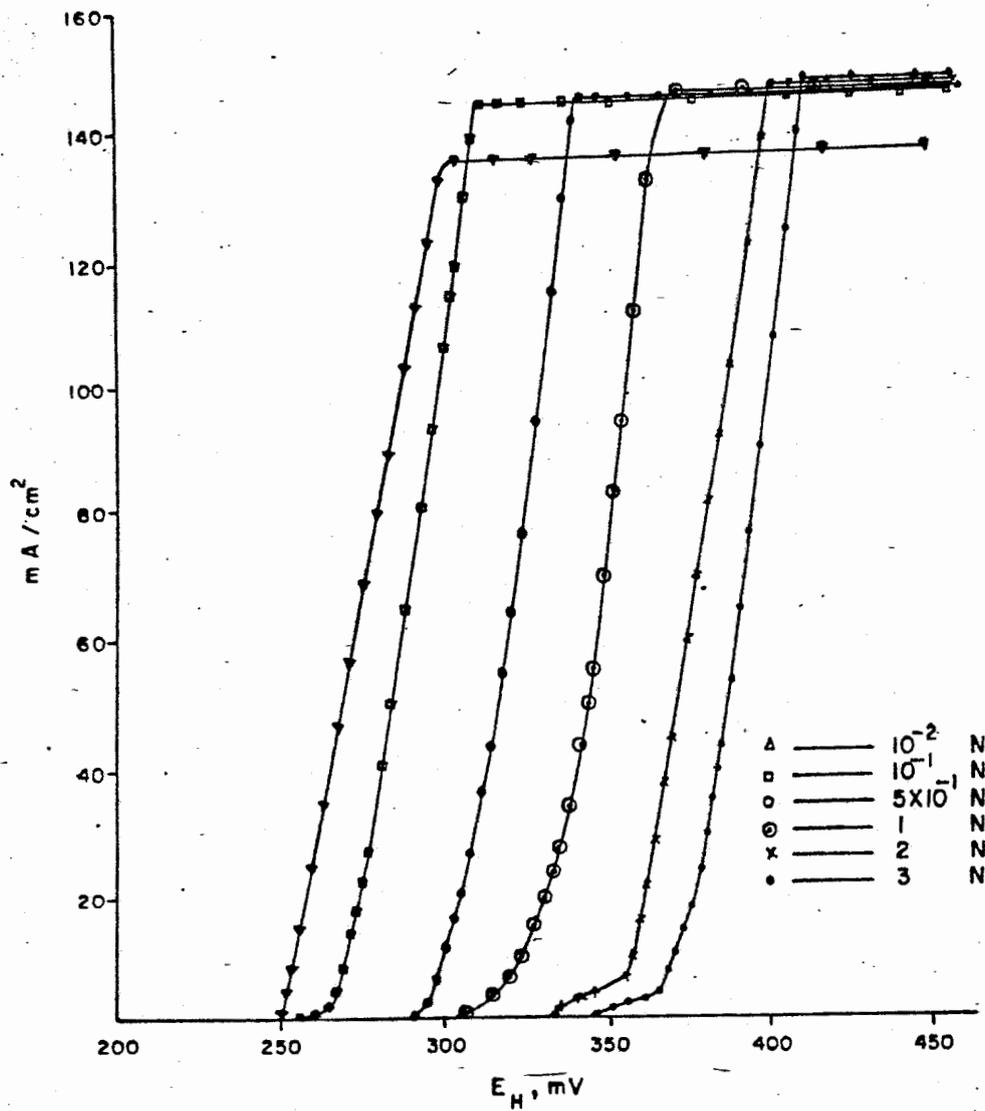
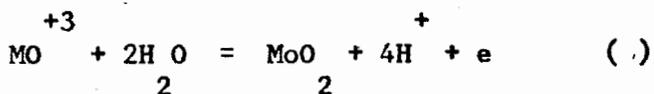
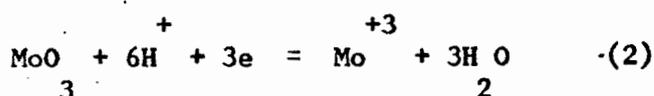
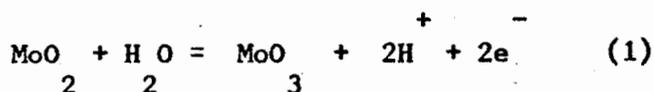


Fig.(1) Potential-Current Curves of Mo-Electrode in Different Concentrations of HClO<sub>4</sub>

250 mV for most of acids studied and 265 for HI and H<sub>2</sub>SO<sub>4</sub>, and a comparison of these data with the results obtained by previous authors, one may conclude that the product of corrosion and anodic polarization was hexavalent molybdenum. In this potential region, hexavalent Mo can be reduced to pentavalent Mo (\*). A process involving this redox reaction must include the reduction of MoO<sub>3</sub> and the formation of MoO<sub>2</sub> since at open circuit, accumulation of hexavalent Mo can be observed (\*). A possible mixed process is the following :



Delahay and Stagg (1952), suggested that oxygen reduction on molybdenum involves a peroxy derivative of Mo which subsequently reduces to water and a normal oxide state of molybdenum. The formation of the peroxy derivative occurs by the reaction of peroxide with a surface oxide. Thus, the rate of production of the hexavalent molybdenum may be limited by the rate of

potentials corresponding to equilibrium of Mo and all its known compounds in 1N H<sub>2</sub>SO<sub>4</sub> is given by Pozdeeva (1966).

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It is noteworthy to mention that, during electrolysis in all test solution—specially at higher concentrations (3N) a dark brown film is formed on the electrode surface. Small portions of the film spalled off the surface and dissolved in the anolyte giving it a light brown colour. These results are in confirmity with those obtained by previous authors (1952 and 1954). Thus Johnson et al (1970) upon their study on the anodic dissolution of Mo in HCl-KCl solutions reported that during electrolysis in 3 and 10 N HCl, a dark blue film formed on the Mo surface. Small portions of the film dissolved in solution giving it a brown colour. In HCl-KCl solutions, the surface oxide film was almost black, but the solutions remained colourless. The films were analyzed using X-ray diffraction techniques, and although they were quite amorphous, lines were found indicating a small amount of the  $\alpha$ -phase oxide (MoO<sub>3</sub>) to be present (\*). The metal surface beneath the surface films remained smooth and shiny at low c.d.s., but become dull at higher values.

During potentiostatic anodic polarization an active-passive transition was observed. The primary potential of

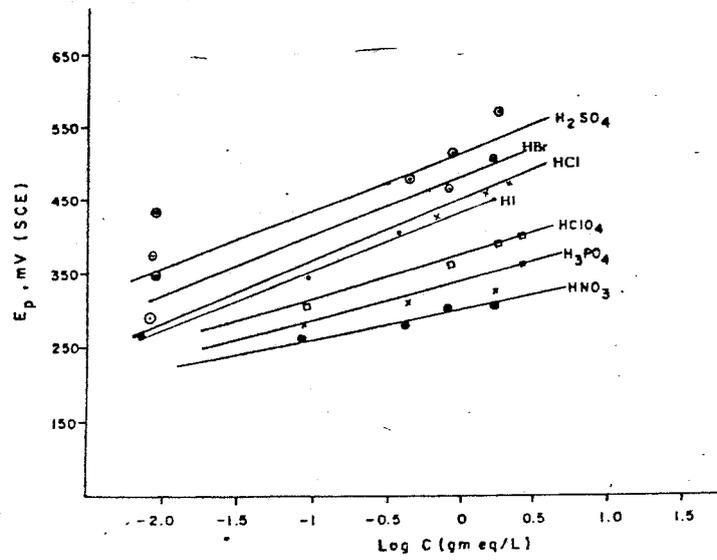


Fig.(3) Variation of Passivation Potential with Log Concentrations of Oxy Acids and Halogen Acids.

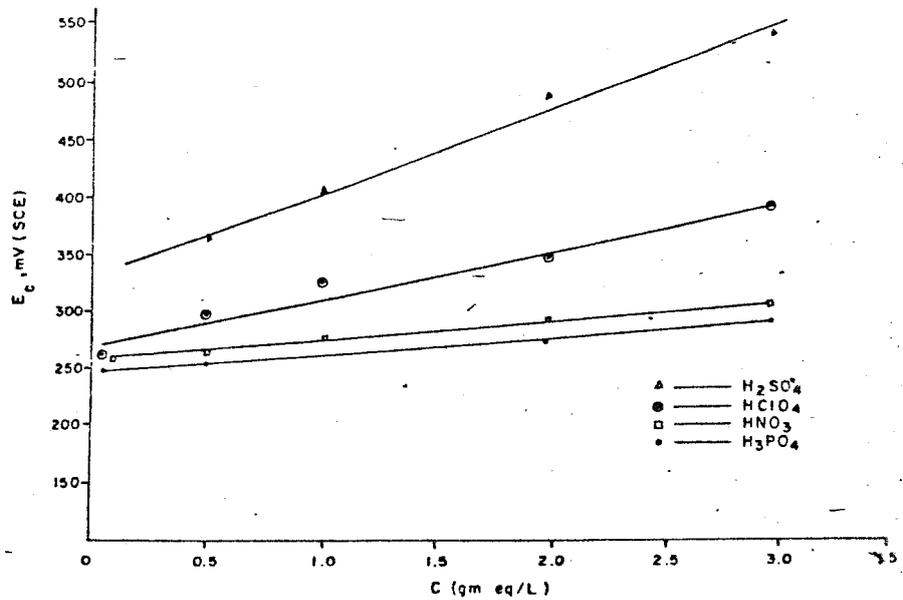
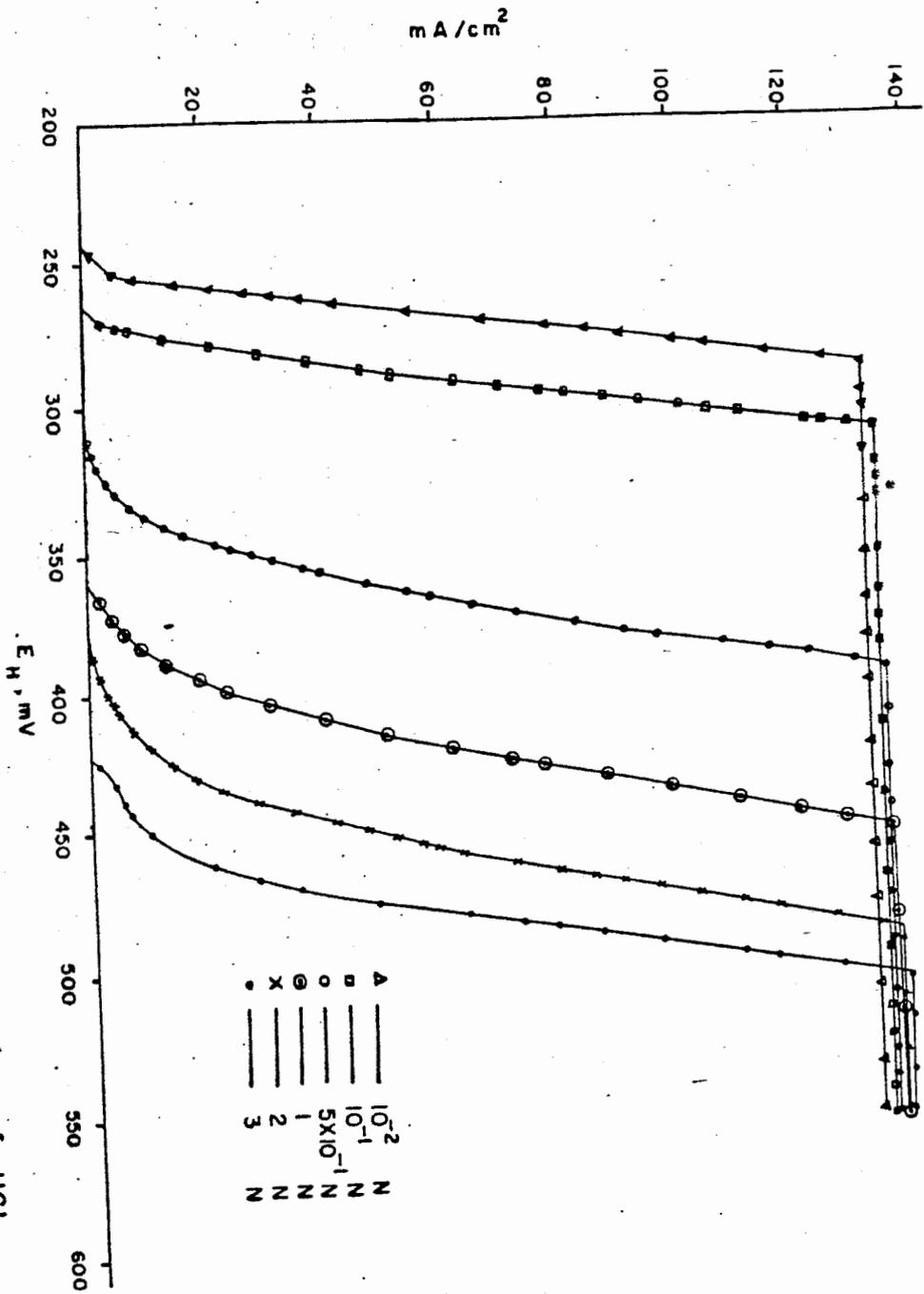
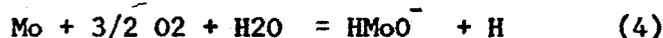


Fig.(4) Variation of Corrosion Potential With Different Concentrations of Oxy Acids.

Fig. (2) Potential - Current Curves of Mo-Electrode in Different Concentrations of HCl

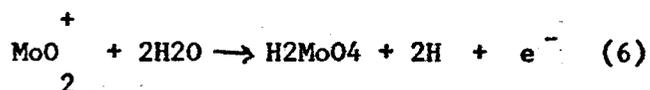
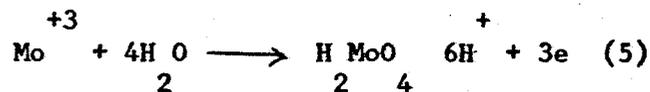


formation or reduction of this peroxy derivative. the over all electrode reaction for the formation of hexavalent molybdenum in aerated H<sub>2</sub>SO<sub>4</sub> may be as follows :



This means that Mo in all acids studied dissolves as molybdenate since it lies in this region. The dissolution of the metal does not cease in the extreme of cathodic region, corresponding to equilibrium of Mo with all its oxide compounds.

In our test solutions the potential of molybdenum electrode which lie in the region from (0.200-0.390 V) may be probably due to dissolution process according to (1966).



i.e. Molybdenic acid  $\text{H}_2\text{MoO}_4$  is formed which, however, prevents dissolution and the metal becomes passive, upon increasing the potential to more positive values, the

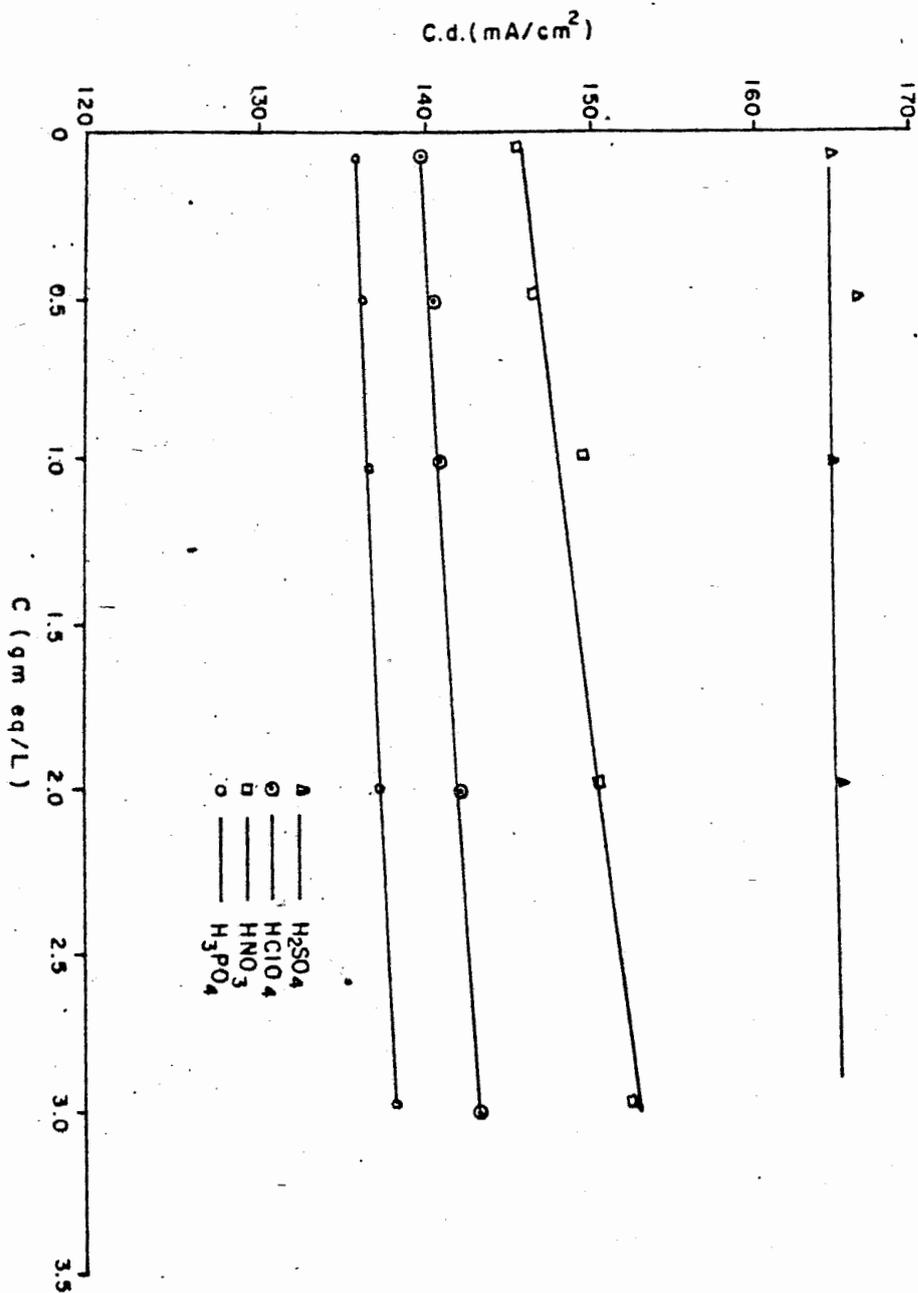


Fig. (5) Variation of Corrosion Current With Different Concentrations of Oxy Acids

filmformed becomes thicker and the thickness of the film depends on the type of the electrolyte and also on concentration.

The passivation potential for Mo electrode at different concentrations of the inorganic acids studied. The passivation potential and log concentration of these acids Fig. (3) was found to follow the equation :

$$E = a + b \log [C]$$

P

Where;

E = passivation potential  
P

a = constant value

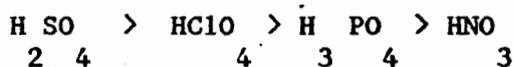
c = concentration of the electrolyte

b = slope of the curve

From the above relation tafel slopes calculated for oxy acids were found to range from 0.04-0.06 V and for halogen acids it ranged from 0.06-0.07 V. This conclusion was in agreement with those obtained by previous investigators (1969 and 1970).

The results revealed also that, the passivation potential increased with increasing concentration in all

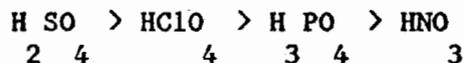
acids studied, and have the following order in case of oxy acids :



While in halogen acids the order was



The relationship between the corrosion potential and concentration for the acids studied gave straight lines with slopes depending on the type of the electrolyte i.e.  $d \log E/d \log C$  is higher with  $\text{H SO}_2 \text{ } ^4$ ,  $\text{HClO}_4$  than  $\text{H PO}_3 \text{ } ^4$  and  $\text{HNO}_3$  Fig. (4). This means that the rate of dissolution of the metal decreased in the following order :



and with halogen acids



Fig. (5) shows the values of corrosion current of molybdenum electrode plotted as a function of concentration of acids used. It is clear from this figure that the corrosion current depends largely on the type of electrolyte.

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