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Potentiometric Determination of the Concentration of Aggressive Anions That Can Be Tolerated by a Certain Passivator

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The effect of various additives of Cl^-, Br^-, and I^- on the potential of a passivated steel electrode was established. In solutions of Na_2CrO_4, Na_2HPO_4, and Na_2WO_4, S-shaped relations were obtained between the steady-state potential and the quantity of the aggressive salt added. The resulting active potentials were established after an induction period which decreases with increase in the concentration of the attacking ions and/or decrease in that of the inhibiting anions. The concentration, C_{agg}, that can be tolerated by a certain concentration of the inhibiting anion, C_{inh}, is given by $\log C_{inh}=K+n \log C_{agg}$, where K and n are constants. The equation was derived theoretically on the basis of the changes produced in the structure of the double layer caused by specific adsorption of both aggressive and passivating ions. In solutions of $KMnO_4$, $NaNO_2$, and $K_3[(Fe(CN)_6)]$, the passivating film could not withstand the corroding action of the halide ions.

The minimum concentration of a certain passivator that can withstand the corroding action of a particular aggressive ion is of importance from theoretical as well as practical points of view.[1-9] The concentration was determined under certain conditions.[2-5,10-14] Only a few fundamental studies being carried out.[6-9,15] Some of the studies are based on time consuming measurements, such as weight loss or visual methods,[6-9,15-17] or on accelerated polarization techniques not in line with natural corrosion conditions.[18-20] It is desirable to establish a simple method to determine such a concentration, in a relatively short time and under natural corrosion conditions.

We have studied the variation of potential of a steel electrode under open circuit conditions, in order to establish the mode which the potential of an electrode, previously equilibrated in a certain passivator, would follow when increasing amounts of a corroding anion such as Cl^-, Br^-, and I^- were added to the solution, and to find a relation between the concentrations of the two counteracting anions. The type of corrosion that occurs always under these conditions is the localized type of attack, the extreme of which is pitting corrosion.[1,9]

Experimental Method and Materials

The steel electrodes (Delta steel Mill company, Cairo) have the same chemical composition as those used:[21,22]

C	Mn	S	P	Si
0.40	0.78	0.045	0.06	0.23%

The metal was machined in the form of short rods; length 2,4 cm, dia. 1 cm. This was fixed to Pyrex glass tubings with neutral wax. Electrical contact was achieved through thick copper wires soldered to the ends of the rods, not exposed to the solution. The electrodes were polished and abraded with the finest grade emery paper. They were then degreased with acetone and washed with triple-distilled water.

Two procedures were followed to achieve the variation of potential of the steel electrode.

Procedure A. The electrode was first equilibrated in a definite volume of the passivating (inhibiting) agent until a constant potential was established. Enough corrosive agent was then introduced into the solution to attain a definite concentration, and the change in potential was again followed with time. The effect of other quantities of the aggressive anions was examined in the same manner, starting always with a fresh solution of the inhibitor and with a newly polished electrode.

Procedure B. Increasing amounts of the aggressive salts were added to the same solution, allowing sufficient time for the establishment of constant potential.

Passivation (inhibition) of the steel electrode was carried out in solutions of different concentrations of Na_2CrO_4, Na_2HPO_4, Na_2WO_4, $KMnO_4$, $NaNO_2$, and $K_3[(Fe(CN)_6)]$. The concentration of the test solution was chosen to induce passivity rather than cause corrosion.[7,8,23,24] NaCl, NaBr and NaI (analytical grade) were used to introduce aggressive anion.

The potential of the steel electrode was measured, to the nearest mV, on Electronic Potentiometer (Metrohm pH meter type 512) relative to a saturated calomel electrode (SCE). This was separated from the main electrolyte by two salt bridges filled with the same passivating solution in order to prevent contamination with Cl^- ion. The steady-state potentials were considered valid when values were obtained, not changing more than 1 mV in 5 min. The electrolyte was stirred, a stream of oxygen, (2—3) bubbles/s) being passed during the course of experiment. Measurements were carried out at 25±1 °C.

Results and Discussion

The curves with black circles in Fig. 1 represent the variation of the potential of the steel electrode with time in solutions of 0.1 M and 0.2 M Na_2CrO_4. The potential shifted towards positive values showing the occurrance of passivity,[23,24] and attained constancy after 160—180 min, following the immersion of the electrode in solution.

When a very small amount of Cl^- ion is introduced into the solution following passivation, the steady state potential remains more or less constant. Low Cl^- ion concentrations have no effect on the dissolution kinetics of the passive film already formed on the electrode surface.[22,25,26]

When the concentration of the Cl^- ion in solution is further increased, a state is soon reached where the Cl^- ion concentration is sufficent to undermine the protective film on the metal surface, causing the potentials of the electrode to change in the negative direction.

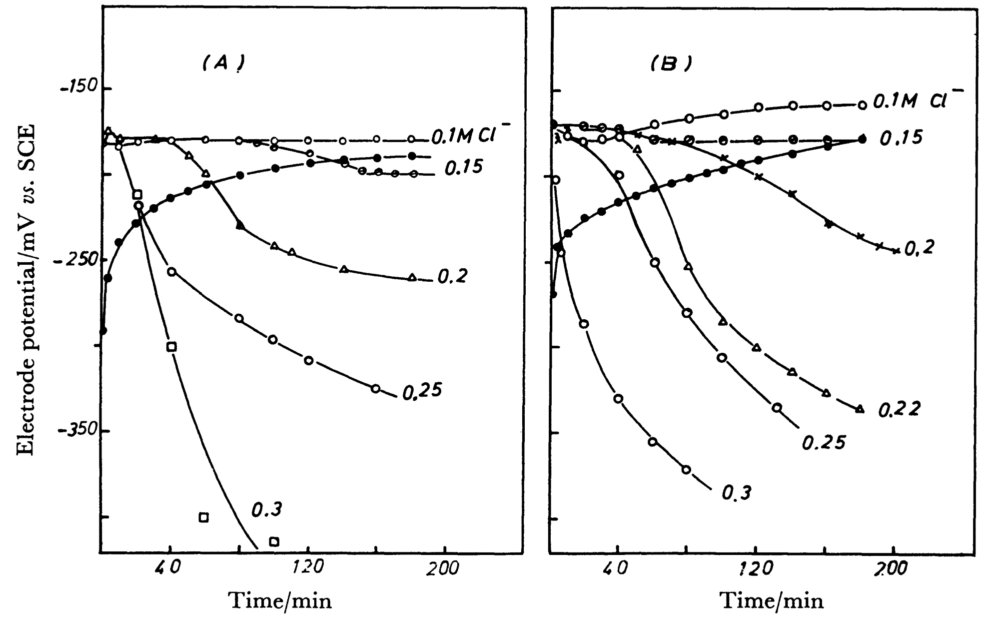

Fig. 1. Variation of the steel electrode potential with time in (A) 0.1 M and (B) 0.2 M Na_2CrO_4 in the presence of different NaCl additions.

Cl^- ions do not attack the passive electrode directly (cuves A and B, Fig. 1). A certain length of time elapses before the potential of the steel electrode changes from that measured in the Cl^--free solution. This is identified as the induction period[18,27] for pitting corrosion to occur. It decreases with the increase of the concentration of the aggressive anion.[18,27] In relatively concentrated Cl^- media, the induction period is too short to be recorded.

In the presence of Cl^- ions, the steel electrode acquires new steady state potentials. For a certain chromate concentration, these potentials become more negative the higher the Cl^- ion content. On the other hand, the potentials developed in equimolar solutions of Cl^- ion depend on the concentration of the passivating ion, being more positive the higher the chromate content.

The curves in Fig. 2 show the variation of the steady state potential of the passive steel electrode with the amount of NaCl, NaBr, and NaI in solutions of Na_2CrO_4 in the range 0.05—0.5 M using procedure (B) for measurements. Figures 3 and 4 represent the same behavior in Na_2HPO_4 and Na_2WO_4 solutions of different concentrations. They are sigmoid, showing normal mode of potentiometric titration, which may be used

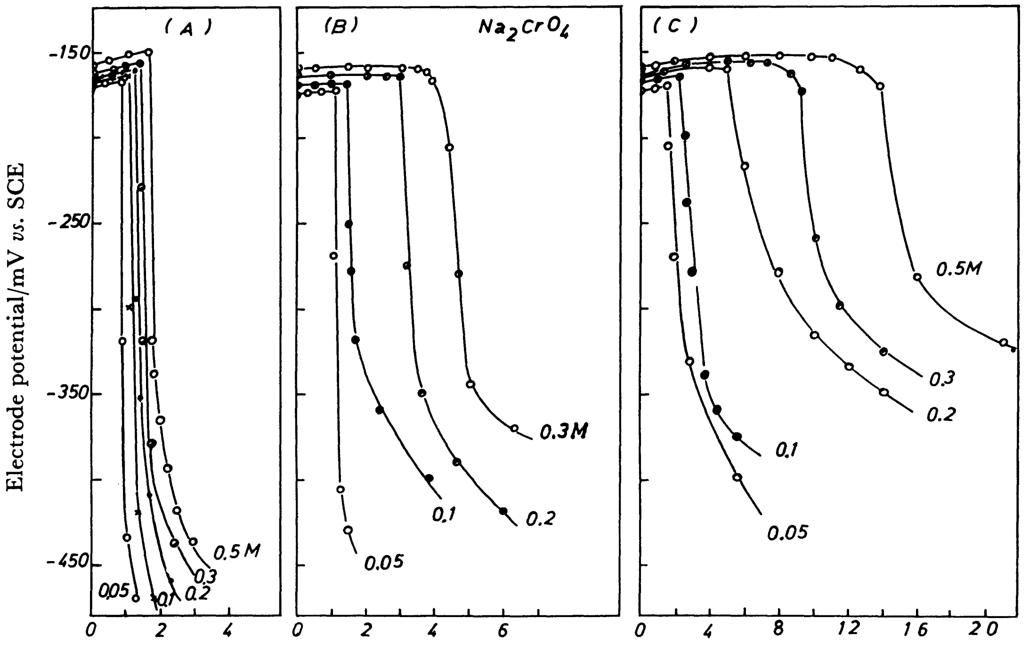

Fig. 2. Variation of the potential of the steel electrode previously passivated in different concentrations of Na_2CrO_4, with additions of NaCl, NaBr, and NaI.

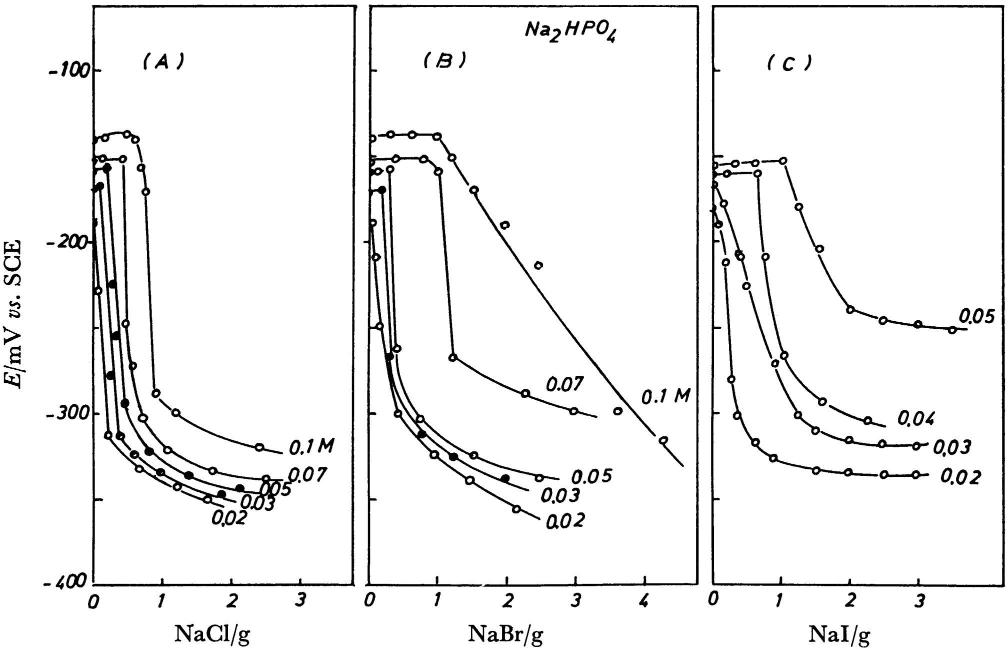

Fig. 3. Variation of the potential of the steel electrode previously passivated in different concentrations of Na_2HPO_4 with additions of NaCl, NaBr, and NaI.

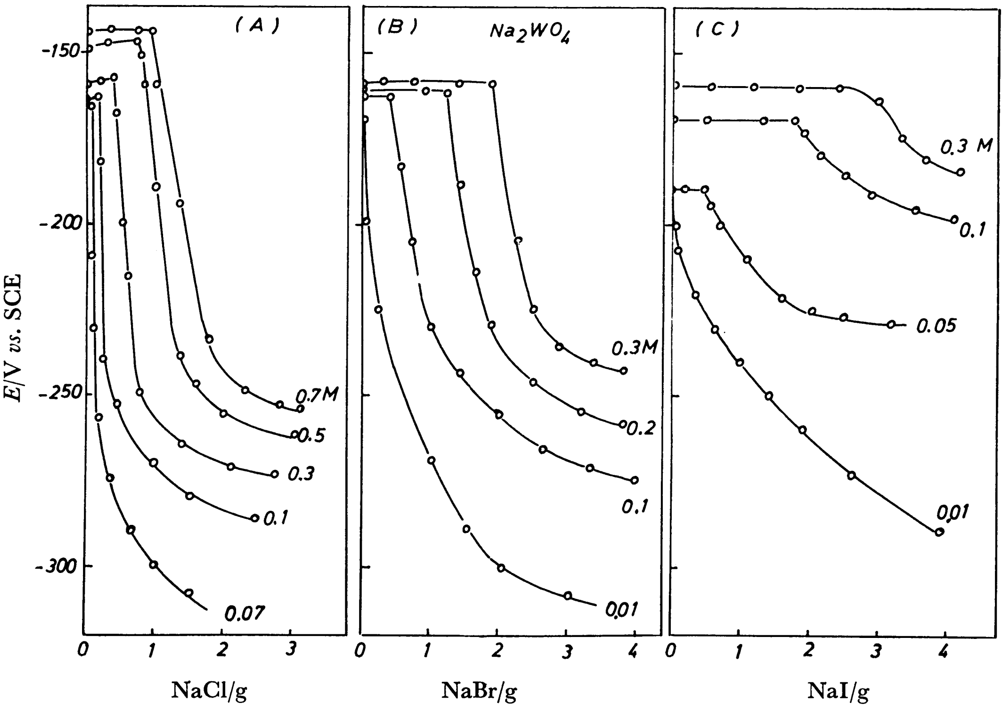

Fig. 4. Variation of the potential of the steel electrode previously passivated in different concentrations of Na_2WO_4 with additions of NaCl, NaBr, and NaI.

to determine the concentration of an inhibitor that can withstand a certain concentration of the aggressive ions. The starting potentials, measured in aggressive-free media, become more positive the higher the concentration of the inhibitor in solution. The rate of potential change at the inflexion point of the curves is inversely proportional to the same parameter. This is to be expected since it is easier to initiate pitting corrosion, which is the type of attack occurring under these conditions, in dilute passivating solutions than in concentrated ones. It appears that as the concentration of the inhibiting agent in solution is raised, more aggressive anion is needed to destroy the protective film on the metal surface and induce pitting corrosion.

The curves in Fig. 5 (A, B, and C) represent the effect of adding Cl^- ions of increasing concentrations

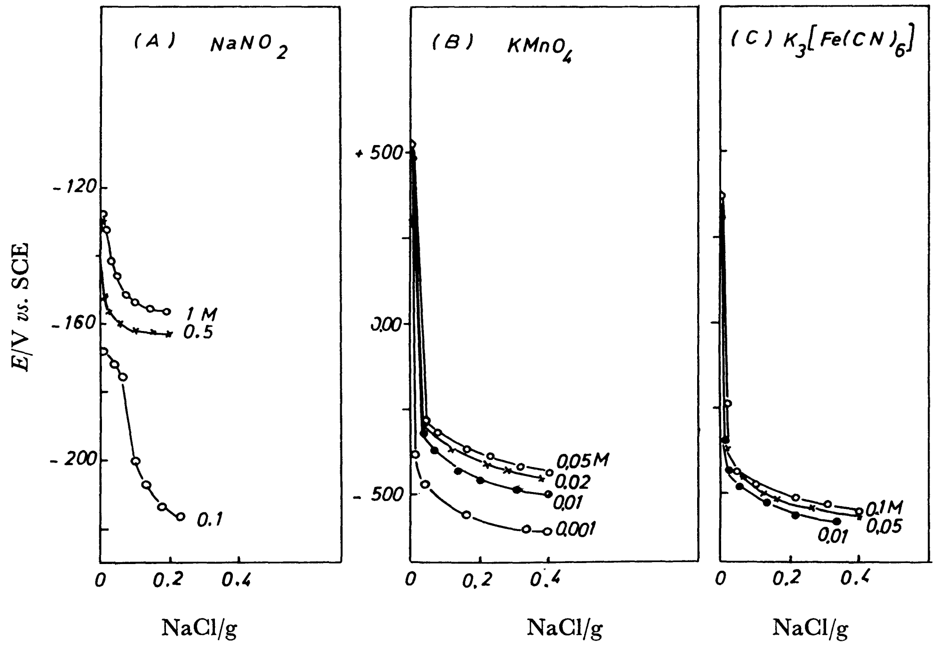

Fig. 5. Variation of the potential of the steel electrode previously passivated in different concentrations of (A) $NaNO_2$, (B) $KMnO_4$, and (C) $K_3Fe(CN)_6$, with the additions of NaCl.

to solutions of $NaNO_2$, $KMnO_4$, and $K_3[(Fe(CN)_6)]$, respectively. Despite the fact that the initial steady state potentials of the steel electrode in these media are equal to or higher than those measured in chromate, phosphate or tungestate solutions of the same concentration, the addition of Cl^- ions to the former solutions causes the potential to shift directly towards more negative values. Apparently treatment of the steel electrode in solutions of these oxidizing agents produces no permenant state of passivity.1) This shows that the function of a certain passivator does not depend primarily on its redox-potential as much as on its ability to form an adhering and stable film on the metal surface. This is not the case with NO_2^-, MnO_4^-, and $[Fe(CN)_6]^{3-}$ anions, the reduction of which at the cathodic sites produces soluble corrosion products. Similar results were obtained in the case of zinc.1)

Inflexion occurs in the potential of the steel electrode when enough aggressive salt is added to the inhibitive solution (Figs. 2—4). The inflexion indicates that the inhibiting film is being destroyed by the aggressive anions. Concentrated solutions of the passivator consume more attacking agent before the potential tends towards more negative values. The relation between the two variables is not linear.1) There is no definite potential,19,27) above which the metal withstands attack, and below which it undergoes corrosion. The choice of such a potential, to be taken as a basis for comparison, is thus arbitrary. Since the initial potential of the steel electrode in aggressive-free media depends on the ambient concentration of the passivator, choice of one and the same potential for all the solutions will not be free from error. It is more plausible, however, to relate this potential to that of the initial value in such a manner that it is common to all curves. Shams El Din and Abd El Haleem1) assumed that the localized type of attack (pitting) is operative to the same extent in all solutions when enough of the aggressive anion is present to displace the initial potential to the negative direction by a constant value. The relation between C_{agg} and C_{inh} is considered at the point of inflexion (0 mV displacement), as well as at some other potentials (more negative to the starting potentials). The plot of the two variables on a double logarithmic scale for chromate solutions is given in Fig. 6. Similar results were obtained with phosphate and tungestate solutions. Parallel straight lines are obtained satisfying the relationship:

$$\log C_{inh} = K + n \log C_{agg}, \qquad (1)$$

where K and n are constants.

The values of the exponent n for solutions of Na_2CrO_4, Na_2HPO_4, and Na_2WO_4 containing the aggressive anion Cl^-, Br^-, and I^- are given in Table 1.

TABLE 1. VALUES OF THE EXPONENT n IN EQ. 1 FOR DIFFERENT INHIBITING-AGGRESSIVE PAIRS

Inhibitor	Na_2CrO_4			Na_2HPO_4			Na_2WO_4		
Aggressive	Cl^-	Br^-	I^-	Cl^-	Br^-	I^-	Cl^-	Br^-	I^-
n	3.25	1.2	0.93	0.72	0.6	0.45	1.0	0.97	0.33

It appears that (Fig. 1 and Table 1)
(1) n is independent of the potential at which it is determined, (2) n depends primarily on the type of the inhibitor, decreasing in the order $Cl^- > Br^- > I^-$, (3) the values of n in Na_2CrO_4 solution is significantly greater than that of the other two inhibitors.

Equation 1 was also obtained by other workers,6–9,15,20) Matsuda and Uhlig15) derived it by assuming the occurrence of competitive adsorption between the aggressive and the inhibiting anions. Brasher *et al.*,9) on the other hand derived it by conferring

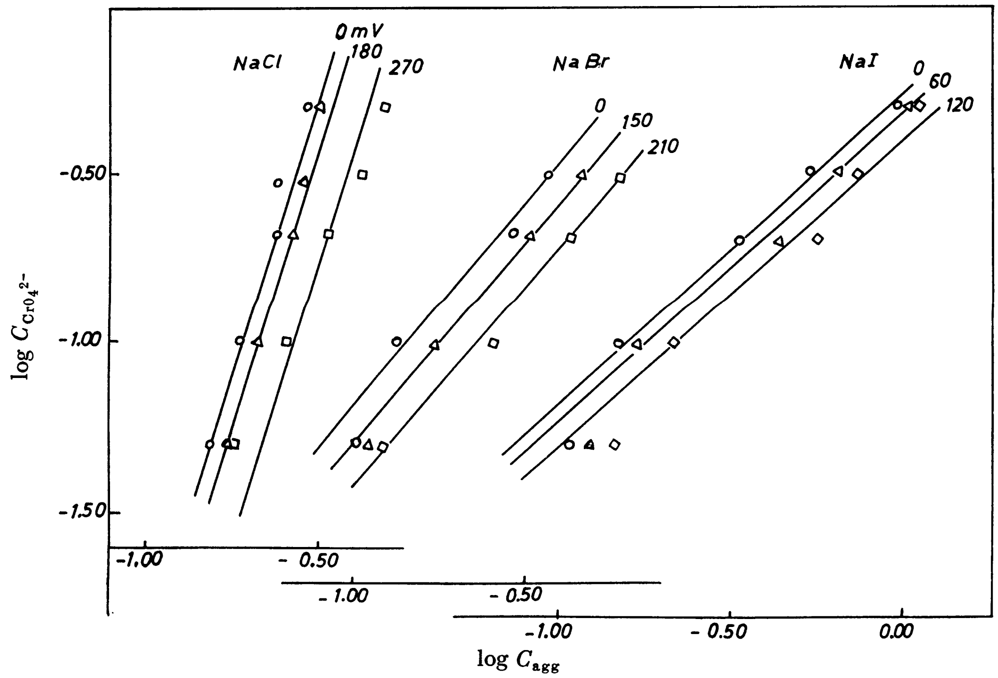

Fig. 6. log $C_{CrO_4^{2-}}$ – log C_{agg} plots at different potentials.

anion exchange properties to the oxide film formed on the metal surface. Selectivity for one or the other of two anions present in solutions was considered to depend on its nature as well as on its concentration. Anderson and Hocking[20] expressed a similar view.

In the present study, Eq. 1 is derived on the basis of the effect produced by both the inhibiting and corrosive anions, when specifically adsorbed on the metal surface, on the structure of the double layer at the metal/solution interface. The derivation is based on the following considerations: (a) In neutral solutions, the corrosive anions attack the passivating oxide film on the metal surface through specific adsorption of the anion,[28–30] their peptizing action on the metal oxide[31] and/or the creation of electrostatic fields through the oxide between opposite charges.[32] One or more of these processes is associated with decrease in the free energy of the system. (b) Inhibiting anions, on the other hand, play their role either by film repair as in the case of CrO_4^{2-} and NO_2^-,[6,7] or by blocking the active sites on the metal surface (benzoate).[8] Both effects involve a decrease in free energy at the metal/solution interface. (c) In solutions containing both the inhibiting and the corrosive anions, the process occurring depends primarily upon which of the two reactions is associated with a larger decrease in free energy. This, in turn, involves a number of associated features such as the concentration and charge of the ions, as well as their adsorbability on the oxide film. (d) The aggressive or the inhibiting anions should be adsorbed on the surface before reacting with the metal. Such adsorption affects both the structure of the double layer at the metal/solution interface, as well as the effective potential necessary for the electrochemical reaction. Figure 7 is a schematic presentation of the structure of the double layer, in which the specifically adsorbed anions occupy the inner Helmholtz plane (IHP), causing a potential drop ψ'. Anions bound only by electrostatic forces occupy the outer plane of the double layer (OHP) with a potential ψ''. The diffuse double layer consisting of ions is dispersed in the direction of solution.

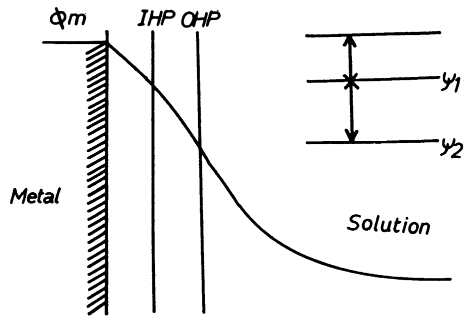

Fig. 7. Schematic presentation of the structure of the double layer at the metal/solution interface.

The relation between the surface concentration, C_s, and the bulk concentration, C_b, of a certain ionic species is given by[1]

$$C_s = C_b \exp(-\Delta G^\circ/RT), \tag{2}$$

where ΔG° is the standard electrochemical free energy change of adsorption, its value depending on the nature of interaction between the ions and the surface as well as their ionic charge, Z. In absence of specific adsorption, we have

$$\Delta\bar{G}^\circ = \pm ZF\psi''. \tag{3}$$

The positive and negative signs in Eq. 3 refer to whether adsorption of anions takes place on the negative or the positive side of the potential of the zero charge of the metal. On the other hand, for anions that are specifically adsorbed we have

$$\Delta\bar{G}^\circ = \Delta G^\circ \pm ZF\psi', \tag{4}$$

where ΔG° represents the standard chemical free energy of adsorption. The surface coverage, θ, with specifically adsorbed anions is given by

$$\theta = X \exp\,(-\Delta\bar{G}^\circ/RT), \tag{5}$$

where X is the mole fraction of the anion in the bulk of solution. However, in solutions of fixed concentration (x), θ is constant and ψ' is given by

$$\psi' = \pm\frac{RT}{ZF}\ln x + \text{constant}. \tag{6}$$

For a metal like iron immersed in a solution of an inhibiting anion (Z_1, X_1), until the establishment of the steady-state potential, a definite fraction of the metal surface is covered by specifically adsorbed anions, adsorbed either on the bare metal surface or on the oxide covering the metal. In this case, ψ_1' at the (IHP) is given by

$$\psi_1' = \pm\frac{RT}{Z_1F}\ln x_1 + \text{const}_1. \tag{7}$$

When an aggressive anion (Z_2) is added in a small amount after the establishment of the steady-state potential in an inhibiting solution, it will first be adsorbed on the free fraction of the surface. On gradual increase in the concentration of the aggressive ion, it will compete with the inhibiting anions for the sites occupied by the latter. Displacement of the inhibiting anions occurs by virtue of the smaller size of the aggressive ions (large charge density) and/or a large drop in the free energy of adsorption. When the concentration of the aggressive anions becomes equal to (X_2), *i.e.* at the end of the horizontal segments (curves, Figs. 2—4), it will represent the maximum amount of the aggressive anion that can be tolerated by the concentration X_1 of the inhibitor. The magnitude of ψ_2' corresponding to the aggressive anion at the (IHP) is given by

$$\psi_2' = \pm\frac{RT}{Z_2F}\ln x_2 + \text{const}_2. \tag{8}$$

Since $\psi_1'=\psi_2'$ apparently at the point of inflexion (Figs. 2—4), we have

$$\frac{RT}{Z_1F}\ln x_1 + \text{const}_1 = \frac{RT}{Z_2F}\ln x_2 + \text{const}_2 \tag{9}$$

or

$$\log X_1 = \frac{Z_1}{Z_2}\log X_2 + \text{constant}. \tag{10}$$

Equation 10 has the same form as that obtained experimentally or derived theoretically.[9,15] From the equation as well as the values of the exponent n (Table 1), we can draw the following conclusions:

1. Equation 10 is based on the idea of competitive adsorption, but unlike the treatment of Matsuda and Uhlig[15] and Brasher *et al.*,[9] it presumes no particular type of adsorption isotherms.
2. The potential of the working electrode remains practically constant until the ψ-potential for the electrode in the inhibiting medium starts to decrease as a result of excessive adsorption of the aggressive anion. The curves (Figs. 2—4) reveal that this is actually the case.
3. The exponent n of Eq. 1 is given here as the ratio of the electrical charges of the inhibiting/aggressive anions. Similar findings were suggested by Brasher *et al.*[9] The values (Table 1) show that this state of affairs is nearly fulfilled when HPO_4^{2-} and WO_4^{2-} are used as inhibitors. An exception is the WO_4^{2-}/I^- system, in which inhibition involves the reduction of the inhibitor with the probable formation of the iodocomplexes of the lower valent W. Concerning the CrO_4^{2-} ions, however, the value of n is almost twice that determined for the other two inhibitors. This is explained on the basis that CrO_4^{2-} reacts preferentially either in the $HCrO_4^-$ or the $Cr_2O_7^{2-}$ forms.[7]
4. Equation 1 holds not only at the inflexion points but also at other more active (negative) potentials, as long as they are referred to the starting potential measured in the aggressive-free media.
5. From the curves (Figs. 2—4) and Eq. 1, we can determine the concentration of the aggressive anion that can be tolerated by a certain concentration of the inhibiting anion, using a simple potentiometric method.

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