Mass Transfer of Components of Zinc Chromating Solutions—Part 1; Mass Transfer of Species Containing Cr(VI), Cr(III) & Zn(II)

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The concentration profiles of the components of a chromating solution were calculated on the basis of a mass transfer model, taking into account the mobile chemical equilibria. The data on the composition model of the diffusion layer, together with the analysis of the solubility of certain Cr(III) and Zn(II) compounds, allowed determination of the composition of conversion coatings formed on the surface of Zn in the chromating solutions.

Conversion coatings containing various compounds of low solubility are formed on the surface of zinc because of chemical interactions between zinc and components of the chromating solution. This improves the corrosion resistance of zinc, as well as enhancing its decorative properties. Certain surface concentrations of the components of the system arise at the zinc/solution interface as a result of the reduction of Cr(VI) to Cr(III) and the coupled oxidation of Zn to Zn(II). This, in turn, leads to the formation of gradients of corresponding concentrations, the magnitude of which determines the rate of diffusive mass transfer. Since the process of zinc corrosion in Cr(VI) solutions usually goes under diffusion control,[1] the quantitative assessment of mass transfer is, without doubt, an important challenge.

Two important problems can be solved by means of mathematical modeling of mass transfer. First, it allows information to be obtained on the surface concentrations of components that determine the rate of redox processes taking place at the interface. Second, the comparison of the data obtained with the solubility products of some low-solubility compounds makes it possible to determine the conditions of formation of conversion coatings in general and to evaluate the thermodynamic probability of formation of these compounds in particular.

The simulation of concentration profiles in the diffusion layer becomes considerably more complicated when chemical interactions occur between the transported components of the initial substances, as well as among the products of electrochemical reactions. Recently, such a problem was generally solved for electrochemical processes involving labile complexes of metals.[2] It is worthwhile, therefore, to analyze in a similar manner the mass transfer of components of zinc chromating solutions.

Theoretical Model

The regularities of mass transfer will be discussed on the assumption that the Nernst model may be applied to steady-state conditions. According to this model, mass transfer is located in the δ thick diffusion layer, beyond which the concentration gradients are absent. Such a layer may be formed both in the conditions of natural and forced convection, though, in the latter case, its thickness can be fairly accurately calculated theoretically.[3]

According to conventional theory, the thickness of the diffusion layer depends on the diffusion coefficients of the components. Consequently, if they are different, every component has its own thickness of diffusion layer. There is another situation, however, when the process of mass transfer is coupled with rather rapid chemical interactions between the components; then the same value of effective diffusion coefficient, *D*, may be ascribed to each component. The physical meaning of this operation was first studied by Kacena and Matousek[4] and may be briefly summarized as follows. Let us assume that one of the transferred species has a higher individual D_j than the others. Because the mobility of such particles is greater, the concentrations exceeding equilibrium will be formed in the direction of the general diffusion flow. This results in a corresponding shift of chemical equilibrium and leads to decrease in their concentrations. The analogous result may be obtained by applying the diffusion coefficient with the lower value. There is a definite correlation between the effective *D* and the individual D_j (see, *e.g.*, Refs. 2 and 4).

Concentration Profiles of the Cr(VI)-containing Species

On dissolving CrO_3 in H_2O, a rather complicated system containing different Cr(VI) oxyions is formed.[5,6] Among the many well-known species, such as H_2CrO_4, $HCrO_4^-$, CrO_4^{-2} and $Cr_2O_7^{-2}$, there are polychromate ions $Cr_3O_{10}^{-2}$, $Cr_4O_{13}^{-2}$, and possibly, other particles of the $Cr_nO_{3n+1}^{-2}$ type. Such substituted chromates as CrO_3Cl^-, $CrSO_7^{-2}$, $HCrPO_7^{-2}$ and $H_2CrPO_7^-$ should also be ascribed to them.[7] Equilibrium characteristics of polychromates and substituted chromates have been discussed by us in Refs. 8 and 9.

Other chemical equilibria between the components of the system are established as well. The number of such equilibria, then, is rather considerable. Therefore, to simplify the mathematical relations, only some will be considered, because the increase of quantity of the equilibria contributes nothing new to the model under investigation. Accordingly, some of the following reactions were selected as typical:

$$CrO_4^- + H^+ \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} H_2CrO_4 \qquad (1)$$

$$CrO_4^- + H^+ \underset{k_{-2}}{\overset{k_2}{\longleftrightarrow}} HCrO_4^- \qquad (2)$$

$$2HCrO_4^- \underset{k_{-3}}{\overset{k_3}{\longleftrightarrow}} Cr_2O_7^{2-} + H_2O \qquad (3)$$

where *k* with the positive indexes represents rate constants of direct reactions (1)-(3), and *k* with the negative indexes represents the relevant reverse reactions.

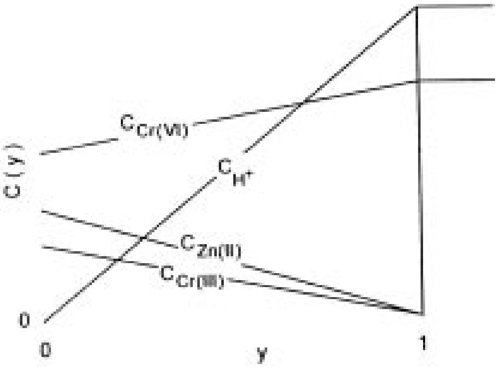

Fig. 1—Corrosion of Zn in solutions of Cr(VI). Diagram of the general concentration profiles of Cr(VI), Cr(III), Zn(II) and labile donors of protons (C_H+) in the diffusion layer simulated according to Nernst. y = x/d, where x is the vertical coordinate, and d is the thickness of the diffusion layer.

Moreover, it is necessary to discuss two important parameters defining the system under investigation. The first is the analytic (total) concentration of the species containing Cr(VI). This value is determined by the quantity of CrO_3 used in preparation of solutions and, consequently, may be easily kept under control.

When restricted to only consideration of processes (1)-(3), the material balance for Cr(VI) can be expressed by the following relationship:

$$[H_2CrO_4] + [HCrO_4^-] + 2[Cr_2O_7^{-2}] + [CrO_4^{-2}] = C_{Cr(VI)} \quad (4)$$

The other parameter describes basic-acidic properties of the system and represents the total concentration, C_H+, of donors and acceptors of protons. As can be seen from Eqs. (1)-(3), the chemical reactions in the system involve H^+ ions. The donors of protons are represented, first, by such species as H_2CrO_4 and $HCrO_4^-$, which are capable of generating H^+ ions. The species $Cr_2O_7^{-2}$ should also be assigned to this group; when the reverse reaction (3) proceeds, two moles of H^+ are generated. On the other hand, the OH^- ions are capable of bonding with H^+ and, therefore, represent acceptors of protons. It follows that the expression for C_H+ could be written in the following way:

$$2[H_2CrO_4] + [HCrO_4^-] + [H^+] + 2[Cr_2O_7^{-2}] - [OH^-] = C_H+ \quad (5)$$

In contrast with $C_{Cr(VI)}$, the parameter C_H^+ is somewhat more abstract. It can be obtained by means of Eq. (5), having previously determined the concentrations of the species containing Cr(VI). The latter procedure is described in detail in Ref. 6. It requires solution of Eq. (4) using the equilibrium constants, *K*, of processes (1)-(3). Having performed the above operations, all information on the distribution of the components in the bulk of the solution can be obtained, which is necessary for calculation of the composition of the diffusion layer.

It is further necessary to discuss the flow of the oxidized forms in the direction of the coordinate *x*, which is transverse to the surface of the Zn electrode. For this purpose, the second Fick's law, complemented by the terms that account for the rate of chemical reactions (1)-(3) (see Refs. 2 and 10), should be written for each species. After procedures described in the Appendix, two simple equations are obtained:

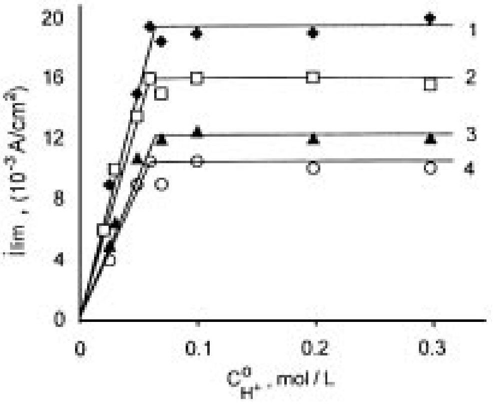

Fig. 2—Dependence of limiting current [i_{lim},(Cr(VI) → Cr(III)] on the general acidity of the Cr(VI) solution. Graphite electrode; Cr(VI) - 0.01, SO_4^{-2} - 0.4 mol/L. Scanning rate, 33.3 mV/sec; rotation velocity of electrode (rpm): (1) 1500; (2) 1000; (3) 500; (4) 300.

$$\partial C_{Cr(VI)}/\partial t = D\, \partial^2 C_{Cr(VI)}/\partial x^2 \quad (6)$$

$$\partial C_H^+/\partial t = D\, \partial^2 C_{H+}/\partial x^2 \quad (7)$$

without any kinetic terms, reflecting the rate of chemical reaction.

Consequently, the total concentrations of Cr(VI)-containing species, as well as those of donors and acceptors of protons, may be described by the same differential equations as simple redox reactions, which proceed under diffusion control. To solve these equations, it is necessary to formulate the appropriate initial and boundary conditions. The latter are determined by means of control of the potential electrode, *E*, or current density, *i*, when the electrode is polarized from the source in the external circuit.[11] In the case of corrosion processes in general, and chromating processes in particular, an overall current via the electrode equals zero. Accordingly, changes in the surface concentrations with time, *t*, will be determined by the kinetics and mechanism of heterogeneous reactions. Those processes, in turn, will form corresponding concentration profiles.

Under the steady-state conditions (when $\partial C/\partial t = 0$) and within the framework of the Nernst model, it follows from Eqs. (6) and (7) that the values of $C_{Cr(VI)}(x)$ and $C_H+(x)$ vary linearly with the coordinate *x*, within the range of $0 \le x \le \partial$. Also, it is necessary to take into account the fact that the oxygen splits from chromate anions during its reduction and interacts with protons, yielding H_2O. This process can be formally described as a reaction $Cr(VI) + \gamma_H H^+ + 3e \rightarrow Cr(III)$, where γ_H is the absolute stoichiometric coefficient, which will be assessed below.

Such an approach allows a simple relationship between the concentration profiles under discussion:

$$\gamma_H dC_{Cr(VI)}/dy = dC_H+/dy \quad (8)$$

where $y = x/\delta$ (when δ is not known, the dimensionless *y* value is more acceptable than *x*). Thus, when one of the concentration profiles is established, the other can be determined on the basis of Eq. (8).

The simplest case occurs when the process proceeds under the conditions of limiting diffusion flow of donors of protons (*i.e.*, when the surface concentration $C_H + (0) = 0$). Because the profile of $C_H + (y)$ can be easily constructed, determina-

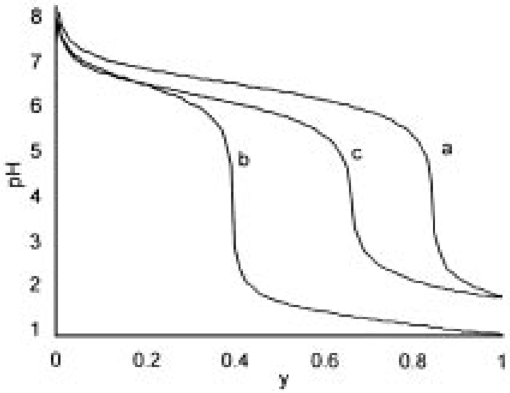

Fig. 3—Calculation of pH within the diffusion layer in the process of Zn corrosion in solution of 0.2 mol/L Cr(VI): a - Cso_4^{-2}, 0.02, C_H^+, 0.23; b - Cso_4^{-2}, 0.00, C_H+, 0.4; c - Cso_4^{-2}, 0.4; C_H^+, 0.279 mol/L.

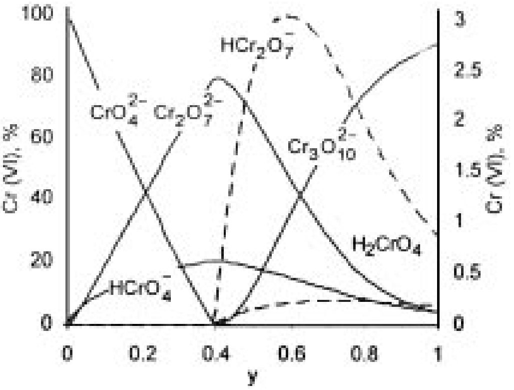

Fig. 4—Corrosion of Zn in solution: Cr(VI), 0.2; C_H+, 0.4 mol/L. Distribution of equilibrium concentration of Cr(VI) species in the diffusion layer.

tion of the profile of $C_{Cr(VI)}$ (*y*) according to Eq. (8) is not difficult. The diagram of the concentration profiles for this case is shown in Fig. 1. Another way could be based on experimental investigation of the corrosion rate of Zn, which allows establishment of the surface concentration of Zn(II). Inasmuch as the processes of oxidizing Zn and reduction of Cr(VI) are conjugated (see below), it is possible to determine the value of $C_{Cr(VI)}(0)$ when $C_{Zn(II)}(0)$ is known.

It follows from the aforesaid that the values of $C_{Cr(VI)}$ and C_H+ are in linear dependence on the coordinate *x* within the framework of the Nernst model. Those dependences may be established by one of the methods mentioned above. It should be emphasized that the concentration profiles of the individual components are, in general, not linear. To calculate them, it is necessary to formulate additional equations, which represent the relations between the concentrations of the components in the diffusion layer.

If reactions (1)-(3) proceed at a rate not notably exceeding the rate of the diffusive mass transfer, the only way to calculate the concentration of the individual species is to solve the system of differential equations given in the Appendix. For this purpose, it is necessary to have information on the *k* values, which are not known for all the reactions.[9] Yet the situation fundamentally changes when the rate of the indicated reactions is high (*i.e.*, when the equilibria are mobile). Thereupon, no significant deviations from equilibrium should be expected in the diffusion layer. The argument to support this assumption could be the kinetic data on the rate of (1)-(3)-type reactions. Accordingly, the required mathematical relations between concentrations of components may be described in terms of constants of respective equilibria:

$$K_1 = [H_2CrO_4] / [HCrO_4^-][H^+] \qquad (9)$$

$$K_2 = [HCrO_4^-] / [CrO_4^{-2}][H^+] \qquad (10)$$

$$K_3 = [Cr_2O_7^{-2}] / [HCrO_4^-]^2 \qquad (11)$$

or values equivalent to them.

Solution of the system of equations (4),(5),(9)-(11) at known values of $C_{Cr(VI)}$, C_H^+ and respective *K* values allows calculation of the concentrations of Cr(VI)-containing species, as well as the concentration of H^+ at any value of $y = x/\delta$.

Values of Extrapolated I = 0 Equilibrium Constants*

Process	**log K_0**
$Cr^{+3} + OH^- \rightarrow CrOH^{+2}$	10.1
$Cr^{+3} + 2OH^- \rightarrow Cr(OH)_2^+$	17.8
$2Cr^{+3} + 2OH^- \rightarrow Cr_2(OH)_4^{+4}$	22.9
$Cr^{+3} + SO_4^{-2} \rightarrow CrSO_4^+ + 4H_2O$	3.2
$2Cr^{+3} + 2OH^- + 2SO_4^{-2} \rightarrow Cr_2(OH)_2SO_4^{+2}$	25.8
$2Cr^{+3} + 4OH^- + 2SO_4^{-2} \rightarrow Cr_2(OH)_4(SO_4)_2$	29.2
$Zn^{+2} + OH^- \rightarrow Zn(OH)^+$	5.04
$Zn^{+2} + 2OH^- \rightarrow Zn(OH)_2$	11.1
$Zn^{+2} + 3OH^- \rightarrow Zn(OH)_3^-$	13.6
$Zn^{+2} + 4OH^- \rightarrow Zn(OH)_4^{-2}$	14.8
$Zn^{+2} + SO_4^{-2} \rightarrow ZnSO_4$	3.1
$H^+ + SO_4^{-2} \rightarrow HSO_4^-$	1.99

* Based on analysis of data from the literature.

Stoichiometry of Reaction of Cr(VI) Reduction

As mentioned, the protons, which are necessary for binding the released oxygen into H_2O, participate in the process of electroreduction of Cr(VI) to Cr(III). In this process, a part of the oxygen may be bound into OH^- anions, yielding Cr(III) hydroxo complexes of $Cr(OH)_n^{+(3-n)}$ type. Accordingly, for each $Cr_mO_{3m+1}^{-2}$ species, a respective charge transfer reaction may be written. The number of such reactions, each of which has its own stoichiometry, depends on the dimensions of the array (*m*, *n*). It may be considered[7] as $m \leq 3$, $n \leq 3$. It can be shown that the stoichiometric coefficient, γ_H, of the specific partial process equals $6\text{-}n + 2/m$. The average stoichiometry coefficient, γ_H, depends on the mole fractions of both Cr(VI) and OH^-, bonded into hydroxocomplexes with Cr(III) species.

Although the distribution of Cr(VI) anions may be calculated on the basis of the model of chromic acid solution,[5,6] it does not concern the distribution of complexes of Cr(III) at the Zn electrode surface. The latter data can only be obtained after calculation of the surface concentrations and can be used for checking the correctness of the assumptions. The experimental method, therefore, is best for establishment of the γ_H value.

We used the method outlined in Ref. 14, the essence of which is measurement of the dependence of density of the limiting cathodic current, i_l, on the concentration of oxidized forms in the solution. The value of i_l may be determined by the diffusion flow of species containing Cr(VI) or by species containing a labile proton. So, for example, keeping the value of $C_{Cr(VI)}$ constant and increasing the acidity of the solution, it is possible to establish the composition of the solution at which i_l becomes independent of C_H+ (or pH). Under such conditions, hereinafter referred to as the equivalent point, Cr(VI) and the donors of protons are in the stoichiometric relationship.

As an example, Fig. 2 shows a typical dependence obtained from the voltamperometric data, a rotating graphite electrode[8] having been employed. The equivalent point corresponds to the ratio of bulk concentrations $C_H+/C_{Cr(VI)}$, which equals 5.9. Similar values were obtained for other compositions of solutions. The analysis shows that the estimated theoretical γ_H value depends to a greater extent on the assumed scheme of Cr(VI) reduction to Cr(III), (*i.e.*, on the value of *n* in the hydroxo- complex, $Cr(OH)_n^{+(3-n)}$), than on the composition of the solution of Cr(VI).

A comparison of the theoretical[8] γ_H value with the experimental one[9] leads to the conclusion that the formed species of Cr(III) may contain 1-2 OH^- ions. It should be noted that, in the course of experiment, such composition of the solutions was used where no conversion coatings on Zn are formed. This allowed minimization of the passivation phenomena at the graphite electrode. Moreover, it was taken into account that the protonized particles, such as HSO_4^- ions, are the donors of protons as well.[15]

Concentration Profiles
Of the Species Containing Cr(III)

The reverse flow of species containing the reduced product [(*i.e.*, ions of Cr(III)] can be analyzed in a similar way. The latter are formed in the process, which, for $HCrO_4^-$, for instance, can be written according to the following generalized scheme:

$$HCrO_4^- + (7-n)H^+ + 3e^- \rightarrow Cr(OH)_n^{(3-n)+} + (4-n)H_2O. \quad (12)$$

Obviously, other species containing Cr(VI) can participate in such reactions. Without a detailed study of the mechanism of the process $Cr(VI) + 3e^- \rightarrow Cr(III)$, we will only note that, in accordance with the above discussed concepts, the total concentration of species containing Cr(III) ($C_{Cr(III)}$) is a linear function of coordinate *x*. Moreover, the dependence of $C_{Zn(II)}$ on *x* is linear, too, as Zn in the investigated corrosion process oxidizes, and the species containing Zn(II) can go into the solution and diffuse into its bulk.

It is necessary to note that, in the course of such reactions as (12), hydroxocomplexes of Cr(III) are formed, which are acceptors of protons. Similar species may be formed during the oxidation of zinc. In this connection, the concentrations of the indicated species with negative sign should be included in such equations as (5). The analysis shows that such corrections are insignificant because of the negligible amount of hydroxocomplexes formed in acid solutions.[9] Moreover, the Cr(III) hydroxocomplexes can hardly be regarded as labile.

When the profile of $C_{Cr(VI)}$ is known, there is no problem in constructing profiles of total concentrations of the reduced species. These relationships may be used for this purpose:

$$dC_{Cr(III)}/dy = -dC_{Cr(VI)}/dy \quad (13)$$

$$dC_{Zn(II)}/dy = 1.5\, dC_{Cr(III)}/dy \quad (14)$$

which follow from consideration of the material balance and the charge conservation. Consequently, the values of total concentrations of Cr(III) and Zn(II) are established for every fixed value of $y = x/\delta$. Subsequently, the solution of the problem is similar to that used for calculation of concentrations of the oxidized species—the equations of material balance, together with the expressions of equilibrium constants, give unambiguous solutions for concentration profiles of the components of the system.

Results & Discussion

The possibility of the existence of a considerably greater amount of species than discussed above was considered in the course of the calculations. As in the case of chromium acid solutions,[5-7] the analysis of literature data on the equilibrium constants for reactions involving various Zn(II)- and Cr(III)-containing species was performed. This was done with the aim of establishing the dependences of those constants on the ionic strength of the solutions and, in particular, to establish the value of K_o related to ionic strength $I = 0$. The details of this analysis are given in Refs. 6 and 9, as well as *K* values for Cr(VI)-containing species. The other data employed are given in the table.

Calculations were made of the concentration profiles at $C_{Cr(VI)} = 0.2$ M and different values of C_{H+}, as well as at different concentrations of SO_4^{-2}ions. An additional relationship written for the total concentration of SO_4^{-2} ions was used in this case.

As an example, we offer a part of the results obtained. The profiles of total concentrations have been shown in Fig. 1. They are linear; however, the profiles of concentrations of individual components are obviously non-linear. The higher the general acidity of the solution, the closer to the surface of the corroding electrode the abrupt change of the free acidity (pH) (Fig. 3). The shape and the pH interval of those curves are actually the same as in the case of the analog curves obtained for alkalimetric titration of chromium acid solution.[6]

The concentration profiles of other components are also rather complicated. Actually, all species containing Cr(VI) can be found in considerable amounts in the diffusion layer (Fig. 4). The amount of CrO_4^{-2} ions decreases with *y*, while the concentration of protonated anions and polychromates increases. These changes are mainly caused by the peculiar changes of pH (Fig. 3). Naturally, when the acidity increases, the fraction of protonated anions increases as well (Fig. 4). The general nature of the concentration profiles, however, remains the same.

The data in Fig. 4 should be considered as a first approximation. These results deserve some further corrections relating to the interplay between the diffusive flows of reactants (*i.e.*, species involving Cr(VI) and H^+) and products of heterogeneous reactions [(*i.e.*, species involving Cr(III) and Zn(II)]. It must be emphasized that the total concentrations of the indicated components do not depend on such interactions and are unambiguously determined by Eqs. (8), (13) and (14). Accordingly, the primary distribution of products in the diffusion layer can be obtained on the basis of linear profiles shown in Fig. 1, with the procedures described above. Once such a simulation is made, Eq. (5) for C_H+ should be supplemented by the negative terms representing the concentrations of generated hydroxocomplexes (see table). Because some species involving SO_4^{-2} ions may be produced (see table), the analogous corrections are also desirable for the total concentration of sulfate. The simulation should then be repeated from the very beginning several times until the next result is obtained. The calculations showed, however, that the first approximation works quite well at sufficiently low pH.

The results obtained by such a procedure have a physical aspect when the calculated concentrations of species do not exceed the values determined by the respective solubility constants. This is not the case for solutions applied for obtaining chromate conversion coatings. Those coatings consist of a number of low-solubility compounds and are formed in the process of oversaturation of the adjacent electrode layer with particular components. The data obtained by this method may serve as the basis for constructing hypotheses on the thermodynamic probability of conversion coatings formation. This problem requires special analysis and will be the subject of our next publication.

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Nomenclature

$C_{Cr(III)}$, $C_{Cr(VI)}$, $C_{Zn(II)}$ - total (analytical) concentrations of species containing Cr(III), Cr(VI) and Zn(II), respectively
C_{H+} - total concentration of donors and acceptors of protons
D - effective diffusion coefficient
D_j - individual diffusion coefficient of certain species
E - electrode potential
i - current density
I - ionic strength
k - rate constant of chemical reaction
K - equilibrium constant
K_o - equilibrium constant at zero ionic strength
t - time
x - coordinate perpendicular to the electrode surface
y - dimensionless coordinate ($y = x/\delta$)
δ - diffusion layer thickness
γ_H - stoichiometric coefficient

Appendix

Analysis of the following equilibria:

$$HCrO_4^- + H^+ \xleftrightarrow[k_{-1}]{k_1} H_2CrO_4 \qquad (A1)$$

$$CrO_4^{-2} + H^+ \xleftrightarrow[k_{-2}]{k_2} HCrO_4^- \qquad (A2)$$

$$2HCrO_4^- \xleftrightarrow[k_{-3}]{k_3} Cr_2O_7^{-2} + H_2O \qquad (A3)$$

$$H^+ + OH^- \xleftrightarrow[k_{-4}]{k_4} H_2O \qquad (A4)$$

The equations of Fick's second law, supplemented by terms describing the rate of chemical reactions, may be written as

$$\partial[H_2CrO_4]/\partial t = D\partial^2[H_2CrO_4]/\partial x^2 + k_1[HCrO_4^-][H^+] - k_{-1}[H_2CrO_4] \qquad (A5)$$

$$\partial[HCrO_4^-]]/\partial t = D\partial^2[HCrO_4^-]/\partial x^2 + k_{-1}[H_2CrO_4] - k_1[HCrO_4^-][H^+] + k_2[CrO_4^{-2}][H^+] - k_{-2}[HCrO_4^-] + 2k_{-3}[Cr_2O_7^{-2}][H_2O] - k_3[HCrO_4^-]^2 \qquad (A6)$$

$$\partial[CrO_4^{-2}]/\partial t = D\partial^2[CrO_4^{-2}]/\partial x^2 + k_{-2}[HCrO_4^-] - k_2[CrO_4^{-2}][H^+] \qquad (A7)$$

$$\partial[Cr_2O_7^{-2}]/\partial t = D\partial^2[Cr_2O_7^{-2}]/\partial x^2 + 0.5k_3[HCrO_4^-]^2 - k_{-3}[Cr_2O_7^{-2}][H_2O] \qquad (A8)$$

$$\partial[H^+]/\partial t = D\partial^2[H^+]/\partial x^2 + k_{-1}[H_2CrO_4] - k_1[HCrO_4^-][H^+] + k_{-2}[HCrO_4^-] - k_2[CrO_4^{-2}][H^+] + k_{-4}[H_2O] - k_4[H^+][OH^-] \qquad (A9)$$

$$\partial[OH^-]/\partial t = D\partial^2[OH^-]/\partial x^2 + k_{-4}[H_2O] - k_4[H^+][OH^-] \qquad (A10)$$

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