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Diffusion and migration in the electropolishing and anodic dissolution of metals

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The solution of the Nernst–Planck equation for the electropolishing of metals is presented. The migration and diffusion equations are solved for the cases where the metal ion is transported independently of the anion of the electrolyte and when ion pairing occurs. It is concluded that under polishing conditions, the surface concentration of acid is decreased by the salt solubility. It is shown that this has important practical consequences for defining the conditions required for electropolishing and in the selection of the acid used.

Nomenclature

C_i, $C_i(X)$	concentration of component i at a distance X from the electrode surface. Subscript i is either M, A or AH, where M represents the metal ion M^{2+}, A is the anion of the acid AH and H is the hydrogen ion H^+
$C_i^{(b)}$	bulk concentration of species i
$C^{(s)}$	solubility of the metal salt formed during anodic dissolution under the conditions prevailing at the electrode surface
$\bar{C}_i$, $\bar{C}_i(X)$	reduced concentration of species i given by $\bar{C}_i = C_i/C^{(s)}$
D_i	diffusion coefficient of species i
F	Faraday constant
f	F/RT
I	current density
j_i	flux of component i. The convention used is to consider that the flux is positive when there is a net flux of i away from the electrode
k_m	mass transfer coefficient
M	molarity
R	gas constant
T	absolute temperature
v_X	velocity of the solution in the X direction
X	distance from the electrode
$\bar{X}$	reduced distance from the electrode $\bar{X} = X/\delta$
Z_i	charge of species i
ΔC	change of concentration between the plane at δ and the electrode surface
$\Delta_\delta^X \phi$	Galvani potential difference between a point at X and the plane δ
δ	distance to the boundary layer; for $X > \delta$, infinite convection is considered whereas for $X < \delta$ only diffusion and migration occurs

1. Introduction

The electropolishing of metals is a well-established industrial process widely employed in the metal finishing industry. However, the mechanism by which a metal surface becomes polished under anodic dissolution conditions is not clear. The original work of Jacquet [1, 2] indicated that a 'viscous' layer was formed on the metal surface during electropolishing. The occurrence of mass transfer-controlled dissolution appears to be a prerequisite for electropolishing [3], although the actual mechanisms for the elimination of micro- and macro-irregularities may be different [4–6]. In particular, the electropolishing of metals appears to occur in the transpassive dissolution region, but at concentrations of acids so large as to mask entirely the active–passive–transpassive transitions. In fact, the rate of anodic dissolution under these conditions appears to be entirely determined by mass transfer [7]. This indicates that during electropolishing, a salt layer is probably present on the electrode surface. In the case of nickel in sulphuric acid, an underlayer of oxide or contaminated oxide appears to exist, but more recent work on electropolishing in non-aqueous media indicates that electropolishing can be carried out in conditions where no oxide layer is present, i.e. in the active dissolution potential region [7].

A central question that needs clarifying to understand the mechanism of electropolishing is the actual concentration of species at the electrode surface. Electropolishing requires high current densities, usually greater than 0.1 A cm^{-2}, as well as high acid concentrations. It is very curious that the equilibrium solubility of the salts formed is generally very small in the media employed. This is the case, for example, for nickel in sulphuric acid [7], copper in phosphoric acid [8] and iron in methanol–sulphuric acid solutions [9]. In the case of nickel in 10 M H_2SO_4, the equilibrium solubility of $NiSO_4$ is of 0.02 M; this very low surface concentration cannot possibly support the high current densities observed in electropolishing, and surface metal ion salt concentrations in excess of 1 M are required to account for the anodic dissolution currents required.

For the Ni–H_2SO_4 system the solubility of $NiSO_4$ decreases sharply for acid concentrations greater than ~ 7.5 M. Electropolishing requires high current densities, and therefore it would be expected that the acid concentration at the surface will differ from that in the bulk. If this were the case, it would be possible to understand the apparent contradiction between equilibrium solubility and bulk acid concentration. This of course is a general problem in electrochemical reactions occurring under mixed diffusion and migration control, and the purpose of this paper is to present the solution of the Nernst–Planck equations for the conditions usually encountered on electrodes operating at high current densities. In particular, we wish to calculate the surface concentration of acid during electropolishing so as to be able to analyse some previous results of the dependence of the electropolishing of nickel on sulphuric acid concentration [7], and to predict the conditions prevailing on the surface of a material being electropolished.

2. The diffusion and migration problem

The model to be considered assumes the presence of a boundary layer of thickness δ, such that infinite convection occurs for distances from the electrode surface $X > \delta$, and pure diffusion and migration for $X < \delta$. Also, a salt layer is considered to be present at the electrode surface in equilibrium with a saturated metal ion salt solution (see Fig. 1). This simple approach is of use when analysing geometries for which the complete solution of the Navier–Stokes equation is not known, and therefore the calculation of the convective terms in the flux equations is not possible. In these cases the use of dimensionless relationships can serve as a basis for the calculation of the parameter δ through the calculation of the Sherwood number for the particular flow condition considered [10].

For every ionic species i, the complete Nernst–Planck equation is given by [11]:

$$j_i = -D_i\left[\frac{dC_i}{dX} + Z_iC_if\frac{d\phi}{dX}\right] + C_iv_X \qquad (1)$$

where j_i = flux of ion i, D_i = diffusion coefficient, C_i = concentration, Z_i = charge number, $f = F/RT$, ϕ = inner potential and v_X = velocity of the solvent in a fixed coordinate system. This relationship is strictly valid either in very dilute solutions, or in the presence of an excess of base electrolyte, i.e. when the activity and the diffusion coefficients are independent of concentration. For electropolishing, the solutions employed are very concentrated and although the activity coefficients will differ considerably from unity, media effects are bound to be fairly constant in the boundary layer when the saturation concentration of the metal salt formed is less than the acid concentration, which would act in this case as the base electrolyte.

In order to describe completely all the ionic fluxes, two further conditions must be satisfied besides the Nernst–Planck Equation 1 for each individual ion in the system [12]. The net current passing through the system, I, must be given by:

$$I/F = \sum Z_ij_i \qquad (2)$$

i.e. it is considered that there are no sources or sinks of charge in the interfacial region. Also, since the system as a whole is electroneutral, the individual ionic concentrations are related through

$$\sum Z_iC_i(X) = 0 \qquad (3)$$

For the purpose of the present discussion it will be considered that Equation 3 is valid for any value of X. Deviations from electroneutrality are small in electrolyte solutions [13] and can be taken into account by the solution of the complete Nernst–Planck–Poisson equation [14]. Since the cases that we analyse in the present work correspond to fairly concentrated solutions, the incidence of these space charge effects on the diffusion and migration of ions is minimal. Also, since we are seeking to solve for the actual concentrations of metal salts and electrolyte under anodic dissolution conditions, we shall further simplify the problem by considering a boundary layer approach, in which case, $v_X = 0$ for $0 > X < \delta$, where v is the velocity component perpendicular to the electrode surface. In general, the values of the velocity profiles for solutions having turbulent hydrodynamic conditions are unknown. In the case of the rotating disc electrode this profile is accurately known, but without any loss of generality the use of a cut-off approximation is preferred as a simple and convenient way of comparing the results for different flow geometries. The solution of the Nernst–Planck equation will depend on the ionic equilibria present [15], and for this reason the different cases of dissociated and partially associated electrolytes will be considered.

3. The system M^{2+}–A^-–H^+

We consider the anodic dissolution of a metal M to yield the divalent ion M^{2+} in the presence of a fully dissociated acid AH (for instance, $A^- = HSO_4^-$, Cl^-, etc.). In the steady state, the Nernst–Planck equations for this system are

$$j_H = 0 = -D_H\left[\frac{dC_H}{dX} + fC_H\frac{d\phi}{dX}\right] \qquad (4)$$

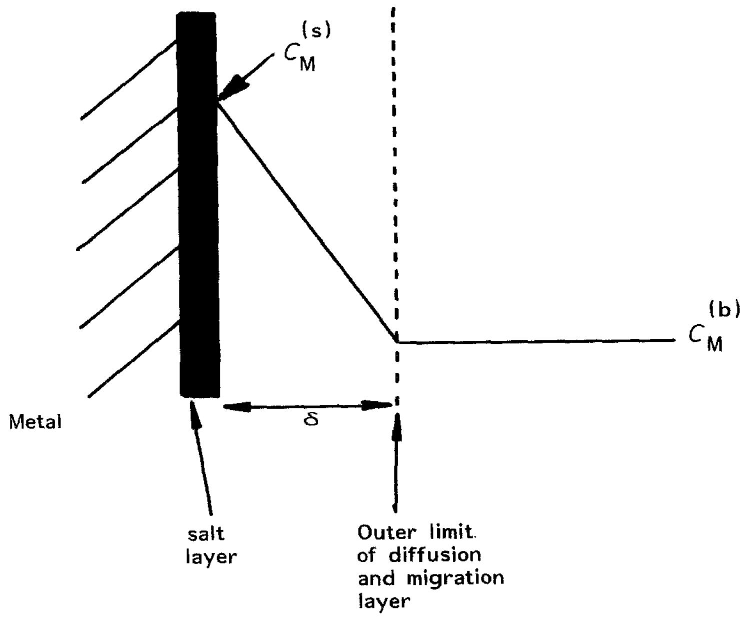

Fig. 1. Schematic diagram of the migration and diffusion region of a metal undergoing electropolishing. δ is the thickness of the diffusion layer.

$$j_M = \frac{I}{2F} = -D_M\left[\frac{dC_M}{dX} + fC_M\frac{d\phi}{dX}\right] \qquad (5)$$

and

$$j_A = 0 = -D_A\left[\frac{dC_A}{dX} - fC_A\frac{d\phi}{dX}\right] \qquad (6)$$

where for simplicity in the notation, $M = M^{2+}$, $H = H^+$ and $A = A^-$. The condition of electroneutrality across the diffusion and migration region is

$$2C_M + C_H = C_A \qquad (7)$$

From Equations 4 and 6

$$\frac{d \ln C_A(X)C_H(X)}{dX} = 0 \qquad (8)$$

and therefore, the product of the concentrations of the anion and the hydrogen ion in the diffusion and migration layer is constant. At $X = \delta$, $C_A = C_H = C^{(b)}$ where $C^{(b)}$ is the bulk stoichiometric concentration of acid and

$$C_A(X)\, C_H(X) = [C_{AH}^{(b)}]^2 \qquad (9)$$

To find the concentration profiles of the ionic species, the system of Equations 4, 5 and 6 subject to conditions 2 and 3 must be solved. It is possible to solve the system of differential Equations 4–6 in a closed form by finding the functional relationship between the derivatives dC_M/dX and dC_H/dX from condition 7 and the flux Equations 4, 5 and 6. Thus

$$-\frac{I}{2FD_M} = 2\frac{dC_H}{dX} + 3\frac{dC_M}{dX} \qquad (10)$$

From Equations 7 and 9

$$\frac{dC_H}{dX} = \left[\frac{C_M}{\sqrt{C_M^2 + (C_{AH}^{(b)})^2}} + 1\right]\frac{dC_M}{dX} \qquad (11)$$

The integration of Equation 11 between a point X within the diffusion and migration layer and the boundary δ leads to

$$\frac{I(\delta - X)}{2FD_M} = (C_M^{(b)} - C_M(X)) + 2\sqrt{C_M(X)^2 + (C_{AH}^{(b)})^2} - 2\sqrt{(C_M^{(b)})^2 + (C_{AH}^{(b)})^2} \qquad (12)$$

where $C_M^{(b)}$ is the bulk concentration of M^{2+}. Considering the usual case where the bulk concentration of metal ion is much smaller than the surface salt concentration required to sustain the high current densities analysed here, the dependence of the concentration of M^{2+} on distance is given by

$$C_M(X) = -\frac{2}{3}\left[\frac{A(X)}{4} + C_{AH}^{(b)}\right] + \frac{2}{3}\sqrt{(C_{AH}^{(b)})^2 + 2A(X)C_{AH}^{(b)} + \left(\frac{A(X)}{2}\right)^2} \qquad (13)$$

with

$$A(X) = \frac{I(\delta - X)}{FD_M} \qquad (14)$$

From Equation 13, setting $X = 0$, it can be easily seen that the product $I\delta$ should be a constant if the concentration of M^{2+} at $X = 0$ is also constant, i.e. if saturation equilibrium of the solid salt of the metal formed at the surface is maintained for different hydrodynamic regimes. From Equation 12 we can derive the relationship between the current density, the bulk acid concentration and the saturation solubility $C^{(s)}$ of the metal ion salt MA_2. This is given by

$$I = \frac{2FD_M}{\delta} = (C^{(s)} - 2C_{AH}^{(b)}) + 2\sqrt{(C_{AH}^{(b)})^2 + (C^{(s)})^2} \qquad (15)$$

Two limiting cases can be considered. When the acid concentration is much larger than the saturation solubility of M^{2+}, the current is given by

$$I = \frac{2FD_M}{\delta}C^{(s)} \qquad (16)$$

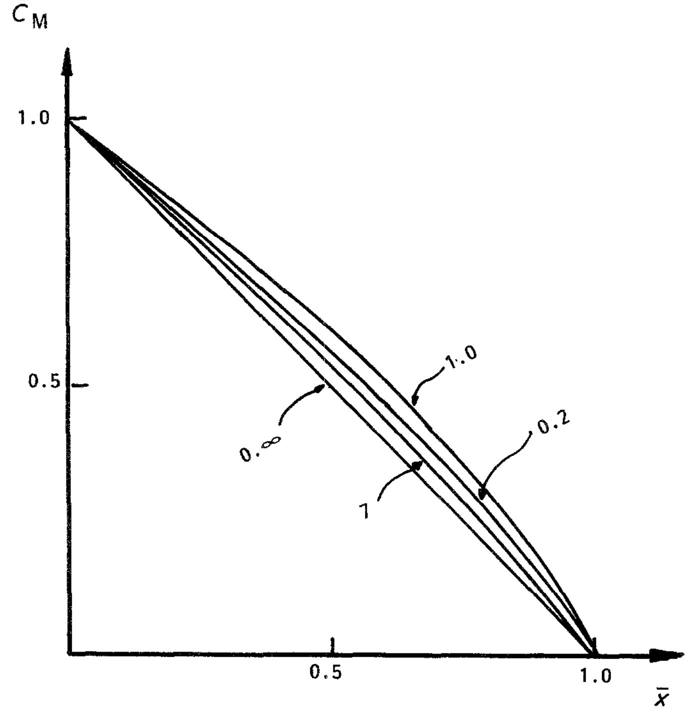

Fig. 2. Reduced concentration of metal ion ($\bar{C}_M = C(X)/C^{(s)}$) as a function of the reduced distance for different values of the ratio $C_{AH}/C^{(s)}$.

which is the usual equation for the trace diffusion case [16]. When $C_{AH} \ll C^{(s)}$, then the current is given by

$$I = \frac{6FD_M}{\delta} C^{(s)} \tag{17}$$

which corresponds to the limiting current for a 2:1 electrolyte [17].

Figure 2 shows the reduced concentration of M^{2+} in the diffusion layer as a function of the reduced distance $\bar{X} = X/\delta$, for different values of the reduced acid concentration ($\bar{C}_{AH} = C_{AH}/C^{(s)}$). As can be seen, the influence of simultaneous diffusion and migration results in significant deviations from linearity when the ratio $C_{AH}/C^{(s)}$ is smaller than 5. For greater values of this concentration ratio, the system is indistinguishable from the trace diffusion case.

The surface concentration of hydrogen ions can be calculated from Equations 7 and 9

$$C_H(0) = -C^{(s)} + \sqrt{(C^{(s)})^2 + (C_{AH}^{(b)})^2} \tag{18}$$

Equation 18 is valid when surface solubility equilibria of the dissolving metal salt is maintained.

Figure 3 shows an example of the dependence of the surface H^+ ion concentration on that of the bulk acid. When the bulk concentration of acid is much greater than the saturation solubility of the salt, the surface concentration of the H^+ ion approaches

$$C_H(0) = C_{AH}^{(b)} - C^{(s)} \tag{19}$$

that is to say, the proton surface concentration is simply given by the difference in concentrations of the acid and the solubility of the metal salt formed. This is the situation that prevails in electropolishing as, for instance, for the nickel–sulphuric acid system [7]. This result shows that the acid concentration at the surface, in the limiting diffusion regime, will depend on the solubility of the metal salt formed and this conclusion can be easily seen in Fig. 3.

In a practical electropolishing situation with some degree of mechanical stirring, the current density will be given by

$$I = ZFk_m\Delta C \tag{20}$$

where k_m, the mass transfer coefficient, will have a value of approximately $5 \times 10^{-4}\,\mathrm{cm\,s^{-1}}$ [18]; ΔC is the concentration difference across the diffusion layer. For a typical dissolution current of $0.2\,\mathrm{A\,cm^{-2}}$, a surface concentration of ~2 M will be required to sustain a fully diffusionally controlled process. For acid concentration lower than the salt solubility, the maximum dissolution rate will be determined by the limiting hydrogen ion concentration compatible with the precipitation of the metal hydroxide.

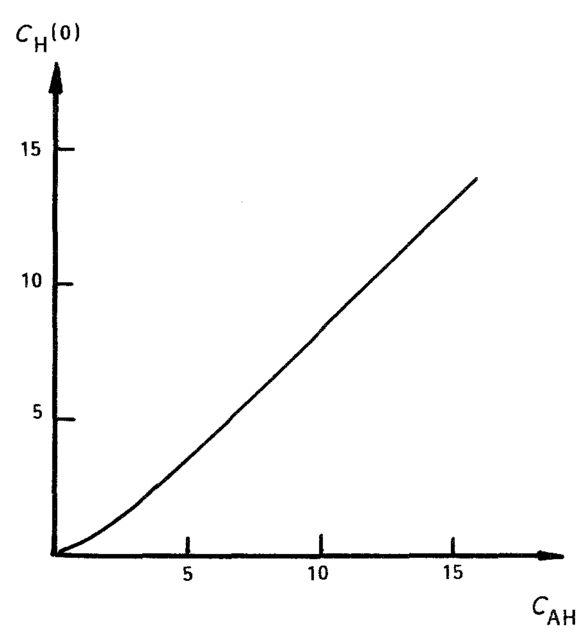

Fig. 3. Surface concentration of H^+ ions as a function of bulk acid concentration when the salt solubility is 2 M, for the diffusionally controlled anodic dissolution of the metal.

These theoretical predictions show that a reaction order greater than zero with respect to the bulk acid as has been previously observed [7] may be simply reflecting the shift in surface concentration of the H^+ ion. These considerations are important not only for electropolishing but in the case of pitting corrosion, in which diffusion-controlled anodic dissolution conditions can be established at the growing pits.

4. The system MA^+-A^--H^+

The previous case refers to a totally dissociated system. In practice, ion pairing between the dissolving metal ion and the anion of the electrolyte is bound to occur, and this section shows how these effects can be taken into account in the solution of the Nernst–Planck equations for the anodic dissolution of a metal to give divalent ions. In this case, the migration and diffusion equations are

$$j_{\mathrm{H}} = 0 = -D_{\mathrm{H}}\left[\frac{\mathrm{d}C_{\mathrm{H}}}{\mathrm{d}X} + fC_{\mathrm{H}}\frac{\mathrm{d}\phi}{\mathrm{d}X}\right] \tag{21}$$

$$j_{\mathrm{MA}} = \frac{I}{2F} = -D_{\mathrm{MA}}\left[\frac{\mathrm{d}C_{\mathrm{MA}}}{\mathrm{d}X} + fC_{\mathrm{MA}}\frac{\mathrm{d}\phi}{\mathrm{d}X}\right] \tag{22}$$

$$j_{\mathrm{A}} = \frac{I}{2F} = D_{\mathrm{A}}\left[\frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}X} - fC_{\mathrm{A}}\frac{\mathrm{d}\phi}{\mathrm{d}X}\right] \tag{23}$$

From Equations 20, 21 and 22 and the condition of electroneutrality, the H^+ ion concentration profile is given by

$$C_{\mathrm{H}}(X) = C_{\mathrm{H}}^{(\mathrm{b})}\left[1 - \frac{I}{4C^{(\mathrm{b})}F} \times \left(\frac{1}{D_{\mathrm{A}}} - \frac{1}{D_{\mathrm{MA}}}\right)(\delta - X)\right]^{(D_{\mathrm{A}}+D_{\mathrm{MA}})/(D_{\mathrm{MA}}-D_{\mathrm{A}})} \tag{24}$$

and it can be shown that the concentration of the anion is given by

$$C_{\mathrm{A}}(X) = C_{\mathrm{A}}^{(\mathrm{b})}\left[1 - \frac{I}{4C_{\mathrm{A}}^{(\mathrm{b})}F}\left(\frac{1}{D_{\mathrm{A}}} - \frac{1}{D_{\mathrm{MA}}}\right)(\delta - X)\right] \tag{25}$$

The important case when the diffusion coefficients of the ion pair and the anion are the same can be easily derived from Equation 24 by taking the limit when $D_{\mathrm{A}} \longrightarrow D_{\mathrm{MA}}$, which leads to:

$$C_{\mathrm{H}}(X) = C_{\mathrm{H}}^{(\mathrm{b})}\exp\left[-\frac{I(\delta - X)}{2C_{\mathrm{A}}^{(\mathrm{b})}DF}\right] \tag{26}$$

and

$$C_{\mathrm{A}}(X) = C_{\mathrm{A}}^{(\mathrm{b})} \tag{27}$$

As discussed before, the concentration of the metal ions at the electrode surface is given by the solubility of the metal salt formed by the anodic dissolution reaction, i.e. $C_{\mathrm{MA}} = C^{(s)}$. From the condition of electroneutrality at the surface, the concentration profile of the proton is given by

$$C_{\mathrm{H}}(X) = (C_{\mathrm{AH}}^{(\mathrm{b})} - C^{(s)})\exp\left[\frac{I}{2DC_{\mathrm{AH}}^{(\mathrm{b})}F}\right] \tag{28}$$

and therefore the surface concentration of acid is given by

$$C_{\mathrm{H}}(0) = C_{\mathrm{AH}}^{(\mathrm{b})} - C^{(s)} \tag{29}$$

Thus, as shown before, for the anodic dissolution of a metal under diffusion control, the concentration of the proton at the surface is decreased with respect to its bulk value by the solubility of the metal salt formed. This result only expresses the fact that the metal cation concentration replaces that of the hydrogen ion at the surface of the dissolving metal.

In terms of the reduced quantities previously defined, the metal cation distribution in the diffusion and migration layer is given by

$$\bar{C}_{\mathrm{M}}(\bar{X}) = \bar{C}_{\mathrm{AH}} - (\bar{C}_{\mathrm{AH}} - 1)(\bar{C}_{\mathrm{AH}}/(\bar{C}_{\mathrm{AH}} - 1))^{\bar{X}} \tag{30}$$

Figure 4 illustrates the reduced concentration profiles of the dissolving salt for different bulk acid concentrations. Again, as shown before, at high acid concentrations with respect to the saturation solubility of the metal salt the concentration profile corresponds to the trace diffusion case. There is however a fundamental difference between the concentration profiles calculated when ion pairing is taken into account and the case where the metal ion can be transported independently of the anion. A strong non-linearity is observed when the bulk acid concentration approaches the saturation value of the metal salt and the system of Equations 21–23 has no solution when $C_{\mathrm{AH}}^{(\mathrm{b})} < C^{(s)}$. The physical origin of this behaviour is the dependence of the flux of the cation on the concentration of the anion, which results from imposing the ion-pairing condition, i.e. that only metal ions associated with the anion can diffuse and migrate (Equation 22). In terms of reduced coordinates, the potential distribution is given by

$$\begin{aligned}\Delta_{\delta}^{X}\phi &= \phi(\bar{X}) - \phi(1)\\ &= -\frac{RT}{F}(1 - \bar{X})\ln[\bar{C}_{\mathrm{AH}}/(\bar{C}_{\mathrm{AH}} - 1)]\end{aligned} \tag{31}$$

The potential decreases linearly with distance in the diffusion and migration layer. From Equation 31 it can be easily seen that the potential drop across this layer will be a function of the bulk acid concentration, increasing rapidly when its value approaches the metal salt solubility. Therefore, very high metals salt solubilities will require very high acid concentrations to achieve electropolishing.

This is an important result for assessing the conditions required for electropolishing and explains problems experienced when it is attempted to use HCl as the electropolishing acid. The chlorides of many metals have a very high solubility and hence, unless very high acid concentrations are employed, the imposed current will not be able to establish the diffusional pattern required for polishing and the surface concentration of metal ions will only reach, in this case, the bulk acid concentration. Thus, under these conditions, the metal will dissolve under mixed kinetic

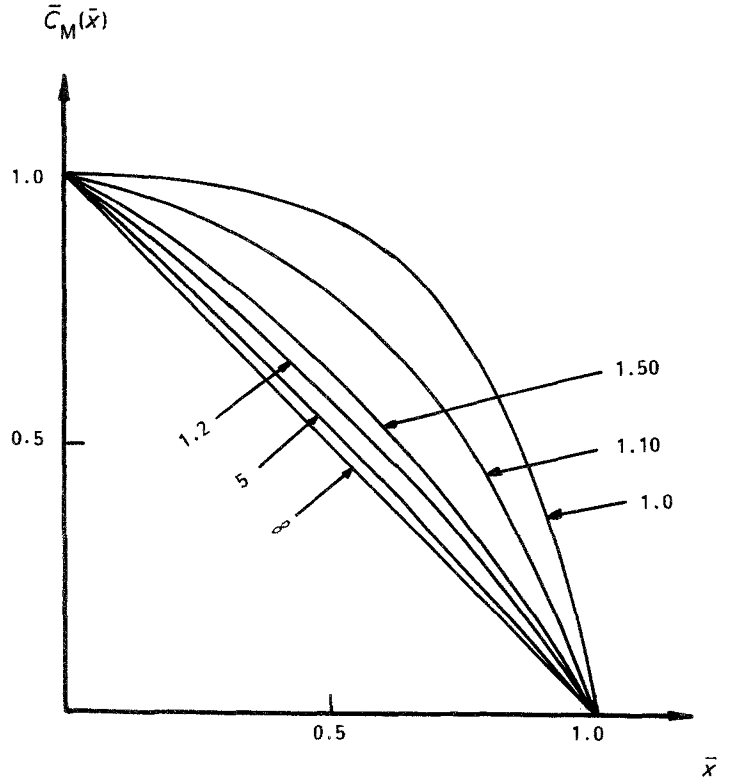

Fig. 4. Dependence of the reduced metal ion concentration ($C(X)/C^{(s)}$) on reduced distance (X/δ) for the anodic dissolution of a metal to give $M^{2+}A^-$ ion pairs with the anion of the acid AH under limiting current conditions.

and diffusional controls and the different anodic dissolution rates of the metal crystal faces will determine to some extent the rate of anodic dissolution. In consequence, crystallographic etching will develop. This analysis gives an explanation for the previous observations regarding the development of crystallographic etching at low H_2SO_4 concentrations in the electropolishing of nickel [7].

Another aspect that this analysis reveals is the importance of the nature of the primary salt formed. As has been discussed elsewhere [7] the primary salt layer formed during electropolishing is not necessarily the salt in equilibrium with the bulk acid. The unusually high surface solubilities observed for $NiSO_4$ for high H_2SO_4 concentrations can be understood in the light of the present results: there is a difference between the surface concentration of H_2SO_4 and that in the bulk given by the solubility of $NiSO_4$, of the order of 2.3 M. Thus, it is not surprising to observe that although the equilibrium solubility of $NiSO_4$ in 10 M H_2SO_4 is approximately 0.02 M, the dissolution currents observed correspond to the salt solubilities observed for more dilute H_2SO_4 concentrations. In fact, according to this analysis, the surface concentration of H_2SO_4 should be 7.7 M in this example. Similar considerations apply to the dissolution of copper in phosphoric acid, and it is proposed that the present analysis is common to all electropolishing situations and that both the acid chosen, and its concentration, must be compatible with the metal salt that would be expected to be formed in order to achieve electropolishing.

5. Conclusions

The solution of the Nernst–Planck equations for the electropolishing of metals leads to a rather simple result regarding the salt and acid concentration profiles in the diffusion and migration layer adjacent to the dissolving metal; this is of practical importance in the design of new electropolishing baths. The surface concentration of acid is lower than that in the bulk by an amount given by the solubility of the primary metal salt formed and an important consequence of this result is that the use of an acid concentration smaller than this solubility will not lead to the establishment of electropolishing conditions.

A second practical important consequence of this analysis is that the use of an acid is not a prerequisite to achieve electropolishing, provided the hydrolysis of the dissolution products is prevented. In this case, as before, the relationship between metal salt solubility and electrolyte concentration must be maintained.

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