CALCULATION OF THE DIFFUSION AND MIGRATION CURRENTS IN SYSTEMS WITH ARBITRARY IONIC CHARGE WHERE METAL ELECTRODEPOSITION OCCURS IN PARALLEL WITH ANION REDUCTION

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UDC 541.138.3

An analytical solution of the electrodiffusion problem was obtained for systems with arbitrary ionic charge where cation reduction occurs in parallel with a process of anion reduction involving hvdrogen ions and producing another kind of anions. The conditions were analyzed where limiting currents can be attained for the first and second process, and the regions of admissible currents were defined where the two processes can occur in parallel in a steady mode.

When electrode processes occur in parallel in systems lacking base electrolyte, one of them may influence another at the stage of reactant transport by diffusion and migration in the diffusion layer. This influence may be unilateral, as e.g. in migration-current exaltation [1, 2], or mutual, as e.g. in correlational exaltation of the migration currents [3]. This influence generally can produce both an increase (exaltation) and a decrease (depression) of the limiting current of a first reaction on account of a second process occurring in parallel.

In [4], electrodiffusion problems were analyzed in systems where metal electrodeposition occurs in parallel with anion reduction in acidified solutions. Schemes were examined where hydrogen ions are involved and a neutral substance is produced in the reaction in which the anions are reduced. This analysis was generalized in [5] to the case of neutral anion reduction products in systems with arbitrary ionic charge.

In the present work we describe the analytical solution for a system with arbitrary ionic charge where the metal cations are reduced in parallel with a process involving hydrogen ions in which the anions are reduced and another kind of anions is produced.

An example of such processes is the reduction of copper in nitrate solutions at solid electrodes:

$$Cu^{2+} + 2e \rightarrow Cu^0\downarrow, \tag{1}$$

when the NO_3^- ions are reduced according to the scheme of

$$NO_3^- + 2H^+ + 2e \rightarrow NO_2^- + H_2O. \tag{2}$$

The general scheme of processes of this type where reduction and the anions being reduced have identical charge [sic] can be written as

$$A_1^{\bar{z}_1+} + \bar{z}_1 e \rightarrow A_1^0\downarrow, \tag{3}$$

$$A_3^{\bar{z}_3-} + pA_2^{\bar{z}_2+} + (p\bar{z}_2)\, e \rightarrow A_4^{\bar{z}_4-} + \sum B_i^0. \tag{4}$$

Here suffixes 1 to 4 correspond to the ions of the metal being deposited, to the cations involved in the second reaction, to the anions being reduced, and to the anions being produced; $A_i^{z_i}$ is the symbol for the corresponding component, B_i^0 are the neutral products of reaction (4), p is the stoichiometric coefficient, and $\bar{z}_i$ is the charge of the corresponding ion (with $\bar{z}_3 = \bar{z}_4$).

A. N. Frumkin Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Elektrokhimiya, Vol. 25, No. 10, pp. 1306—1312, October, 1989. Original article submitted July 13, 1988; revision submitted April 21, 1989.

The system of electrodiffusion equations which describes the scheme of (3) and (4) is given by

$$\frac{dc_1}{dx}+\tilde{z}_1c_1\frac{d\bar{\psi}}{dx}=\frac{1}{\tilde{z}_1}\frac{i_1L}{FD_1c^0}=j_1, \tag{5}$$

$$\frac{dc_2}{dx}+\tilde{z}_2c_2\frac{d\bar{\psi}}{dx}=\frac{1}{\tilde{z}_2}\frac{i_2L}{FD_2c^0}, \tag{6}$$

$$\frac{dc_3}{dx}-\tilde{z}_3c_3\frac{d\bar{\psi}}{dx}=\frac{1}{p\tilde{z}_2}\frac{i_2L}{FD_3c^0}=j_2, \tag{7}$$

$$\frac{dc_4}{dx}-\tilde{z}_3c_4\frac{d\bar{\psi}}{dx}=\frac{-1}{p\tilde{z}_2}\frac{i_2L}{FD_4c^0}, \tag{8}$$

$$\tilde{z}_1c_1+\tilde{z}_2c_2=\tilde{z}_3(c_3+c_4). \tag{9}$$

Here c_i are the corresponding concentrations made dimensionless through concentration c_0 of the metal ions in the bulk solution, D_i are the corresponding diffusion coefficients, $\bar{\psi}= FE/RT$ is the dimensionless potential, x is the dimensionless coordinate ($0< x < L$), L is the thickness of the Nernst diffusion layer, and $j_1 > 0$ and $j_2 > 0$ are dimensionless currents. At the limits of the diffusion layer the values of potential and component concentrations are given as

$$c_1(1)=1,\ c_2(1)=k,\ c_3(1)=(\tilde{z}_1+k\tilde{z}_2)/\tilde{z}_3,\ c_4(1)=0,\ \bar{\psi}(1)=0. \tag{10}$$

We take into account that the diffusion coefficients of the original and resulting anions are sufficiently close so that $D_3 \approx D_4$. Moreover, to simplify the notation we shall introduce relative charges z_1 and z_2 and the relative potential Ψ defined as

$$z_1=\tilde{z}_1/\tilde{z}_3,\ z_2=\tilde{z}_2/\tilde{z}_3,\ \Psi=\tilde{z}_3\bar{\psi}. \tag{11}$$

Quantities z_1, z_2, and Ψ coincide with the common quantities when $\bar{z}_3 = 1$, which is true in particular in the scheme of (1) and (2).

Using (11) we can rewrite Eqs. (5) to (9) as

$$\frac{dc_1}{dz}+z_1c_1\frac{d\Psi}{dx}=j_1, \tag{12}$$

$$\frac{dc_2}{dx}+z_2c_2\frac{d\Psi}{dx}=j_2\nu, \tag{13}$$

$$\frac{dc_3}{dx}-c_3\frac{d\Psi}{dx}=j_2, \tag{14}$$

$$\frac{dc_4}{dx}-c_4\frac{d\Psi}{dx}=-j_2, \tag{15}$$

$$z_1c_1+z_2c_2=c_3+c_4, \tag{16}$$

where the parameter $\nu = pD_3/D_2$. Combining (14) and (15) and introducing the notation of

$$c_5=c_3+c_4, \tag{17}$$

we obtain the equation

$$\frac{dc_5}{dx}-c_5\frac{d\Psi}{dx}=0. \tag{18}$$

The system of Eqs. (12), (13), (16), and (18) with boundary conditions (10) describes the correlational exaltation of migration currents. It has been analyzed in detail in [3]. Following the solution scheme described in [3] we obtain below a solution for c_1, c_2, c_5, and Ψ, and then find concentrations c_3 and c_4 by using Eqs. (14) and (16).

Using linear combinations of the Eqs. (12) to (16) we can write quantity $dx/d\Psi$ in terms of component concentrations, thus:

$$\frac{dx}{d\Psi}=\frac{z_1(z_1-z_2)c_1+(1+z_2)c_5}{j_1z_1+j_2z_2}. \tag{19}$$

Substituting (19) into Eqs. (12) and (18) and changing to the new independent variable Ψ, we obtain a system of two linear first-order equations for c_1 and c_5. We shall seek a solution of this system in the form of $c \sim \exp(\lambda\Psi)$. The resulting equation for the characteristic values λ has simple solutions; one of them is unity, the other

$$\lambda = -\frac{z_1 z_2 (1+J)}{z_1 + z_2 J}, \tag{20}$$

where $J = \nu j_2/j_1$ is the flux ratio of the second and first kind of cations. The profiles of concentrations c_1 and c_5 can be found as linear combinations of the exponentials obtained. Allowing for boundary conditions (10) we can write them as

$$c_5 = (z_1 + kz_2) e^{\Psi}. \tag{21}$$

$$c_1 = \frac{(1+z_2)(z_1+kz_2)e^{\Psi} + z_2[J(z_1+1) - k(z_2+1)]e^{\lambda\Psi}}{z_1(z_2+1) - z_2 J(1+z_1)} \tag{22}$$

Concentration c_2 can now be found from (21) and (22) and the electroneutrality condition (16). Thus, c_1, c_2, and c_5 have been determined as functions of potential Ψ.

To find these concentrations as functions of coordinate x we must write the latter in terms of potential Ψ. Substituting (21) and (22) into (19) we obtain

$$\frac{dx}{d\Psi} = \frac{1}{j_1}(Ae^{\Psi} + B\lambda e^{\lambda\Psi}), \tag{23}$$

where A and B are constants which are independent of Ψ and x:

$$A = \frac{(z_1+kz_2)(1+z_1)(1+z_2)}{z_1(z_2+1) - z_2 J(z_1+1)}, \tag{24}$$

$$B = \frac{(z_1-z_2)[k(z_2+1) - J(z_1+1)]}{(1+J)[z_1(1+z_2) - Jz_2(1+z_1)]}. \tag{25}$$

Integrating (23) while allowing for the boundary condition (10) we can define the implicit coordinate dependence of potential as

$$x - 1 = \frac{1}{j_1}[A(e^{\Psi} - 1) + B(e^{\lambda\Psi} - 1)]. \tag{26}$$

We change to the independent variable Ψ in (14) in order to find the individual distributions of concentrations c_3 and c_4 (not merely that of their sum, c_5). Substituting (23) into (14) and integrating while allowing for (10) we obtain

$$c_3 = e^{\Psi}\left\{(z_1+kz_2) + A\Psi - B\frac{\lambda}{\lambda-1}[1 - e^{(\lambda-1)\Psi}]\right\} \tag{27}$$

The expression for c_4 is obtained from (17), (27). and (21). Thus, through the parameter Ψ concentrations c_1, c_2, c_3, and c_4 were found as parametric functions of coordinate x for arbitrary values of currents j_1 and j_2.

We shall now analyze the limitations imposed upon currents j_1 and j_2 because of the possibility that the concentrations of individual solution components become zero at the electrode. Setting $x = 0$ in (26) we find an equation which defines the value of potential, Ψ_0, at the electrode:

$$j_1 = A(1 - e^{\Psi_0}) + B(1 - e^{\lambda\Psi_0}). \tag{28}$$

Under the condition of $c_1(x=0) = 0$ which corresponds to the partial limiting current with respect to the metal ions, and eliminating Ψ_0 with the aid of (22) and (28), we find a relation linking quantities $j_1^{(1)}$ and J:

$$j_1^{(1)} = \frac{1}{1+J}\left\{(z_1+1) + k(z_2+1) - (z_1+kz_2)\left(\frac{1+z_2}{z_2}\right) \times \right. \\ \left. \times \left[\frac{k(z_2+1) - J(z_1+1)}{(z_2+1)(z_1+kz_2)}\right]\left[\frac{z_1+z_2 J}{z_1+z_2 J+z_1 z_2(1+J)}\right]\right\}. \tag{29}$$

Here and in the following, the superscripts in $j_1^{(i)}$ and $j_2^{(i)}$ indicate that the current is defined for the condition of $c_i(0) = 0$. The link between the currents in the case where the condition of $c_2(0) = 0$ is realized at the electrode can be obtained in a similar way:

$$j_1^{(2)} = \frac{1}{1+J}\left\{ (z_1+1)+k(z_2+1)-(z_1+kz_2)\left(\frac{1+z_1}{z_1}\right)\times \right.$$
$$\left. \times\left[\frac{z_1(J(z_1+1)-k(z_2+1)}{J(z_1+1)(z_1+kz_2)}\right]\left[\frac{z_1+z_2J}{z_1+z_2J+z_1z_2(1+J)}\right]\right\}. \tag{30}$$

It follows from (27) that the condition of $c_3(0) = 0$ leads to the following link between J and Ψ_0:

$$(z_1+kz_2)\nu/J+A\Psi_0-B\frac{\lambda}{\lambda-1}[e^{(\lambda-1)\Psi_0}-1]=0, \tag{31}$$

which generally does not admit an analytical expression for Ψ_0 in terms of J. After finding Ψ_0 from this equation by numerical solutions for given values of parameter J we can calculate the current $j_1^{(3)}$ from (28).

Finally consider the limitations imposed upon the currents through the condition of $c_4(x=0) = 0$. In this case concentration c_4 near the electrode should be a rising function, i.e., it should have a positive derivative ($dc_4/dx\,|_{x\to 0} > 0$). The quantity on the right-hand side of (15) will be negative because j_2 is positive. This is feasible only when the migration term in (15) always remains an essentially negative quantity, which for $c_4 \to 0$ is possible only when $d\Psi/dx \to +\infty$. It is easy to see that the latter condition can be satisfied only when in addition to $c_4 \to 0$ all other concentrations (c_1, c_2, and c_3) become zero at the electrode at the same time and $\Psi \to -\infty$. Therefore, relative to the limitations already discussed, the condition of $c_4(0) \geq 0$ imposes no additional limitations on the limiting currents in the system.

We point out that relations (23) to (26) had been obtained in [3] in a slightly different form, while relations (29) and (30) have been reported in [3]* in the form of an implicit connection between j_1 and j_2 which, for the construction of functions $j_1^{(1,2)}(j_2^{(1,2)})$, would require numerical solution of the equations for $j_1^{(1,2)}$ at a number of fixed values of $j_2^{(1,2)}$. In the present work we use a parametric specification of these functions in terms of the independent parameter J, viz., $j_1^{(1,2)} = j_1^{(1,2)}(J)$ and $j_2^{(1,2)} = J/\nu \cdot j_1^{(1,2)}(J)$, allowing these curves to be constructed directly.

Curves of $j_1^{(i)}(j_2^{(i)})$ corresponding to the conditions of $c_i(0) = 0$ and i = 1, 2, 3 are shown in Fig. 1 for a number of values of the dimensionless parameters employed.

The curve $j_1^{(1)}(j_2^{(1)})$ starts at $j_2^{(1)} = 0$ from a point N corresponding to the generalized Eucken relation for the case of arbitrary ionic charge [6], and ends at point Q with the coordinates $j_1 = z_1 + I$, $j_2 = (z_2 + 1)k/\nu$ where it is joined by the analogous curve of $j_1^{(2)}(j_2^{(2)})$ issuing from point M. Here the curves $j_1^{(1)}(j_2^{(1)})$ can either rise (Fig. **la**) or have a minimum, and point Q can be located, both above (Fig. lb) and below (Fig. Id) the point N. Explorations showed that point Q will be below point N under the conditions of

$$k > \frac{z_1}{z_2}(z_2^{1/z_1}-1)^{-1}, \quad z_2>1. \tag{32}$$

We point out that in [3] only the possibility of a monotonic rise of $j_1^{(1)}(j_2^{(1)})$ was described.

The behavior of function $j_1^{(3)}(j_2^{(3)})$ proved to be not at all trivial. Plots of this function have two branches separated by a cusp W. Point W generally can be located, both above (Figs. la and Ic) and below (Fig. Ib) the line of $j_1^{(1)}(j_2^{(1)})$. Then curves $j_1^{(1)}(j_2^{(1)})$ and $j_1^{(3)}(j_2^{(3)})$ either have two points of intersection or they do not intersect. Point R of intersection of the curve $j_1^{(3)}(j_2^{(3)})$ with the horizontal axis of j_2 can be further to the left (Figs. 1*b* and 1*c*) and further to the right (Fig. la) of the point M where curve $j_1^{(2)}(j_2^{(2)})$ intersects with the axis of j_2, so that curves $j_1^{(3)}(j_2^{(3)})$ and $j_1^{(2)}(j_2^{(2)})$ either intersect in a single point or they do not intersect. Finally, for $\Psi_0 \to -\infty$ all three curves of $j_1^{(i)}(j_2^{(i)})$ merge in point Q, while it can be shown that curve $j_1^{(3)}(j_2^{(3)})$ is below the curve $j_1^{(1)}(j_2^{(1)})$ but above the curve of $J = k(z_2 + 1)/(z_1 + 1)$.

Values of currents j_1 and j_2 which satisfy the conditions of $c_i(0) \geq 0$ are those in region I of Figs. 1a and 1*c* including the coordinate origin, and in addition those in region *II*. When point W is below the curve $j_1^{(1)}(j_2^{(1)})$ (Fig. 1*b*), the resulting region of physically realizable currents is simply connected. The additional region *II* which arises when W is located above the curve $j_1^{(1)}(j_2^{(1)})$ is physically realizable in principle but cannot be reached by gradually increasing the currents j_1 and j_2 starting from zero; it can only be reached from a transient state.

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*we point out that in the relations of [3] which correspond to relations (24) to (26) and (29) of the present work, misprints exist in the symbols for the indices of charge which are eliminated in the present paper.

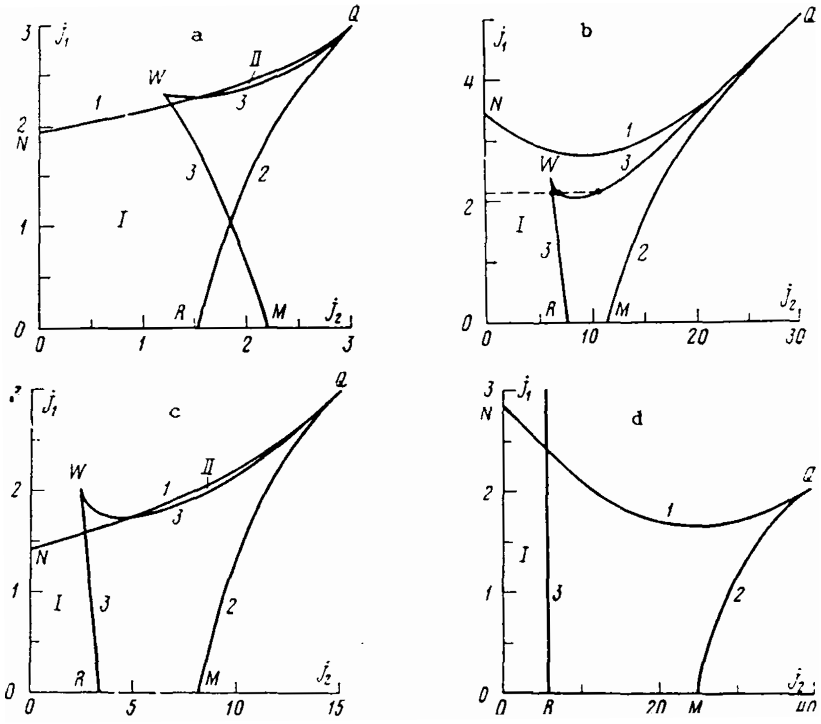

Fig. 1. Situation of curves $j_1^{(i)}(j_2^{(i)})$ in the plane (j_2, j_1) in the case of $\nu = 0.2$: I) $j_1^{(1)}(j_2^{(1)})$, 2) $j_1^{(2)}(j_2^{(2)})$, 3) $j_1^{(3)}(j_2^{(3)})$; (a) $z_1 = 2$, $z_2 = 1$, k = 0.3; (b) $z_1 = 4$, $z_2 = 2$, $k = 2$; (c) $z_1 = 2$, $z_2 = 1$, $k = 2$; and (d) $z_1 = 1$, $z_2 = 2$, k = 2.5.

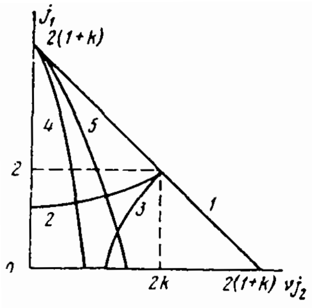

Fig. 2. Relative positions of curves in the plane $(j_1$, uj,): I) curve corresponding to (42), 2) curve corresponding to (39), 3) curve corresponding to (40). 4) curve corresponding to (41) when inequality (43) holds, and 5) curve corresponding to (41) when inequality (43) does not hold.

In the case of $z_1 < z_2$ the relative disposition of curves $j_1^{(i)}(j_2^{(i)})$ is as shown in Fig. 1*d*. Here curve $j_1^{(3)}(j_2^{(3)})$ has a single branch issuing from the point *R*, and asymptotically approaches to the axis of j_1. We notice that for $z_1 < z_2$, again cases are possible where the point R is located further to the right or left of point M, and where point Q can be located above or below the point N.

In conclusion, we shall discuss the chief results of the above investigation. When cation reduction occurs as the only process at the electrode and $j_2 = 0$, the condition of $c_1(0) \geq 0$ defines the region of discharge currents $j_1 \leq j_1^{(1)}(j_2{=}0)$ which is physically realizable, i.e.. the current should be smaller than or equal to the limiting diffusion and migration current. When anion reduction according to scheme (4) is the only process that is realized at the electrode and $j_1 = 0$, the physically realizable values of current are determined by the conditions of $c_2(0) \geq 0$ and $c_3(0) \geq 0$ (exploration showed that the condition of $c_4(0) \geq 0$ does not give rise to any additional limitations). Depending on the values of parameters u, k, $\overline{z}_1$, $\overline{z}_2$, and $\overline{z}_3$, a limitation of the current of process (4) in the absence of process (3) is possible, either on account of the condition of $c_2(0) = 0$ or on account of the condition of $c_3(0) = 0$. In the first case concentration $c_2(0)$ decreases with increasing current, and at $c_2(0) = 0$ we have $c_3(0) > 0$ and $j_2 = j_2^{(2)}$. In the second case the decrease in concentration $c_3(0)$ is faster than the increase in current j_2, and at $c_3(0) = 0$ we have $c_2(0) > 0$ and $j_2 = j_2^{(3)}$.

The situation regarding the values of currents which are accessible becomes much more complicated when processes 73) and (4) occur simultaneously, which is due to the mutual influence produced by migration of the components. It can be said in general that the region of accessible currents in the plane of (j_2, j_1) is defined by the set of conditions $c_i(0, j_1, j_2) \geq 0$. The above investigation has shown that this region can be simply or multiply connected, i.e., it can consist of two (or more) nonoverlapping regions.

Curves $j_1^{(i)}(j_2^{(i)})$ which correspond to the links between the currents of processes (3) and (4) under conditions where $c_i(0) = 0$ and constitute the boundaries of the region of physically realizable currents can have falling and rising sections. These sections can be interpreted as a manifestation of local "depression" and local "exaltation" of the migration current when the limiting value of one of the currents decreases or increases because the other current has been increased.

We point out that owing to the complex behavior of curve $j_1^{(3)}(j_2^{(3)})$, three values of the limiting current for process (4) may exist in the system within a certain region of prelimiting currents j_1 for process (3) (the dashed line in Fig. Ib). This is due to the fact that concentration $c_3(0)$ when considered as a function of current j_2 at fixed values of the current j_1 has nonmonotonic behavior. One of the possible values of the limiting current $j_2^{(3)}$ (the central one) can be attained only when coming from higher currents, which is quite unexpected.

Thus, the above analysis has shown that depending on the parameters involved, effects of an exaltation or depression of the migration current may be displayed when processes (3) and (4) occur in parallel.

In conclusion we wish to discuss the particular case of $z_1 = z_2$ where B = 0. Equation (31) for Ψ_0 has a single root $\Psi_0 = -AJ/\nu(z_1 + kz_2)$, from which upon substitution into (28) one can find an explicit parametric expression for $j_1^{(3)}$.

Moreover, in cases where all ions have the same charge one can find the distributions of all concentrations, directly from (12) to (16). Combining (12) to (15) and integrating while allowing for (16) we obtain for $c_3 + c_4$:

$$c_3+c_4=(1+k)y, \tag{33}$$

where $y = 1 + (j_1 + \nu j_2)(x - 1)/(2 + 2k) \geq 0$ is a linear function of x. With the aid of (18) we hence find $d\Psi/dx$:

$$d\Psi/dx=\ln y. \tag{34}$$

Substituting (34) into Eqs. (12) to (15) we can integrate the linear Eqs. (12) to (15), and obtain the concentration distributions $c_i(X)$, with i = 1 to 4, in an explicit form:

$$c_1(x)=[j_1(x-1)(1+y)/2+1]/y, \tag{35}$$

$$c_2(x)=[\nu j_2(x-1)(1+y)/2+k]/y, \tag{36}$$

$$c_3(x)=[2(1+k)\ln y/(\nu+j_1/j_2)+1+k]y, \tag{37}$$

$$c_4(x)=-2y(1+k)\ln y/(\nu+j_1/j_2). \tag{38}$$

Setting $c_i = 0$ for $x = 0$ in (35) to (37) we obtain expressions for the corresponding partial currents:

$$j_1^{(1)}=2(1+k)+\nu j_2^{(1)}/2+[(2+2k+\nu j_2^{(1)})^2-4(1+k)]^{1/2}, \tag{39}$$

$$\nu j_2^{(2)}=2(1+k)-j_1^{(2)}/2-[(2+2k-j_1^{(2)}/2)^2-4k(1+k)]^{1/2}, \tag{40}$$

$$2\ln[1-(j_1^{(3)}+\nu j_2^{(3)})/(2+2k)]=-j_1^{(3)}/j_2^{(3)}-\nu. \tag{41}$$

The function $j_1^{(3)}(\nu j_2^{(3)})$ defined by relation (41) is shown in Fig. 2. For $j_2 = 0$, curve $j_1^{(3)}(\nu j_2^{(3)})$ issues from the point of $j_1 = 2(1 + k)$ tangent to the straight line

$$j_1+\nu j_2=2(1+k). \tag{42}$$

At $j_1 = 0$, the curve $j_1^{(3)}(\nu j_2^{(3)})$ terminates in the point $\nu j_2 = 2(1 + k)[1 - \exp(-\nu/2)]$. This point can be located, both to the left and to the right of the point $\nu j_2 = 2(1 + k) - 2\sqrt{(1 + k)}$ from which issues the curve (40). In the former case, which is realized when

$$1+k>\exp\nu, \tag{43}$$

curves (40) and (41) do not intersect, and the joint reduction of anions and metal cations can be limited only via conditions (39) and (41). In the second case when a condition which is the opposite of (43) holds true, curves (40) and (41) intersect and three possibilities exist for limitations of the resultant process, which correspond to the conditions (39) to (41). The maximum current of metal ion reduction is always found when conditions (40) and (41) are fulfilled simultaneously.

We notice that the left-hand side of inequality (43) depends through the parameter k on solution composition only, while the right-hand side through the parameter ν depends, both on the stoichiometry of reduction reaction (4) and on the ratio of diffusion coefficients of the anions and cations.

Thus, the maximum partial current of metal electrodeposition is between a lowest value of $j_1 = 2(1 + k) - 2\sqrt{[(1 + k)k]}$ and a highest value of $j_1 = 2$. This result arises from the joint effects of a lowering of the limiting current of metal ion reduction which occurs when a second kind of cations are added to the system, and of a correlational exaltation of the migration current [2, 4] which leads to a higher limiting current of cation reduction.

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