

*The electrodiffusion problem is solved for the case where metal cations are reduced in parallel with anions. hydrogen ions are involved in reduction of the anions, and ionic charge is arbitrary. The resulting behavior of the limiting diffusion and migration current includes both a depression of migration, caused by the addition of acid to the solution, and an enhancement of migration caused by correlational exaltation of the migration current. The "totally" limiting currents are calculated as functions of the stoichiometric coefficients, the solution composition, and the diffusion coefficients of the ionic components.*

When several electrode reactions occur in parallel in a system lacking base electrolyte, they influence each other. Examples of such an influence are the migration-current exaltation observed when cations and a neutral substance are reduced at the same time [1-3], and the correlational exaltation of migration currents displayed when several types of cations undergo parallel reduction in processes of the same type [2, 4].

In the present work a general approach is developed which allows the mutual influence of metal electrodeposition and anion reduction to be analyzed in systems where the ions carry arbitrary charge.

Consider the case where reduction of metal cations



occurs in parallel with a process of reduction of anions  $A_3^{z_3-}$  which involves cations  $A_2^{z_2+}$ :



where  $n_2$  and  $n_3$  are the corresponding stoichiometric coefficients,  $z_1$ ,  $z_2$ , and  $z_3$  are the ionic charges, and  $\Sigma B_i$  denotes the set of neutral products of reaction (2). We shall limit the present analysis to processes of the type of (2) where the products are neutral, and the solution contains two types of cations and one type of anions. Examples of such reactions occurring in acidified nitrate solutions in copper electrodeposition have been reported in [5].

The system of electrodiffusion equations describing reduction of metal cations (1) and the parallel reduction of anions which follows the scheme of (2) involving cations, is given by

$$\frac{dc_1}{dx} + z_1 c_1 \frac{F}{RT} \frac{d\Phi}{dx} = \frac{i_1 L}{z_1 F D_1 c_1^0} = j_1 \quad (3)$$

$$\frac{dc_2}{dx} + z_2 c_2 \frac{F}{RT} \frac{d\Phi}{dx} = \frac{n_2}{n_2 z_2 - n_3 z_3} \frac{i_2 L}{F D_2 c_1^0} = v j_2 \quad (4)$$

$$\frac{dc_3}{dx} - z_3 c_3 \frac{F}{RT} \frac{d\Phi}{dx} = \frac{n_3}{n_2 z_2 - n_3 z_3} \frac{i_2 L}{F D_3 c_1^0} = j_2 \quad (5)$$

$$z_3 c_3 = z_1 c_1 + z_2 c_2 \quad (6)$$

Here  $c_1$ ,  $c_2$ , and  $c_3$  are the concentrations of cations  $A^{z_1+}$ , cations  $A^{z_2+}$ , and anions  $A^{z_3-}$ , respectively, which have been made dimensionless through the concentration  $c_1^0$  of cations  $A^{z_1+}$  in the solution,  $D_i$  are the corresponding diffusion

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coefficients,  $\Phi$  is the electric potential,  $F$  is the Faraday constant,  $R$  is the gas constant,  $T$  is the absolute temperature,  $x$  is the dimensionless coordinate ( $0 < x < 1$ ),  $L$  is the thickness of the Nernst diffusion layer,  $i_1$  and  $i_2$  are the current densities of reactions (1) and (2), respectively, and  $\nu = n_2 D_3 / n_3 D_2$ . We point out that quantities  $j_1$ ,  $j_2$ , and  $\nu j_2$  are positive since the fluxes of all three sorts of ion are toward the electrode. Equation (6) is a statement of the condition of local electroneutrality. At the limits of the diffusion layer ( $x = 1$ ) the values of potential and component concentrations are given as

$$c_1(1) = 1, \quad c_2(1) = k, \quad c_3(1) = Z_1 + kZ_2, \quad \Phi(1) = 0. \quad (7)$$

where  $k = c_2^0 / c_1^0$  is the dimensionless concentration of ions  $A_2^{z_2+}$  in the bulk solution, and for a more convenient formulation relative ionic charges  $Z_1 = z_1 / z_3$  and  $Z_2 = z_2 / z_3$  have been introduced.

In the electrochemical system being considered, a "partial" limiting current with respect to the metal ions can be realized, which corresponds to the condition of  $c_1(0) = 0$ , or a "partial" limiting current with respect to the cations involved in parallel reaction (2) which corresponds to the condition of  $c_2(0) = 0$ . It follows from (6) that a limiting current with respect to the anions being discharged can exist only when all three concentrations tend toward zero at the electrode, i.e., when  $c_1(0) = c_2(0) = c_3(0) = 0$ . This state of a "totally" limiting current is associated with particular values of ionic fluxes  $j_1$  and  $j_2$ .

It is the aim of the present investigation to find the distributions of concentrations, potential, and ionic fluxes under the conditions of a totally limiting current.

Combining Eqs. (3) to (6) and integrating while allowing for boundary conditions (7), we obtain

$$c_1(x) + c_2(x) + c_3(x) = [j_1 + j_2(\nu + 1)](x - 1) + 1 + k + Z_1 + Z_2 k. \quad (8)$$

For  $x = 0$  it follows from expressions (8) and (6) that

$$j_2 = \frac{(1 + Z_1)(1 - f_1) + (1 + Z_2)(k - f_2)}{1 + J + \nu}, \quad (9)$$

where  $J = j_1 / j_2$  is the flux ratio,  $f_1 = c_1(0)$  and  $f_2 = c_2(0)$  are the notation for the cation concentrations at the electrode. One must set  $f_1 = 0$  in (9) and find  $f_2$  as a function of parameter  $J$  in order to calculate flux  $j_2$  under the conditions of the limiting current with respect to metal cations. The state of the totally limiting current corresponds to conditions of  $f_1 = f_2 = 0$  and to some particular value of  $J$ .

Multiplying Eq. (3) by  $z_1$ , Eq. (4) by  $z_2$ , and Eq. (5) by  $-z_3$ , adding, and allowing for (6) we obtain an expression for the dimensionless electric field strength,  $-E = d\Psi/dx$ :

$$\frac{d\Psi}{dx} = \frac{j_2 \beta}{c_1 + \alpha c_2}, \quad (10)$$

where  $\Psi = z_3 F \Phi / RT$  is the dimensionless potential, and the following notation for combinations of parameters has been introduced:

$$\alpha = \frac{Z_2 Z_2 + 1}{Z_1 Z_1 + 1} > 0, \quad (11)$$

$$\beta = \frac{J}{Z_1 + 1} + \frac{Z_2 \nu - 1}{Z_1(Z_1 + 1)} \quad (12)$$

It follows from (10) and (12) that quantity  $\beta$ , and thus also quantity  $d\Psi/dx$ , at  $Z_2 \nu < 1$  can assume both positive and negative values.

We change to the new independent variable  $\Psi$  in Eqs. (3) and (5). and substitute  $dx/d\Psi$  from (10):

$$\frac{dc_1}{d\Psi} + Z_1 c_1 = \frac{J}{\beta} (c_1 + \alpha c_2), \quad (13)$$

$$\frac{dc_2}{d\Psi} + Z_2 c_2 = \frac{\nu}{\beta} (c_1 + \alpha c_2). \quad (14)$$

An equation for  $c_3$  need not be included in this system since it is obtained as a result of (13), (14) and (6), (10). We shall seek the solution of Eqs. (13) and (14) in the form of  $\exp(\lambda\Psi)$ ; this corresponds to a characteristic equation for the eigenvalues  $\lambda$  given by

$$\beta\lambda^2 + \lambda[(Z_1 + Z_2)\beta - J - \nu\alpha] - (1 + J + \nu)Z_2/(Z_1 + 1) = 0. \quad (15)$$

The absolute term in Eq. (15) is always negative; therefore, at  $\beta > 0$  the equation has two roots differing in sign. For an exploration of the case of  $\beta < 0$  we rewrite the characteristic Eq. (15) with (12) as

$$\lambda^2(1-b) + \lambda(b-a+Z_1+Z_2) + (Z_1Z_2+a) = 0, \quad (16)$$

where

$$b = JZ_1 + \nu Z_2, \quad a = (J + \nu)Z_1Z_2. \quad (17)$$

It is readily seen from (12) that the condition of  $\beta < 0$  is equivalent to the condition of

$$0 < b < 1, \quad (18)$$

while from (17) and (18) we can obtain the limits imposed on  $a$ :

$$0 < a < b \cdot \max(Z_1, Z_2). \quad (19)$$

Considering  $J$  and  $\nu$ ,  $Z_1$ , and  $Z_2$  as formal, positive parameters we notice that (16) and (17) are symmetric with respect to a simultaneous change of variables:  $Z_1 = Z_2$ ,  $\nu = J$ . Therefore, it will suffice to examine the case of  $Z_1 > Z_2$  in order to demonstrate that the discriminant is positive. The discriminant of Eq. (16) can be written as

$$D = (b-a+Z_1+Z_2)^2 - 4(Z_1Z_2+a)(1-b) = (a+b-Z_1+Z_2)^2 + 4(Z_2+1)(bZ_1-a). \quad (20)$$

The last term in parentheses in (20) is nonnegative because of condition (19), hence the entire discriminant is nonnegative. It is easy to show that the discriminant becomes zero only under the condition of  $J = \sigma = 0$ , where

$$\sigma = Z_2\nu(Z_1+1) + Z_2 - Z_1. \quad (21)$$

It also follows from (18) and (19) that  $a < Z_1 + Z_2$ . Hence all coefficients of Eq. (16) are positive. Therefore, characteristic Eq. (16) has always two negative roots when  $\beta < 0$ :

$$\lambda_1 = \frac{-(b-a+Z_1+Z_2) + \sqrt{D}}{2(1-b)}, \quad \lambda_2 = \frac{-(b-a+Z_1+Z_2) - \sqrt{D}}{2(1-b)} \quad (22)$$

For  $\beta > 0$  the quantities  $\lambda_1$  and  $\lambda_2$  satisfy inequalities  $\lambda_2 > 0 > \lambda_1$ . The case of  $\beta = 0$  corresponds to  $d\Psi/dx \equiv 0$ , which implies that there is no migrational transport in the system.

We shall write the concentrations in a form which will satisfy the boundary conditions (7) for  $x = 1$ :

$$c_1 = g_1 e^{\lambda_1 \Psi} + (1-g_1) e^{\lambda_2 \Psi}, \quad (23)$$

$$c_2 = g_2 e^{\lambda_1 \Psi} + (k-g_2) e^{\lambda_2 \Psi}. \quad (24)$$

Substituting (23) and (24) into (13) or (14) and equating the coefficients of the corresponding exponentials to the left and right of the resulting equation we obtain a linear system for  $g_1$  and  $g_2$  which has the solution:

$$g_1 = \frac{\lambda_2 \beta + Z_1 \beta - J - k \alpha J}{\beta(\lambda_2 - \lambda_1)}, \quad g_2 = \frac{\lambda_2 \beta k + Z_2 \beta k - \nu - k \alpha \nu}{\beta(\lambda_2 - \lambda_1)} \quad (25)$$

Thus, expressions (23) and (24) with values substituted from (17), (22), and (25) yield the distributions of concentrations  $c_1$ , and  $c_2$  (and via the condition of electroneutrality, also that of concentration  $c_3$ ) as functions of  $\Psi$ . Substituting (23) and (24) into (10) and integrating we can obtain an expression for  $x(\Psi)$  which, together with (23) and (24), parametrically specifies concentrations  $c_1$  and  $c_2$  as functions of the coordinate.

Let us now discuss the possible limiting-current modes in the system being examined. Concentrations  $c_1(0)$  and  $c_2(0)$  at the electrode are given by the relations

$$f_1 = g_1 e^{\lambda_1 \Psi_0} + (1 - g_1) e^{\lambda_2 \Psi_0}, \quad (26)$$

$$f_2 = g_2 e^{\lambda_1 \Psi_0} + (k - g_2) e^{\lambda_2 \Psi_0}, \quad (27)$$

where  $\Psi_0$  is the dimensionless potential drop across the diffusion layer.

In the mode of limiting current with respect to the first kind of cations we have  $f_1 = 0$ , and we obtain from (26) and (27):

$$f_2 = \left( \frac{g_1}{g_1 - 1} \right)^{\lambda_1 / (\lambda_2 - \lambda_1)} \left[ g_2 - (g_2 - k) \frac{g_1}{g_1 - 1} \right]. \quad (28)$$

Substituting  $f_1 = 0$  and (28) into expression (9) we obtain the explicit function  $j_2 = j_2^1(J)$  which, together with  $j_1 = Jj_2$ , parametrically defines the function  $j_2 = j_2^1(j_1^1)$  for  $f_1 = 0$ .

Similarly, when the limiting current with respect to the second kind of cations is attained we have  $f_2 = 0$ , and  $f_1$  is given by the expression

$$f_1 = \left( \frac{g_2}{g_2 - 1} \right)^{\lambda_1 / (\lambda_2 - \lambda_1)} \left[ g_1 - (g_1 - 1) \frac{g_2}{g_2 - k} \right]. \quad (29)$$

Moreover, from (9) we obtain the parametric connection of the currents,  $j_2^2 = j_2^2(j_1^2)$ . The superscripts in  $j_1^i$  and  $j_2^i$  imply currents limited by the  $i$ -th component.

The above functions and the coordinate axes define in the plane ( $j_1 > 0$ ,  $j_2 > 0$ ) a closed region within which each point ( $j_1$ ,  $j_2$ ) corresponds to a particular state of the electrochemical system. Consider in more detail the points of intersection of the curves  $j_2^1(j_1^1)$  and  $j_2^2(j_1^2)$  with the coordinate axes  $j_1 = 0$  and  $j_2 = 0$ , i.e., the limiting currents attained when one of the electrode reactions is missing.

Suppose that  $j_1 = 0$  or  $J = 0$ . Then it is easy to find the roots of the characteristic equation of system (13), (14), and solutions for the concentration profiles which satisfy the boundary conditions (7) for  $x = 1$  can be written down as

$$c_1 = \exp(-Z_1 \Psi), \quad (30)$$

$$c_2 = g_0 \exp(-Z_1 \Psi) + (k - g_0) \exp \left[ - \frac{Z_2(v+1)\Psi}{1 - Z_2 v} \right]. \quad (31)$$

Constant  $g_0$  can be found when substituting (30) and (31) into (14):

$$g_0 = -v(Z_1^2 + Z_1) / \sigma. \quad (32)$$

It is obvious from expression (30) that inequality  $c_1 > 0$  is strictly valid for all finite  $\Psi$ , i.e., a partial limiting current with respect to only the second kind of ions can exist:  $c_2(x=0) = 0$ . After finding the potential drop  $\Psi_0$  from this condition with the aid of (31), and substituting it into (30), we obtain the value of  $f_1$ , and hence can immediately calculate  $j_2^2(0)$  with the aid of (9).

Let us define the conditions under which all concentrations will become zero at the electrode while  $\Psi \rightarrow \infty$ . A necessary condition for this situation is a positive coefficient for the leading exponential in (31) (this is the exponential in which the exponent has the smaller absolute value). For  $\sigma > 0$  the first exponential in (31) falls off more slowly than the second, which implies that its coefficient ought to be positive, which is in contrast with (32). For  $\sigma < 0$ , to the contrary, the second exponential falls off more slowly, and hence the condition of  $g_0 < k$  should be satisfied.

Thus, in this specific case of a totally limiting current (where  $j_1^{12} = 0$ ), we obtain from (9) an expression for  $j_2^{12}$ :

$$j_2^{12} = (1 + Z_1 + k + kZ_2) / (1 + v), \quad j_1^{12} = 0. \quad (33)$$

We shall now analyze the limiting currents in the case of  $j_2 = 0$ . In this case only metal electrodeposition occurs. From Eqs. (4) and (5) and boundary conditions (6) we immediately find the distributions of the electroactive ions:  $c_2 = k \exp(-Z_2 \Psi)$  and  $c_3 = (Z_1 + Z_2 k) \exp \Psi$ . Function  $c_1(\Psi)$  can then be obtained with the aid of electroneutrality condition (6). After manipulations analogous to those reported above, we can find  $j_1^1(j_2=0)$  in the mode of a limiting current with respect to cations, of  $c_1(0) = 0$ . The function  $j_1^1(k)$  corresponds to the Eucken relation generalized to the case of ions of arbitrary charge [6, 7]. In the expressions reported above, the exponents in the exponential terms have different signs; therefore, a totally limiting current cannot be realized when  $j_2 = 0$ .

Let us now find the values of fluxes  $j_1^{12}$  and  $j_2^{12}$  in the mode of a totally limiting current, of  $f_1 \rightarrow 0$  and  $f_2 \rightarrow 0$ . Setting  $f_1 = 0$  in relation (29) we find that the expressions in the first or second set of parentheses on the right-hand side

should be zero. Suppose that  $\beta < 0$ , and the first expression in parentheses is zero. Then the exponent  $\lambda_1/(\lambda_2 - \lambda_1)$  is a positive number, since  $\lambda_2 < \lambda_1 < 0$ , and hence  $g_2 = 0$ . However,  $f_2$  which is given by relation (28) also becomes zero, so that we can conclude that  $g_1 = 0$ . Therefore, the expressions in the second sets of parentheses in (28) and (29) are practically always zero. We readily see from (23) and (24) that this implies that  $c_1$  and  $c_2$  are mutually proportional, and since because of the condition of electroneutrality  $c_3$  is a linear combination of  $c_1$  and  $c_2$ , concentration  $c_3$  is also proportional to  $c_1$ . Hence from expression (8) we obtain the linear concentration profiles which, in the mode of the totally limiting current, can be written as

$$c_1 = x, \quad c_2 = kx, \quad c_3 = (Z_1 + kZ_2)x. \quad (34)$$

In the case of  $\beta > 0$ , eigenvalues  $\lambda_1$  and  $\lambda_2$  have different signs, so that in the mode of the totally limiting current only the exponential term with a negative exponent need be retained in the solution (23), (24). This also leads to proportionality of  $c_1$  and  $c_2$ , and yields (34). For  $\beta = 0$ , finally, solutions (34) follow directly from (3) to (5).

Substituting (34) into (10) we have

$$\frac{d\Psi}{dx} = \frac{j_2\beta}{x(1+\alpha k)}. \quad (35)$$

After substituting (34), (35) into (3) and (5) we obtain a system of two linear equations for  $j_1$  and  $j_2$ ; the solution of this system yields the values of the fluxes under the conditions of the totally limiting current:

$$j_1^{12} = \frac{Z_2\nu(Z_1+1) + Z_2 - Z_1 + \nu Z_1(Z_1+1)/k}{Z_2(1+\nu) + \nu Z_1/k}, \quad (36)$$

$$j_2^{12} = \frac{(Z_2+1) + (Z_1+Z_2)k}{Z_2(1+\nu) + \nu Z_1/k}. \quad (37)$$

The condition under which solutions (36), (37) exist is a positive numerator in (36), which is equivalent to  $g_0 > k$  ( $g_0$  is a combination of constants  $Z_1$ ,  $Z_2$ , and  $\nu$  defined by relations (32) and (21)).

Thus, depending on the relative values of parameters  $g_0$  and  $k$ , values  $j_1^{12}$  and  $j_2^{12}$  are given either by expressions (33) or by expressions (36), (37). Under the conditions of a totally limiting current, the concentration profiles can be linear functions (34) (when  $g_0 > k$ ) or nonlinear functions (when  $g_0 < k$ ). In the latter case, moreover, the inequality of  $c_1 \ll c_2, c_3$  holds at  $x \ll 1$ .

We stress that a situation is possible where reaction (1) cannot occur owing to diffusion, migration, and stoichiometric limitations while reaction (2) proceeds relatively vigorously. According to the above relations (36) and (37), when the concentration of the second kind of cations ( $A_2^{z_2+}$ ) increases while that of the first kind of cations ( $A_1^{z_1+}$ ) remains unchanged, current  $j_1$  will experience a depression. For instance, when ions of the second sort are not present in the system we have  $k = 0$  and (36) yields

$$j_1^{12}|_{k=0} = 1 + Z_1, \quad (38)$$

which is the result known for binary solutions. When there is an excess of cations of the second kind we have  $k \rightarrow \infty$ , and the current tends toward the value of

$$j_1^{12}|_{k \rightarrow \infty} = 1 + Z_1 - Z_1(1 + 1/Z_2)/(1 + \nu). \quad (39)$$

which is lower than the value defined by relation (38).

We shall now apply the results obtained to one of the possible  $\text{NO}_3^-$  reduction reactions during copper electrodeposition from nitrate solutions [5]:



For these reactions  $z_1 = 2$ ,  $z_2 = z_3 = 1$ ,  $n_2 = 3$ ,  $n_3 = 1$ ,  $D_{\text{NO}_3^-} = 1.92 \cdot 10^{-5} \text{ cm}^2/\text{s}$ , and  $D_{\text{H}^+} = 9.34 \cdot 10^{-5} \text{ cm}^2/\text{s}$ , whence  $\nu = 0.617$ . Under the conditions of the totally limiting current, the concentration profiles are linear functions of the type of (34), and the dimensionless fluxes are given by the relations:

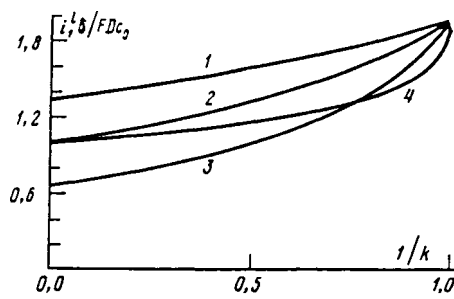


Fig. 1. Limiting currents of metal deposition,  $j_1^{12}$ , as functions of solution composition according to relation (48) with  $z_1 = z_2 = z_3 = 1$  and the following values of parameter  $\nu$ : 1)  $\nu > 1$ , 2)  $\nu = 1$ , and 3)  $\nu < 1$ . Curve 4 corresponds to relation (51).

$$j_1^{12} = (0.85k + 3.7) / (1.617k + 1.23), \quad j_2^{12} = 2k(k + 2) / (1.617k + 1.23). \quad (42)$$

As  $k$  increases quantity  $j_1^{12}$  decreases until it attains a value of  $j_1^{12} \approx 0.5$ , which implies that the system exhibits an incomplete depression of the limiting current with respect to the first kind of cations.

We point out that when all ions in the system have the same charge:  $z_1 = z_2 = 1$ , a mathematically simpler method exists for solving the system (3) to (7). In this case (8) changes to an expression for the concentration  $c_3(x)$ :

$$c_3(x) = (1 + k) + (x - 1)(j_1 + j_2(1 + \nu)) / 2, \quad (43)$$

whence, with the aid of (5), we readily find the expression

$$d\Psi/dx = (j_1 - j_2 + \nu j_2) / (2c_3(x)). \quad (44)$$

Integration of (44) while allowing for the boundary condition of  $\Psi(1) = 0$  yields

$$Y(x) = \tau \ln [1 + (x - 1)(j_1 + j_2(1 + \nu)) / (2 + 2k)], \quad (45)$$

where  $\tau = (j_1 - j_2 + \nu j_2) / (j_1 + j_2 + \nu j_2)$ . Substituting  $\Psi(x)$  into Eq. (3) we can find the cation concentration distribution  $c_1(x)$ :

$$c_1(x) = \left[ 1 + \frac{(x - 1)(j_1 + j_2(1 + \nu))}{2(1 + k)} \right]^{-\tau} \times \left( \int_1^x dx j_1 \left\{ 1 + \frac{(x - 1)(j_1 + j_2(1 + \nu))}{2(1 + k)} \right\}^{\tau} + 1 \right) \quad (46)$$

We notice that parameter  $\tau$  generally can assume both positive and negative values. In the limiting-current mode with respect to the cations  $c_1(x=0) \rightarrow 0$ . In the case of  $\tau < 0$ ,  $c_1(0)$  can tend toward zero, both on account of the first factor in (46) [which, according to (5), additionally implies that  $c_3 \rightarrow 0$ ] and on account of the second factor. But in the case of  $\tau > 0$  we find that  $c_1(0) \rightarrow 0$  under the condition of

$$1 - [1 - (j_1 + j_2 + \nu j_2) / (2k + 2)]^{\tau + 1} = [1 + (\nu + 1)j_2 / j_1] (\tau + 1) / (2k + 2). \quad (47)$$

Condition (47) generally implies that quantity  $c_1(0)$  tends toward zero, while concentrations  $c_2(0) = c_3(0) > 0$ .

The totally limiting current  $i^{12}$  implies that the conditions (47) and  $c_3(0) = 0$  are simultaneously fulfilled. Then we can obtain from (43) and (47):

$$j_1^{12} = 2\nu(1 + k) / (k + \nu + k\nu), \quad (48)$$

$$j_2^{12} = 2k(1 + k) / (k + \nu + k\nu), \quad (49)$$

$$i^{12} = \frac{2F_c c_1^0}{L} \frac{1+k}{k+\nu+k\nu} (\nu D_1 + k D_2). \quad (50)$$

It follows from relation (50) that when  $k = 0$ , i.e., when no hydrogen ions are present in the solution,  $i^{12}$  coincides with the limiting current of  $2FD_1c_1^0/L$  in binary solutions. The contribution coming from the second term in parentheses in (50) increases with increasing  $k$ , while the contribution which comes from the first term and describes the current of cation reduction decreases. The physical meaning of this result is as follows. Increasing values of  $k$  imply the realization of two competing effects. First, adding acid to the system causes the limiting current to fall to the values given by Eucken's relation:

$$i^{12} = FD_1 c_1^0 / L 2(1+k)(1 - \sqrt{1 - 1/(1+k)}). \quad (51)$$

This value of  $i_1^{12}$  follows as well from relation (47) when  $j_2 = 0$ . Secondly, concurrent anion reduction causes a change in limiting current  $i_1^{12}$  analogous to that described by the theory of correlational migration-current exaltation [2, 4]. Functions  $j_1^{12}(k)$ , which were determined with relations (48) and (51) for a number of values of the parameter  $\nu$ , are shown in Fig. 1. It can be seen here that  $j_1^{12}$  assumes values which are higher than those given by relation (51) when  $\nu > 1$ . The values of  $j_1^{12}$  given by relation (48) are higher than those given by (51) at sufficiently small  $k$  when  $\nu < 1$ . Thus, here both the stoichiometry of the process and the relative values of the component diffusion coefficients, which are contained in  $\nu$ , are of importance.

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