Generalized Theory of Steady-State Voltammetry without a Supporting Electrolyte. Effect of Product and Substrate Diffusion Coefficient Diversity

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A generalized theory of the steady-state voltammetric response of a microelectrode in the absence of supporting electrolyte and for any values of diffusion coefficients of the substrate and the product of an electrode process is presented. The treatment applies to any reasonable combination of the charge numbers of the substrate, its counterion, and the product. A way to incorporate the activation polarization into the model is also demonstrated. It has been shown that the height, position, and shape of the migrational voltammogram are affected by the ratio of the product to substrate diffusivity (θ). In particular, for the electrode processes with sign retention, unequal diffusivities of electroactive species influence both characteristic points of the voltammogram (the limiting current and the half-wave potential). For charge neutralization processes (uncharged product), the changes in θ parameter are accompanied only by a shift in the half-wave potential. The most dramatic changes in the $I-E$ relation can be observed for the charge reversal processes. In this case, a consecutive increase in θ results in the transition of the voltammogram shape from rapid exponential growth ($\theta < 1$), through ramp shape ($\theta = 1$), to common wave shape ($\theta > 1$). On the basis of the expressions derived for the limiting current (exact and linearized), a possibility of the determination of the diffusion coefficient of the electrode reaction product is demonstrated. In addition, the ranges of θ where the assumption of equal diffusivities of the substrate and the product is obeyed within an insignificant error have been determined quantitatively. The theory has been experimentally verified using voltammetric oxidation of hexacyanoferrate(II).

There is no doubt that the demonstrated simplicity of the expression describing steady-state diffusional current at microelectrodes[1] resulted in numerous analytical applications of microelectrodes. These applications, however, are usually assigned to the presence of significant excess of supporting electrolyte.

It turns out that the elimination of supporting electrolyte opened new possibilities in electrochemical and electroanalytical experiments. They are presented in a recent review.[2] The absence of excess supporting electrolyte revealed a great diversity in the voltammetric behavior as a result of different responses to the charge numbers of electroactive species and the supporting electrolyte concentration. The authors that aim at development of the general theories describing this phenomenon have to cope with the complexity of the transport equations, which contain both diffusional and migrational terms.[3−7] Therefore, to make the transport equations solvable and, in consequence, to derive analytical solutions, several assumptions were undertaken. The most restrictive assumption, in our view, is that of equal diffusivities of the two electroactive species. This simplification eliminates an extra source of diversity in the voltammetric behavior and may lead to difficulties in interpretation of the experimental data. There are some approaches published that do not impose this simplification; however, they either are limited to a specific class of electrode reactions[8−11] or employ the numerical simulation.[12−17] We believe that knowledge of the exact relations for steady-state voltammetry under the diffusion−migration conditions would strengthen the analytical applications of microelectrodes in various media (e.g., low polar solvents, environmental samples, solid samples, ionic liquids).[18−27]

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This work is concerned with the derivation of a theory of the steady-state voltammetric response of a microelectrode in the absence of supporting electrolyte and for any values of diffusion coefficients of the product and the substrate of an electrode process. The analytical expressions found for the limiting current, the limiting ohmic potential drop, the limiting resistance, and the half-wave potential are generalized versions of those derived by Oldham.[6] In the derivation process, we have assumed that electroneutrality is satisfied at any point in the solution, all ions obey the Nernst−Einstein relation, the heterogeneous process is not coupled to any homogeneous reactions, the electrode process is of 1 to 1 stoichiometry, no reproportionation or disproportionation reactions take place, and the steady-state conditions are established. The assumption of steady-state conditions at sufficiently large overpotential makes the conclusions obtained for the limiting current at hemispherical electrodes applicable to disk microelectrodes.[28]

This paper also demonstrates that the diffusion coefficient of the electrode reaction product can be determined straightforwardly from the steady-state limiting current. This possibility may be treated as an approach supplementary to that presented in our previous paper.[29] Finally, this work provides an answer to the question of what the phrase "comparable diffusion coefficients of the electroactive species" (which is often used in the transport-based models) means quantitatively.

The derivation scheme presented in this work can be extended to any level of ionic support. However, the analytical solutions will not be available for any substrate and product charge numbers. This problem is currently under analysis.

THEORETICAL SECTION

Model Cell. A two-electrode system with a hemispherical working microelectrode placed on an infinite insulating plane is assumed. The second electrode is placed infinitely far from the working electrode (which in practical situations corresponds to more than several millimeters)[30] and is infinitely large. The solution contains the electrode process substrate (S) of charge z_S, which is accompanied by counterions (X) of opposite charge z_X. It is assumed that the product (P) is initially absent in the solution.

The electrode process, $S^{z_S} \rightarrow P^{z_P} + ne$ (where z_P is the product charge number and n is the number of electrons transferred per molecule equal to $z_P - z_S$, positive for oxidation and negative for reduction), proceeds in a single step and is not coupled to any chemical reaction. It is also assumed that the size of the microelectrode is not too small, so that the thickness of the double layer is an insignificant fraction of the diffusion layer thickness. Under such the conditions, the electroneutrality principle holds throughout the solution.[31−33]

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No restrictions are imposed on the magnitudes of the diffusion coefficients of all species.

Formulation of the Problem. In a system containing no added inert electrolyte, both diffusion and migration contribute to the total flux (J) of the transported substance. The flux can be represented by the Nernst−Planck equation which, when applied to the transport field of spherical symmetry, has the form

$$J_i = -D_i \frac{\partial C_i}{\partial r} - D_i \frac{z_i F}{RT} C_i \frac{\partial \Phi}{\partial r} \tag{1}$$

where i numbers all species present in the system (here $i = $ S, P, X), D_i and C_i denote ith species diffusion coefficient and concentration, respectively, Φ is the electrostatic potential in the solution, r is the radial distance from the electrode surface, and F, R, and T have their usual meanings.

Under steady-state conditions, the fluxes of all species are constant and are equal to the specific value at the electrode surface. For electroactive species, this value is proportional to the current (I) flowing through the interface due to electrooxidation or electroreduction, while for electroinactive species, it is equal to zero. Equation 1 adopted for the steady-state conditions and written for each of the three solutes (S, P, X) constitutes a system of three differential equations

$$\frac{dC_S}{dr} + \frac{z_S F}{RT} C_S \frac{d\Phi}{dr} = -\frac{I}{2\pi nF D_S r^2} \tag{2}$$

$$\frac{dC_P}{dr} + \frac{z_P F}{RT} C_P \frac{d\Phi}{dr} = \frac{I}{2\pi nF D_P r^2} \tag{3}$$

$$\frac{dC_X}{dr} + \frac{z_X F}{RT} C_X \frac{d\Phi}{dr} = 0 \tag{4}$$

Although no limitations on counterion diffusion coefficient are imposed, it will, in fact, have no influence on the steady-state concentration profiles and electrostatic potential.

The set of eqs 2−4 contains four unknown functions, i.e., C_S, C_P, C_X, and Φ. It can be made solvable by adding an extra relation, e.g., the electroneutrality principle

$$z_S C_S + z_P C_P + z_X C_X = 0 \quad \text{any} \quad r \tag{5}$$

and the following boundary conditions

$$r \rightarrow \infty: \quad C_S \rightarrow C_S^b, \quad C_P \rightarrow 0,$$

$$C_X \rightarrow C_X^b = -\frac{z_S}{z_X} C_S^b, \quad \Phi \rightarrow \Phi^b \tag{6}$$

where superscript b is related to the bulk of the solution.

To make the transport equations more concise and convenient for the solving process, we make them dimensionless using the following definitions

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$$c_i = C_i/C_S^b \qquad i = \text{S, P, X} \tag{7}$$

$$\theta = D_P/D_S \tag{8}$$

$$\chi = r/r_e \tag{9}$$

$$\Psi = (F/RT)(\Phi - \Phi^b) \tag{10}$$

where r_e is the microelectrode radius.

The next step is to replace the independent distance variable χ by its reciprocal denoted by y according to the following rule: $\chi^2 \, d/d\chi \equiv d/d(1/\chi) \equiv d/dy$. Finally, the new independent variable Ψ is introduced.[34] The latter is called, by some authors, the quasi-potential transformation.[8,9] It is worth noting that such a transformation of the electrostatic potential with additional mathematical operations eliminates the necessity of using the principle of uniform total concentration that was employed in several papers.[6,7,35]

All the above rearrangements lead to the following form of the set of eqs 2−4

$$\left(\frac{dc_S}{d\Psi} + z_S c_S\right)\frac{d\Psi}{dy} = -\frac{I}{I_d^L} \tag{11}$$

$$\left(\frac{dc_P}{d\Psi} + z_P c_P\right)\frac{d\Psi}{dy} = \frac{I}{\theta I_d^L} \tag{12}$$

$$\left(\frac{dc_X}{d\Psi} + z_X c_X\right)\frac{d\Psi}{dy} = 0 \tag{13}$$

where I_d^L is the limiting current at hemispherical electrodes for the purely diffusional conditions. I_d^L is equal to $2\pi n F D_S C_S^b r_e$.

The boundary conditions (6) take the form

$$y \to 0: \quad c_S \to 1, \quad c_P \to 0, \quad c_X \to c_X^b = -\frac{z_S}{z_X}, \quad \Psi \to 0 \tag{14}$$

Elimination of the Electrostatic Potential Gradient. The term $d\Psi/dy$ can be obtained by summing the dimensionless versions of eqs 2−4 multiplied by the corresponding charge of the species and using the electroneutrality condition

$$\frac{d\Psi}{dy} = \frac{I}{I_d^L}\left(\frac{z_P}{\theta} - z_S\right)(z_S^2 c_S + z_P^2 c_P + z_X^2 c_X)^{-1} \tag{15}$$

One may notice that the electric field expressed by eq 15 will vanish when θ is equal to z_P/z_S. As a result the diffusion−migration, eqs 2−4 reduce to the diffusional ones. Thus, the limiting current for any level of ionic support (including absence of supporting electrolyte) will be equal to that for the purely diffusional conditions (sufficient excess of supporting electrolyte), if θ equals z_P/z_S.[36]

Integration of the Transport Equations. By multiplying eqs 11−13 by the reciprocal of eq 15 one eliminates the potential

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gradient in the left-hand sides of these equations and, finally, obtains the set of linear differential equations with respect to Ψ. They can be easily integrated, as shown in Supporting Information (eqs 16−23), and the following solutions are obtained

$$c_S = e^{\lambda\Psi} + \frac{z_S\theta(z_P - z_X)}{z_S z_P(\theta - 1) - z_X(z_S\theta - z_P)}(e^{-z_X\Psi} - e^{\lambda\Psi}) \tag{24}$$

$$c_P = \frac{z_S(z_S - z_X)}{z_S z_P(\theta - 1) - z_X(z_S\theta - z_P)}(e^{\lambda\Psi} - e^{-z_X\Psi}) \tag{25}$$

$$c_X = -\frac{z_S}{z_X}e^{-z_X\Psi} \tag{25}$$

where

$$\lambda = z_S z_P(\theta - 1)/(z_P - z_S\theta)$$

Equations 24−26 are the general solutions of the equation set 2−4. They describe the potential dependencies of the concentrations of the substrate, the product, and the counterion, respectively.

To find out how the electrostatic potential varies with the current and the distance from the electrode surface one has to integrate relation 15 using the lower limit corresponding to the bulk of the solution ($\Psi = 0 = y$). The result is the following

$$\frac{Ir_e}{I_d^L r} = \frac{\theta}{z_P - z_S\theta}\left\{\frac{z_S}{\lambda}(z_S - z_P)(1 - \alpha)(e^{\lambda\Psi} - 1) - \frac{z_S}{z_X}[(z_S - z_P)\alpha + z_P - z_X](e^{-z_X\Psi} - 1)\right\} \tag{27}$$

for $\lambda \neq 0$, that is, for $z_S z_P(\theta - 1) \neq 0$, where $\alpha = z_S\theta(z_P - z_X)/[z_S z_P(\theta - 1) - z_X(z_S\theta - z_P)]$.

For $z_S z_P(\theta - 1) = 0$ this relation has the form

$$\frac{Ir_e}{I_d^L r} = \frac{\theta}{z_P - z_S\theta}\left\{z_S(z_S - z_P)(1 - \alpha)\Psi - \frac{z_S}{z_X}[(z_S - z_P)\alpha + z_P - z_X](e^{-z_X\Psi} - 1)\right\} \tag{28}$$

where α is simplified to $z_S\theta(z_X - z_P)/[z_X(z_S\theta - z_P)]$.

It is worth taking a closer look at the conditions fulfilling the equality $z_S z_P(\theta - 1) = 0$, since they introduce significant changes to the I versus Ψ relation (one exponential term is replaced by the linear one). It is evident that $z_S z_P(\theta - 1)$ vanishes when either θ is equal to 1 (equal diffusion coefficients of electroactive species, any z_S, z_P, $z_S \neq z_P$), z_S is zero (uncharged substrate, any θ and z_P, and $z_S \neq z_P$), or z_P is zero (uncharged product, any θ and z_S, and $z_P \neq z_S$). The case of equal diffusion coefficients has been extensively studied by Amatore et al.[3,4] and Oldham et al.[5−7] The two other conditions indicate the θ−insensitivity of the limiting current for the electrode process of the charge production−and the charge neutralization class. An additional discussion is presented in the next section.
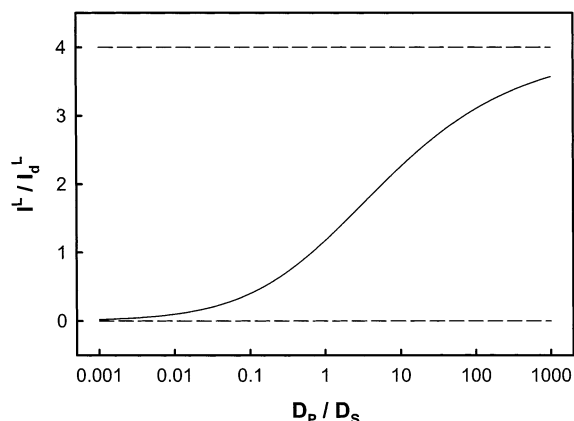
Figure 1. Limiting current versus the ratio of diffusion coefficients of product and substrate for the electrode processes $S^{3+} = P^{2+} - e$ with univalent counterion in the absence of supporting electrolyte. The current is made dimensionless with respect to the limiting current for the purely diffusional conditions. Horizontal dashed lines represent asymptotes of the relation shown.

Equations 27 and 28 express the variation of Ψ in an implicit form. They apply to any point in the solution under steady-state conditions, including the most useful point, the one located at the solution−electrode interface (i.e., at $r = r_e$, where $\Psi = \Psi^s$). The surface electrostatic potential, Ψ^s, treated as a macroscopically observed ohmic potential drop, varies from zero at the voltammogram foot to its limiting value, where the substrate surface concentration drops to zero (total concentration polarization of the substrate) and the current approaches its limit.

Setting $c_S = 0$ in eq 24 generates the following expression for the limiting electrostatic potential at the interface (limiting ohmic potential drop across the cell)

$$\Psi^L = \frac{z_P - z_S\theta}{z_S\theta(z_P - z_X) - z_P(z_S - z_X)} \ln\left[\frac{z_S(z_P - z_X)}{z_P(z_S - z_X)}\theta\right] \quad (29)$$

This expression is valid for any θ, z_S, z_P, and z_X values with the exception of the charge reversal reactions (sgn(z_S) $\neq$ sgn(z_P), $z_S \neq 0$, $z_P \neq 0$). In the absence of supporting electrolyte, the processes with charge reversal cannot reach the limiting conditions, since the electroneutrality principle would be violated for $c_S = 0$. It can be noticed that the Ψ^L parameter is infinite for charge neutralization ($z_P = 0$) and charge production ($z_S = 0$) processes. For other groups of electrode processes (reactions with sign retention: sgn(z_S) = sgn(z_P), $z_S \neq 0$, $z_P \neq 0$), it is seen that Ψ^L is indeterminate when θ is equal to the reciprocal of the argument of the logarithm in eq 29. In such a case, the expression of 0/0 type is obtained. Using the de l'Hospital rule, it can be shown that Ψ^L will reach a limit $(z_S - z_X)^{-1} - (z_P - z_X)^{-1}$ when θ tends to $z_P(z_S - z_X)/[z_S(z_P - z_X)]$. Since the limit found is finite, one can conclude that Ψ^L, and in consequence I^L, are continuous in this point.

By combing eq 29 with eqs 27 and 28, one can find expressions for the limiting current. For $z_S z_P(\theta - 1) \neq 0$ and sgn(z_S) = sgn(z_P), the corresponding expression can be written as

$$\frac{I^L}{I_d^L} = \frac{\theta}{\theta - 1}\left[\frac{z_X - z_S}{z_X} + \frac{z_S(z_P - z_X)}{z_X z_P}e^{-z_X\Psi^L}\right] \quad (30)$$

where Ψ^L is given by eq 29, and for $z_S z_P(\theta - 1) = 0$, it looks as follows

$$\frac{I^L}{I_d^L} = 1 - \frac{z_S\theta(z_S - z_P)}{z_X(z_S\theta - z_P)}\left\{1 - \frac{z_P(z_S\theta - z_X)}{z_X(z_S\theta - z_P)}\ln\left[\frac{z_P(z_S\theta - z_X)}{z_S\theta(z_P - z_X)}\right]\right\} \quad (31)$$

As was mentioned earlier, equality $z_S z_P(\theta - 1) = 0$ is satisfied for three cases which, when applied to eq 31, yield the following simplified expressions for the limiting current

$$\frac{I^L}{I_d^L} = 1 - \frac{z_S}{z_X}\left\{1 - \frac{z_P(z_S - z_X)}{z_X(z_S - z_P)}\ln\left[\frac{z_P(z_S - z_X)}{z_S(z_P - z_X)}\right]\right\} \quad \text{for} \quad \theta = 1,$$
$$\text{any} \quad z_S, z_P, z_S \neq z_P \quad (32)$$

$$\frac{I^L}{I_d^L} \to 1 \quad \text{for} \quad z_S = 0, \quad \text{any } \theta \quad \text{and } z_P, z_S \neq z_P \quad (33)$$

$$\frac{I^L}{I_d^L} = \frac{z_X - z_S}{z_X} \quad \text{for} \quad z_P = 0, \quad \text{any } \theta \quad \text{and } z_S, z_P \neq z_S \quad (34)$$

It is noteworthy that for θ very close to 1, eq 30 approaches eq 32, which was earlier derived analytically by Amatore et al.[3,4] and Oldham et al.[6] In other words, eq 32 is a special case of eq 30.

To visualize the course of the function given by eq 30, an example calculated for the process: $S^{3+} = P^{2+} - e$ with an univalent counterion has been chosen. This example reveals the main features of the I^L versus θ relations observed for various z_S, z_P, z_X combinations. The corresponding plot is given in Figure 1. It is seen in Figure 1 that the limiting current changes logarithmically with θ. Rescaling the abscissa, one finds that the I^L versus $\ln(\theta)$ dependence is of asymmetrical wave shape. This dependence has two horizontal asymptotes described by the following equations

$$I^L/I_d^L = 0 \qquad \theta \to 0 \quad (35)$$

$$I^L/I_d^L = (z_X - z_S)/z_X \qquad \theta \to \infty \quad (36)$$

These two extreme limits of θ, i.e., 0 and infinity, obviously have no experimental significance. They were introduced to show the theoretical boundaries (minimum and maximum values) of the limiting current function. We want to stress here that eq 36 is identical with the result for the limiting current for the corresponding charge neutralization process.

Summary and Simplification of the Expression for the Limiting Current. Let us summarize the main results derived so far. The solutions of the transport equations in the form of the potential dependencies of the species concentrations are given by eqs 24−26. The changes of the current intensity with electrostatic potential at any point in the solution, including the solution−electrode interface, are expressed by eqs 27 and 28. At

Table 1. Numeric Values of the Coefficients of the Linear Relation Given by Eq 37: I_1^L/I_d^L and a, and the Ranges of θ (D_P/D_S) of the Relation Applicability (See Text for Details). $z_X = \mp 1$

z_S	coefficients/ θ range	z_P 0	± 1	± 2	± 3	± 4	± 5	± 6
± 1	I_1^L/I_d^L	2		0.84927	0.78360	0.74666	0.72294	0.70641
	a	0		0.21677	0.19730	0.18504	0.17668	0.17063
	θ range	$(0, +\infty)$		(0.30, 11.20)	(0.29, 12.57)	(0.27, 11.49)	(0.26, 10.00)	(0.24, 8.76)
± 2	I_1^L/I_d^L	3	1.2739		0.87991	0.81214	0.76856	0.73817
	a	0	0.40780		0.29011	0.26292	0.24437	0.23095
	θ range	$(0, +\infty)$	(0.39, 8.57)		(0.45, 73.94)	(0.44, 95.02)	(0.43, 90.45)	(0.42, 72.22)
± 3	I_1^L/I_d^L	4	1.5672	1.1732		0.90215	0.83918	0.79525
	a	0	0.55856	0.44229		0.33268	0.30382	0.28292
	θ range	$(0, +\infty)$	(0.45, 10.73)	(0.51, 3.50)		(0.51, 2.99)	(0.50, 3.14)	(0.49, 3.38)
± 4	I_1^L/I_d^L	5	1.8666	1.3536	1.1277		0.91780	0.86043
	a	0	0.70716	0.54894	0.45750		0.36078	0.33238
	θ range	$(0, +\infty)$	(0.48, 12.41)	(0.55, 2.75)	(0.56, 2.47)		(0.55, 2.50)	(0.54, 2.58)
± 5	I_1^L/I_d^L	6	2.1688	1.5371	1.2588	1.1014		0.92924
	a	0	0.85481	0.65459	0.53897	0.46626		0.38076
	θ range	$(0, +\infty)$	(0.50, 13.73)	(0.57, 2.48)	(0.58, 2.25)	(0.58, 2.22)		(0.57, 2.29)
± 6	I_1^L/I_d^L	7	2.4724	1.7224	1.3917	1.2046	1.0841	
	a	0	1.0020	0.75971	0.61989	0.53197	0.47200	
	θ range	$(0, +\infty)$	(0.51, 14.76)	(0.58, 2.33)	(0.60, 2.12)	(0.60, 2.09)	(0.59, 2.10)	

the total concentration polarization of the substrate (the limiting conditions), the limiting value of the surface electrostatic potential is described by eq 29. The corresponding value of the current as it approaches its limit is given by eqs 30 and 31. By dividing the surface electrostatic potential (unified with the ohmic potential drop across the cell) by the limiting current, one can easily calculate the cell resistance at the limiting conditions. For the charge neutralization processes, the steady-state cell resistance is infinite in the absence of supporting electrolyte. For other processes with sign retention, its value is dependent on θ.

The general expression 30 relating the limiting current and the θ parameter (D_P/D_S) is too complex to be very conveniently applied to the analysis of the experimental data obtained for θ values close to unity. By expanding the limiting current into a series about the point $\theta = 1$, one obtains the limiting current in the form of a power series of the $(\theta - 1)$ term. In addition, we have found numerically that the replacement of the $(\theta - 1)$ term by $\ln(\theta)$ expands the range of θ values of the applicability of the linearized expression. Therefore, the linearized expression for the limiting current can be represented as

$$I^L/I_d^L = I_1^L/I_d^L + a \ln(\theta) \tag{37}$$

where I_1^L is the limiting current calculated for a supporting electrolyte-free solution with the assumption of equal diffusion coefficients of the substrate and the product and a is a function of z_S, z_P, and z_X generated by the Taylor expansion. The numeric values of I_1^L/I_d^L and a for a monovalent counterion and for various z_S and z_P combinations likely to be encountered in practice are listed in Table 1.

It turns out that eq 37 approximates the exact function very well (with the maximum error of 2%) for the average θ range of 0.35−3.0. In some cases, the θ range of the equation applicability is significantly wider. This is shown in Table 1.

The convenient form of the linear expression of I^L versus $\ln(\theta)$ will make feasible the determination of the product diffusion coefficient, if the values of the limiting currents recorded in the system containing no and excess supporting electrolyte are known. For the voltammetric experiments without added supporting electrolyte, it is vital to maintain the ratio of ionic impurities concentration to the substrate concentration at a very low level (smaller than 1×10^{-3}).[37] This support ratio, usually undefined, may change the magnitude of the limiting current[7] and, in consequence, may lead to poorer accuracy of the determined product diffusivity. To improve the accuracy of D_P determination, one may decrease this support ratio by increasing the substrate concentration.

Finally, it is also possible to find out what the "comparable diffusion coefficients of the substrate and the product" phrase means quantitatively. Using either eq 30 or its linearized version, it is possible to determine the maximum and minimum θ values that cause an insignificant (below 2%) change in the limiting current derived with the assumption of diffusion coefficient equality. In other words, one may evaluate the error introduced to the limiting current (and electrostatic potential as well) by the assumption of equal diffusivities of electroactive species. The ranges of θ values that cause no more than 2% change in the limiting current derived with the assumption of $\theta = 1$ are collected in Table 2. It is seen that the width of the applicable θ ranges depends on the charge numbers of all species present in the system and is the largest for a monovalent substrate (excluding the charge neutralization processes).

Construction of a Steady-State Voltammogram. In general, under the conditions of supporting electrolyte deficit, the potential imposed to the electrode is divided into two main parts: the potential that results from the concentration or activation overpotential and the ohmic potential drop

$$E = (E_r - E^{0\prime}) + (RT/F)\Psi^s \tag{38}$$

where E is the potential applied to the working electrode from

(37) Hyk, W.; Stojek, Z. *J. Electroanal. Chem.* **1997**, *422*, 179.

Table 2. Ranges of D_P/D_S Values That Cause No More Than 2% Change in the Limiting Current Derived with the Assumption of Equal Diffusion Coefficients ($D_P = D_S$)

		z_P						
z_S	z_X	0	±1	±2	±3	±4	±5	±6
±1	∓1	(0, +∞)		(0.9246, 1.0814)	(0.9236, 1.0825)	(0.9224, 1.0839)	(0.9214, 1.0852)	(0.9206, 1.0863)
	∓2	(0, +∞)		(0.8950, 1.1180)	(0.8962, 1.1164)	(0.8961, 1.1165)	(0.8956, 1.1171)	(0.8951, 1.1178)
	∓3	(0, +∞)		(0.8668, 1.1561)	(0.8701, 1.1511)	(0.8710, 1.1496)	(0.8712, 1.1493)	(0.8711, 1.1495)
±2	∓1	(0, +∞)	(0.9394, 1.0643)		(0.9410, 1.0623)	(0.9399, 1.0635)	(0.9389, 1.0647)	(0.9379, 1.0658)
	∓2	(0, +∞)	(0.9155, 1.0930)		(0.9246, 1.0814)	(0.9246, 1.0814)	(0.9242, 1.0819)	(0.9236, 1.0825)
	∓3	(0, +∞)	(0.8926, 1.1226)		(0.9086, 1.1010)	(0.9096, 1.0995)	(0.9098, 1.0992)	(0.9097, 1.0994)
±3	∓1	(0, +∞)	(0.9453, 1.0575)	(0.9482, 1.0542)		(0.9470, 1.0554)	(0.9461, 1.0565)	(0.9452, 1.0575)
	∓2	(0, +∞)	(0.9258, 1.0805)	(0.9337, 1.0708)		(0.9356, 1.0685)	(0.9353, 1.0688)	(0.9348, 1.0694)
	∓3	(0, +∞)	(0.9071, 1.1039)	(0.9196, 1.0877)		(0.9244, 1.0817)	(0.9247, 1.0813)	(0.9246, 1.0814)
±4	∓1	(0, +∞)	(0.9485, 1.0540)	(0.9517, 1.0503)	(0.9517, 1.0502)		(0.9502, 1.0519)	(0.9494, 1.0528)
	∓2	(0, +∞)	(0.9313, 1.0741)	(0.9394, 1.0643)	(0.9413, 1.0620)		(0.9414, 1.0618)	(0.9410, 1.0623)
	∓3	(0, +∞)	(0.9149, 1.0943)	(0.9273, 1.0785)	(0.9310, 1.0740)		(0.9327, 1.0718)	(0.9327, 1.0718)
±5	∓1	(0, +∞)	(0.9504, 1.0519)	(0.9540, 1.0478)	(0.9542, 1.0475)	(0.9537, 1.0481)		(0.9522, 1.0497)
	∓2	(0, +∞)	(0.9347, 1.0701)	(0.9429, 1.0603)	(0.9450, 1.0578)	(0.9455, 1.0572)		(0.9450, 1.0577)
	∓3	(0, +∞)	(0.9197, 1.0884)	(0.9322, 1.0728)	(0.9360, 1.0682)	(0.9374, 1.0665)		(0.9380, 1.0658)
±6	∓1	(0, +∞)	(0.9517, 1.0504)	(0.9555, 1.0461)	(0.9559, 1.0456)	(0.9555, 1.0460)	(0.9549, 1.0467)	
	∓2	(0, +∞)	(0.9370, 1.0674)	(0.9453, 1.0575)	(0.9476, 1.0549)	(0.9482, 1.0542)	(0.9482, 1.0542)	
	∓3	(0, +∞)	(0.9230, 1.0844)	(0.9355, 1.0690)	(0.9394, 1.0643)	(0.9409, 1.0625)	(0.9375, 1.0618)	

the potentiostat, E_r is the true electrode potential, $E^{0\prime}$ is the formal potential of the redox couple, and the last term represents the ohmic potential drop across the cell (Ψ^s denotes the dimensionless electrostatic potential at the electrode−solution interface).

Both terms at the right-hand side of eq 38 depend on the magnitude of the current flowing through the interface (I). Therefore, to find the expression describing the migrational voltammogram, in the form of either E versus I or I versus E, one has to know how E_r and Ψ^s vary with the current flowing through the cell. The Ψ^s-I relation is described implicitly by eqs 27 and 28, and the form of the E_r-I relation depends on the electrode process mechanism. For the Nernstian conditions (reversible processes), the ($E_r-E^{0\prime}$) term is expressed as

$$E_r - E^{0\prime} = RT/(nF) \ln(c_P^s/c_S^s) \tag{39}$$

where superscript s refers to the interface and the ratio of product and substrate concentrations is a function of the current

When the process is quasi-reversible, the Butler−Volmer conditions must apply. Hence, ($E_r-E^{0\prime}$) is given in the implicit form

$$\frac{I}{I_d^L} = k\left\{ c_S^s \exp\left[\frac{\beta nF(E_r - E^{0\prime})}{RT}\right] - c_P^s \exp\left[\frac{(1-\beta)nF(E_r - E^{0\prime})}{RT}\right]\right\} \tag{40}$$

where β is the electron-transfer coefficient and k is the dimensionless standard heterogeneous rate constant (equal to $k_s r_e/D_S$).

For a totally irreversible electrode process eq 40 simplifies to

$$E_r - E^{0\prime} = \frac{RT}{\beta nF} \ln\left(\frac{I}{I_d^L k c_S^s}\right) \tag{41}$$

In general, it is not possible to derive an analytical expression for

the migrational voltammetric curve (with the exception for some special cases discussed later); however, we have all the equations that are needed to construct a theoretical steady-state voltammogram for any combination of θ, z_S, z_P, and z_X. The calculation procedure is similar to that presented by Myland and Oldham.[7] It consists of several steps to be performed:

1. Select the initial value and the increment of the dimensionless surface electrostatic potential, Ψ^s. The former should be zero while the latter may be equal to Ψ^L/N (where N is the number of points of the voltammetric curve and Ψ^L is given by eq 29). If Ψ^L is infinite, choose arbitrarily a small number either positive (oxidation) or negative (reduction) for the potential increment.

2. Increase the actual value of Ψ^s by adding the potential increment.

3. Calculate the dimensionless current (I/I_d^L) via eq 27 (or 28).

4. Using the actual value of Ψ^s, calculate surface concentrations of the substrate and the product (eqs 24 and 25).

5. Compute the true electrode potential ($E_r - E^{0\prime}$) using the appropriate expression (eq 39, 40, or 41) for the selected electrode process mechanism.

6. Evaluate the potential imposed to the electrode (the total electrode potential, E) by adding the value calculated in step 5 to $RT\Psi^s/F$.

7. Add the dimensionless current from step 3 to the plot of the current against the total electrode potential from step 6.

8. Check whether c_S^s is equal to or less than zero. If so, the voltammogram is completed; otherwise, go to step 2.

A few examples of the theoretical steady-state voltammograms, computed for four reversible electrode processes of different classes carried out in supporting electrolyte-free solutions, are presented in Figures 2−5. They involve the following reactions: $S^+ = P^{3+} + 2e$ (charge increase process, $z_X = -1$, Figure 2), $S^{4-} = P^{3-} + e$ (charge decrease process, $z_X = 1$, Figure 3), $S^{2-} = P^0 + 2e$ (charge neutralization process, $z_X = 2$, Figure 4), and $S^- = P^+ + 2e$ (charge reversal process, $z_X = 1$, Figure 5). Each figure contains two sets of three voltammograms obtained for θ equal
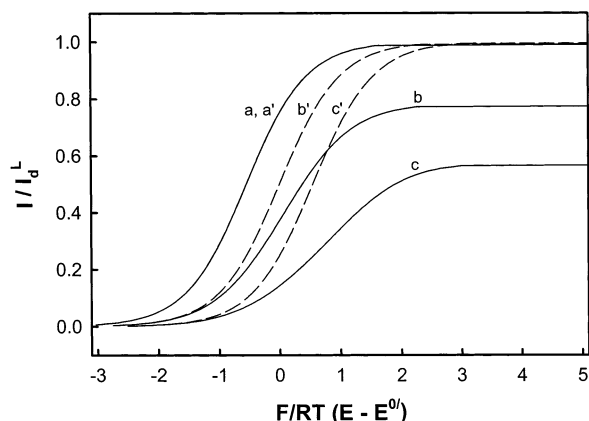
Figure 2. Steady-state voltammograms for the reversible process $S^+ = P^{3+} + 2e$ (charge increase process, monovalent counterion) for several θ values: 3 (a, a'), 1 (b, b'), $^{1}/_{3}$ (c, c'). Curves marked with a, b, and c (solid lines) refer to the supporting electrolyte-free solution while those marked with a', b', and c' (dashed lines) refer to the purely diffusional conditions. The current is made dimensionless with respect to the limiting current for the purely diffusional conditions.
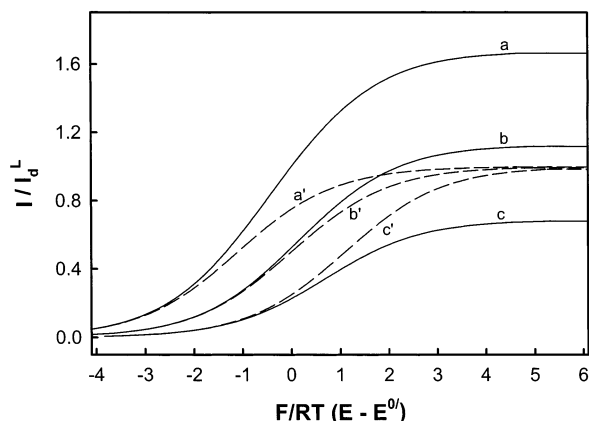

Figure 3. As for Figure 2, but for the reversible process $S^{4-} = P^{3-} + e$ (charge decrease process, monovalent counterion).

to 3, 1, and $^{1}/_{3}$. Each first set (solid lines) corresponds to the supporting electrolyte-free solution while the second (dashed lines) corresponds to the purely diffusional conditions (sufficient excess of supporting electrolyte). For the diffusional conditions, the voltammetric wave equation has the familiar form[38]

$$E = E^{0\prime} - \frac{RT}{nF} \ln(\theta) - \frac{RT}{nF} \ln\left(\frac{I_d^L - I}{I}\right) \qquad (42)$$

As seen in Figures 2 and 3, for the processes with the sign retention, both characteristic points on the steady-state voltammogram (i.e., $E_{1/2}$ and I^L) are affected by θ, if supporting electrolyte is eliminated. For the charge neutralization processes, the changes in diffusion coefficients of the electroactive species are accompanied only by a shift in half-wave potential (see Figure 4). The most dramatic changes, however, can be observed for the charge reversal process. The increase in θ from 1 to 3 causes the transformation of the ramp-shaped voltammogram to the common wave-shaped curve (see Figure 5). This result suggests that a quasi-limiting conditions may be established when the
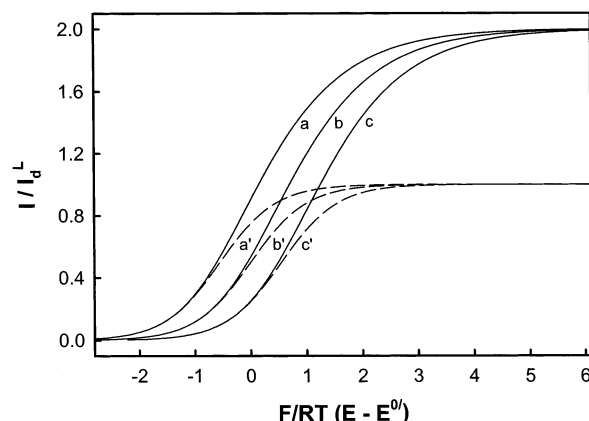
(38) Oldham, K. B.; Zoski, C. G. *J. Electroanal. Chem.* **1988**, *256*, 11.

Figure 4. As for Figure 2, but for the reversible process $S^{2-} = P^0 + 2e$ (charge neutralization process, divalent counterion).
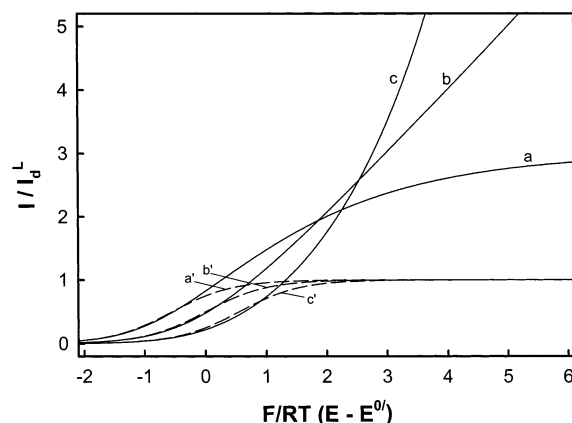

Figure 5. As for Figure 2, but for the reversible process $S^- = P^+ + 2e$ (charge reversal process, monovalent counterion).

product is transported faster than the substrate. If the product diffusivity is infinite, the true limiting conditions ($c_S^s = 0$) will occur and the current will approach the limit predicted by eq 36. A totally different behavior can be noticed for the case of θ less than 1. In such a situation, the increase in the product concentration, due to its slower transport in the depletion layer, enhances the transport of the substrate compared to the case of equal diffusivities. As a result, the current grows even faster than can be predicted by Ohm's law. This law is obeyed for charge reversal processes with equal diffusivities of electroactive species at potentials larger than $E^{0\prime}$.

The results presented in Figures 2−5 were generated using the procedure for voltammogram construction presented above. However, it is possible to obtain an explicit Ψ^s-I relation and, in consequence, to derive analytical expressions of $E-I$ dependence for two cases: $z_P = 0$ (charge neutralization processes) and $z_P = z_X$ (charge reversal processes). The results for the reversible reactions are as follows

$$E = E^{0\prime} + \frac{RT}{z_S F} \ln\left(\frac{I_d^L}{I}\theta\right) + \frac{RT}{z_S F}\frac{I^L}{I_d^L} \ln\left(\frac{I^L - I}{I^L}\right) \qquad (43)$$

$$E_{1/2} = E^{0\prime} + \frac{RT}{z_S F} \ln\left(\frac{2I_d^L}{I^L}\theta\right) - \frac{RT}{z_S F}\frac{I^L}{I_d^L} \ln 2 \qquad (44)$$

for charge neutralization processes, where

$$I^L/I_d^L = (z_X - z_S)/z_X$$

and

$$E = E^{0/} + \frac{RT}{nF} \ln\left[\frac{z_S}{z_P}\left(1 + \frac{z_P(\theta - 1)}{\theta(z_S - z_P)} \frac{I}{I_d^L}\right)^\gamma - \frac{z_S}{z_P} \right] +$$

$$\frac{RT}{F} \frac{(z_P - z_S\theta)}{z_S z_P(\theta - 1)} \ln\left[1 + \frac{z_P(\theta - 1)}{\theta(z_S - z_P)} \frac{I}{I_d^L}\right] \quad (45)$$

for charge reversal processes, where

$$\gamma = (z_S - z_P)/[z_S(\theta - 1)]$$

EXPERIMENTAL SECTION

To verify the expressions derived, steady-state voltammograms were recorded for the oxidation of $Fe(CN)_6^{4-}$ in aqueous solutions containing no and sufficient excess of supporting electrolyte. The approach for the evaluation of the product diffusivity, proposed in this paper, was also examined.

Instrumentation and Chemicals. Voltammetric measurements were performed using an AutoLab potentiostat, model PGSTAT 20, which was controlled via a personal computer. Two pieces of platinum foil were used as the counter and the quasi-reference electrodes to eliminate a possible leak of ions from the bridge. A platinum disk microelectrode of 5.0 ± 0.2 μm ($r_e \pm s(r_e)$) in radius (Project Ltd., Warsaw) was used as the working electrode.

Before each experiment, the working electrode was polished with aluminum oxide powders of various sizes (down to 0.05 μm) on a wet pad and was rinsed with a direct stream of Milli-Q, Millipore-quality water (conductivity of ~0.056 μS/cm). The electrodes were dried using ethyl alcohol. After the measurements, the electrode surface was inspected optically with an Olympus, model PME 3, inverted metallurgical microscope. To minimize the electric noise, the electrochemical cell was kept in a grounded aluminum foil Faraday cage.

Electroactive species, potassium hexacyanoferrate(II) trihydrate ($K_4Fe(CN)_6 \cdot 3H_2O$, 99+%) and potassium chloride (99+ %), used as supporting electrolyte, were purchased from Aldrich. The chemicals were used as received.

Voltammetric measurements were performed at room temperature (21 °C) in 20 mM aqueous solutions of the redox system, $Fe(CN)_6^{4-}$, containing either no or 40-fold excess of KCl. Ten replicates of the background-corrected voltammograms were recorded at the scan rate of 10 mV/s. The reproducibility of the results was very good, with the coefficient of variation of the steady-state current less than 1.5%.

To make sure that electroactive species do not adsorb during the $Fe(CN)_6^{4-}$ oxidation process, we have correlated the limiting current with the microelectrode radius (5.0, 10.9, 12.5, 25.0 μm). The dependence found was linear with the generalized regression coefficient $r^2 = 0.998$ and the slope of 5.22 nA/μm. By taking the accepted literature value of D_S, equal to 6.32×10^{-10} m^2/s, the theoretical value of the slope ($4FD_SC_S^b$) was calculated to be 4.91 nA/μm. The good agreement between theoretical and experimental values indicates the transport-controlled nature of the

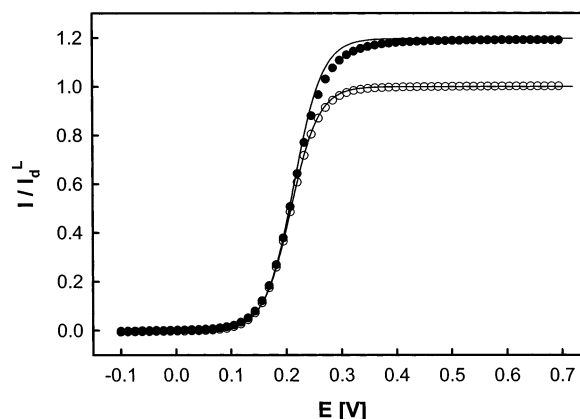**Figure 6.** Steady-state voltammograms of the oxidation of 20 mM $Fe(CN)_6^{4-}$ without supporting electrolyte (filled circles) and with 0.8 M KCl (empty circles). The theoretical voltammograms (solid lines) were calculated using the ratio of diffusion coefficients of the product and the substrate ($D(Fe(CN)_6^{3-})/D(Fe(CN)_6^{4-})$) determined from the limiting currents. The voltammetric currents are made dimensionless with respect to the diffusional limiting current.

process examined. The perfectly flat and very well reproducible voltammetric wave plateaus serve as additional proof for the absence of $Fe(CN)_6^{4-}$ adsorption at the concentration magnitude used.

In addition, to avoid the photochemical decomposition of hexacyanoferrate(II),[39] the electrochemical cell was always shielded from light.

RESULTS

The substrate tested, $Fe(CN)_6^{4-}$, gives a 1e wave-shaped voltammetric response as shown in Figure 6. It should be noted that the limiting current for the process $Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + e$ carried out under the absence of supporting electrolyte is increased compared to the purely diffusional conditions. Assuming equal diffusion coefficients of the substrate and the product, the theoretical value of the ratio of the limiting currents recorded in the absence of supporting electrolyte and in the presence of its excess is equal to 1.128. According to the theoretical derivation presented in this paper, the inequality of the substrate and the product diffusivities, which is the case for hexacyanoferrates, should make this ratio distinctly larger.

For the redox species examined, the experimental value of the ratio of the limiting currents obtained in the system with no supporting electrolyte to that in the presence of excess supporting electrolyte ($I^L/I_d^L \pm s(I^L/I_d^L)$, where $s(I^L/I_d^L)$ denotes the standard deviation of the currents ratio and represents the uncertainty of its determination) is 1.195 ± 0.021. This ratio determines the ratio of the product to substrate diffusivity as it is predicted by eqs 30 and 37. The number we found for $D(Fe(CN)_6^{3-})/D(Fe(CN)_6^{4-})$ is 1.16 ± 0.05. This result combined with the diffusion coefficient of the electrode process substrate (($6.15 \pm 0.18) \times 10^{-10}$ m^2/s, determined from the height of the diffusional voltammogram) yields the value of the $Fe(CN)_6^{3-}$ diffusivity. The number obtained at 21 °C is $(7.13 \pm 0.37) \times 10^{-10}$ m^2/s. It is in a good agreement with the values found in the literature: $7.17 \times$

(39) Eisenberg, M.; Tobias, C. W.; Wilke, C. R. *J. Electrochem. Soc.* **1954**, *101*, 306

10^{-10} (~1 mM $Fe(CN)_6^{3-}$, 0.5 M KCl, $T = 25$ °C), 7.4×10^{-10} (10 mM $Fe(CN)_6^{3-}$, no supporting electrolyte, $T = 20$ °C), 7.61×10^{-10} (1 M KCl, $T = 25$ °C).[40-42]

The experimental value of the ratio of diffusion coefficients of the product and the substrate ($D(Fe(CN)_6^{3-})/D(Fe(CN)_6^{4-})$) was used for the computation of the theoretical voltammograms. The results obtained are superimposed on the experimental curves in Figure 6. It is seen that both experimental and theoretical voltammetric curves fit each other very well.

(40) Baur, J. E.; Wightman, R. M. *J. Electroanal. Chem.* **1991**, *305*, 73.
(41) Zhou, H.; Shi, Z.; Dong, S. *J. Electroanal. Chem.* **1998**, *443*, 1.
(42) Ikeuchi, H.; Kanakubo, M. *J. Electroanal. Chem.* **2000**, *493*, 93.

SUPPORTING INFORMATION AVAILABLE

Details of the integration of the transport equations. This material is available free of charge via the Internet at http://pubs.acs.org.