INFLUENCE OF PARTIAL BLOCKING OF THE ELECTRODE SURFACE ON THE TRANSFER COEFFICIENTS

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Partial blocking of the transport surface under the stagnant (Nernst) layer is simulated by periodically alternating bands of perfectly insulating zones and active zones with a constant potential of the driving force. The numeric solution of the corresponding two-dimensional elliptic problem is represented by a simple empirical correlation for the transfer coefficients. The result is interpreted in terms of a simple electrochemical problem about limiting diffusion currents at electrodes with non-uniform surface activity.

In solving problems of charge, heat and mass transfer between a homogeneous medium and a wall, the usual assumption is that the interface is a homogeneous, two-dimensional continuum. For a negligible interface resistance or for a sufficiently rapid surface reaction at the interface the electric potential, temperature and concentration at the whole interface are considered known and constant. This is, however, at variance of reality, e.g. when electric current or heat passes between two contacting coarse blocks of a solid material or when a catalytic reaction proceeds at the solid surface. The fraction of the active part of the surface may be even less than 1% of the geometric interface area.

The notion of partial blockade of the surface was introduced in electrochemistry to elucidate the drop in activity of solid electrodes in the limiting diffusion current regime. Landsberg and Thiele[1] start from the Nernst model of stagnant diffusion layer and they model the non-uniform surface activity by assuming the existence of circular active zones surrounded by inert regions. The model involves three parameters: thickness of the diffusion layer, radius of fictitious circular zones with an active centre which occupy the whole electrode surface, and the fraction of the active part of the surface in the fictitious circular region. An obvious drawback of the model is the assumption of complete occupation of the surface by circular regions, however this makes possible to use the known solution of the two-dimensional problem of electric current conduction through a cylinder terminated by a circular contact[2]. Also Levart and coworkers[3] start from the model of Nernst stagnant layer. Their model of non-uniformly active surface consist of a regular arrangement of square-shaped active zones and the model parameters again characterize the diffusion thickness, the period of the inhomogeneites, and the fraction of the active part of the surface. The problem of three-dimensional diffusion in a stagnant medium is solved by using Fourier series whose coefficients are determined in nodes of the square grid on the transport surface. Drawbacks of this work are too large steps of the grid on the electrode surface (at most 15 × 15 points per period) and limitation to macroheterogeneous surfaces with a heterogeneity period equal or larger than the diffusion thickness. The two works mentioned were criticized by Filinovskii[4], who considered the notion of Nernst stagnant layer as doubtful, and proposed a diffusion layer approach of the transport model involving the influence of convection at the expense of neglection of longitudinal diffusion.

The present work is based on the Nernst stagnant layer approach together with the notion of additional diffusion path, formulated implicitly by Smythe[2]. The purpose is to solve a simple model of a partially blocked surface a one-dimensional periodic structure of active and inactive bands. The criticism of Filinovskii[4] is evaluated in the Discussion.

THEORETICAL

The geometry of the transport model considered is illustrated in Fig. 1*a*. We assume that the transport resistance between the wall and the streaming liquid is concentrated in a layer of constant diffusion thickness, δ, on whose outer boundary, *B*, the concentra-

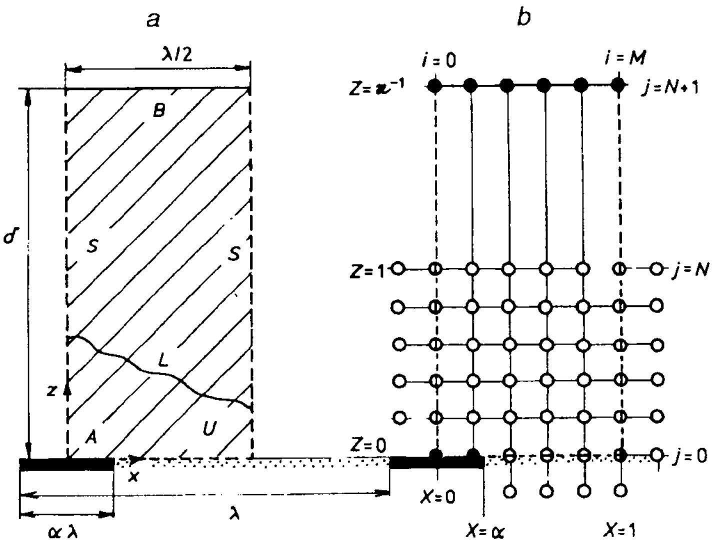

FIG. 1

Diffusion layer on periodically blocked surface: *a* Geometric parameters: *A* active surface, *U* blocked surface, *S* symmetry planes. Shaded area denotes integration domain of the concentration field. *b* Grid for integration of harmonic equation: ○ inner grid points (with unknown *C* values), ● points with known boundary values of *C*, ⊖ ⦶ ⊕ points at boundaries with mirror symmetry tion is equal to that in the bulk of the streaming liquid, $c = c_B$. Partial blockade of the surface is simulated by periodically alternating bands of a perfectly permeable interface, A, of known constant concentration, $c = c_A$, and of a perfectly blocked interface, U, with zero permeability, $\partial_Z c = 0$. The period of this structure is λ, and the fraction of the active area is $\alpha = A/(A + U) \leq 1$.

Owing to periodicity and symmetry of the concentration field, it is sufficient to consider the integration domain denoted in Fig. 1*a* by shading. By using dimensionless variables (cf. Symbols), the problem can be formulated mathematically as follows:

$$\partial^2_{XX}C + \partial^2_{ZZ}C = 0 \qquad \text{for } 0 < X < 1\,, \quad 0 < Z < 1/\kappa \tag{1}$$

$$C = 1/\kappa \qquad \text{for } 0 < X < 1\,, \quad Z = 1/\kappa \tag{2a}$$

$$C = 0 \qquad \text{for } 0 < X < \alpha\,, \quad Z = 0 \tag{2b}$$

$$\partial_Z C = 0 \qquad \text{for } \alpha < X < 1\,, \quad Z = 0 \tag{2c}$$

$$\partial_X C = 0 \qquad \text{for } X = 0\,, \quad 0 > Z > 1/\kappa \tag{2d}$$

$$\partial_X C = 0 \qquad \text{for } X = 1\,, \quad 0 > Z > 1/\kappa\,. \tag{2e}$$

Thus, we have to deal with a two-dimensional elliptic problem with two geometrical simplexes, $0 < \alpha < 1$, $\kappa > 0$. For a fully active wall, $\alpha = 1$, the solution is obviously

$$C = Z\,. \tag{3}$$

In the general case, $\alpha < 1$, no analytical solution has been found. Owing to the mixed character of the boundary conditions, no conformal mapping is known which would transform the given problem into an ordinary differential equation. Therefore, the solution was carried out numerically. To find the total diffusion current, the following procedure was chosen. The curve integral

$$E = \int_L (\partial_Z C \, \mathrm{d}X - \partial_X C \, \mathrm{d}Z)\,, \tag{4}$$

where L denotes an arbitrary curve separating the active zone from the outer boundary of the diffusion layer, is constant as a result of the properties (*1*), (*2c* – *2e*). It is apparent that E is equal to the ratio of the diffusion current – a particular case to that for a fully active wall, $\alpha = 1$. The accuracy of the solution was tested by comparing the values of E obtained by integration along several suitably chosen curves.

Numerical Solution

The given problem was solved by the finite-difference method. The values of C_i^j at the grid points for $Z < 1/\kappa$ are defined on an isotropic rectangular grid, $Z^{j+1} - Z^j = X_{i+1} - X_i = 1/M$,

$$C_i^j = C(X_i, Z^j)\,, \quad X_i = i/M\,, \quad Z^j = j/N\,, \quad 0 \le i \le M\,, \quad 0 \le j \le N\,. \tag{5}$$

The values in the corresponding grid points can therefore be calculated according to the usual second-order difference scheme for harmonic equation

$$C_i^j = \frac{1}{4}(C_i^{j+1} + C_i^{j-1} + C_{i+1}^j + C_{i-1}^j)\,. \tag{6}$$

For $\kappa > 1$, i.e. for surface non-uniformity with a long period compared to the diffusion layer thickness (case of a macroheterogeneous blockade), we have $N < M$ with the given choice of the grid steps. We will be concerned mainly with the microheterogeneous blockade, $\kappa << 1$, in which case the use of an equally spaced grid would result in a too high total number of grid points with respect to the required grid density near the active surface (i.e. for a given value of M). This obstacle can be eliminated, with regard to the asymptotic linear concentration profile for $Z \to 1/\kappa$ according to Eq. (3), by the choice of an unequally spaced grid for $Z > 1$. Thus, for $1/\kappa > 1 + 1/M$, the interval $1 \le Z \le 1/\kappa$ was bridged by a single step as shown in Fig. 1*b*. The corresponding formula for the calculation of the grid point values for $j = N$ ($Z = 1$) is

$$C_i^N = [(1 + \beta)(C_{i-1}^N + C_{i+1}^N) + 2\beta(\beta C_i^{N+1} + C_i^{N-1})]/2(1 + \beta)^2\,, \tag{7}$$

where

$$\beta \equiv (Z^N - Z^{N-1})/(Z^{N+1} - Z^N) = [M(\kappa^{-1} - 1)]^{-1} < 1 \tag{8}$$

and $C_i^{N+1} = 1/\kappa$ in accord with the boundary condition (*2a*).

In the lateral columns, $i = 0$ and $i = M$, we use the symmetry relations to eliminate the grid point values outside the integration domain

$$C_{-1}^j = C_1^j\,, \qquad C_{M+1}^j = C_{M-1}^j \tag{9}$$

and the grid point values on the boundary are calculated according to Eqs (*6*) and (*7*).

Thus, a system of $M(M + 1)$ equations of the type (*6*) and (*7*) must be solved. The solution was carried out by iterations using the superrelaxation method, based on the relationship

$$(C_i^j)_{new} = s(C_i^j)_{new} + (1-s)\,(C_i^j)_{old}\,. \tag{10}$$

As usual with problems of the boundary layer theory, the system of equations solved behaves as a "stiff" system. To increase the rate of convergence at points near the outer boundary of the diffusion layer, it was therefore necessary to use extremely high values of the relaxation coefficient, $1.9 < s < 1.999$. The iterations were substantially accelerated by gradual halving of the grid with linear interpolation of the grid point values. The maximum grid dimension, conditioned by simple addressing of the computer within one memory section, was limited to $M = 120$, i.e. more than 14 000 grid points. The program was written in TURBO-Pascal and a PC/XT type computer with an arithmetic coprocessor was used. The grid point values were stored as 4-byte real variables of the type **single**. About 200 – 2 000 iterations were necessary to obtain stable values of the local gradients to 4 – 5 valid digits, and the time necessary for the calculation of one variant was 1 – 200 min.

The retardation factor E defined by Eq. (*4*) was calculated from the concentration gradients in each internal row of the grid, $1 \le j \le N - 1$:

$$E^j = \frac{1}{4}(C_0^{j+1} - C_0^{j-1} + C_M^{j+1} - C_M^{j-1}) + \frac{1}{2}\sum_{i=1}^{M-1}(C_i^{j+1} - C_i^{j-1})\,. \tag{11}$$

The value of E^j for $j = N - 2$ converged most rapidly to a constant value during iterations and gradual halving of the grid. The found values of E^{N-2} for the smallest grid steps, $M = 60$ and 120, were in mutual agreement to 3 – 4 valid digits. These values are summarized in Table I and represent the main result of this work.

TABLE I
Values of retardation factor $E = E(\kappa, \alpha)$

κ	α					
	0.750	0.500	0.250	0.125	0.050	0.025
2	0.914	0.713	0.471	0.335	0.249	0.197
1	0.954	0.827	0.624	0.484	0.387	0.317
0.5	0.979	0.904	0.763	0.647	0.537	0.482
0.2	0.991	0.960	0.890	0.816	0.742	0.702
0.1	0.996	0.980	0.941	0.906	0.852	0.827
0.05	0.998	0.990	0.971	0.949	0.919	0.905

Analytical Approximations of the Concentration Field

The most interesting are such situations in which the surface structure can be considered as microheterogeneous and strongly blocked, i.e. $\kappa < 1$, $\alpha << 1$. The characteristic features of the concentration field are then apparent from Figs 2 and 3, corresponding to numerical data for $\kappa = 0.1$, $\alpha = 0.25$, $E = 0.941$.

The whole integration domain, $0 < X < 1$, $0 < Z < 1/\kappa$, can be divided into three subdomains:

In the outer diffusion layer, $Z > 1$, the concentration field is sufficiently smoothed out by longitudinal diffusion, $\partial_X C << \partial_Z C$, and it is therefore one-dimensional with a constant gradient equal to E:

$$C \approx (1 - E)/\kappa + E Z . \tag{12}$$

The linear concentration profile according to Eq. (*12*) is shown in Fig. 3 by the dotted line.

In the region adjacent to the active surface, the concentration field is close to the course given by the solution of a harmonic equation with constant concentrations at the active surface and at a confocal elliptical cylinder[5] corresponding to the outer boundary of the diffusion layer:

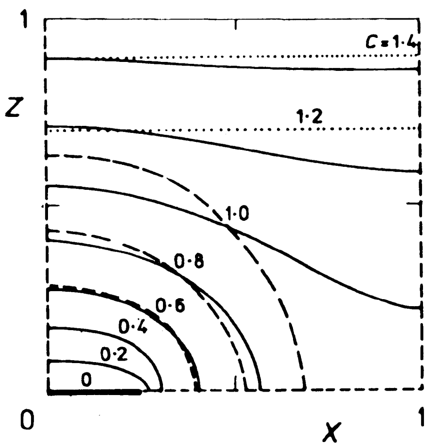

FIG. 2
Concentration field for the case of $\kappa = 0.1$, $\alpha = 0.25$: Solid lines denote numerical results for M, $N = 120$, dashed lines correspond to analytical approximation close to the active surface, dotted line to analytical approximation close to outer limit of the boundary layer

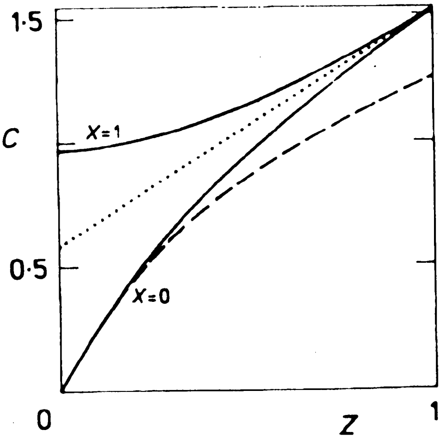

FIG. 3
Normalized concentration profiles. The meaning of the particular lines is the same as in Fig. 2

$$C \approx a \ln [\sigma + (\sigma^2 - 1)^{1/2}] , \quad (13)$$

where σ and τ are orthogonal curvilinear coordinates of elliptic cylinders[5] with foci at the points $Z = 0$, $X = \pm \alpha$, i.e.

$$X^2 = \alpha^2 \sigma^2 \tau^2 , \qquad Z^2 = \alpha^2 (\sigma^2 - 1)(1 - \tau^2) \quad (14)$$

and a is a constant depending on the boundary conditions beside the active surface. It can be found from the condition that the concentration fields (*12*) and (*13*) give the same values of the total diffusion current, i.e. parameter E in Eq. (*4*):

$$a = 2E/\pi . \quad (15)$$

By comparing the approximate representation (*13*) with the numerical solution for $\kappa < 1$, $\alpha < 1$ we can conclude that the approximate solution represents satisfactorily the concentration field in the region of $C < 0.6$, corresponding approximately to a quarter-circle with centre $X = Z = 0$ and radius α. In Fig. 2 are shown the lines of constant concentration according to Eqs (*13*) and (*15*).

Between the two asymptotic regions mentioned there is a transitory region, where the concentration profiles are smoothed out as a result of interactions of periodically placed active bands. The character of this transition is also apparent from Fig. 2.

RESULTS AND DISCUSSION

The values of $E = E(\kappa, \alpha)$ in Table I are equal to the ratio of the transfer coefficient, k, under given conditions to its value for a fully active surface, $k_0 = D/\delta$ ($\alpha = 1$). The tabulated values are for $\kappa \leq 1$ represented by the semiempirical function

$$E(\kappa, \alpha) = 1/[1 + 0.6\kappa(1 - \alpha) \ln (1/\alpha)] \quad (16)$$

with an accuracy to 0.2%. On introducing the additional diffusion path, l, for smoothing out the concentration field by longitudinal diffusion, Eq. (*16*) can be rewritten as

$$k/k_0 = \delta/(\delta + l) , \quad (17)$$

where

$$l = 0.3\lambda(1 - \alpha) \ln (1/\alpha) . \quad (18)$$

The additional diffusion length, l, is of the same order of magnitude as the distance between two neighbouring active zones, $\lambda(1 - \alpha)$. If the latter quantity is sufficiently small, then the additional diffusion resistance becomes negligible even if the active zones participate very little on the whole transport surface, $\alpha << 0.1$. In other words, an estimate of the scale $\lambda(1 - \alpha)$ is necessary if the effect of partial blockade is to be estimated, since the transport near the boundaries between active and inert surface zones is controlled by longitudinal diffusion.

It should be noted that the above analysis, which is formally limited to a stagnant diffusion layer of constant thickness, can also be used to estimate additional diffusion resistance in convective diffusion between a streaming liquid and a micro-heterogeneously blocked convective electrode, $\lambda(1 - \alpha) << \delta$. This can be substantiated as follows. The influence of microheterogeneities on the concentration profiles is, according to the above analysis, equalized in an adhering layer of thickness roughly equal to $\lambda(1 - \alpha)$ (Fig. 2), hence much smaller than δ. The influence of convection on the concentration field in this region, $z << \delta$, is represented with a sufficient accuracy by the Nernst diffusion thickness δ: $c \approx (c_B - c_A)z/\delta$. It can therefore be expected that the correction for the additional resistances in the form of Eq. (*17*) can be used with a moderate accuracy even in the case of convective diffusion. Except for so-called uniformly accessible configurations, the quantities δ and E must be understood in a local sense, since the thickness of the diffusion layer depends on the distance from the leading edge[6].

A drawback of our model is doubtlessly its one-dimensional structure. Sample calculations, however, allow us to conclude that the one-dimensional model gives qualitatively the same results as two-dimensional models of surface inhomogeneity[1,3], if a given diffusion thickness δ, fraction of active surface α, and distance between active zones $\lambda(1 - \alpha)$ are considered. As long as adequate methods for independent determination of the phenomenological parameters λ, α will not be found, minor qualitative deviations between the two models can be tolerated.

The published analyses of the effect of non-uniformly active surface on convective diffusion, based on the concentration boundary layer approach[4,7] with negligible effect of longitudinal diffusion, can only be adequate in cases where the partial blockade measure, λ, is comparable with the local diffusion thickness, δ, or is larger. It is known[8,9] that for convection electrodes of length equal to or smaller than $(9D/\gamma)^{1/2}$ the longitudinal diffusion is the controlling transport mechanism, the effect of longitudinal convection is negligible, and the concentration boundary layer approach is therefore inadequate. For convection electrodes under common conditions, e.g. rotating disc electrode or electrodiffusion friction sensors, we have $D \approx 10^{-9}$ m^2 s^{-1} and $\gamma \approx 10^3$ s^{-1}, hence a prevailing effect of longitudinal diffusion on equalizing the influence of surface inhomogeneity on the concentration profile can be expected already for $\lambda < 10$ μm. The model of the boundary layer type is adequate for nonuniformities of length larger than 10 μm, e.g. in analysis of the influence of insulating insertions between the segments of direction-sensitive electrodiffusion friction sensors[7] or velocity sensors[10].

CONCLUSIONS

To judge the influence of non-uniform catalytic activity or transport resistance of the surface on the total intensity of charge, heat or mass transfer, it is not sufficient to know only the fraction of the active surface α. Another important factor is the characteristic non-uniformity period λ in relation to the local diffusion thickness δ.

Macroscopic surface heterogeneities, whose dimensions λ are equal to or larger than the diffusion thickness, δ, or the internal measure of longitudinal diffusion, $(9D/\gamma)^{1/2}$, must be distinguished from microscopic heterogeneities, which are overlapped by the concentration boundary layer, $\lambda(1 - \alpha) < \delta$, $\lambda(1 - \alpha) < (9D/\gamma)^{1/2}$. In describing the influence of macroscopic heterogeneities, use can be made of the concentration boundary layer approach, while in the case of microheterogeneities the influence of tangential diffusion components must be taken into consideration.

Numerical solution of the problem of linear periodic microheterogeneities leads to a practically applicable correlation Eqs (*16*), (*17*).

SYMBOLS

a	parameter of asymptotic solution, Eqs (*13*), (*15*)
c	concentration
c_A	concentration at the active surface
c_B	concentration in the bulk of the liquid
C	normalized concentration $\kappa^{-1}(c - c_A)/(c_B - c_A)$
D	diffusivity
E	retardation factor, Eq. (*4*), equal to k/k_0
k	local transfer coefficient
k_0	value of k for fully active surface
l	additional diffusion thickness, Eq. (*17*)
M, N	numbers of grid steps (Fig. 1*b*)
x	length coordinate
X	dimensionless longitudinal coordinate, equal to $2x/\lambda$
z	normal coordinate
Z	dimensionless normal coordinate, equal to $2z/\lambda$
α	fraction of active surface
γ	velocity gradient at the wall
δ	diffusion thickness for completely active surface
κ	normalized distance between active centres, equal to $\lambda/2\delta$
λ	distance between active centres on surface
σ, τ	orthogonal curvilinear coordinates of elliptic cylinder

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