

CONVECTIVE DIFFUSION TOWARD ROTATING POLAR SPHERICAL ELECTRODE

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Results are given of a theoretical and experimental study of a convective mass exchange in the regime of limiting diffusion current toward the polar surface of a rotating sphere, for a creeping and boundary-layer type of flow near the surface.

Rotation of bodies in a Newtonian liquid induces a flow in the direction from the axis toward the periphery. Depending on the Reynolds number, one can have three qualitatively different regimes: turbulent or laminar boundary layer or the creeping flow. They correspond to characteristic forced convective diffusion regimes. It should be noted that, for intermediate angular velocities of rotation of the bodies ($\Omega < 200 \text{ rad}\cdot\text{sec}^{-1}$) in highly viscous liquids ($\nu > 10^{-5} \text{ m}^2 \text{ sec}^{-1}$), or for bodies with small radii ($R < 10^{-3} \text{ m}$), the Reynolds numbers Re are considerably smaller than those which correspond to the boundary-layer flow. It is therefore of interest for electrochemical diagnostics of heat- and mass-exchange processes, to consider convective diffusion toward rotating bodies (electrodes) in the creeping flow regime ($Re < 10$).

Up until now, this problem has not been considered [1]. The use of a rotating disk for $Re < 10$ is difficult because of the absence of a theoretical solution of the corresponding hydrodynamic problem [2]. However, a number of authors [3-7] determined theoretically the field of secondary meridian velocities for a rotating sphere. In our investigations of the electrochemical diagnostics of the mass exchange, we used the spherical electrode configuration (Fig. 1). Below, this will be called the rotating polar spherical electrode. This setup has the following advantages:

- 1) In any regime of forced convective diffusion, the surface of the rotating electrode remains equally accessible for diffusion.
- 2) In contrast with the equatorial region, the kinematics of flow in the polar region is known not only for the creeping regime but also for the laminar boundary-layer regime.
- 3) Near the pole opposite the point where the supporting pin is fixed, the velocity field is least affected by the secondary effects.

In the analysis of convective diffusion toward the spherical surface, we used the usual assumptions of the theory of concentration boundary layer and of the corresponding Lighthill computational scheme [1, 8].

In axisymmetric conditions, the meridian velocity components play the dominant role. The solution of the problem of flow near a rotating sphere at low values of Re [3-7] yields the following relation for the gradient of meridian velocities at the wall:

$$\partial_r U_\theta |_{r=R} = \gamma(\Theta) = \frac{1}{4} \Omega Re \sin \Theta \cos \Theta \xi_c \xi_w. \quad (1)$$

The coefficient ξ_c reflects the effect of finite but sufficiently small values of Re [5]. For $\Theta \ll 1$, one can use the approximation

$$\xi_c = 1 - 0.00215 Re^2. \quad (2)$$

The coefficient ξ_w takes into account the effect of stationary walls of the vessel which are, for simplicity, assumed spherical with radius R_b . In practically important situations $R/R_b < 0.25$, and the correction is expressed by the formula

$$\xi_w = 1 - 26.75 (R/R_b)^3 + 67.50 (R/R_b)^4. \quad (3)$$

For an axisymmetric segment of the active area on a slowly rotating sphere, defined by a pair of axial circles $\Theta = \Theta_0, \Theta = \Theta_1$, one can use the kinematic description (1) and a method developed in [8], to obtain the following expression for the mass-

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exchange coefficient:

$$\text{Sh} = \frac{IR}{F_m C_0 D} = \xi_E (\xi_w \xi_c)^{1/3} 0.4891 \text{Re}^{2/3} \text{Sc}^{1/3}, \quad (4)$$

where

$$\xi_E = \left(3 \int_{\Theta_0}^{\Theta_1} \sin^2 x \cos^{1/2} x dx \right)^{2/3} / 2 \int_{\Theta_0}^{\Theta_1} \sin x dx. \quad (5)$$

For a rotating polar spherical electrode, i.e., for $\Theta_0 = 0$, $\Theta_1 \ll 1$, the quantity ξ_E can be approximately expressed by the formula

$$\xi_E = 1 - 0.15 (R_E/R)^2. \quad (6)$$

It follows from the dependence (6) that for $\sin \Theta_1 = R_E/R \leq 0.5$, the values of the mean current density I deviate by no more than 4% from the limiting value at the pole where the conditions of equal accessibility are satisfied fairly accurately. Corrections for effects that are neglected in the scheme of concentration boundary layer were analyzed in detail in [9]. As a result, for sufficiently large Peclet numbers

$$\text{Pe} = (R_E/R)^3 \text{Re}^2 \text{Sc}/12 \gg 10 \quad (7)$$

one can obtain the dependence

$$\beta \equiv \text{Sh} \text{Sc}^{-1/3} = \xi_V \xi_D \xi_E (\xi_w \xi_c)^{1/3} 0.4891 \text{Re}^{2/3}. \quad (8)$$

Here the coefficient ξ_V expresses the effect of the deviation of the real velocity profile from linear [9]:

$$\xi_V = 1 + 2 \text{Re}^{-4/3} \text{Sc}^{-2/3} \exp(-\text{Re}^2 \text{Sc}/12). \quad (9)$$

When conditions (7) hold, this effect is clearly negligible. The coefficient ξ_D takes into account the effect of longitudinal diffusion at the boundaries of the electrode $\Theta = \Theta_1$ where the transport conditions at the wall change in a steplike manner. Using the analysis [10], ξ_D can be expressed in the form

$$\xi_D = 1 + 0.8 \text{Pe}^{-1/2}. \quad (10)$$

The use of the definition of the Peclet number (7) which differs from the traditional expression $\text{Pe} = \text{Re}C_s$ is due to the specific mechanism of convective transport with a characteristic meridian velocity proportional to Re^2 .

For a complete analysis of the data on mass exchange on a rotating sphere, it is convenient to consider not only forced convection in a creeping flow force but also other transport regimes.

In the approximation of laminar and turbulent boundary layers, convective diffusion was considered by a number of authors [1, 8, 10]. It was shown that the conditions for forced convection near the pole are qualitatively identical to the conditions for a rotating disk [1, 8, 10]. For relatively low values of Re and Pe , however, the following corrections should be introduced in the original equation:

$$\beta = \lambda_D \lambda_E (\lambda_c)^{1/3} 0.6205 \text{Re}^{1/2}. \quad (11)$$

Corrections for the curvature of the spherical surface will be taken approximately in the form

$$\lambda_E = 1 - 0.19 (R_E/R)^2. \quad (12)$$

According to [10], the effect of longitudinal diffusion near the edges of a disk electrode can be written as

$$\lambda_D = 1 + 0.55 \text{Pe}^{-1/2} \text{Re}^{1/4}. \quad (13)$$

In the usual transport conditions ($\text{Sc} > 1000$, $10 < \text{Re} < 100$), the most important is the effect of secondary flows in the laminar boundary layer. Their relative contribution is proportional to $\text{Re}^{-1/2}$. Equating the values for β calculated using (8) and (11) for $\text{Re} = 10$ which contain the corrections ξ_c and λ_c , we obtain the empirical estimate

$$\lambda_c = 1 + 0.7 \text{Re}^{-1/2}. \quad (14)$$

In the whole range of Re for a laminar forced convective transport, the inclusion of the secondary convective effects is given by the relation

$$\beta = \beta^*(\text{Re}) = \begin{cases} 0.4891 (\xi_0)^{1/3} \text{Re}^{2/3}, & \text{Re} < 10, \\ 0.6205 (\lambda_c)^{1/3} \text{Re}^{1/2}, & \text{Re} > 10. \end{cases} \quad (15)$$

However, for very small Re, the forced convection is insignificant in comparison with the free or purely molecular diffusion. For the latter, the mean diffusion current density at the rotating spherical polar electrode is given by the relation

$$\text{Sh} = (4/\pi)(R/R_E). \quad (16)$$

Using formula (16) together with the expression for the developed free convection toward a spherical surface [1, 11] or a horizontal disk [1, 12] gives the semiempirical formula

$$\text{Sh}_F = (R/R_E)(1.27 + 0.54(\text{Ra})^{1/4}). \quad (17)$$

The regime for which the forced convection (15) or the free convection (17) are equal, will be called the critical regime.

An estimate of the corresponding critical Reynolds number can be obtained from the condition

$$\beta^*(\text{Re}_{\text{cr}}) = \text{Sc}^{-1/3} \text{Sh}_F. \quad (18)$$

For the correct evaluation of the Rayleigh number

$$\text{Ra}_E = \frac{g R_E^3}{\nu D} \cdot \frac{\Delta \rho}{\rho} \quad (19)$$

it is necessary to take into account realistic concentration conditions near the electrode surface. In equimolar solutions of potassium ferro-ferricyanides, the mass exchange with the cathode or anode by an oxidation–reduction reaction is characterized by the Selmin density correction [13]:

$$\frac{\Delta \rho}{\rho} = 0.167(0 - C_{\text{ferri}}) + 0.226(2C_{\text{ferro}} - C_{\text{ferri}}) = 0.059C_0, \quad (20)$$

where $D_{\text{ferro}} = D_{\text{ferri}}$ and $C_{\text{ferro}} = C_{\text{ferri}} = C_0$. In contrast with the anode region, the solution in the cathode region is denser than in the volume of the liquid.

The aim of the experiments is to test the theoretical dependence $\beta^*(\text{Re})$ given by formula (15). The measurements are based on the cathode reduction of ferricyanide ions from water solutions. In addition to the equimolar quantities of $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ and $\text{K}_3\text{Fe}(\text{CN})_6$, these solutions contained various quantities of supporting electrolyte K_2SO_4 to increase the electrical conductivity, and glycerin and saccharose to increase the viscosity of the electrolyte. All components were technically pure, and the solution was carefully filtered. In particular, the saccharose solutions were boiled for 0.5 h before the reagents were added and were filtered at an increased temperature. In the experiments, we used electrolytes which were 4 h-3 days old after their preparation. No special measures were taken to remove dissolved oxygen. The measurements were done at the ambient temperature which, in the duration the 2 months when the experiment was carried out, remained within the limits from 15 to 23°C. In this range, the parameters of the temperature corrections to the density and viscosity,

$$\rho(T)/\rho(T_r) = \exp(-K_\rho(T - T_r)), \quad (21a)$$

$$\nu(T)/\nu(T_r) = \exp(-K_\nu(T - T_r)) \quad (21b)$$

were determined experimentally. The temperature correction to the diffusion coefficient was done using (21b) according to the widely accepted formula

$$D(T)\nu(T)/T = \text{const}. \quad (22)$$

In the analysis of experimental data, the characteristic temperature was taken as $T = 20^\circ\text{C}$. The data on the composition and some properties of the solution are given in Table 1.

For the given conditions (electrode, electrolyte, angular velocity of rotation), the experiment reduces to the registration of the transient $I-t$ characteristic, i.e., to the determination of the dependence of the density of the electric current I on time t after a discontinuous change of the polarization voltage in the cell (see Fig. 1a) from $\Delta U = 0$ to a constant, previously specified, value ΔU .

The principal diagram of the apparatus is shown in Fig. 1. The rotating electrode was made from a platinum wire of diameter 2 mm. After assembly, the target was polished in the form of a sphere. The experimental bodies were plastic spheres of diameters 20 and 10 mm, and also a disk of diameter 30 mm. The test bodies were positioned in the holder

TABLE 1. Main Data* on the Electrolytes

Solution	Thickener	Thickener concentration, %	ρ	K_ρ	$10^6 \nu$	K_ν	C_0	x_f
01	Standard solution		1038	0,002	1,10	0,023	0,026	4,0
02	«							
03	«							
11	Glycerin	66	1174	0,003	15,9	0,048	0,00865	0
12	«	84	1213	0,003	64,8	0,064	0,0227	0
13	«	82	1210	0,004	56,2	0,062	0,0222	0,02
14	«	76	1200	0,004	36,0	0,056	0,0334	0,04
15	«	70	1188	0,003	23,2	0,050	0,0397	0,05
16	«	65	1173	0,003	13,4	0,046	0,0287	0,4
17	«	55	1163	0,003	7,1	0,041	0,0284	0,4
22	Saccharose	40	1200	0,003	5,6	0,037	0,0301	0,18
23	«	60	1286	0,003	41,8	0,056	0,0320	0,08

*All data are in the principal SI units (see Notation) and are reduced to the temperature 20°C.

of the rotor of viscosimeter RHEOTEST II which allows a stepwise variation of the velocity of rotation from 0.03 to 25.0 rad/sec. The wobble of the electrode did not exceed 0.1 mm. To collect the current from the rotating electrode, we used a graphite brush and a brass ring. The auxiliary electrode from nickel foil of area 0.02 m² was positioned in the volume of the electrolyte near the wall of the glass vessel of diameter 100 mm. The transient I-t curves were registered by various methods. When the time needed to reach the steady-state diffusion current was short (up to 4 sec), we used a loop oscillograph N700. For long times, we used a linear pen recorder of the polarograph Lp7e (Czechoslovak make). In some cases, the measurements were done visually by a galvanometer. Figure 1b shows the volt-ampere characteristics for three solutions when the transition times did not exceed 60 sec. In all these cases, the rate of increase of the voltage was kept constant and equal to 6.67 mV/sec. For sufficiently slow rate of increase of the voltage, with the current increase not more than 10% in the range from $\Delta U = 0.2$ V to $\Delta U = 0.8$ V, analogous volt-ampere characteristics were observed for concentrated glycerin solutions without addition of supporting electrolyte. All subsequent measurements were done at the voltage $\Delta U = 0.7$ V. In the analysis of the transient I-t curves, we determined three parameters I_∞ , t_0 , and t_E which were used for the theoretical description of the transition process in the static potential conditions. The theoretical results which are presented more accurately in [14, 15], lead to the following relations:

$$I(t) = I_\infty N(\Theta), \quad \Theta = (t - t_E)/t_0, \quad (22a)$$

$$N(\Theta) = \begin{cases} \Theta^{-1/2} (1 + 0.025\Theta^3) + \Theta(0.1700 - 0.0029\Theta^3), & \Theta < 1, \\ 1 + 1.0075e^{-1.832\Theta} + 0.81e^{-4.61\Theta} + 0.7e^{-7.9\Theta}, & \Theta > 1. \end{cases} \quad (23)$$

The parameter I_∞ is the steady-state current density. The parameter $I_\infty^2 t_0$, which is independent of the convective conditions, describes the initial stage of the transition process when the following asymptotic relationship holds:

$$\lim_{t \rightarrow 0} (I^2 t) = I_\infty^2 t_0 = (F_m C_0)^2 D / \pi, \quad (24a)$$

and hence we have for the diffusion coefficient

$$D = D_0 = (I_\infty^2 t_0) \pi / (F_m C_0)^2. \quad (24b)$$

The empirical parameter t_E characterizes the various dynamical affects associated with fast changes of the magnitude of the electric current during the initial stage of the transition process. An analysis of the experimental data confirmed the assumption that these phenomena are affected mainly by the retardation of the recording instrument. For example, for very different I-t curves with values of t_0 which differ by decimal orders, the quantities t_E for one particular system of registration were approximately equal. In particular, for the loop oscillograph $t_E = 0.005$ -0.01 sec, and for the linear pen recorder 0.2-0.4 sec which agrees well with the specifications of this instrument. The graphical analysis of the results was done in two stages. The first stage, which gives estimates of t_E and $(I_\infty^2 t_0)$, is based on the linear dependence

$$I^{-2} = (I_\infty^2 t_0)^{-1} (t - t_E), \quad (25a)$$

which is applicable to $t - t_E < 0.1 t_0$. In the second stage, we determined the parameters $(I_\infty^2 t_0)$ and t_0 using the formula

$$(t - t_E)^{1/2} \cdot I = (I_\infty t_0^{1/2}) \left[1 - 0.17 \left(\frac{t - t_E}{t_0} \right)^{3/2} \right], \quad (25b)$$

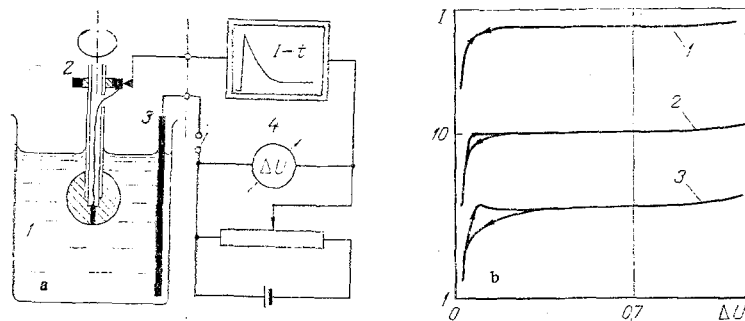


Fig. 1. Diagram of the experimental apparatus (a) and the measured volt-ampere characteristics (b). 1) Electrolyte under study; 2) rotating polar spherical electrode; 3) auxiliary electrode; 4) supply and registration. (b) 1) Solution 01; 2) solution 17; and 3) solution 23. The parameters were $R = 5 \text{ m}$ and $\Omega = 25.5 \text{ rad}\cdot\text{sec}^{-1}$.

TABLE 2. Diffusion Coefficients of the Depolarizer at 20°C , Including Standard Deviations of the Resulting Values

Solution	Thickener	$10^{12}D_0$	$10^{12}D_c$	$10^{12}D_{bl}$	$10^{18}D_{ov}$
01	—	606 ± 15	—	631 ± 10	606
11	Glycerin	35,0	$33,7 \pm 0,5$	$35,6 \pm 0,3$	554
12	«	$6,8 \pm 0,2$	$8,37 \pm 0,4$	—	440
13	«	$8,9 \pm 0,3$	$9,8 \pm 0,2$	9,5	500
14	«	$12,6 \pm 0,1$	$13,4 \pm 0,2$	13,9	450
15	«	$20,6 \pm 0,4$	$20,6 \pm 0,3$	—	478
16	«	39,1	$38,3 \pm 1,8$	$40,6 \pm 0,5$	525
17	«	$76,2 \pm 0,8$	$76,5 \pm 0,8$	$78,7 \pm 1,8$	540
22	Saccharose	$122 \pm 2,6$	125 ± 12	119 ± 1	683
23	«	$18,4 \pm 0,5$	$20,7 \pm 0,9$	$20,5 \pm 1,1$	769

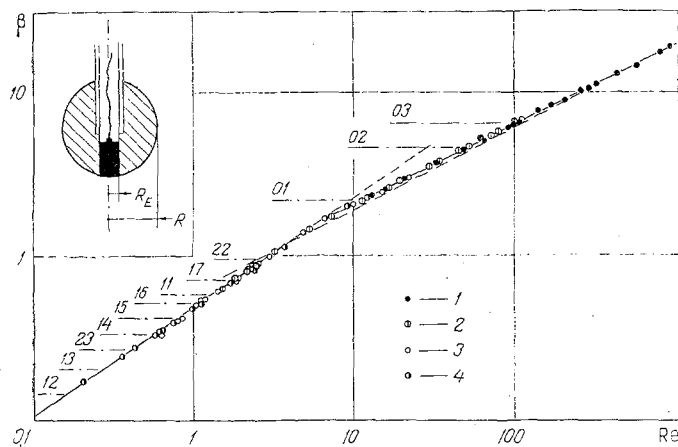


Fig. 2. Results of the experiment $\beta = \beta(\text{Re})$. The full line is the theoretical $\beta^*(\text{Re})$, dashed lines are the asymptotes for the boundary-layer and creeping regimes, and the dash-dot horizontal lines numbered by the electrolytes in Table 1 are the critical values of β for free-convection conditions (Eq. (18)). 1) $\nu = (1-2) \times 10^{-6} \text{ m}^2\cdot\text{sec}^{-1}$; 2) $\nu = (4-5) \times 10^{-6} \text{ m}^2\cdot\text{sec}^{-1}$; 3) $\nu = (14-20) \times 10^{-6} \text{ m}^2\cdot\text{sec}^{-1}$; 4) $\nu = (40-80) \times 10^{-6} \text{ m}^2\cdot\text{sec}^{-1}$.

which is applicable for $t - t_E < t_0$. The quantity t_E was assumed known from the first stage of the numerical and graphical analysis. The final analysis of the experimental data was done on a computer using a nonlinear regression analysis. The obtained quantities D_0 together with the statistical estimate of scatter and the resulting values of D_c (for the creeping regime) and D_{bl} (for the boundary-layer regime) are shown in Table 2. The latter values are calculated using formulas (8) and (11), and regression estimates of the parameter I_∞ .

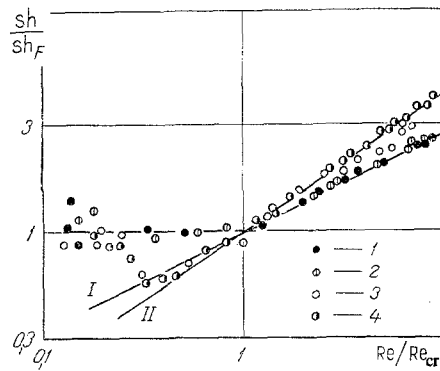


Fig. 3. Functional dependence $Sh(Re)$ in the critical region $Re = Re_{cr}$. Curve I is the asymptote for a boundary-layer flow ($Re \gg 10$), and curve II is the asymptote for creeping flow ($Re \ll 10$). The points 1-4 have the same meaning as in Fig. 2.

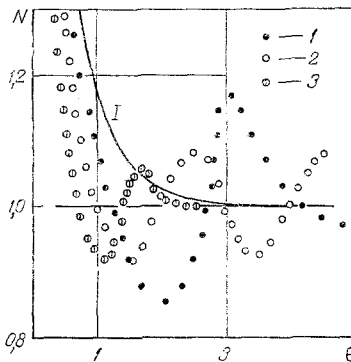


Fig. 4. Normalized transient characteristics in the critical region. 1) Water, $\Omega = 0.4 \text{ rad}\cdot\text{sec}^{-1}$; 2) glycerin, $\Omega = 0.6 \text{ rad}\cdot\text{sec}^{-1}$; 3) water, $\Omega = 0$; I) theory according to (23).

The main aim of this work is to test the theory of steady-state convective diffusion during the creeping rotational flow around rotating sphere and, in particular, to confirm Eq. (8). In the analysis of the data on $I_{\infty} = I_{\infty}(\Omega)$, we therefore used only the values of the diffusion coefficient which were determined independently of the convective conditions of transport.

The statistical analysis of the data in the range $Re_{cr} < Re < 10$, and for a set of 150 separate values of I_{∞} , gave an unexpectedly small scatter. The relative standard deviation of the results did not exceed 3%. This is due mainly to the fact that the obtained values of D_0 contain the random errors of measuring the depolarizer concentration, size of the electrodes, etc.

Consequently, the theoretical results based on Eqs. (8) and (15) can be considered as experimentally confirmed with the above accuracy. Some of the experimental data on $I_{\infty} = I_{\infty}(\Omega)$ shown in Fig. 2 make it possible to estimate the influence of the corrections ξ_c and λ_c . The horizontal dash-dot lines in Fig. 2 show the values $\beta = \beta^*(Re_{cr})$ which correspond to the limiting free-convection current densities. For electrolytes without addition of the thickener, the numbers 01, 02, and 03 denote the corresponding electrodes of diameters 1, 2, and 3 cm. Figure 3 shows the data on the subcritical region ($Re < Re_{cr}$) normalized by the values Sh_F and Re_{cr} according to Eqs. (17) and (18). The results confirm the reliability of the estimates of the values $Sh = Sh_F$ under free-convection conditions ($Re < Re_{cr}$), with accuracy of $\pm 20\%$. For high-viscosity electrolytes, the forced convection regime dominates even at $\Omega = 0.5\Omega_{cr}$. It should be noted that since the complex νD is constant, the critical velocity of rotation Ω_{cr} depends on the viscosity of the electrolyte. In particular, for equimolar ferro-ferricyanide systems for $Re_{cr} < 10$,

$$\Omega_{cr} = 6 \cdot 10^{-8} R^{-1/2} R_E^{-3/2} (1.27 + 3200 Re^{3/4} C_0^{1/4})^{3/2}. \quad (26)$$

For the variation of the parameters R , R_E , and C_0 in the experiment, the critical value of the angular velocity varied from 0.4 to 0.8. For electrolytes with the viscosity of water, the values of Re are in this case so large that the transition from the forced to free convection takes place completely in the laminar boundary-layer regime. It is probable that this is the reason why electrochemists who are interested in low-viscosity electrolytes did not find it necessary to study the conditions of forced convection at very low Re . It follows from Fig. 2 and Table 1 that, for solutions with viscosity of the order $10^{-5} \text{ m}^2 \cdot \text{sec}^{-1}$, there exists a wide range of velocities of rotation with developed creeping flow regime already at relatively high values of R_0 and C_0 . The conditions for the transition from the free to forced convection follow explicitly also from Fig. 3. In the region $Re < Re_{cr}$ for $I(t) < 1.5(I_\infty)$, one observes a deviation of the transient $I-t$ characteristic from the theory (23). Figure 4 shows the $I-t$ characteristics normalized in the usual fashion. The nonmonotonic character of the curve is probably due to the competing interactions of the centrifugal forces and the forces which arise on account of the density gradient. The development of $I-t$ characteristics with one minimum is typical for a stationary electrode. When the behavior of transient characteristics is close to periodic, the periods of oscillation are close to t_0 .

NOTATION

C_0 , molar concentration of the depolarizer; D , diffusivity of the depolarizer; D_0 , D_c , and D_{bl} , experimental diffusion coefficients found from the transient $I-t$ characteristics; F_m , charge transferred to the test electrode by 1 kmole of the depolarizer; I , mean electric current density at the test electrode; r , θ , and φ , spherical coordinates; R , radius of the sphere; R_E , polar electrode radius; T , temperature; x_p , concentration of the supporting electrolyte; γ , gradient of the meridian velocities near the wall; ν , kinematic viscosity; ρ , density; and Ω , angular velocity of the rotating body.

LITERATURE CITED

1. T. Z. Fahidy and S. Mohanta, "Mass transport in electrochemical systems," in: *Advances in Transport Processes* (editors A. S. Mujumdar and R. A. Mashelkar), Vol. 1, Wiley Eastern, New Delhi (1980), p. 276.
2. D. F. Griffith, D. T. Jones, and K. Walters, "A flow reversal due to edge effects," *J. Fluid Mech.*, **36**, Pt. 1, 161-175 (1969).
3. W. G. Bickley, "The secondary flow due to sphere rotating in viscous fluid," *Philos. Mag.*, **25**, No. 170, 746-752 (1938).
4. M. A. Gol'dshtik, "Secondary flows around a sphere during its rotation in viscous fluid," *Inzh.-Fiz. Zh.*, **3**, No. 3, 79-85 (1960).
5. W. L. Haberman, "Secondary flow about a sphere rotating in a viscous fluid inside a coaxially rotating spherical container," *Phys. Fluids*, **5**, No. 5, 625-626 (1962).
6. W. D. Collins, "Viscous flow induced by slow rotating of a sphere," *Mathematics*, **2**, 42-53 (1955).
7. H. Takagi, "Viscous flow induced by slow rotating of a sphere," *J. Phys. Soc. Jpn.*, **42**, No. 1, 319-325 (1977).
8. J. Newman, "Mass transfer to a rotating sphere at high Schmidt numbers," *J. Electrochem.*, **119**, No. 1, 69-71 (1972).
9. O. Wein, "Transient convective diffusion for the hydrodynamic stagnant region with an applicability to electrochemistry," *Coll. Czech. Chem. Commun.*, **46**, 3221-3231 (1981).
10. W. H. Smyrl and J. Newman, "Limiting current on a rotating disc with radial diffusion," *J. Electrochem. Soc.*, **118**, No. 7, 1079-1081 (1971).
11. C. Schütz, "Natural convection mass transfer measurements on spheres and horizontal cylinders by an electrochemical method," *Int. J. Heat Mass Transfer*, **6**, No. 10, 873-879 (1963).
12. A. A. Wragg, "Free convection mass transfer at horizontal electrodes," *Electrochim. Acta*, **13**, No. 12, 2159-2165 (1968).
13. J. R. Selman and J. Newman, "Free convection mass transfer with supporting electrolyte," *J. Electrochem. Soc.*, **118**, No. 7, 1070-1079 (1971).
14. V. S. Krylov and V. N. Babak, "Nonstationary diffusion toward the surface of a rotating disc," *Élektrokimiya*, **7**, No. 5, 649-655 (1971).
15. K. Nisanioglu and J. Newman, "Transient convective diffusion to a disk electrode," *J. Electroanal. Chem.*, **50**, No. 1, 23-29 (1974).