CONVECTIVE DIFFUSION TO A SLOWLY ROTATING SPHERICAL ELECTRODE; BASIC MODEL FOR $Re \to 0$, $Pe \to \infty$

Ondřej WEIN

Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, 165 02 Prague 6

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Theory has been formulated of a convective rotating spherical electrode in the creeping flow regime ($Re \to 0$). The currently available boundary layer solution for $Pe \to \infty$ has been confronted with an improved similarity description applicable in the whole range of the Peclet number.

Application of a rotating spherical electrode under the convective conditions of the hydrodynamic boundary layer[1-5], *i.e.* for $Re \gg 10$, offers no advantages over the known[6] rotating disc electrode. A different situation arises in the case of viscous liquids, rotating microelectrodes or in region of low speeds of rotation. In all these cases the Reynolds number, $Re = \Omega R^2 \varrho/\eta$, may assume subcritical values, $Re \ll 10$, when the character of the flow is that of the creeping motion. The hydrodynamic theory of three dimensional creeping rotational flow past a slowly rotating sphere has remained so far the only in detail examined case of this type of the secondary creeping flow[7-11]. Based on the knowledge of the field of meridional velocities, theory can be formulated for this case of the convective diffusion. This theory has been used earlier to interpret some absolute electrochemical measurements in high viscosity liquids using a polar electrode mounted flush on a rotating spindle[12,13]. For similar purposes the disc electrode has been so far inapplicable as the field of meridional velocities for $Re \to 0$ has been in this case unknown.

The present paper explains the earlier experimentally utilized[12,13], yet so far unpublished theory of convective diffusion to a slowly rotating sphere ($Re \to 0$) under the conditions allowing utilization of the concentration boundary layer concept ($Pe \to \infty$).

THEORETICAL

The Axially Symmetric Concentration Boundary Layer

The mathematical theory of convective diffusion is generally coupled with the study of the boundary value problems of the elliptic type. An important exception to this rule represent problems of convective diffusion in the flow past a wall where a constant concentration of the transported solute is maintained. For a broad region of controlling conditions (velocity of liquid, dimensions of the transport active surface, diffusion coefficient of the transported solute) the transport of the solute takes place only within a thin shell adherring to the wall (the concentration boundary layer, CBL) while the composition of the core of liquid remains essentially unaffected. Under such circumstances the problem may be formally simplified as follows: *1*) neglect diffusional fluxes parallel to the wall compared to the lateral diffusional fluxes; *2*) neglect effects of curvature of CBL in the convective and diffusional terms; *3*) linearize profile of the longitudinal velocity in CBL; *4*) take concentration of the transported solute outside CBL constant, $c = c_0$.

The simplifications *1* and *4* reduce the studied problem to a parabolic one, while the simplifications *2* and *3* enable similarity solution to be obtained in a simplified closed form. For twodimensional systems with planar symmetry corresponding similarity transformation has been formulated by Lighthill[14]; for axially symmetric problems his results have been modified by Acrivos[15]. Certain applications of these transformations to problems of electrochemical convective diffusion under the conditions of limiting diffusion current have been published in Newman's surway[16].

For axially symmetric cases[15,16] the results of the theory of CBL may be summarized as follows. In local Cartesian coordinates (x, y), (Fig. 1) and after the above mentioned simplifications the equation of convective diffusion takes the form:

$$\gamma y(\partial_x c - \partial_x[\ln(r_0 \gamma)^{1/2}]\, y \partial_y c) = D\, \partial_{yy}^2 c\,, \tag{1}$$

where $r_0 = r_0(x)$ determines the profile of the rotationally symmetric wall confining the flow and $\gamma = \gamma(x)$ designates local gradient of longitudinal velocity on the wall, $\gamma = \partial_y v_x|_{y=0}$. Solution of this parabolic equation with the boundary conditions as

$$c = 0 \quad \text{for} \quad y = 0 \quad \text{and} \quad x > 0 \tag{2a}$$

$$c = c_0 \quad \text{for} \quad y = \infty \quad \text{or} \quad x = 0 \tag{2b}$$

may be expressed in the form with a single independent variable

$$c = c_0 \int_0^{\xi} \exp(-s^3)\, ds \Big/ \int_0^{\infty} \exp(-s^3)\, ds\,, \tag{3}$$

$$\xi = y D^{-1/3} \varkappa(x)\,, \tag{4}$$

where

$$\varkappa(x) = (r_0 \gamma)^{1/2} \left[9 \int_0^x (r_0^3 \gamma)^{1/2}\, dx \right]^{-1/3}. \tag{5}$$

The resulting local and mean fluxes may then be expressed by simple explicit formulas

$$J(x) \equiv D\,\partial_y c\big|_0 = D^{2/3} c_0\, \varkappa(x)/\Gamma(4/3) \tag{6}$$

$$\bar{J}(L) \equiv \int_0^L J(x)\, r_0(x)\, \mathrm{d}x \Big/ \int_0^L r_0(x)\, \mathrm{d}x = D^{2/3} c_0\, \bar{\varkappa}(L)/\Gamma(4/3) \tag{7}$$

where, according to (5) and (7)

$$\bar{\varkappa}(L) = \frac{1}{6}\left[9\int_0^L (r_0^3\gamma)^{1/2}\,\mathrm{d}x\right]^{2/3} \Big/ \int_0^L r_0(x)\,\mathrm{d}x\,. \tag{8}$$

The Nernst mean thickness of the concentration boundary layer is introduced by the usual definition as $\delta = Dc_0/\bar{J}$. If γ_L is a characteristic mean value of the gradient of meridional velocity on the wall, then we have clearly from Eqs (7), (8)

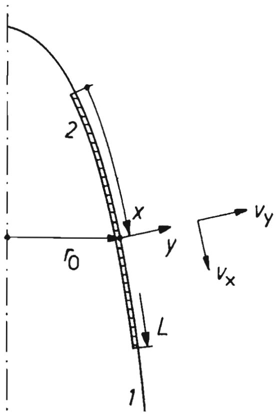

FIG. 1

Boundary layer coordinates on an axially symmetric body. *1* Body, *2* sunk electrode

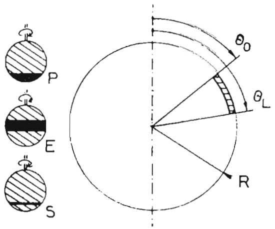

FIG. 2

Geometry of a spherical rotating electrode (RSE). P Polar RSE, E equatorial RSE, S sandwich RSE the following proportionalities $\delta/L \sim D^{1/3}\gamma_L^{-1/3}L^{-2/3}$. These relations lead in accord with the current definition of the Péclet number, to a general expression as

$$Pe_L = \gamma_L L^2 D^{-1} . \tag{9}$$

A successful application of the concentration boundary layer theory is thus limited by the condition $Pe_L \to \infty$.

Let us consider now the case of convective diffusion to an electrode formed by a symmetric part of the slowly rotating spherical spindle, (Fig. 2). The hydrodynamic theory[7-11] of the creeping flow, $Re \to 0$, of unconfined Newtonian liquids, induced by a slow rotation of a sphere, offers the following description of the meridional velocity gradient on the surface of the wall in spherical coordinates (r, θ, φ):

$$\gamma(\theta) = \partial_r v_\theta \big|_{r=R} = \tfrac{1}{4}\Omega Re \sin\theta \cos\theta . \tag{10}$$

In spherical coordinates, we clearly have $x = R(\theta - \theta_0)$, $r_0 = R \sin\theta$, for spherical surface of the electrode (Fig. 2). The resulting general relations (3), (6), (7) may thus be used in the given case with the following expression of the kinematic parametes $\varkappa$, $\bar{\varkappa}$:

$$\varkappa = (\Omega^2 R\varrho/\eta)^{1/3}\, 12^{-1/3} G(\theta_0, \theta) , \tag{11a}$$

$$\bar{\varkappa} = (\Omega^2 R\varrho/\eta)^{1/3}\, 12^{-1/3} \bar{G}(\theta_0, \theta_L) , \tag{11b}$$

where

$$G(\theta_0, \theta) = (\sin^2\theta \cos\theta)^{1/2}\, H^{-1/3}(\theta_0, \theta) , \tag{12a}$$

$$\bar{G}(\theta_0, \theta_L) = 0{\cdot}5 H^{2/3}(\theta_0, \theta_L)/(\cos\theta_0 - \cos\theta_L) , \tag{12b}$$

$$H(\theta_0, \theta) = 3 \int_{\theta_0}^{\theta_L} \sin^2 s \cos^{1/2} s \, ds . \tag{13}$$

The integral $H(\theta_0, \theta)$ can be computed with sufficient accuracy from the following expansions:

$$H(0, \theta) \doteq \begin{cases} \theta^3(1 - 0{\cdot}35\theta^2 + 0{\cdot}03125\theta^4) , & \theta \leqq 1 \\ 1{\cdot}43777 - 2q^{3/2}(1 - 0{\cdot}4643q^2 + 0{\cdot}25q^4) ; & 1 < \theta \leqq \pi/2 , \end{cases} \tag{14}$$

where it is $q = \pi/2 - \theta$ in the second expression.

In the special, and probably the most interesting case of a rotating spherical polar electrode[12,13], when $\theta_0 = 0$, $\theta_L \ll 1$, one can find the following approximate expression for the mean diffusional fluxes

$$\overline{Sh} = 0{\cdot}4891(Re^2Sc)^{1/3}(1 - 0{\cdot}15\sin^2\theta_L - 0{\cdot}09\sin^4\theta_L)\,. \tag{15}$$

For the case of the electrode being formed by the whole surface of the rotating sphere the corresponding exact expression of the mean diffusional fluxes is

$$\overline{Sh} = 0{\cdot}3115(Re^2Sc)^{1/3}\,. \tag{16}$$

An Improved Similary Description of the Convective Diffusion to a Sphere

An exact description of the axially symmetric steady convective diffusion past a spherical surface may be generally given as:

$$-\partial_\theta\chi\,\partial_r c + \partial_r\chi\,\partial_\theta c = D\sin\theta[r^{-2}(r^2\,\partial_r)^2\,c + \sin^{-2}\theta(\sin\theta\,\partial_\theta)^2\,c] \tag{17}$$

where $\chi(r, \theta)$ is a spherical stream function

$$v_\theta = (r\sin\theta)^{-1}\,\partial_r\chi\,,\quad v_r = (r^2\sin\theta)^{-1}\,\partial_\theta\chi\,. \tag{18a,b}$$

For the meridional flow induced by a slow rotation of a sphere, $Re \to 0$, in an unconfined Newtonian liquid there exists an exact expression for the stream function[7-11]

$$\chi = \tfrac{1}{4}\Omega R^3 Re\sin^2\theta\cos\theta Y^2/2\,, \tag{19}$$

where

$$Y = 1 - R/r\,. \tag{20}$$

Substituting Eq. (*19*) into Eq. (*17*) and introducing a new quasi-similarity variable $c(r, \theta) = c_0 C(Z, \theta)$ where

$$Z = Pe^{1/3}YG\,, \tag{21}$$

with Y being given by Eq. (*20*), $G = G(\theta_0, \theta)$ by Eq. (*12a*) and

$$Pe = Re^2Sc/12\,, \tag{22}$$

the transport equation (*17*) modifies to the form

$$\partial^2_{ZZ}C + 3Z^2\,\partial_Z C = M_C[C] - M_D[C]\,, \tag{23}$$

where

$$M_C[C] = 3\sin\theta\cos\theta G^{-3}Z\,\partial_\theta C \tag{24}$$

expresses some secondary convective effects away from the surface of the sphere and

$$M_D[C] = Pe^{-2/3}G^{-2}(1 - Y)^{-2} \sin^{-2}\theta\,[\sin\theta\,\partial_\theta + \sin\theta G^{-1}G'Z\,\partial_Z]^2 C \quad (25)$$

incorporates the complete effect of longitudinal diffusion.

In this work we shall neglect both mentioned secondary effects assuming that $M_D = 0$, $M_C = 0$. The resulting solution of the improved similarity problem with the boundary conditions apparent from Eqs (*20*) and (*21*)

$$C = 0 \quad \text{for} \quad Z = 0\,, \quad (26a)$$

$$C = 1 \quad \text{for} \quad Z = p \equiv Pe^{1/3}G \quad (26b)$$

takes a similar structure as the similarity solution in the boundary layer approximation:

$$C = \int_0^Z \exp(-s^3)\,ds \Big/ \int_0^p \exp(-s^3)\,ds\,, \quad (27)$$

$$Sh(\theta) = p \Big/ \int_0^p \exp(-s^3)\,ds\,. \quad (28)$$

In the last expression one can use with the accuracy better than 0·5% the following approximation

$$Sh(\theta) \approx \begin{cases} 1 + 0{\cdot}25p^3\,; & p < 1{\cdot}1 \\ 1{\cdot}120p(1 + 0{\cdot}37p^{-2}\exp(-p^3))\,; & p > 1{\cdot}1\,. \end{cases} \quad (29)$$

DISCUSSION AND CONCLUSION

The assessment of the accuracy of the improved similarity solution (*28*), (*29*) through a detailed study of the boundary value problem (*23*), (*26a,b*), with eventually additional conditions, appears difficult and particularly more so far the practically important case of high values of p. Relatively easily it is seen that if $p \gg 1$ then $M_D \sim \sim Pe^{-2/3}$, while $M_C \sim \exp(-Pe)$. Examination of the secondary convective effects, without simultaneous incorporation of the effect of longitudinal diffusion, thus clearly is not adequate. Numerical solution of this problem[17] for the special case of polar electrode, $\theta_0 = 0$, $\theta_L \ll 1$, however, suggests that already for $p = 2{\cdot}5$ all side effects, associated with the terms $M_C \neq 0$, $M_D \neq 0$ in Eq. (*23*), may be neglected while preserving the accuracy of the result, according to Eq. (*29*), better than 0·5%. This excellent accuracy of the improved similarity description may be explained by the fact that the transport equation $\partial^2_{ZZ}C + 3Z^2 \partial_Z C = 0$ incorporates exactly all radial diffusional and convective terms of the original transport equation and the effect of longitudinal convection is slightly distorted by the assumption of $M_C = 0$ only in the region outside the concentration boundary layer. From this originates also the finding that the model yields correct answers ($Sh = 1$) also for $Pe = 0$.

The principal result of the presented analysis is the conclusion that for $p \geqq 1{\cdot}5$, *i.e.* roughly for $Re^2Sc \geqq 40$, the results of the boundary value solution of the problem may be regarded as sufficiently accurate. For current values of $Sc > 1\,000$ the measurements on polar rotating spherical electrodes may thus be safely carried out still in the region of $Re \approx 0{\cdot}2$ and even lower[13]. The real limitations of the range of operating parameters – the electrode diameters, speed of rotation, viscosity – toward $Re \to 0$ are usually set by other factors, most often by the effect of free convection. Free convection dominates as soon as the estimate of the mean diffusional fluxes due to the free convection from current correlations[16,17] exceeds the value of $\bar{J}$ following from the boundary value description of the forced convective diffusion effects, Eq. (*15*).

LIST OF SYMBOLS

c	concentration of the transport solute
c_0	concentration in the bulk liquid
D	diffusivity
$G, \bar{G}$	function defined in Eq. (*12a,b*)
$J, \bar{J}$	local and mean diffusional flux, Eqs. (*6*), (*7*)
L	longitudinal transport length of the electrode (Fig. 1)
p	parameter, defined in Eq. (*26b*)
$Pe = \Omega^4 R^2 \varrho/(12D\eta)$	
r	spherical radius
r_0	local axial radius of the wall (Fig. 1)
R	radius of sphere
$Sh = JR/(c_0D)$	
$\overline{Sh} = \bar{J}R/(c_0D)$	
$Re = \Omega R^2 \varrho/\eta$	
$Sc = \eta/(\varrho D)$	
x, y	boundary layer coordinates (Fig. 1)
γ	gradient of meridional velocity
η	viscosity
ϱ	density
θ	meridional angle (Fig. 2)
θ_0, θ_L	geometrical parameters of electrode (Fig. 2)
Ω	angular speed of rotating electrode

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