CONVECTIVE DIFFUSION TO THE DISC ELECTRODE ROTATING SLOWLY IN A VISCOELASTIC LIQUID

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Received April 23rd, 1986

Limiting diffusion currents toward the rotating disc electrodes are determined theoretically for the cases of low Reynolds numbers, Re $\ll$ 10, and for viscoelastic liquids with non-zero normal stress differences, Ab $>$ 0. The case of Newtonian fluid, Ab $=$ 0, at low Re is considered in details and is tested by comparing the theoretical prediction with experimental data.

Measurement of elastic normal stresses in dilute polymer solutions at low shear rates is an extremely difficult experimental task which assumes the indirect determination of pressure differences of the order of magnitude $10^{-4}-10^{-2}$ Pa.

For such an aim, all known mechanical methods[1,2] are hopelessly rough and therefore they are applicable merely to cases of rather concentrated polymer solutions (over 1 000 ppm) or rather high shear rates (over 100 s^{-1}).

One of possible indirect methods of determination of normal stress differences consists in investigation of the meridional flow generated by a slowly rotating spindle in a pool of quiescent viscoelastic liquid[3-5]. The meridional flow of centrifugal nature can be supressed significantly for viscoelastic liquids or even can change its direction to so-called centripetal streaming. The well-known visual observation of the centripetal streaming in highly concentrated polymer solutions can be used for determination of their elastic properties[6-8]. The electrodiffusion measurement[9-11] of the meridional velocity gradients at the wall of a rotating spindle seems to be substantially more sensitive because it indicates even a slight suppresion of the centrifugal streaming due to the liquid elasticity.

The said electrodiffusion measurements were conducted by using spherical spindles as the only existing theory has been developed for the primary flow with the spherical symmetry. This is rather strong limitation because sensitivity of the method is inversely proportional to the square of spindle radius and it is impossible to prepare spherical spindles of radiuses below 1 mm. On the other hand there is no trouble to prepare rotating disc electrodes with a cylindrical spindle with 100 μm in dia-

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meter. Therefore it seems to be of some interest to develop a corresponding theory, which is lacking even for the relatively simple case of low-Re rotational flow of Newtonian liquids.

The main purpose of this study is to develop the theory of steady convective diffusion to a disc-like spindle rotating slowly (Re $\ll 10$) in a viscoelastic liquid with the constant material parameters η, ν_1, ν_2. The theory is compared with experimental data on steady limiting current densities for Newtonian fluids in the region Re < 100. As the result, a semiempirical modification is suggested of the well-known Levich's formula in the low-Re region.

THEORETICAL

Convective Diffusion to a Rotating Disc Electrode at Re $\to 0$, Ab > 0

The limiting diffusion current[9–12] detected at electrochemical mass transfer measurements is fully controlled by convective diffusion in a thin diffusion layer close to the surface of an electrode. In particular, local current density $J(r)$ at the surface of RDE (rotating disc electrode) of a known radial profile of meridional velocity gradient

$$\partial_z v_r|_{z=0} = \gamma_M(r)\,, \tag{1}$$

is given by the equation[12–14]

$$J(r) = nFD^{2/3}c^B\varkappa(r)\,, \tag{2}$$

where the parameter

$$\varkappa(r) = \frac{(r\gamma_M(r))^{1/2}}{\Gamma(4/3)}\left\{9\int_0^r (r_1^3\gamma_M(r_1))^{1/2}\,dr_1\right\}^{-1/3} \tag{3}$$

characterizes intensity of the convective mass transfer. For so-called electrodes with uniformly accessible surface[12–14] the meridional velocity gradient γ_M is proportional to the distance to axis of rotation, $\gamma_M = A\,.\,r$ and Eq. (3) is reduced to the relation $\varkappa(r) = (A/3)^{1/3}$. Such kinematics is typical *e.g.* for the laminar boundary layer flow of a Newtonian liquid around a rotating disc for $2\,.\,10^2 <$ Re $< 2\,.\,10^5$. In this case there holds[12] $A = 0{\cdot}51023\Omega^{3/2}(\eta/\varrho)^{-1/2}$ and according to Eq. (2)

$$J = j = 0{\cdot}6502nFD^{2/3}c^B\Omega^{1/2}(\eta/\varrho)^{-1/6}\,. \tag{4}$$

The dynamics of rotational flow of viscoelastic liquid is governed by three viscometric material functions[5,15]

$$\tau_{12} = \eta\gamma\,,$$

$$\tau_{11} - \tau_{22} = \nu_1 \gamma^2 , \qquad (5)$$
$$\tau_{22} - \tau_{33} = \nu_2 \gamma^2 ,$$

which can be determined by mechanical measurements under viscometric conditions of flow, for which $v_1 = \gamma x_2$. Assuming the meridional component of velocity field sufficiently small, $\gamma_M \ll \Omega$, and the material coefficients η, ν_1, ν_2 constant, the kinematics of the meridional streaming under creeping flow conditions, Re → 0, is fully characterized by the pair of rheodynamic similarity criteria

$$\mathrm{Re} = \Omega R^2 \varrho / \eta , \qquad (6)$$

$$\mathrm{Ab} = (\nu_1 + 2\nu_2)/(\varrho R^2) . \qquad (7)$$

An explicite solution on steady rotational flow of viscoelastic (second order) liquid is known for spherical[3,4] and spheroidal[16,17] spindles under simplifying asymptotic conditions Re → 0, $0 \leqq \mathrm{Ab} < 1$.

By starting with the results[16,17] it is possible to develop the following expression for the meridional velocity gradient γ_M at the surface of an infinitely oblate spheroid of radius R (a disc):

$$\gamma_M(r) = \Omega \, \mathrm{Re} \, Y[a_v \sqrt{(1 - Y^2)} + (b_v - b_E \, \mathrm{Ab})/\sqrt{(1 - Y^2)}] \qquad (8)$$

with $Y = r/R$, and

$$a_v = \frac{128}{\pi^3} - \frac{38}{3\pi} = 0{\cdot}09627 , \qquad (9a)$$

$$b_v = \frac{27}{12\pi} - \frac{12}{\pi^3} = 0{\cdot}59444 , \qquad (9b)$$

$$b_E = \frac{14}{\pi} - \frac{16}{\pi^3} = 3{\cdot}94031 . \qquad (9c)$$

Substitution of Eq. (8) into Eq. (3) gives an explicit expression of the limiting current densities in the form generally suggested in Eq. (2). It is necessary to know the overall current I or the corresponding mean current density j over the surface of the working electrode of radius $R_w < R$

$$I = \int_0^{R_w} J(r) \, 2 \, \pi r \, \mathrm{d}r = j \, \pi R_w^2 , \qquad (10)$$

where

$$j \equiv \frac{I}{\pi R_w^2} = nFD^{2/3} c^B \bar{\varkappa}(R_w) \qquad (11)$$

and[12,13]

$$\bar{\varkappa}(R_w) = \frac{1}{3R_w^2}\left\{9\int_0^{R_w}(r^3\gamma_M(r))^{1/2}\,dr\right\}^{2/3}. \qquad (12)$$

By expanding $\gamma_M(r)$ according to Eq. (8) into the Taylor series and by integrating the results according to Eq. (12), an approximate expression of $\bar{\varkappa}$

$$\bar{\varkappa}(R_w) \approx \left(\frac{\Omega \mathrm{Re}}{3R_w}(a_v + b_v - b_E\,\mathrm{Ab})\right)^{1/3} \cdot \left(1 - \frac{1}{10}\frac{a_v + b_E\,\mathrm{Ab}}{a_v + b_v - b_E\,\mathrm{Ab}}\left(\frac{R_w}{R}\right)^2\right) \qquad (13)$$

can be obtained which guarantees the accuracy better than $\pm 1\%$ of the resulting $\bar{\varkappa}$ for $\mathrm{Ab} < 0.15$ and $R_w/R < 0.5$.

Genfralized Levich Formula for Newtonian Liquids

Newtonian liquids with constant material coefficients $\eta > 0$, $\nu_1 = \nu_2 = 0$ represent a special case of the considered class of viscoelastic liquids. In this case Eq. (13) is reduced to a form which can be arranged to the following expression of the mean current density

$$j = 0.6864 nFD^{2/3}c^B\left(\frac{\Omega^2 R\varrho}{\eta}\right)^{1/3}. \qquad (14)$$

The second order term $0(R_w/R)^2$ has been neglected in the expression (14) as it represents less than 0.5% of the total value of j for Newtonian liquids with $(R_w/R) < 0.5$.

By introduction of dimensionless parameters, the final asymptotic results (4) and (14) for the Newtonian liquids can be represented in the following form

$$\beta \approx \begin{cases} 0.6864\,\mathrm{Re}^{2/3}\,; & \mathrm{Re} \ll 1 \\ 0.6205\,\mathrm{Re}^{1/2}\,; & \mathrm{Re} \ll 1\,, \end{cases} \qquad (15a,b)$$

where

$$\beta \equiv jR/[nFc^B D^{2/3}(\eta/\varrho)^{1/3}]\,. \qquad (16)$$

The main purpose of the following part of this study is to match two asymptotes in a reasonable way. From general properties of perturbation schemes for the creeping flow asymptotes[5,9,18] and the boundary-layer flow asymptotes[19] it can be deduced that the first neglected terms in expressions for $\gamma_M(r)$ are of the order of $0(\mathrm{Re}^2)$ and $0(\mathrm{Re}^{-1/2})$ for $\mathrm{Re} \to 0$ and $\mathrm{Re} \to \infty$, respectively. The following formulas

$$\beta(\mathrm{Re}) \approx \begin{cases} 0{\cdot}6864\ \mathrm{Re}^{2/3}(1 + \lambda_0\ \mathrm{Re}^2)^{1/3}\,; & \mathrm{Re} < \mathrm{Re}_t \\ 0{\cdot}6205\ \mathrm{Re}^{1/2}(1 + \lambda_\infty\ \mathrm{Re}^{-1/2})^{1/3}\,; & \mathrm{Re} > \mathrm{Re}_t \end{cases} \qquad (17a,b)$$

with the pair of adjustable parameters λ_0, λ_∞ could present a sound base for semiempirical matching procedure because the proportionality $\beta \sim \gamma_M^{1/3}$ follows from the general formulas (2) and (3). Two of the parameters λ_0, λ_∞ and Re_t can be adjusted by requiring continuity and smoothness of the function $\beta = \beta(\mathrm{Re})$ in the neighbourhood of the transient point Re_t. It is known[20] that the kinematics of the boundary layer flow, $\mathrm{Re} \gg 1$, near the poles of a spindle is identical for both spherical and disc-like bodies. Therefore it is possible to accept $\lambda_\infty = 0{\cdot}7$ from the previous analysis[9] for spherical electrodes. Then, by applying the said smoothing conditins the remaining two parameters in the formula (17) can be adjusted with the following result:

$$\beta(\mathrm{Re}) \approx \begin{cases} 0{\cdot}6864\ \mathrm{Re}^{2/3}(1 - 0{\cdot}055\ \mathrm{Re}^2)^{1/3}\,; & \mathrm{Re} < 2 \\ 0{\cdot}6205\ \mathrm{Re}^{1/2}(1 + 0{\cdot}7\ \mathrm{Re}^{-1/2})^{1/3}\,; & \mathrm{Re} > 2\,. \end{cases} \qquad (18a,b)$$

RESULTS AND DISCUSSION

This semiempirical formula was tested by measuring the limiting current densities for two types of rotating electrodes which are shown in Fig. 1 as the type D (disc-like spindle) and type C (cylindrical spindle). Altogether, two electrodes of the type C ($R = 10$ mm and $R = 20$ mm with common $R_w = 1{\cdot}025$ mm) and two electrodes of the type D ($R = 4$ mm, $R_w = 2{\cdot}240$ mm and $R = 2$ mm, $R_w = 1{\cdot}025$ mm) were used in the mass transfer experiments. The experimental arrangement was the same as in the other reported experimental studies[9,10].

TABLE I
Properties of used solutions

Solution	S1	S2
Saccharose content, mass %	55·0	82·0
$K_3Fe(CN)_6$ content, mol m^{-3}	25·0	25·0
$K_4Fe(CN)_6 \cdot H_2O$ content, mol m^{-3}	25·0	25·0
K_2SO_4 content, mol m^{-3}	57·0	57·0
Temperature, K	298·3	298·3
D, $m^2\ s^{-1}$	$56{\cdot}2\ 10^{-12}$	$17{\cdot}2\ 10^{-12}$
η/ϱ, $m^2\ s^{-1}$	$14{\cdot}0\ 10^{-6}$	$55{\cdot}6\ 10^{-6}$

The model Newtonian liquids were prepared from concentrated saccharose–water solutions by adding appropriate amounts of ferro-ferricyanide depolarizers and potassium sulphate as a supporting electrolyte[9,10]. Diffusivity of the working depolarizer $Fe[(CN)_6]^{3-}$ was determined in an independent mass-transfer experiment, by measuring the transient current-time characteristics under potentiostatic conditions[21]. The relevant properties of the used solutions are given in Table I.

The steady limiting cathodic currents at the constant overpotential − 700 mV were measured in dependence on the speed of rotation of a spindle within limits 0·5 – 500 rad s^{-1}. The results of treating these data are shown in Fig. 1.

For electrodes of the type D, the results agree well with the semitheoretical prediction, Eq. (*18*), within deviations less than ±5%. Substantially lower current densities in the low-Re region Re < 100 were found for electrodes of the type C. By fitting these experimental data to general correlation formula (*17*) under the continuity and smoothing conditions, the following empirical formula was obtained

$$\beta = \begin{cases} 0{\cdot}44\ \mathrm{Re}^{2/3}\ ; & \mathrm{Re} < 2 \\ 0{\cdot}62\ \mathrm{Re}^{1/2}(1 - 0{\cdot}7\ \mathrm{Re}^{-1/2})^{1/3}\ ; & \mathrm{Re} > 2\,. \end{cases} \qquad (19a,b)$$

The last result is also demonstrated in Fig. 1 by the curve C.

CONCLUSIONS

A theoretical prediction of the intensity of convective diffusion to a disc-like spindle rotating slowly in a Newtonian liquid was checked experimentally. Good agreement

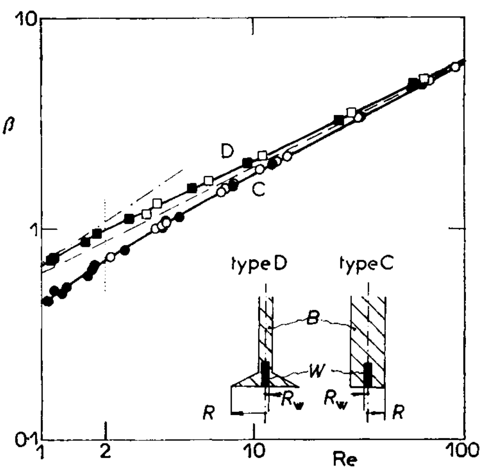

FIG. 1

Verification of the generalized Levich formula. D — theory for the disc-like electrode, type D, Eqs (*18a,b*); C — correlation for cylindrical electrode, type C, Eqs (*19a,b*); B — body of a rotating electrode; W — working electrode. ○ solution S1, electrode of the type C, ● solution S2, electrode of the type C, □ solution S1, electrode of the type D, ■ solution S2, electrode of the type D. Dotted line: Re = Re_t = 2, dashed line: asymptote for Re → ∞, dash and dotted line: asymptote for Re → 0. *R* — radius of spindle, R_w — radius of working electrode was found between the theory and the experiment for the type D of electrodes. Consequently, the theoretical formulas (*19*) and (*13*) could be applicable for a more general case of viscoelastic liquids. Experimental data for the type C of electrodes show strong disagreement with the theoretical prediction. It should be therefore concluded that formulas (*11*) and (*13*) are not applicable for treatment of data obtained by using cylindrical microelectrodes of the type C.

LIST OF SYMBOLS

Ab	Aberystwyth number, Eq. (7)
c^B	concentration of working depolarizer in the bulk of liquid
D	diffusivity of working depolarizer
I	total current
J	local current density
j	mean current density
nF	the charge corresponding to 1 mole of working depolarizer
Re	Reynolds number, Eq. (*6*)
R	radius of rotating body
R_w	radius of working electrode
r	radial coordinate
v_i	Cartesian velocity components
v_r	radial velocity
x_i	Cartesian coordinate
$Y = r/R$	
z	axial coordinate
β	normalized mass-transfer coefficient, Eq. (*16*)
γ	shear rate of a viscometric flow
γ_M	meridional component of the velocity gradient at wall
η	viscosity
ν_1, ν_2	coefficients of the elastic normal stresses, Eq. (*5*)
$\lambda_0, \lambda_\infty$	adjustable parameters in Eq. (*17a,b*)
ϱ	density of the liquid
τ_{ij}	stress components in a viscometric flow i, j (1 — direction of flow, 2 — direction of velocity gradient, 3 — indifferent direction)
Ω	angular speed of rotation

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Translated by M. Rylek.