CONVECTIVE MASS TRANSFER OF A CONE IN A NONLINEAR VISCOUS FIELD WITH CONSIDERATION OF HETEROGENEOUS REACTION KINETICS

Z. P. Shul'man, N. A. Pokryvailo,
and T. V. Yushkina

UDC 532.135:532.517.2:541.138

Convective mass transfer of a cone in a flow of a nonlinear viscous fluid with consideration of a first-order heterogeneous reaction was investigated.

Recently a new direction has developed in the technique of hydrodynamic measurements in fluids, including non-Newtonian, namely, electrodiffusion tensoanemometry [1-5]. This method allows determining the local instantaneous flow velocity on the basis of the magnitude of the current of the electrochemical reaction. The method is based on the fact that the value of the maximum current at the output of the transducer depends just on convective diffusion, provided that the rate of reaction of the ions on the surface of the electrode far exceeds the rate of delivery of these ions from the solution into the reaction zone, i.e., the reaction occurs in a diffusion regime and the concentration on the surface of the control electrode is equal to zero.

The transducers-electrodes used in these measurements usually have a conical, wedge, or spherical shape and are made small for increasing the sensitivity.

The surface of such electrodes is not equally accessible in the sense of the transport of matter — the thickness of the diffusion boundary layer near the leading edge of the electrode approaches zero, the intensity of mass transfer is very great, and the electrochemical reaction rate has a finite value. The electrode therefore at some part of its surface is not polarized and the reaction occurs in a mixed kinetics regime.

The effect of a finite electrochemical reaction rate is especially substantial for small transducers.

In [6] the problem of determining the concentration field and intensity of mass transfer with consideration of a first-order electrochemical reaction was solved for a flat transducer of fluctuations of the tangential stress on the wall, which was embedded flush in the wall of the channel past which the electrolyte flowed.

Let us consider mass transfer of a conical electrode with generatrix length L and vertex angle 2α located in the general case in a flow of an incompressible nonlinear viscous fluid with an exponential rheological equation of state [7-8]

$$\tau = k\left|\frac{\partial u}{\partial y}\right|^{n-1}\frac{\partial u}{\partial y}. \tag{1}$$

We will consider mass transfer to be of low intensity (the concentration field of the diffusing admixture does not affect the dynamics of the flow). The thickness of the dynamic boundary layer is assumed to be much smaller than the radius of curvature of the cone. We will direct the x axis along the generatrix of the cone and the y axis perpendicular to it.

Let us assume also that a first-order reaction occurs on the electrode's surface.

The mathematical formulation of the problem is represented by the system of equations

---

Institute of Heat and Mass Transfer, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 30, No. 1, pp. 80-85, January, 1976. Original article submitted March 25, 1975.

$$u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}=V\frac{dV}{dx}+\frac{k}{\rho}n\left|\frac{\partial u}{\partial y}\right|^{n-1}\frac{\partial^2 u}{\partial y^2}, \tag{2}$$

$$\frac{\partial (ux)}{\partial x}+\frac{\partial (vx)}{\partial y}=0, \tag{3}$$

$$u\frac{\partial C}{\partial x}+v\frac{\partial C}{\partial y}=D\frac{\partial^2 C}{\partial y^2} \tag{4}$$

with boundary conditions

$$u(x,\ 0)=v(x,\ 0)=0;\quad u(x,\ \infty)=V=bx^m, \tag{5}$$

$$C(x,\ \infty)=C_0;\ C(0,\ y)=C_0;\ D\left.\frac{\partial C}{\partial y}\right|_{y=0}=k_1C(x,\ 0). \tag{6}$$

Parameter m in the law of the potential flow velocity is related with the quantity α by the approximate dependence [9]

$$m=\frac{4}{\pi^2}\alpha^2.$$

The dynamic problem (2), (3), (5) is self-similar. The velocity component and the self-similar variable have the form

$$u=bx^mF'(\eta),$$

$$\eta=\left(\frac{b^{2-n}\rho\,[m(2n-1)+n+2]}{k\,(n+1)}\right)^{\frac{1}{1+n}}yx^{\frac{m(2-n)-1}{n+1}}=yx^{\frac{m(2-n)-1}{n+1}}M^{\frac{1}{1+n}}, \tag{7}$$

$$v=-bM^{\frac{1}{1+n}}x^{\frac{m(2n-1)-n}{n+1}}\left[\frac{m(2n-1)+n+2}{n+1}F+\frac{m(2-n)n}{n+1}\eta F'\right].$$

We will proceed in (4) to variables x, Ψ, where Ψ is the stream function.

We obtain

$$\frac{\partial C}{\partial x}=Dx^2\frac{\partial}{\partial \Psi}\left[u\frac{\partial C}{\partial \Psi}\right]. \tag{8}$$

The large values of the diffusion Prandtl number characteristic for diffusion processes in liquids permits approximating the velocity profile within the diffusion boundary layer by a linear approximation

$$\frac{u}{V}=\left.\frac{\partial (u/V)}{\partial y}\right|_{y=0}y=a\eta,$$

where a is the dynamic form parameter whose values were found by means of a transformation (of Stepanov–Mangler type [8]), and are given in Table 1.

TABLE 1. Values of the Form Parameter a for Various m, n

m	n				
	0,2	0,4	0,6	0,8	1
0,1	0,0922	0,1532	0,219	0,285	0,3486
0,2	0,1669	0,252	0,336	0,4145	0,4857
0,4	0,3086	0,4166	0,5136	0,5956	0,6662
0,6	0,4525	0,5619	0,6538	0,73	0,792
0,8	0,6059	0,6977	0,775	0,8389	0,8913
1	0,7746	0,8285	0,883	0,9308	0,9726

Using (7), we find

$$u = [2aVM^{\frac{1}{1+n}} x^{\frac{m(2-n)-(n+2)}{n+1}} \Psi]^{1/2}. \tag{9}$$

By introducing the variables

$$\zeta = \frac{1}{4N} Bx^N; \quad z = \frac{2}{3} \Psi^{3/4}; \; N = \frac{3m+5n+4}{2(n+1)}; \tag{10}$$

$$B = [2abM^{\frac{1}{1+n}}]^{1/2} D$$

we reduce (8) to the form

$$\frac{\partial^2 C}{\partial z^2} + \frac{1}{3z} \cdot \frac{\partial C}{\partial z} = \frac{\partial C}{\partial \zeta} \tag{11}$$

with system of boundary conditions

$$\frac{3^{1/3}}{4^{2/3}} B^{\frac{4(n+1)}{3m+5n+4}} \left[\frac{2(3m+5n+4)}{n+1} \zeta \right]^{\frac{3m+n}{3m+5n+4}} \lim_{z\to 0} \left(z^{1/3} \frac{\partial C}{\partial z} \right) = k_1 \lim_{z\to 0} C(\zeta, z), \tag{12}$$

$$\lim_{z\to\infty} C(\zeta, z) = C_0; \quad \lim_{\zeta\to 0} C(\zeta, z) = C_0.$$

An equation of form (8) was solved in [10] by the Sutton method [11] for the case of mass transfer of a plate. Having used this method and omitting intermediate calculations, we obtain

$$j(x, 0) = \frac{k_1 C_0}{\Gamma(2/3)} \int_0^\infty e^{-\gamma t^{2/3}} e^{-t} t^{-1/3} dt, \tag{13}$$

where the dimensionless quantity

$$\gamma = \frac{3^{2/3} \Gamma(1/3) k_1 x^{\frac{n+2-3m}{3(n+1)}}}{\Gamma(2/3) B^{2/3} \left[\frac{2(3m+5n+4)}{n+1} \right]^{1/3}}, \tag{14}$$

in particular,

$$\gamma = \frac{3^{1/3} \Gamma(1/3) k_1 x^{\frac{1-m}{2}}}{\Gamma(2/3) B^{2/3} (m+3)^{1/3}} \quad \text{for} \quad n = 1. \tag{14a}$$

Expanding (13) in a series for small and large values of the parameter γ [10], we can show that when $\gamma << 1$ the flow of matter toward the transducer is determined exclusively by the reaction rate, and when $\gamma >> 1$ the diffusion kinetics regime is determining and the flow toward the surface of the transducer is described by the dependence

$$j = \left[\frac{3m+5n+4}{36(n+1)} B^2 \right]^{1/3} C_0 x^{-\frac{2n-6m+4}{6(n+1)}} [1/3\Gamma(1/3)]^{-1}. \tag{15}$$

Before this limiting case is realized there is a certain intermediate region where the reaction occurs in a mixed kinetics regime.

On the basis of the aforesaid, we can estimate the limiting length of the generatrix of the transducer on which a substantial role will be played by the electrochemical reaction rate:

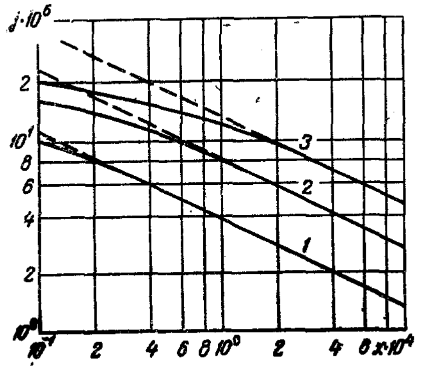

Fig. 1

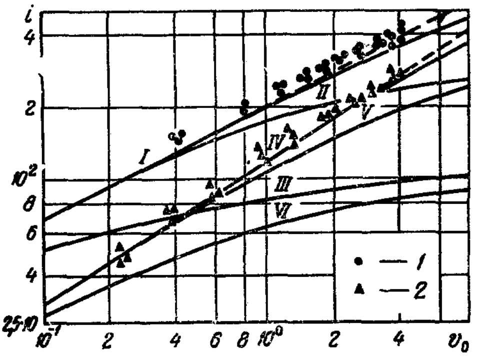

Fig. 2

Fig. 1. Local diffusion flow to conical electrode; n = 0.6, m = 0.1; 1,2,3) v_0 = 0.5, 2, and 5 m/sec, respectively; x is in m.

Fig. 2. Current vs velocity; L = $0.53 \cdot 10^{-3}$ m, m = 0.1. 1,2) Results of experiment in 0 and 1.5% solutions of Na-CMC, respectively; I,II,III) n = 1, k_1 = $0.9 \cdot 10^{-4}$, $0.5 \cdot 10^{-4}$, $0.12 \cdot 10^{-4}$ m/sec, respectively; IV,V,VI) n = 0.6, k_1 = $0.9 \cdot 10^{-4}$, $0.5 \cdot 10^{-4}$, $0.12 \cdot 10^{-4}$ m/sec, respectively; i, μA; v_0, m/sec.

$$L_n = \left\{ \frac{\Gamma(2/3)\, B^{2/3} \left[\frac{2(3m+5n+4}{n+1} \right]^{1/3}}{\Gamma(1/3)\, k_1 3^{2/3}} \right\}^{\frac{3(n+1)}{n+2-3m}}; \tag{16}$$

for the case of a Newtonian fluid Eq. (16) has the form

$$L_n = \left\{ \frac{\Gamma(2/3)(m+3)^{2/3} \left[2ab \left(\frac{b\rho}{k} \cdot \frac{m+1}{n+1} \right)^{1/2} \right]^{2/3}}{\Gamma(1/3)\, k_1 3^{1/3}} \right\}^{\frac{2}{1-m}}. \tag{16a}$$

The estimate obtained shows that L_n changes depending on the properties of the fluid, flow velocity, and reaction rate constant k_1. In a Newtonian fluid (n = 1), as we see from (14a), the region of the leading critical point of an axisymmetric body (m = 1) is an equally accessible surface and the regime in which the electrochemical reaction occurs is not related with the distance from the leading critical point.

The integral flow toward the transducer-electrode and, accordingly, the current are described by the dependences

$$I = 2\pi \sin\alpha \int_0^L xj\,dx = 2\pi \sin\alpha \frac{k_1 C_0}{\Gamma(2/3)} \int_0^L x \int_0^\infty e^{-\gamma t^{2/3}} e^{-t} t^{-1/3} dt\, dx, \tag{17}$$

$$i = I\bar{z}F. \tag{17a}$$

In the limiting case of diffusion kinetics (17), (17a) take on the form

$$I_n = \frac{\pi \sin\alpha\, C_0}{1/3\Gamma(1/3)} (6B^2)^{1/3} L^{\frac{3m+5n+4}{3(n+1)}} \left(\frac{n+1}{3m+5n+4} \right)^{2/3}, \tag{18}$$

TABLE 2. Rheological Parameters of the Solution

Solution 0,025 M $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]+$ $+0,5 M K_2SO_4+$ Na-CMC, %	$\rho \cdot 10^{-3}$ kg/m³	$k \cdot 10^3$ kg·sec^{n-2}/m	n	$D \cdot 10^9$ m²/sec
0	1,015	1,16	1	0,625
1,5	1,04	870	0,604	0,469

$$i_n = I_n \bar{z}F. \qquad (18a)$$

The calculation by Eqs. (13), (15) was made on a Minsk-22 computer for a transducer with a generatrix length $L = 0.7 \cdot 10^{-3}$ m and vertex angle $2\alpha = 53°$.

To investigate the effect of rheological properties we used the results of viscometry of two electrochemical solutions: 0.025 M aqueous solution of ferrous ferricyanide (supporting electrolyte 0.5 M K_2SO_4) and a 1.5% aqueous solution of the polymer sodium carboxymethylcellulose (Na-CMC) in the presence of the electrolyte indicated above. Table 2 presents the parameters of the power law of the investigated systems.

Figures 1 and 2 show the dependence of the local flow and current of the transducer on the velocity, reaction rate constant k_1, and properties of the fluid.

The calculation by Eqs. (15), (18a) is shown by dashes. Also plotted in Fig. 2 are the data of the experiment carried out together with A. S. Sobolevskii on the basis of measuring the limiting diffusion current by a conical platinum electrode ($L = 0.7 \cdot 10^{-3}$ m, $2\alpha = 53°$) in the aforementioned solutions, where an oxidation–reduction reaction occurs:

$$\mathrm{Fe(CN)}_6^{-3} + e^- \rightleftarrows \mathrm{Fe(CN)}_6^{-4},$$

the order of the reaction of reduction of ferricyanide on the platinum electrode being equal to unity [12]. The coefficients of diffusion of the $\mathrm{Fe(CN)}_6^{-3}$ ions were measured by the "surge current" method [13]. For a qualitative comparison of experiment with the calculation we used the value of the rate constant of the electrochemical reaction $k_1 = 9 \cdot 10^{-4}$ m/sec obtained in [14] for a system of ferrous ferricyanide (supporting electrolyte 1 M KCl) and platinum electrode.

We see from Fig. 1 that the extent of the unpolarized surface of the electrode increases with an increase of the flow velocity.

The data of Fig. 2 show that when $k_1 = 9 \cdot 10^{-4}$ m/sec the contribution of the unpolarized parts of the investigated electrode to the total current becomes noticeable already at velocities of 1.5 and 3 m/sec for $n = 1$ and 0.6, respectively, and the difference between the current and diffusion current amounts to 10% at velocities of about 4 and about 7 m/sec.

The data of the experiment in the investigated range of velocities agree sufficiently well with the theory and indicate that the reaction rate constant that occurred in the experiment is most likely higher than $k_1 = 9 \cdot 10^{-4}$ m/sec.

It is obvious that with an increase of the size of the electrode the contribution of the unpolarized areas to the total current will be increasingly less substantial.

We also see from Fig. 2 that a decrease of the electrochemical reaction rate related, for example, with contamination of the transducer can lead to a decrease of the value of the limiting current and departure of the process from a diffusion regime.

It is also necessary to note that the conditions of polarization of the electrode in fluids with $n < 1$ are slightly better than when $n = 1$.

NOTATION

C, concentration; C_0, concentration in the flow; x,y, coordinates; u,v, velocity components with respect to the x and y axes, respectively; V, velocity value at the edge of the boundary layer; k, measure of consistency; n, index of the non-Newtonian behavior of the fluid; D, diffusion coefficient; k_1, reaction rate constant; v_0, velocity of the incident flow; $\bar{z}$, charging number; F, Faraday number.

LITERATURE CITED

1. V. P. Popov, N. A. Pokryvailo, and L. K. Gleb, in: Investigation of Unsteady Heat and Mass Transfer [in Russian], Nauka i Tekhnika, Minsk (1966).
2. G. V. Vasil'chenko, Izv. Sibirsk. Otd. Akad. Nauk SSSR, No. 3, 13 (1969).
3. R. Sh. Nigmatullin and G. P. Gabsalyamov, Control Instruments and Systems [in Russian] (1970), pp. 3, 27.
4. V. P. Popov, N. A. Pokryvailo, L. K. Gleb, S. S. Kutateladze, B. G. Pokusaev, V. A. Kuz'min, V. E. Nakoryakov, and A. N. Burdukov, Author's Certificate No. 266,287, Byull. Izobret., No. 11 (1970).

5. N. A. Pokryvailo, É. F. Saenko, A. P. Yakimakho, A. S. Soboloevskii, and A. S. Pashik, in: Heat and Mass Transfer, Vol. 1, Part 3 [in Russian], Minsk (1972), p. 3.
6. S. S. Kutateladze (editor), Investigation of Turbulent Flows of Two-Phase Media [in Russian], Novosibirsk (1973).
7. M. Reiner, Lectures on Theoretical Rheology, North Holland (1960).
8. Z. P. Shul'man and B. M. Berkovskii, Boundary Layer of Non-Newtonian Fluids [in Russian], Nauka i Tekhnika, Minsk (1966).
9. Z. P. Shul'man, in: Heat and Mass Transfer, Vol. 10 [in Russian], Minsk (1968).
10. V. G. Levich, Physicochemical Hydrodynamics [in Russian], Fizmatgiz (1959).
11. W. G. L. Sutton, Proc. Roy. Soc., 182, 48 (1943).
12. S. Azim and A. C. Riddiford, J. Polarogr. Soc., No. 12, 20 (1966).
13. E. M. Skobets and N. S. Kavetskii, Zh. Fiz. Khim., 25, 1468 (1950).
14. J. E. B. Randless and K. W. Somerton, Trans. Faraday Soc., 48, 937 (1952).

THIN-FILM FLOW OF A QUASIVISCOUS FLUID OVER THE SURFACE OF A ROTATING NOZZLE

V. P. Kostromin, V. G. Kuznetsov,
and K. D. Vachagin

UDC 532.135+532.54

Problems of the flow of a quasiviscous fluid with an arbitrary rheological law over the surface of a rapidly rotating nozzle are investigated.

The problem being investigated is of great practical value, since a thin-film flow of fluids over surfaces of rotating nozzles is often encountered in processes of dispersion, evaporation of solutions, mixing, absorption, scrubbing of gases, molecular distillation, etc. The flow of ordinary viscous fluids and fluids with quite complex rheological characteristics occurs in this case. One of the main parameters characterizing the flow process is the thickness of the fluid film on the surface of the rotating nozzle. Relationships for determining the thickness of the film of an ordinary viscous fluid [1-3] and for a non-Newtonian fluid only with a rheological power law [4] are known in the literature.

In this connection it is of interest to examine the problem of determining the thickness of the film of a quasiviscous fluid whose viscosity properties are expressed by an arbitrary rheological law in the form

$$\eta_e = f_1(\tau) = f_2(\dot{\gamma}). \tag{1}$$

The fluid is fed to the center of a rotating nozzle with a sharp edge and flows over it in a radial direction as a thin continuous laminar film under the effect of the centrifugal force. The movement of the fluid is examined in a cylindrical coordinate system r, φ, z rigidly associated with the center of the disk (Fig. 1). The following assumptions are made:

1) the flow of the fluid over the disk is steady;

2) the thickness of the fluid film is much less than the radius at which the flow is investigated, i.e., $\delta/r \ll 1$;

3) the effect of the gravitational force, surface tension forces, and frictional forces on the ambient medium is insignificant as a consequence of their smallness in comparison with the centrifugal forces.

Kazan Scientific-Research Technological and Design Institute of the Chemical-Photographic Industry. S. M. Kirov Kazan Chemical Technological Institute. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 30, No. 1, pp. 86-91, January, 1976. Original article submitted February 26, 1975.