TRANSIENT CONVECTIVE MASS TRANSFER AT A DISC ROTATING IN A NON-NEWTONIAN FLUID

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Results are shown of a theoretical and experimental study concerning the transient convective mass transfer at a disc rotating in a non-Newtonian fluid.

I. We consider the transient process of convective diffusion of a low-molecular substance in the case of a disc rotating steadily in an infinitely large and anomalously viscous medium characterized by a power-law rheological equation of state. The mass transfer process is usually described by the following equation [1]:

$$\frac{\partial c}{\partial t}+v_r\frac{\partial c}{\partial r}+\frac{v_\varphi}{r}\cdot\frac{\partial c}{\partial \varphi}+v_z\frac{\partial c}{\partial z}=D\left(\frac{\partial^2 c}{\partial z^2}+\frac{\partial^2 c}{\partial r^2}+\frac{1}{r}\cdot\frac{\partial^2 c}{\partial \varphi^2}\right). \quad (1)$$

When the process occurs within the confines of a diffusion boundary layer whose characteristic dimension is much smaller than the disc radius, and if it is assumed that $v_z(\partial c/\partial z) \gg v_r(\partial c/\partial r)$, then Eq. (1) may be written as

$$\frac{\partial c}{\partial t}+v_z\frac{\partial c}{\partial z}=D\frac{\partial^2 c}{\partial z^2} \quad (2)$$

with the axial symmetry taken into account here.

Assuming further that the concentration of the low-molecular substance at the surface is a certain specified function of time and that the edge effects at the disc periphery are negligible [1], we write the initial and the boundary conditions as follows:

$$c(0,\ t)=f(t),\qquad c(\infty,\ t)=c_0,\qquad c(0,\ 0)=c_0. \quad (3)$$

For the solution of system (2)-(3) we will use the results in [2], where the problem of fluid flow due to a steady rotation of a disc in a medium characterized by a power-law rheological equation of state [12]

$$\tau_{ij}=-p\delta_{ij}+k\left|\frac{1}{2}\dot{e}_{rm}\dot{e}_{mr}\right|^{\frac{n-1}{2}}\dot{e}_{ij} \quad (4)$$

has been solved numerically.

The constraint problem in [2] is analyzed by applying the Karman hypothesis of similarity between profiles, with the automorphous variables becoming

$$\xi=z\left(\frac{\omega^{2-n}r^{1-n}}{N}\right)^{\frac{1}{1+n}}, \quad (5)$$

$$v_r(r,\ z)=\omega rF(\xi), \quad (6)$$

$$v_\varphi(r,\ z)=\omega rG(\xi), \quad (7)$$

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$$v_z(r,\ z) = [r^{n-1}\omega^{2n-1}N]^{\frac{1}{1+n}}\ H(\xi). \tag{8}$$

The continuity equation is written as

$$2F + H' + \left(\frac{1-n}{1+n}\right)F'\xi = 0. \tag{9}$$

Here the primes indicate derivatives with respect to ξ.

In our case the Prandtl number is quite high. Consequently, it is permissible to approximate the profile of radial velocities within the diffusion boundary layer by a linear relation:

$$F = a\xi, \quad \text{where} \quad a = \left(\frac{\partial F}{\partial \xi}\right)_{\xi=0} = F'(0). \tag{10}$$

From Eq. (9) we find

$$H(\xi) = -a'\xi^2; \qquad \text{here} \qquad a' = a\left[1 + \frac{1}{2}\left(\frac{1-n}{1+n}\right)\right]. \tag{11}$$

From (8) and (11) one can derive an expression for the mean axial velocity:

$$\langle v_z \rangle = -az^2\left[\frac{\omega^3 R^{1-n}}{N}\right]^{\frac{1}{1+n}}. \tag{12}$$

Inserting (12) into (2) yields

$$\frac{\partial c}{\partial t} - az^2\left[\frac{\omega^3 R^{1-n}}{N}\right]^{\frac{1}{1+n}}\frac{\partial c}{\partial z} = D\frac{\partial^2 c}{\partial z^2}. \tag{13}$$

It has been assumed here that the coefficients in the rheological equation of state (4) do not depend on the concentration in the diffusion boundary layer of the substance.

The expression for the mean flow density of a steady stream against a disc rotating in an infinitely large power-law medium is [3]:

$$j(R) = \left(\frac{a'}{3}\right)\frac{1}{\frac{1}{3}\Gamma\left(\frac{1}{3}\right)}\left[\frac{6n+6}{5n+7}\right]c_0 D^{2/3}\, N^{-\frac{1}{3}\left(\frac{1}{1+n}\right)} R^{\frac{1}{3}\left(\frac{1-n}{1+n}\right)}\omega^{\frac{1}{1+n}}. \tag{14}$$

We now rewrite (14) as follows:

$$\frac{j(R)}{Dc_0} = \left(\frac{a'}{3}\right)\frac{1}{\frac{1}{3}\Gamma\left(\frac{1}{3}\right)}\left[\frac{6n+6}{5n+7}\right]\frac{1}{D^{1/3}}\, N^{-\frac{1}{3}\left(\frac{1}{1+n}\right)} R^{\frac{1}{3}\left(\frac{1-n}{1+n}\right)}\omega^{\frac{1}{1+n}} \tag{15}$$

or

$$\frac{j(R)}{Dc_0} = \frac{1}{\delta_{\text{mean}}}, \quad \text{where} \quad \delta_{\text{mean}} = \left(\frac{3}{a'}\right)^{1/3}\frac{\left[\frac{1}{3}\Gamma\left(\frac{1}{3}\right)\right]D^{1/3}}{N^{-\frac{1}{3}\left(\frac{1}{1+n}\right)} R^{\frac{1}{3}\left(\frac{1-n}{1+n}\right)}\omega^{\frac{1}{1+n}}}\left[\frac{5n+7}{6n+6}\right]. \tag{16}$$

The quantity δ_{mean} has the dimension of length and, according to V. G. Levich [1], it will be treated as the thickness of the diffusion boundary layer in the case of a steady convective mass transfer at a disc rotating in a power-law fluid.

The variables t and z will be replaced by the dimensionless variables

$$x = \frac{z}{\delta_{\text{mean}}}; \qquad \tau = \frac{Dt}{\delta^2_{\text{mean}}}; \qquad g(z,\ t) = \frac{[c_0 - c(z,\ t)]}{c_0}, \tag{17}$$

and, accordingly, the original equation (13) will be transformed into

$$\frac{\partial g}{\partial \tau} - \alpha(n)x^2\frac{\partial g}{\partial x} = \frac{\partial^2 g}{\partial x^2}, \tag{18}$$

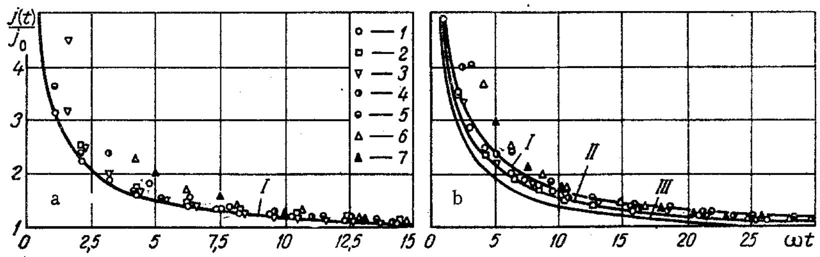

Fig. 1. Transient convective mass transfer at the 20 mm (diameter) rotating disc. (a) 0% Na–KM (CN), theory (I); (b) 0.75% Na–KM (CN), theory 100 rpm (I), 500 rpm (II) 2500 rpm (III): 100 rpm (1), 200 rpm (2), 500 rpm (3), 1000 rpm (4), 1500 rpm (5) 2000 rpm (6), 2500 rpm (7).

where

$$\alpha(n) = 2{,}128\,\frac{2(1+n)}{3+n}\left(\frac{5n+7}{6n+6}\right)^3.$$

The initial and the boundary conditions will be written as follows:

$$\begin{gathered} g\to 0,\quad x\to\infty,\quad \tau\geqslant 0,\\ g(0,\ \tau)=\varphi(\tau),\quad x=0,\quad \tau>0,\\ \varphi(\tau)=\frac{[c_0-f(t)]}{c_0}\,. \end{gathered} \tag{19}$$

The constraint problem can now be solved by the method shown in [4].

With the aid of the Laplace–Carson transformation

$$G(x,\ p)=p\int_0^\infty e^{-p\tau}\,g(x,\ \tau)\,d\tau \tag{20}$$

Eq. (18) becomes

$$pG=\frac{d^2G}{dx^2}+\alpha(n)\,x^2\,\frac{dG}{dx} \tag{21}$$

with the boundary conditions

$$G\to 0\quad \text{at}\quad x\to\infty,\quad G=\Phi(p)\quad \text{at}\quad x=0, \tag{22}$$

where $\Phi(p)$ is the Laplace transform of function $\varphi(\tau)$.

Inserting

$$G(x,\ p)=\Psi(x,\ p)\exp\left[-\frac{\alpha(n)\,x^3}{6}\right] \tag{23}$$

TABLE 1. Parameters of the Power Law and Diffusivity of $Fe(CN)_6^{3-}$ Ions

Solution $2\cdot10^{-3}$ M $K_3[Fe(CN)_6]$ + $2\cdot10^{-1}$M $K_4[Fe(CN)_6]$ +Na–KM(CN), %	$\rho\cdot10^{-3}$, kg/m^3	$k\cdot10^3$, kg/m·sec^{-2}	n	$D\cdot10^9$, m^2/sec
0	1,015	1,16	1,00	0,625
0,75	1,028	78	0,74	0,536
1,00	1,032	264	0,65	0,510
1,50	1,040	950	0,57	0,484

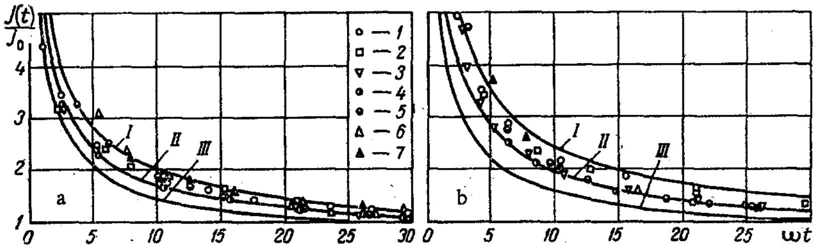

Fig. 2. Transient convective mass transfer at the 20 mm (diameter) rotating disc. (a) 1% Na–KM (CN), (b) 1.5% Na–KM(CN); theory 100 rpm (I), 500 rpm (II), 2500 rpm (III); 100 rpm (1), 200 rpm (2), 500 rpm (3), 1000 rpm (4), 1500 rpm (5), 2000 rpm (6), 2500 rpm (7).

into (21) yields an equation which does not contain the first derivative, namely

$$\frac{d^2\Psi}{dx^2}-\left[p+\alpha(n)x+\frac{\alpha^2(n)x^4}{4}\right]\Psi=0 \tag{24}$$

with the boundary conditions

$$\Psi\to 0 \quad \text{at} \quad x\to\infty, \quad \Psi\to\Phi(p) \quad \text{at} \quad x=0.$$

As has been mentioned earlier, of interest here is the solution to the problem for the region directly adjacent to the disc surface, i.e., for the layer where $x \leq 1$. Consequently, we may assume that the solution to Eq. (24) approximates the solution to the equation

$$\frac{d^2\Psi_1}{dx^2}-[p+\alpha(n)x]\Psi_1=0 \tag{25}$$

with the boundary conditions

$$\Psi_1\to 0 \quad \text{at} \quad x\to\infty, \quad \Psi_1=\Phi(p) \quad \text{at} \quad x=0. \tag{26}$$

Equation (25) is the well known Airy equation. Its solution [4]

$$\Psi_1(x,\ p)=\mathrm{Ai}\left[\frac{p+\alpha(n)x}{\alpha(n)^{2/3}}\right]+\mathrm{Bi}\left[\frac{p+\alpha(n)x}{\alpha^{2/3}(n)}\right] \tag{27}$$

is expressed in terms of Airy functions Ai and Bi. With the constants determined from the boundary conditions (26), we have

$$\Psi_1(x,\ p)=\Phi(p)\ \frac{\mathrm{Ai}\{[p+\alpha(n)x]/\alpha^{2/3}(n)\}}{\mathrm{Ai}\,[p/\alpha^{2/3}(n)]}\ . \tag{28}$$

The Laplace representation for a stream of a substance diffusing toward the disc surface is

$$L\left[D\left(\frac{\partial c}{\partial z}\right)_0\right]=-j(R)\left(\frac{\partial\Psi}{\partial x}\right)_0\approx j(R)\Phi(p)\ \frac{\mathrm{Ai}'\,[p/\alpha^{2/3}(n)]}{\mathrm{Ai}\,[p/\alpha^{2/3}(n)]}\,\alpha^{2/3}(n). \tag{29}$$

Applying the interpolation formula to the logarithmic derivative of the Airy function [4],

$$\frac{\mathrm{Ai}'(y)}{\mathrm{Ai}(y)}\approx-\frac{1+y}{\sqrt{1{,}877+y}}\ , \tag{30}$$

we perform an inverse Laplace transformation [5] and obtain as a result

$$j(\tau)=D\left(\frac{\partial c}{\partial z}\right)_0=j(R)\frac{d}{d\tau}\int\limits_0^\tau\varphi(\tau-\lambda)\times$$

$$\times\left[\frac{\exp(-1{,}877\alpha^{2/3}(n)\lambda)}{\sqrt{\pi\tau}}+\frac{\alpha^{2/3}(n)}{\sqrt{1{,}877\alpha^{2/3}(n)}}\ \mathrm{erf}\sqrt{1{,}877\alpha^{2/3}(n)\lambda}\right]d\lambda, \tag{31}$$

where $\varphi(\tau)$ is determined from condition (19).

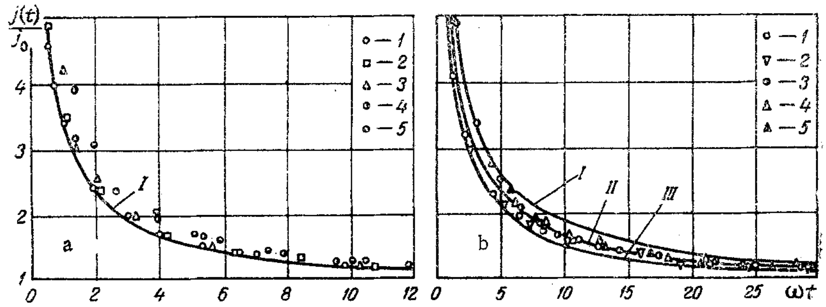

Fig. 3. Transient convective mass transfer at the 5 mm rotating disc. (a) 0% Na–KM (CN), theory (I), 100 rpm (1), 200 rpm (2), 500 rpm (3), 1000 rpm (4), 1500 rpm (5). (b) 0.75% Na–KM (CN), theory 100 rpm (I), 500 rpm (II), 2500 rpm (III); 100 rpm (1), 500 rpm (2), 1000 rpm (3), 2000 rpm (4), 2500 rpm (5).

We next consider the transient mass transfer at $f(\tau) = c(0, t) = 0$. In ordinary variables, then, Eq. (31) yields

$$\frac{j(t)}{j(R)} = \frac{\exp\left[-\frac{a^{2/3}\omega t}{0{,}531\,(\mathrm{Pr}'_D)^{1/3}}\right]}{\sqrt{\frac{\pi\omega t}{\Phi(n)\,(\mathrm{Pr}'_D)^{1/3}}}} + 0{,}94\sqrt[3]{\frac{2(1+n)}{3+n}} \times \frac{5n+7}{6n+6}\,\mathrm{erf}\sqrt{\frac{a^{2/3}\omega t}{0{,}531\,(\mathrm{Pr}'_D)^{1/3}}}, \tag{32}$$

where

$$\mathrm{Pr}'_D = \frac{1}{D}\left[N^2 R^{2(n-1)}\omega^{3(n-1)}\right]^{\frac{1}{1+n}} \tag{33}$$

is the universal Prandtl diffusion number and

$$\Phi(n) = 0{,}89\left(\frac{3}{a'}\right)^{1/3}\left(\frac{5n+7}{6n+6}\right); \quad \frac{1}{3}G\left(\frac{1}{3}\right) = 0{,}89.$$

Relation (32) allows us to evaluate the approach to a steady state. Initially, at time $t \ll 0.531\,(\mathrm{Pr}'_D)^{1/3}/a^{2/3}\omega$, the flow of the substance is purely diffusive in nature and convection is negligible:

$$j(t) = j(R)\frac{1}{\sqrt{\frac{\pi\omega t}{\Phi(n)\,(\mathrm{Pr}'_D)^{1/3}}}} = \frac{Dc_0}{\sqrt{\pi D t}}. \tag{34}$$

At time $t \gg 0.531\,(\mathrm{Pr}'_D)^{1/3}/a^{2/3}\omega$ the mode of mass transfer becomes steady:

$$j(t) = 0{,}94\sqrt[3]{\frac{2(1+n)}{3+n}}\left(\frac{5n+7}{6n+6}\right)j(R). \tag{35}$$

The characteristic transient time is defined as

$$T = \frac{0{,}531\,(\mathrm{Pr}'_D)^{1/3}}{a^{2/3}\omega}. \tag{36}$$

It follows from expressions (33) and (36) that, with all other factors the same, the transient time decreases as the fluid becomes more pseudoplastic. Thus, at $n = 1$, $\omega = 100\ \mathrm{sec}^{-1}$, $R = 10^{-2}$ m, and $D = 10^{-9}\ \mathrm{m}^2/\mathrm{sec}$ the characteristic transient time $T \approx 1$ sec, while at $n = 0.5$ it is $T \approx 0.5$ sec. As the fluid becomes more dilatant, the trend reverses. We note that at $n = 2$ the characteristic transient time does not depend on the rotational speed of the disc.

II. The experimental study of the transient mass transfer at a disc rotating in an anomalously viscous fluid was made with the apparatus shown in [6]. The electrochemical test method seemed most applicable here because, first of all, stepwise changes in the boundary conditions differentiating this process from the quasisteady mode could be reliably effected by it and, secondly, the mass transfer

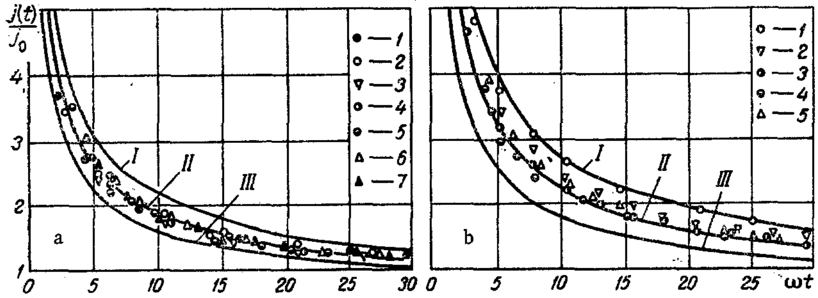

Fig. 4. Transient convective mass transfer at the 5 mm rotating disc. (a) 1% Na–KM (CN), 80 rpm (1), 100 rpm (2), 500 rpm (3), 1000 rpm (4), 1500 rpm (5), 2000 rpm (6), 2500 rpm (7). (b) 1.5% Na–KM (CN), 100 rpm (1), 500 rpm (2), 1000 rpm (3), 1500 rpm (4), 2000 rpm (5). For a and b theory 100 rpm (I), 500 rpm (II), 2500 rpm (III).

parameters could be thus recorded within short time intervals. At the same time, the invariability of boundary conditions (2) was also ensured [10]. The latter circumstance made it feasible to use appropriate mathematical models for the analysis of test data and, particularly, for the theoretical analysis outlined earlier.

It has been noted already [7, 10] how very reliable the electrochemical method is for measuring the parameters of transient mass transfer in a stable laminar stream of a Newtonian fluid. However, its application to the study of convective mass transfer in a non-Newtonain fluid calls for some caution and for the fulfilment of certain specific prerequisites [6, 8].

As test fluids we used aqueous solutions of the Na–KM (CN) polymer in various concentrations and containing also the electrolytes $K_3[Fe(CN)_6]$ ($2 \cdot 10^{-3}$ kg-mole/m^3) and $K_4[Fe(CN)_6]$ ($2 \cdot 10^{-1}$ kg-mole/m^3) as background components. The purpose of these electrolytic compounds was to allow the mass transfer rate to be measured during the reversible oxidation–reduction reaction

$$Fe(CN)_6^{3-} + e \rightleftharpoons Fe(CN)_6^{4-}.$$

in the system. At the same time, the aqueous solutions of Na–KM (CN) containing these electrolytes retained their pseudoplastic properties within the requisite range of shearing rates. The values of the power-law parameters for this system, listed in Table 1, were obtained with a capillary viscosimeter and the corresponding diffusivity of the $Fe(CN)_6^{3-}$ ions was measured with the instrument shown in [9]. All these values were obtained at 20°C.

It is well known that at the electrode–electrolyte interface there appears an electric double-layer which, while governing the ion exchange rate, plays an important role in the kinetics of electrode processes [11]. Since an electric double-layer is, in effect, a capacitor, hence it inevitably affects the transient process – especially during the initial period. The capacitance of such a double-layer as well as other parameters depend also on the area of the active electrode surface and, therefore, an optimum design of the apparatus geometry and the circuit parameters is very important. In our experiment the test objects (probes) were platinum discs 5 and 20 mm in diameter, embedded concentrically in the ends of a Plexiglas cylinder. With such probe dimensions and with the aid of the described instrument, it was possible to measure the parameters of transient mass transfer 0.01 sec after the beginning [7]. The tests were preceded by an alternate anode–cathode polarization of the active probe surface in a 1 N KOH solution. The test solution, which had been produced from distilled water, was purged with nitrogen for 30 min and in this way cleared of dissolved oxygen. Before a recording of each curve, the active probe surface was also depolarized by short-circuiting the main and the auxiliary electrode. A constant voltage was then applied to the electrodes, in order to ensure a diffusive mode of probe performance. Both the initial and the boundary conditions (3) were maintained here, with $f(t) = 0$ [7].

The process was recorded on a model N-700 light-beam oscillograph. The test data were evaluated in terms of the relation

$$\frac{j(t)}{j(R)} = f(\omega t).$$

The results of measurements pertaining to the transient mass flow are shown in Fig. 1 for various rotational speeds of the 20 mm disc in an aqueous electrolytic solution containing no polymer. Included here is a curve representing Eq. (32) for $n = 1$. A close correlation between test data and Eq. (32) is noted over a wide range of speeds.

The data shown in Fig. 1b and Fig. 2 generalize the test results pertaining to the transient mass transfer at a disc which rotates in electrolytic solutions with nonlinear flow characteristics. The solid lines correspond to the analytical expression (32). Since in this case the dimensionless group Pr'_D, which appears as a parameter in Eq. (32), depends on the disc speed, hence the curves based on Eq. (32) tend to disperse. This tendency is somewhat weaker in the case of the test curves. This deviation from theory amounts to 2.5-15%, depending in the Na–KM (CN) concentration. These are then the accuracy limits of the electrochemical method of measuring the transient transfer processes during their initial stages. It follows from expression (36) that, when $n = 1$, the characteristic transient time does not depend on the size of the reaction surface of the disc, unlike in the case of an external flow around a disc or of a flow in a channel [7]. As the fluid becomes more dilatant, i.e., as n increases, the characteristic time according to expression (36) becomes longer for larger discs. Pseudoplastic fluids exhibit the opposite trend. This conclusion, which has been predicted by theory, agrees with the test results.

The test results pertaining to the transient convective mass transfer at the 5 mm disc-electrode are shown in Figs. 3 and 4. Here the process in a pseudoplastic fluid stabilized slower than with the 20 mm disc (see Figs. 2b and 4b), especially in the 1.5% Na–KM (CN) solution. The solid curves correspond to theoretical calculations based on Eq. (32). For discs rotating in a solution containing no polymer, according to Figs. 1a and 3a, the transient time is independent of the disc radius.

Thus, our experimental study of the transient mass transfer at a disc rotating in a nonlinear purely viscous fluid indicates that the analytical solution (32) to the problem represents an adequate generalization of test data for the entire range of Na–KM (CN) concentrations considered in this experiment.

NOTATION

c	is the concentration;
c_0	is the concentration in the volume of electrolyte;
r, φ, z	are the cylindrical coordinates;
v_r, v_φ, v_z	are the velocity components along the respective cylindrical coordinate axes:
t	is the time;
D	is the diffusivity;
j	is the mass flow density;
ω	is the angular velocity;
n	is the exponent characterizing the non-Newtonian behavior of the fluid;
k	is the measure of consistency;
ξ	is the automorphous variable
$N = k/\rho$;	
ρ	is the density of the substance;
R	is the disc radius;
$j(R)$	is the mean flow density against disc;
a	is the quantity defined by Eq. (9);
a'	is the quantity defined by Eq. (10);
x, τ, g	are the dimensionless variables: space coordinate, time, and concentration respectively;
Ai	is the Airy function;
τ_{ij}	is the stress tensor;
δ_{ij}	is the Kronecker delta;
$\dot{e}_{rm}, \dot{e}_{mr}, \dot{e}_{ij}$	are the rate of-shear tensors.

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