RHEODYNAMICS AND MASS TRANSFER OF A DISK ROTATING IN A NON-NEWTONIAN FLUID

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The results are given from an experimental study of the rheodynamics and mass transfer associated with a disk rotating in dilute aqueous solutions of high polymers. The possibility of determining the non-Newtonian behavior index and diffusion coefficient by the electrochemical method is demonstrated. Visualization techniques are used to exhibit the fluid flow pattern near the surface of the disk and to analyze the centripetal effect in a viscoelastic medium.

Rotating mechanisms are enjoying increasing applications both in industry and in basic research in rheometry, rheodynamics, and heat and mass transfer. A very special representative of such mechanisms is the rotating disk, which serves as an effective tool for physicochemical studies of the kinetics of chemical and electrochemical reactions, the determination of diffusion coefficients, the quantitative analysis of materials, etc. The rotating disk problem is one of the few problem for which exact solutions have been obtained to the equations of motion as well as the heat- and mass-transfer equations for the case of a Newtonian medium. The integrability of these equations for flowing systems of a more complex nature is primarily dependent upon the rheological equations governing the systems. A numerical solution of the equations of motion for a disk or cone rotating in a non-Newtonian power-law fluid is given in [1]. Hansford and Litt [2] used the results of Mitschka to integrate the convective diffusion equations on the assumption of a linear velocity profile inside the diffusion boundary layer. They obtained the following analytical expression for the mass flow to the disk:

$$I(R)=\left(\frac{a'}{3}\right)\left[\frac{1}{\frac{1}{3}\Gamma(1/3)}\right]\left[\frac{6n+6}{5n+7}\right]C_0D^{2/3}N^{-\frac{1}{3}\left(\frac{1}{1+n}\right)}R^{\frac{1}{3}\frac{1-n}{1+n}}\omega^{\frac{1}{1+n}}. \tag{1}$$

As implied by Eq. (1), the surface of the rotating disk in this case is not equally accessible in the diffusion respect. It can be shown, however, that this fact does not severely limit the serviceability of the disk for the investigation of diffusion kinetics in fluids having comparatively mild pseudolaminar and dilatative attributes in mass-flow measurements on narrow annular regions of the disk surface. Thus, for a ring with $r_{in}=1$ cm and $r_{out}=2$ cm, all other conditions being equal, the difference between the local mass flows at the edges is about 8% for $n = 0.5$ and about 2.5% for $n = 0.8$. Hansford and Litt [2] determined the mass flow from the rate of dissolution of a disk made of solid benzoic acid in aqueous solutions of carboxymethylcellulose (CMC) and polyethylene oxide (polyox). The method is not precise, as it only permits one to estimate the average mass-transfer rate over a relatively long period of time. The authors showed that the results of j-measurements agree satisfactorily with Eq. (1) for large disk revolutions per minute. For low revolutions per minute the data of Hansford and Litt exhibit a sharp deviation from their own theory. This fact is attributable to the inception of viscoelastic properties in the solution, which form secondary currents near the disk surface. Giesekus [3] investigated in detail the secondary flows about a sphere and a cone rotating in a polyacrylamide solution and bounded by a nonmoving plane. Visualization was realized by the injection of dyes toward the surface of the rotating body. In both cases the motion of the fluid about

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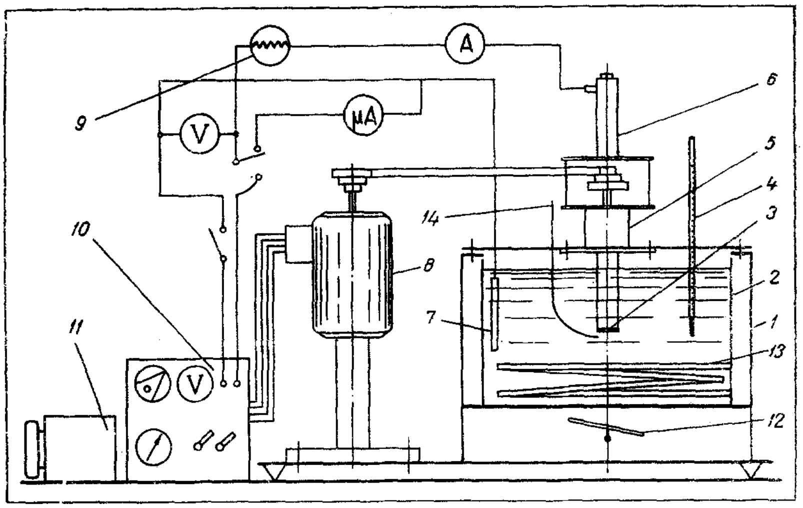

Fig. 1. Rotating disk electrode. 1) Housing; 2) tank; 3) platinum disk (cathode); 4) thermometer; 5) rotation assembly; 6) mercury current collector; 7) anode; 8) dc motor; 9) loop oscillograph; 10) control section; 11) oscilloscope; 12) mirror; 13) heater; 14) nitrogen injection tube for visualization.

the surface of the body due to the normal stress effect was directed along the surface parallel to the axis of rotation, whereas in more distant regions the centrifugal effect prevailed. Hill and co-workers [4] used a similar method to study the motion of a fluid about a rotating disk bounded by a cylindrical jacket. Motion of the fluid toward the center of the disk (centripetal effect) took place for a polyox solution. In glycerin and carboxypolymethylene the motion remained centrifugal.

Our experimental investigation of the mass transfer and fluid flow near the surface of a rotating disk was carried out on the apparatus illustrated in Fig. 1. The speed of the disk could be continuously controlled in the tests between 20 and 5000 rpm by means of a regulation system. A highly polished platinum plate was cemented to the end of a rotating ebonite cylinder 40 mm in diameter. The cylinder was mounted in precision roller bearings, and the maximum play of its end surface was 0.02 mm. The tank was made of Plexiglas with dimensions of 300 × 250 mm. It was shown in [2] that the influence of the walls and bottom of the tank was nil with these overall dimensions for the disk and tank. In order to visualize the fluid flow at the periphery of the rotating disk a thin tube was inserted for the injection into the fluid of fine nitrogen bubbles, which were entrained by the motion of the medium. The flow pattern was photographed through the mirror 12 under high-intensity side illumination. The remaining components of the apparatus are associated with the electrochemical method used to measure the j-currents. The arrangement for measurement of the diffusion flows (Fig. 1) consisted of a platinum cathode bonded to the end of the cylinder, a platinum grid anode with a contact surface area of about 150 cm^2, a dc source, and a rheostat. The twenty-channel mercury current collector 6 was mounted coaxially with the rotating cylinder. The diffusion current was recorded with a milliammeter or N-700 multichannel loop oscillograph (11). The electrodes could be connected into the electrical circuit with a predetermined voltage. The nonstationary diffusion currents were measured only after careful depolarization of the electrodes, which was monitored with a microammeter with the anode and cathode shorted through the instrument. Dissolved oxygen was removed from the distillate-prepared solution by nitrogen purging. The temperature of the solution during the tests was maintained constant within ±0.2°C limits.

The reversible oxidation–reduction reaction $Fe(CN)_6^{3-} + e \rightleftharpoons Fe(CN)_6^{4-}$ was used to measure the mass flows and diffusion coefficients [5, 6]. The advantage of this system, with the participation of $5 \cdot 10^{-3}$ kmole/m^3 of $K_3Fe(CN)_6/K_4Fe(CN)_6$ and additives of 0.3 NK_2SO_4 (background), is that, first, the electrochemical reaction takes place in the diffusion region over a wide range of variation of the parameters and, second, deposits do not form on the electrodes and the concentrations of the reacting components are practically invariant during the tests. It is important to note that electrochemical methods based on mass-flow measurements by means of diffusion-monitored oxidation–reduction reactions stand apart from other known

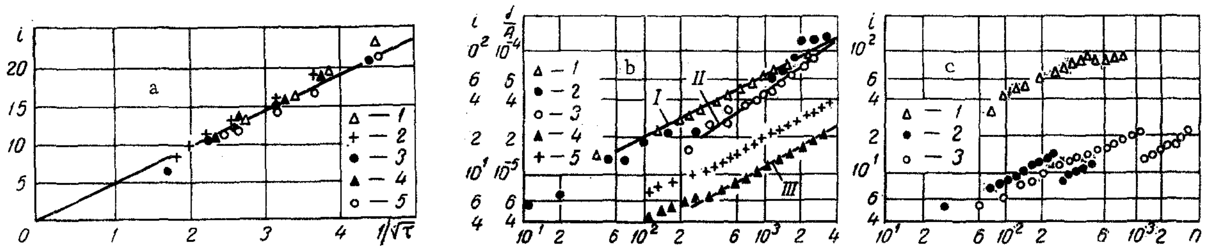

Fig. 2. Limiting mass flow onto the disk [i, mA; $1/\sqrt{\tau}$, $\sec^{-1/2}$; n, rpm; j/A, $kg/m^2 \cdot sec$; curve III and points 4 and 5 are given in coordinates i – n; the remaining curves and points are in coordinates (j/A) – n]. a) Time variation of limiting current: 1) $C_{Na-CMC} = 0\%$, n = 275 rpm; 2) 0.75 and 0; 3) 0 and 25; 4) 1 and 0; 5) 1 and 110, respectively; b) limiting mass-flow density versus rpm (Na–CMC): I, II, III) theoretical curves for, respectively, $C_{Na-CMC} = 0\%$ from [13]; 1.5% from [2]; 0.75% from [2]; 1, 2, 3, 4, 5) experimental data for, respectively, $C_{Na-CMC} = 0\%$; 1.5% from [2]; 1.5%, 0.75%; 0.25%; c) limiting current density versus disk rpm (polyox): 1, 2, 3) experimental data for $C_{pol} = 0.1\%$ and disk diameter 31 mm; 0.25% and 15 mm; 0.5% and 15 mm, respectively.

j-measurement techniques by virtue of their accuracy, simplicity, ability to record nonstationary processes (including rapid processes), and the applicability of standard instrumentation without amplifying devices. The use of these methods, however, for high-polymeric solutions, which are readily degradable in acid and alkali media, calls for extreme caution. It is well known that the specifics of the mechanical behavior of polymeric solutions are due to the properties of the flexible chain macromolecules. The basic factors responsible for the enhanced nonlinear viscosity and high rubberlike elasticity of such solutions are the degree of polymerization of the high-molecular substance, the polymer concentration of the solution, the temperature, the character of the solvent, and, in the case of ionic polymers, the pH of the medium. Thus, in strong acid or strong alkali solutions the effective (Newtonian) shear viscosity falls off rapidly as the pH of the medium is varied from its neutral values. In addition to striving for conditions such that the liquid preserves strict Newtonian characteristics, it is required to ensure optimum conditions for the electrochemical processes. The possible influence of adsorption of certain surface-active substances on the electrode processes has been demonstrated in [7]; a variation of the longitudinal diffusion current was also observed, even for extremely minute additions of such substances. The electrode processes tend to be inhibited by the fact that a definite activation energy is required in order to overcome the additional energy barrier due to the presence of the adsorbed film and, hence, to allow ions to be transmitted through that film. Geirovskii [8] has shown, however, that this effect is manifested primarily in the discharge of multivalent cations. None of the surface-active agents that he investigated had any effect on reversible electrode processes involving a single electron, such as $Fe^{2-} \rightleftharpoons Fe^{3-}$. In our experiments the composition of the solution yielded a pH = 6 (neutral medium). At the same time, the non-Newtonian properties of the solution were preserved throughout the entire experiment. The absence of electrode process inhibition was confirmed by plotting the polarization curves for a platinum disk electrode with very small (0.0005 to 0.001%) additives of Na–CMC and polyox, as well as by running control D-measurements in the nonstationary diffusion regime. It is important to note that measurements of the diffusion coefficients of low-molecular compounds in a high-molecular medium, such as Na–CMC and polyox, is of considerable interest, both scientifically and engineeringwise. Indeed, the classical diaphragm diffusion cell method proves unsuccessful under the conditions of high-viscosity fluids. Consequently, a number of researchers have attempted to determine the diffusion coefficients from measurements of convective mass transfer in viscous fluids. For example, Clough and co-workers [9], using the non-Newtonian analog of the Graetz–Leveque equations, determined the diffusion coefficients of medium-soluble solids in the flow of viscous fluids in a tube. Hansford and Litt [2] determined the diffusion coefficients of benzoic acid in CMC and polyox solutions by comparing the measured rate of dissolution of the disk with the theoretical relation (1). However, these methods are rather complicated, lack precision, and, as pointed out by the authors themselves [2], are not independent.

In our measurements of the diffusion coefficients we used the surge technique of [10]. But, departing from [10], we fixed the nonstationary diffusion current beginning with very small buildup transient times (0.02 sec) for the mass-transfer process. For such small times the equations describing convective diffusion toward the surface of a rotating disk reduce to an equation of the thermal conduction type, whose solution is well known [11]:

$$j = \frac{C_0 D^{1/2}}{\sqrt{\pi\tau}}. \tag{2}$$

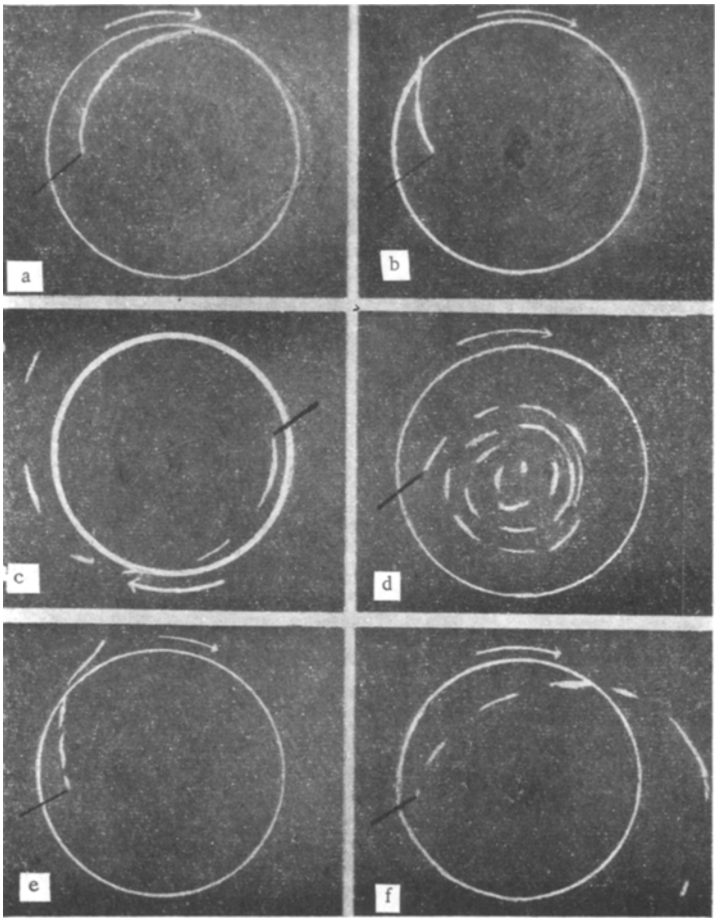

Fig. 3. Fluid flow near the disk surface. a) $C_{Na-CMC} = 0.75\%$, $n = 187$ rpm; b) 0.75 and 650, respectively (at the surface in cases a and b); c) 0.25 and 190 (4 mm from the surface); d) 0.25 and 190 (at the surface); e) 0.25 and 190 (8 mm from the surface); f) 0.25 and 700 (4 mm from the surface).

Or, recognizing that $i = jzF$,

$$i = \frac{C_0 z F D^{1/2}}{\sqrt{\pi\tau}}. \tag{3}$$

Immediately after the application of voltage to the electrodes of the cell the current magnitude in the external circuit is determined by the electrochemical factors associated with the transient process in the double electric layer at the solid wall. Given an intelligent choice of circuit parameters, the length of this transient process can, however, be shortened to a few microseconds. Therefore, if an oscilloscope is used to record the time variation of the current $i = f(\tau)$ after the instant application of voltage to the electrodes, one can calculate the diffusion coefficient from Eq. (3). If the experimental i-values are plotted on a graph with abscissa $1/\sqrt{\tau}$, then $\tan\alpha = i\sqrt{\tau}$ and, hence, D can be determined graphically in the linear approximation of the experimental points. It is clear from Fig. 2a that for small time values the limiting diffusion current is determined by nonstationary molecular diffusion on both the rotating and the stationary disk. This fact makes it possible, by contrast with the methods described in [2, 9], to determine the diffusion coefficient of the reacting component without knowing the rheological model of the fluid.

The results of our mass-flow measurements by the electrochemical method are presented in Fig. 2b for solutions without Na–CMC additives and with 1.5, 0.75, and 0.25% additives of this polymer. Also shown for comparison are the results of Hansford and Litt's theoretical calculations and experimental j-measurements. As the figure indicates, in the solution without polymer additives the measured values of the diffusion currents coincide with those calculated according to Levich's equation [13]. For the 1.5%

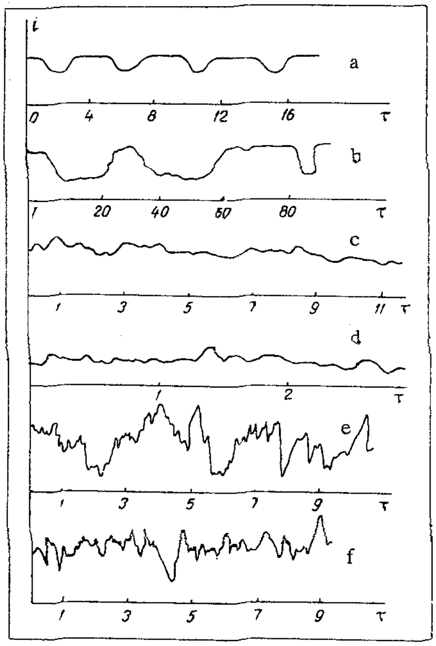

Fig. 4. Oscillograms of the limiting current (τ, sec; i, mA). a) $C_{pol} = 0.25\%$, n = 287 rpm; b) 0.25 and 400, respectively; c) 0.25 and 630; d) 0.25 and 1042; e) 0.1 and 780; f) 0.1 and 1185. a, b, c, d) disk diameter 15 mm; e, f) 31 mm.

Na–CMC solution our data (light circles) fall below the experimental points (dark circles) of Hansford. In our experiments the diffusion coefficient of the component reacting on the disk is lower than in Hansford's experiments. Also, the values of the rheological parameters n and K differ appreciably for the solutions used. Consequently, the agreement of the results in the range of disk speeds from 500 to 1500 rpm is deemed satisfactory. Our experimental data are in considerably better agreement with the theoretical solution of Hansford (curve II). In comparing the results we used our values of $K = 170 \cdot 10^{-3}$ kg-wt $\cdot \sec^{n-2}/\mathrm{m}$ and n = 0.58 according to viscosimetric measurements and the diffusion coefficient $D = 0.5 \cdot 10^{-9}$ $\mathrm{m}^2/\mathrm{sec}$ obtained from stationary measurements of the diffusion current. The scatter of the experimental points for n > 500 rpm in the cited paper is probably attributable to errors associated with distortion of the initially plane surface of the disk as it enters into solution: the buildup of irregularities, indentations along the streamlines, and curving of the surface. The latter effect stems from the fact that for purely viscous nonlinear fluids the surface of the rotating disk is not equally accessible in the diffusion respect.

The measurement of the diffusion current onto a disk electrode rotating in a purely viscous nonlinear fluid is significant from the point of view of determining the non-Newtonian behavior index n. Determining the power exponent in the relation $i = \mathrm{const}\,\omega^m$ from the experimental data in Fig. 2a and 2b and making use of expression (1), we obtain $m = 1/(1 + n)$. The values thus found for n are consistent with the viscosimetric data. In the range of low disk speeds (20 to 300 rpm), as is evident from Fig. 2b, the experimental points deviate from expression (1). Hansford and Litt [2] observed a similar result. In their experiments, unlike our own, this deviation showed up as a sharp reduction in the rate of dissolution of the disk and a large scatter of the experimental points. The authors of [2] attributed this anomaly to the inception of viscoelastic properties of the Na–CMC solution, as reflected in a change of direction of the fluid flow, namely from centripetal to centrifugal. In order to study this effect we implemented visualization of the fluid flow about the disk. It is apparent from the photographs (Fig. 3a and 3b) that the fluid flow was directed from the center toward the periphery over the entire range of disk revolutions per minute in Na–CMC solutions. We postulate that this discrepancy with the effect observed by Hansford is due to the disparity in the rheological properties of the particular Na–CMC solutions used.

The motion of the fluid about the surface of a disk rotating in a polyox WSR-301 solution is illustrated in the photographs of Fig. 3c-3f. Here the inception of viscoelastic properties is witnessed by a deviation of the gas bubble trajectory toward the disk axis. This trend grows stronger as the revolution per minute is increased, until finally the motion of the fluid becomes completely centripetal (Fig. 3d). Far from the disk surface, however (~10 mm), the flow remains centrifugal (Fig. 3e). It is interesting to trace the convective diffusion process toward the disk in this case. It is clear in Fig. 2c that as the disk revolution per minute is increased the diffusion current increases monotonically until a critical value of the revolution per minute is reached, after which it is seen to fall off abruptly. An oscillographic trace of the diffusion current (Fig. 4) made it possible to exhibit a new and very intriguing effect: for comparatively small effective values of the number $\mathrm{Re}_{ef} = 900$ strong pulsations begin to appear. It is well known that for purely viscous linear fluids the flow about a well-centered disk remains laminar up to values of $\mathrm{Re} = 5 \cdot 10^4$. This fact is also borne out by our j-measurements in water (see Fig. 2b). Here the transition to pulsation conditions is normally attended by an intensification of mass transfer. It is evident from Fig. 4a and 4b that the onset of the diffusion current fluctuation regime corresponds to a simultaneous reduction in its average value. At these revolutions per minute the visualization operation disclosed flow instability near the disk surface and a reduction in the flow velocity. With a further increase in the revolution per minute the average value of the mass flow increases monotonically. The initiation of unstable low-frequency fluctuations with sporadic turbulent pulsation intervals of higher frequency is noticeable in Fig. 4a-4c. With a further increase in the revolution per minute (Fig. 4d-4f) the pulsations acquire a more stable character, and their frequency increases. It is difficult to account for the nature of this new phenomenon in terms of the conventional notions concerning the onset of turbulence. Clearly, the early transition to a large-scale pulsation regime of fluid motion about the surface of the rotating disk is due to interaction of the centripetal and centrifugal flows and is elicited by a certain critical ratio of the tangential and normal stresses inherent in the shear flow of viscoelastic systems. Vinogradov and co-workers [12] submit similar causes as responsible, in particular, for the destabilization of the flow of viscoelastic polymer melts upon emergence from a pipe, relying on their proposed "elastic turbulence" model.

NOTATION

C_0	is the concentration of active agent in the electrolyte volume;
D	is the diffusion coefficient;
r	is the radial coordinate;
n	is the non-Newtonian behavior index of the fluid or disk revolution per minute;
R	is the disk radius;
j	is the total current onto the disk;
a'	is the constant defined in [2];
$N = K/\rho$;	
K	is the consistency index;
ρ	is the density;
τ	is the time;
z	is the ion charge;
F	is the Faraday number;
i	is the limiting current density;
Re	is the Reynolds number.

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