THE EFFECT OF THE PHYSICAL PARAMETERS OF POLYMER SOLUTIONS ON THE REDUCTION OF DRAG IN TURBULENT FLOW

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By measurements in the ultracentrifuge, rotational viscosimeter, photogoniodiffusometer and in an apparatus with coaxial cylinders, it is shown that in solutions which possess the Toms effect, particles of the polymer have an asymmetric shape with an elongation equal to 5 approximately. A model of a medium with anisotropic viscosity is demonstrated for explaining the phenomenon.

As a result of investigations of the reduction of frictional drag in the case of turbulent flow of dilute solutions of high-molecular polymers in tubes between rotating cylinders, and also in the case of streamlined flow round disks, plates and other bodies (Toms effect), it was established that the magnitude of the reduction depends on the polymer concentration, its molecular weight and type and that polymers of a chain structure without significant side branches have the greatest efficiency.

In order to explain the phenomenon, various models of continuous media have been proposed [1-7]. Their basis requires consideration of the structure of dilute solutions of high-molecular polymers, both in the absence of and in the presence of a velocity gradient. The results of measurements are given in this paper of the molecular weight distribution of samples of polyethylene oxide (PEO), the dependence of the specific viscosity on the velocity gradient, determination of the average molecular weight and linear size of molecules of the potassium salt of polyacrylic acid in the photogoniodiffusometer at different values of the pH value. The effect of reduction of drag and friction pulsations at the wall was determined for these same solutions. The experimental results obtained give new facts for explaining this phenomenon.

The reduction of friction drag during flow of the prepared solutions was studied in an equipment with coaxial cylinders, of which the outer one rotated (the diameter of the outer cylinder was 110 mm and the gap between the cylinders was 10 mm) [8]. The range of solution concentrations from 10^{-4} to 10^{-1} % enabled both the start of the action of the polymer on the flow and the action at high concentrations to be recorded, when there is interaction of the dissolved macromolecules.

The molecular weight distribution of samples of polyethylene oxide, synthesized under various conditions, was determined on the basis of centrifugation in the "Veskmap" ultracentrifuge at a rotor speed of 44,770 rpm, using Bailey's relation [9] and Gasting's method [10]. The weighted-mean molecular weight was then calculated. This approach ensured against the error of the viscosimeter method of determining the molecular weight, as it was not known beforehand how the molecular weight distribution differs from Gaussian.

The molecular weight distribution of the samples investigated is plotted in Fig. 1. It can be seen that, for a weighted-mean molecular weight of $(3-7)\cdot 10^6$, with certain samples quite a large quantity of molecules have a molecular weight of $(10-20)\cdot 10^6$. As the degree of drag reduction in turbulent flow depends on the molecular weight, then in exact calculations and analyses of the efficiency of the samples, the molecular weight distribution must be taken into account. With the samples shown in Fig. 1, although the form of the molecular weight distribution differs considerably, the Schultz coefficient of nonuniformity is equal to 0.3 to 0.5, i.e., it is close to a Gaussian distribution.

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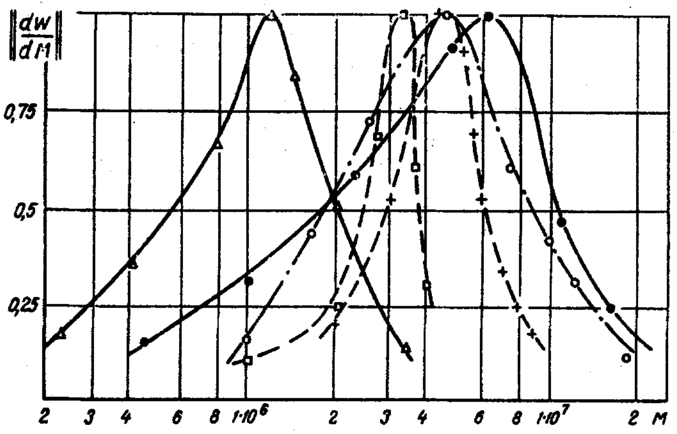

Fig. 1. Normalized molecular weight distribution ||dW /dM|| of samples of polyethylene oxide.

Over a certain narrow range of change of concentration and Reynolds number, the effect of molecular weight distribution can be neglected. This can be seen clearly in Fig. 2, in which for 10 samples it proved possible to construct a simple relation (curve 1) between the degree of drag reduction and the weighted-mean molecular weight M_W. The scale of the mean-square size of a micromolecule $\overline{(h^2)}^{1/2}$ is also plotted on the axis of abcissa, and therefore curve 1 as shown can be considered also as a function of the size of a macromolecule.

The mean-square size was determined by the well-known formula

$$\overline{(h^2)}^{3/2} = \frac{[\mu]_0 M_w}{\Phi_0} \tag{1}$$

($[\mu]_0$ was measured in the capillary viscosimeter).

It can be seen that particles with a linear size of order (1 to 2)$\cdot 10^3$ Å lead to a significant drag reduction.

In order to understand the structure of the solution, in addition to the size of the particles, it is essential to know their shape. It is well-known that these data can be obtained from the dependence of the viscosity of the solution on the velocity gradient. We determined these relations for solutions of polyethylene oxide with different molecular weights in the rotation viscosimeter, type KD, in which the gap between the cylinders was reduced to 0.1 mm. The solution concentration was equal to $5 \cdot 10^{-2}$% and the velocity gradient was varied over the range from $7 \cdot 10^3$ to $5 \cdot 10^4$ sec^{-1}. The measurement error amounted to ±3%.

The results of the experiment are shown in Fig. 3 for two solutions of polyethylene oxide with $M_W = 1.3 \cdot 10^6$ and $4.1 \cdot 10^6$. Values of $\alpha_{rot} = g/4D_{rot}$ are plotted along the axis of abcissa; g is the velocity gradient and D_{rot} is the coefficient of rotational diffusion, calculated for an axisymmetrical ellipsoid with an elongation of 4.9. The calculated curves for rigid, impermeable, asymmetrical ellipsoids with elongations of p = 5 and p = 10 are also plotted, using Kuhn's formula [11, 12].

A comparison between the experimental data and the calculations, shows that the orientation of the actual molecules of polyethylene oxide polymers is close to the orientation of axisymmetrical ellipsoids with an elongation slightly greater than 5 (it is well-known, that the conformation of a chain with a Gaussian distribution of the segments has the shape of a broad-bean with a maximum elongation of 4.9). It can be seen, in addition, that with increase of the velocity gradient, the asymmetry of the particles increases. As a result of orientation and stretching of the macromolecules, the specific viscosity of actual polyethylene oxide solutions is reduced by a factor of 1.7 to 1.8 approximately. Over the range of variation of the weighted-mean molecular weight of the samples investigated, the reduction of the specific viscosity increases with increase of the molecular weight.

It follows from the data given that, in a dilute solution of polyethylene oxide with a molecular weight of (1-6)$\cdot 10^6$, the particles have axisymmetrical shape with an elongation equal to 5 approximately, and a linear size of order (1 to 2)$\cdot 10^3$ Å.

Curve 1 in Fig. 2 also shows the increase of the effect of drag reduction with increase of the linear size of the particles, in this case however the increase of linear size was achieved due to the

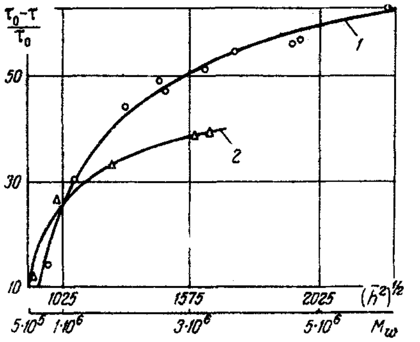

Fig. 2

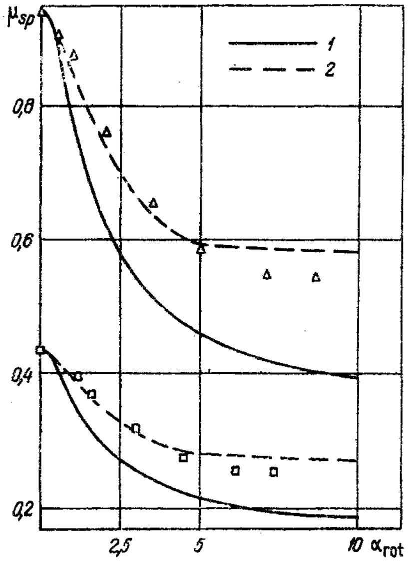

Fig. 3

Fig. 2. Dependence of the drag reduction effect $\tau_0 - \tau/\tau_0$, %, on the molecular weight M_W (curve 1) and the size of the molecules $(\bar{h}^2)^{1/2}$, Å (curve 2).

Fig. 3. Effect of shear velocity α_{rot} on the specific viscosity of the solutions μ_{sp}: 1) calculation for an ellipsoid with elongation 10; 2) calculation for an ellipsoid with elongation 5.

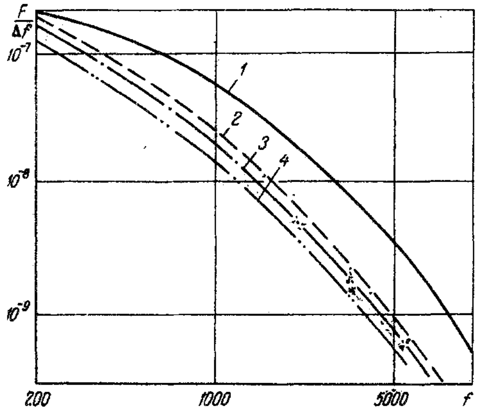

Fig. 4. Dependence of ratio of distribution function to pass band of filter F(f)/Δf on the concentration of polyethylene oxide solution: 1) 0 (water); 2) $2\cdot10^{-3}$; 3) $5\cdot10^{-5}$; 4) $2\cdot10^{-4}$.

increase of molecular weight of the polyethylene oxide. Therefore, one understands the necessity for obtaining the dependence of the effect only on the linear size at constant molecular weight.

In the apparatus with coaxial cylinders described, the reduction of friction drag was measured in solutions of polyelectrolyte — potassium salt of polyacrylic acid $(C_2H_3COOK)_n$ with concentrations of 0.01%. The solutions differed in pH over the range 1.1-10, which was achieved by means of standard fixanals with identical ionic strength equal to 0.02. The experiments showed that, with increase of the pH of the solution from 1.1 to 10, the degree of drag reduction increases from 14 to 36%. As the increase of pH over the range investigated causes an increase of the linear size $(\bar{h}^2)^{1/2}$ of the macromolecular coil, then this also is a basic cause of the increase of efficiency of the polymer.

The variation of $(\bar{h}^2)^{1/2}$ was determined quantitatively in a photogoniodiffusiometer, made by the firm "Fica," according to standard procedure. The molecular weight of the polymer was also determined by the method of double extrapolation with respect to light diffusion in an acetate buffer (pH = 4.2) and was equal to (1.5 to 1.6) $\cdot 10^6$. It was established that an increase of pH from 1.1 to 10 leads to an increase of the linear size $(\bar{h}^2)^{1/2}$ from 590 to 1550 Å.

The results are plotted in Fig. 2, where the dependence of the Toms effect on the molecular weight and, correspondingly, on the linear size of the polyethylene oxide molecules already is represented. Curve 2 shows that, in the general case, not only the molecular weight of the polymer should be taken into account, but also its conformation in solution.

We emphasize, that in these experiments the linear size of the particles in solution which possess the Toms effect, was measured directly. It increased from 590 to 1550 Å with the change of pH, i.e., it was in the same range as the particle sizes in the polyethylene oxide solution, which also gave a reduction of the drag.

The data shown on the particle sizes obtained by direct measurement using the methods tested in numerous investigations of solutions of different polymers, permitted the requirements for a model of the medium in which the effect of drag reduction is observed to be quite specifically formulated (we are speaking only of dilute solutions): the polymer is in solution in the form of particles with a linear size of order 10^3 Å, having an asymmetrical shape with an elongation of approximately 5; the particles are in the solvent at distances from one another which far exceed the linear dimensions of the particles.

These requirements confirm the model of a medium with anisotropic viscosity proposed by one of the authors. The essence of the physical foundations of this model will follow [4].

Under the action of a large average velocity gradient in the boundary zone of turbulent flow, the prolate particles have the most probable orientation along the flow (along the fairing). For pulsation turbulent motion, such a medium has an anisotropic viscosity (the viscosity along the normal is greater than along the surface). The increased lateral viscosity strongly decreases the lateral velocity pulsations and, correspondingly, the turbulent shear stress, but the small longitudinal viscosity (only slightly in excess of the viscosity of the solvent), causes no significant increase of the laminar friction component. Then, on the assumption that the solution concentration is small and that the conformation of the macromolecules has a strongly elongated shape, the following relation can be obtained for the two-layer model of turbulent flow [4]:

$$\frac{\Delta U}{U_0} \sim \frac{[\mu]_0 c}{(\mathrm{Re})^{n/2}}, \tag{2}$$

U_0 is the velocity at the outer edge of the boundary layer (for flow in a tube, it can be converted to mean flow rate); ΔU is the velocity increase at the outer edge of the boundary layer, due to the action of the polymer at constant frictional stress at the wall.

Taking account of Eq. (1), we have in place of Eq. (2)

$$\frac{\Delta U}{U_0} \sim \frac{\bar{\Phi}_0 (\overline{h^2})^{3/2} c}{(\mathrm{Re})^{n/2} M_w}. \tag{3}$$

For polymers of a single homologous series, the dependence of the Toms effect on the weighted-mean molecular weight can be obtained by using the Mark—Kuhn—Hauwink formula

$$\frac{\Delta U}{U_0} \sim \frac{K_\mu M_w^\alpha c}{(\mathrm{Re})^{n/2}} \tag{4}$$

(α for polyethylene oxide is equal to 0.78).

In the model described, no consideration is taken that a chain macromolecule, which assumes the shape of a statistical coil in solution, in a field of variable pressures and velocities must experience deformation with a defined frequency. A method of calculating these pulsations is proposed in [7].

The effect of polymer additives on the velocity and pressure pulsations in turbulent flow has been investigated by various methods [13, 14]. We measured the pulsations of frictional stress at the wall in the apparatus described above, with coaxial cylinders, at various concentrations of the polyethylene oxide polymer.

The grazing friction sensor was made in the Institute of Hydrodynamics. It consists of a rod of quartz glass, carrying on the polished end surface a sensitive element — a film with dimensions 2.5 × 0.2 mm and thickness 1 to 2 μ. The measurements were carried out with a thermoanemometer type 5501 (of the firm "Disa"); the a.c. component of the signal was fed to a type 212 ("Bruel and Kjoer") spectral frequency analyzer and simultaneously recorded on a type 2305 pen-recorder.

Figure 4 shows the distribution functions F(f), related to the pass band of the filter, in water and in polyethylene oxide solutions at a linear speed of the outer cylinder of 34.5 m/sec. From the graphs, it follows that the friction pulsations at the wall in solutions with concentrations at which the Toms effect is observed, are reduced considerably over the frequency range from 200 to 5000 Hz.

NOTATION

M_w	is the weighted-mean molecular weight;
$(\overline{h^2})^{1/2}$	is the mean-square linear size;
c	is the concentration;

$[\mu]_0$	is the characteristic viscosity with zero velocity gradient;
μ_{sp}	is the specific viscosity;
g	is the velocity gradient;
$\alpha_{rot} = g/4D_{rot}$	is the shear velocity;
D_{rot}	is the coefficient of rotational diffusion;
Φ_0	is the Flori coefficient;
K_μ	is the Kuhn—Hauwink coefficient;
α	is the index, describing the conformation of a macromolecule;
U_0	is the average velocity;
ΔU	is the increment of average velocity;
Re	is the Reynolds number;
n	is the exponent in the hydrodynamic drag law;
$F(f)$	is the distribution function.

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