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EFFECT OF THE MOLECULAR WEIGHT OF POLYETHYLENE OXIDE ON THE DYNAMICS OF REDUCTION OF RESISTANCE

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A study is carried out to investigate experimentally the dynamics of reduction of the friction resistance over the length of a tube in the case of a flow of solutions of polyethylene oxide with different molecular weights.

When water-soluble polymers are used to decrease friction resistance, contradictory requirements are established for the molecular weight of the polymer. In [1] it is found that the effectiveness of reduction of friction increases rapidly with the molecular weight, followed by saturation at $M_w \approx (1-3)\cdot 10^6$. As shown in [2], the effectiveness of reduction of friction is a function of $cM_w^{0.85}$, which means that as the concentration c is decreased to save on the amount of polymer, the molecular weight of the polymer should be increased. On the other hand, it is reported (see the review [3]) that the destruction rate of these polymers increases and their solubility decreases as M_w increases.

In [4] it is shown that during a turbulent flow a polymer solution changes its hydrodynamic effectiveness in a complicated manner: there is a section of growing effectivenees, a section of manifestation of maximum reduction of the resistance, and a section of a destructive drop. As the concentration of the solution increases, the section of the maximum effectiveness is shifted to the end of the tube, and as the velocity increases, it is shifted to the beginning of the tube. Thus, the effectiveness of the action of the polymer cannot be defined by one quantity; it is a function of the duration and intensity of interaction of the polymer macromolecules with the turbulent flow.

We continue to study the dynamics of reduction of friction resistance with account for the effect of the molecular weight of polyethylene oxide (PEO).

The scheme of the setup is described in detail in [4]. It differs from the present one by the use of an additional fifth measuring section, a tube 12.5 cm in length, for more thorough investigation of the effectiveness in the starting length of the tube. Moreover, a thermostating system is used in the setup to maintain a constant specified temperature of 25°C.

The molecular weight of the PEO was measured in an Ubbelode viscometer with a tube of length 2 mm and a diameter of the capillary of 1 mm at a shear rate of 22–25 sec^{-1}.

The measurements were taken at 30°C. The molecular weight M_w was determined from the measured characteristic viscosity $[\eta]$, using the formula

$$[\eta] = 1.25\cdot 10^{-4}\, M_w^{0.78}\,.$$

For hydrodynamic measurements PEO samples with the following molecular weights were chosen: $0.3\cdot 10^6$ ($[\eta] = 2.2$ dl/g), $0.8\cdot 10^6$ (5 dl/g), $1.93\cdot 10^6$ (10 dl/g), and $3.25\cdot 10^6$ (15 dl/g). The first three samples are of domestic production, and the fourth one is produced by the Bulgarian company Badimol. Working solutions with a concentration of $5\cdot 10^{-5}$ were prepared from the basic solution a day before their use.

Reduction of the friction resistance was measured in five sections of the tube: 0.125–0.25 m, 0.25–0.5 m, 0.5–1 m, 1–2 m, and 2–4 m. It was not measured in the starting length of the tube since the turbulent flow was formed there.

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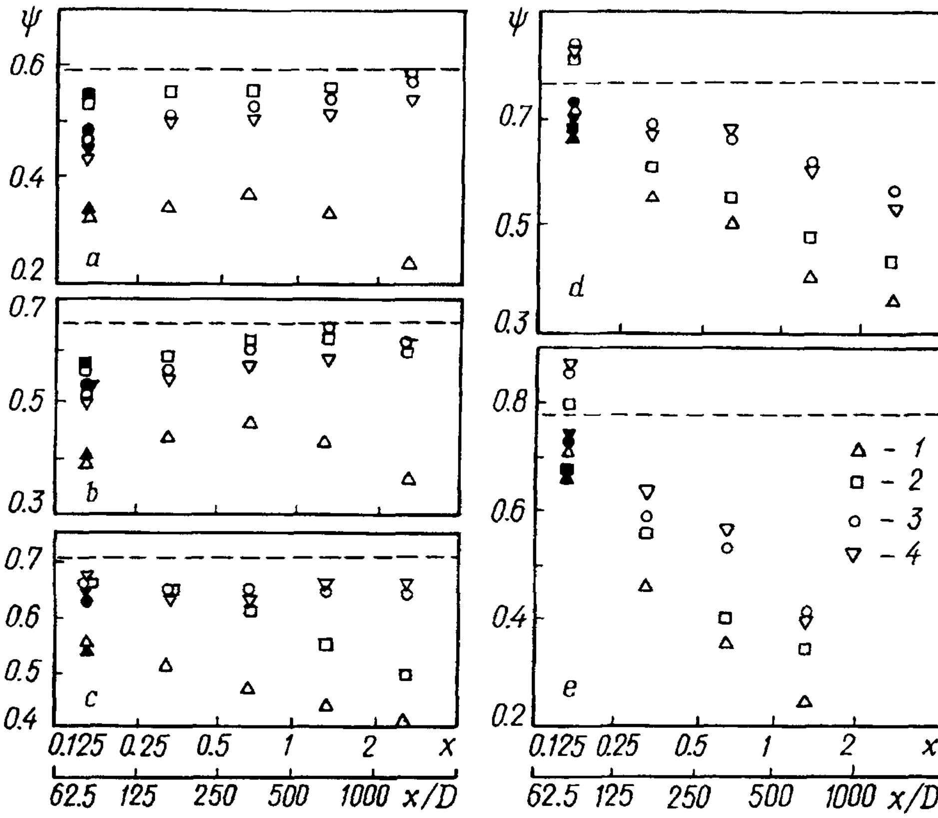

Fig. 1. Dynamics of the effectiveness of reduction of friction along the length of a tube in a flow of solutions of PEO with different molecular weights: 1) $M_w = 0.3 \cdot 10^6$; 2) $0.8 \cdot 10^6$; 3) $1.96 \cdot 10^6$; 4) $3.25 \cdot 10^6$; dark points) corrected values; a) Re = $6 \cdot 10^3$; b) 10^4; c) $2 \cdot 10^4$; d) $4 \cdot 10^4$; e) $7 \cdot 10^4$. x, m.

Results of the measurements are shown in Fig. 1. In the graphs points are placed in the middle of the sections. As in [4, 5], here three areas with different behavior of the effectiveness can be distinguished. The first is characterized by an increase in the effectiveness of the action of the polymer along the length of the tube. For a concentration of PEO $c = 5 \cdot 10^{-5}$ this is especially pronounced at low velocities (Fig. 1a, b). A section of growth is observed for all four samples with different molecular weights, and the growth is more pronounced with increasing M_w.

The section where the maximum effectiveness is attained is shifted to the beginning of the tube with increase in the velocity. For example, at a velocity of 3 m/sec (Fig. 1a), the solutions with $M_w = (0.8, 1.93, 3.25) \cdot 10^6$ show that the effectiveness increases over the entire length of the tube, i.e., the chosen length of the tube (4 m) is not sufficient for manifestation of a maximum effectiveness by these solutions. At a flow velocity of 5 m/sec (Fig. 1b), the solution of PEO with $M_w = 0.8 \cdot 10^6$ exhibits maximum effectiveness in the section 0.5–1.0 m, the solution of PEO with $M_w = 1.93 \cdot 10^6$, in the section 1–2 m, and the solution of PEO with $M_w = 3.25 \cdot 10^6$, beyond the length of the tube.

The maximum reduction of the friction approaches a limiting value ψ_{lim}, which corresponds to propagation of Virk's velocity profile [6] to the axis of the tube, and is defined by the formula suggested in [4]

$$\psi_{\text{lim}} = 0.554 \arctan (0.024 \sqrt{\text{Re}}) . \tag{1}$$

As can be seen from the present data, the limiting reduction of friction is independent of the molecular weight of the polymer, if it exceeds a certain value. In particular, the solution of PEO with $M_w = 0.3 \cdot 10^6$ cannot attain the limiting reduction of friction. However, at higher Reynolds numbers (Fig. 1d, e) the friction is reduced to an extent that exceeds the limiting value. The reason for this phenomenon is analyzed below.

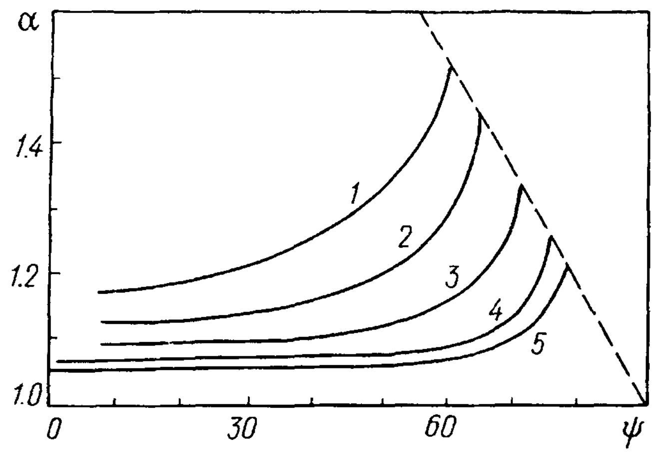

Fig. 2. Plot of the Coriolis coefficient versus the reduction of friction resistance at: 1) Re = $6 \cdot 10^3$; 2) 10^4; 3) $2 \cdot 10^4$; 4) $4 \cdot 10^4$; 5) $7 \cdot 10^4$. ψ, %.

Finally, at high flow velocities or at low velocities at the end of the tube, the decrease in the effectiveness by many authors is observed (see the review [7]).

To find out why the observed reduction of the friction resistance exceeds the limiting value, we analyze the method of calculating the friction, based on measurement of the pressure drop. In accordance with the general Bernoulli equation, the applied pressure is expended on work against friction forces and on changing the kinetic energy of the flow

$$\Delta P = \frac{2l}{R}\tau + 0.5\rho U^2(\alpha_{x+l} - \alpha_x) . \tag{2}$$

Here ΔP is the pressure drop in the section of the tube from x to $x + l$, τ is the shear friction averaged over the measuring section, and α is the Coriolis coefficient, defined by the formula $\alpha = \oint_S u^3 dS/SU^3$, where u is the local velocity in the cross-sectional area S.

For a fully developed turbulent flow of water, in which the velocity profile remains unchanged over the length of the tube, the kinetic energy of the flow does not change over the measuring section, and the following relation is valid:

$$\Delta P = \frac{2l}{R}\tau .$$

The situation can change drastically for a flow of non-Newtonian liquids. For example, for the given present case of $D = 2R = 2 \cdot 10^{-3}$ m, $U = 20$ m/sec, and for the first measuring section of the tube $x/D = 62.5-125$, $\psi_{x/D=62.5} = 70\%$, $\psi_{x/D=125} = 60\%$, and $\overline{\psi} = 65\%$ are assumed. For a flow of a non-Newtonian liquid at different Reynolds numbers a computational algorithm for the Coriolis coefficient is given in [8]. In Fig. 2 one can see a family of curves $\alpha(\psi)$ for the Reynolds numbers of the analyzed velocity regimes. The dashed line shows the limiting reduction of friction. For the present example $\alpha_{\text{ini}} = \alpha(\psi = 70\%) = 1.27$ and $\alpha_{\text{fin}} = \alpha(\psi = 60\%) = 1.16$.

Using Blasius's law for a flow of water $\tau_0 = (0.3164/8)(\text{Re})^{-1/4}\rho U^2$, formula (2) can be transformed to the form

$$\Delta P = \frac{2l}{R}\tau_0 \left[(1 - \psi) + \frac{2R}{0.3164l}(\text{Re})^{1/4}(\alpha_{\text{fin}} - \alpha_{\text{ini}})\right] . \tag{3}$$

Substitution of the values of the parameters gives

$$\Delta P \cong \frac{2l}{R}\tau_0 (0.35 - 0.08) .$$

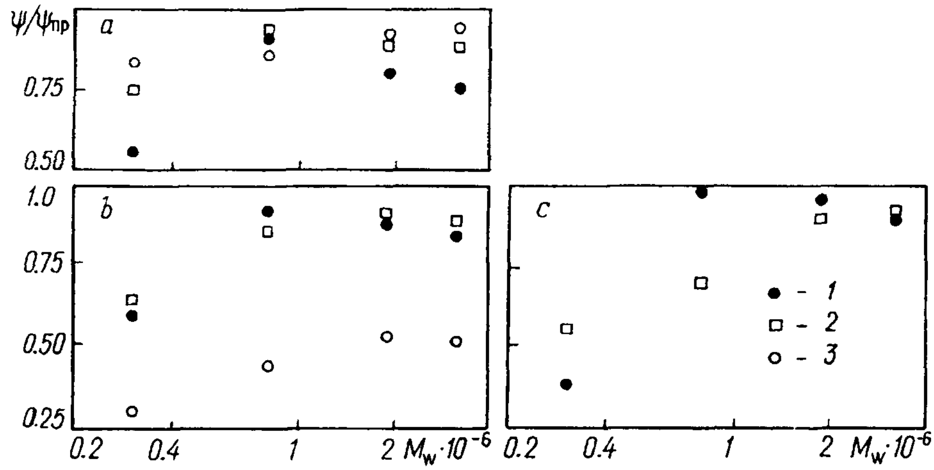

Fig. 3. Plot of the relative effectiveness of reduction of friction versus the molecular weight at different distances from the beginning of the tube: a) $x/D = 62.5-125$; b) 250–500; c) 1000–2000; 1) $\mathrm{Re} = 6 \cdot 10^3$; 2) $2 \cdot 10^4$; 3) $7 \cdot 10^4$.

Thus, in the present example the contribution of the change in the kinetic energy of the flow to the pressure drop amounts to 22.5% of the friction losses. Neglect of this contribution results in an 8% overestimation of the true effectiveness of reduction of friction.

If in the measuring section of the tube the effectiveness is found to decrease (in the case of a low concentration of the solution or a high flow velocity), the contribution of the change in the kinetic energy of the flow has the opposite sign.

As can be seen from an analysis of formula (3), the effect of a change in the kinetic energy of the flow becomes quite substantial in two cases: 1) at high effectivenesses of reduction of friction ($\psi > 0.5$), when the first term in brackets in formula (3) decreases, and 2) when at a short distance l, the velocity profile changes substantially. Since this profile depends on the local effectiveness of reduction of friction, this effect is especially pronounced in the starting length of the tube [4].

In the general case, for correct measurement of the friction, it is necessary to determine not only the pressure drop in the measuring section but also the velocity profile at the beginning and end of this section. Figure 1 also shows corrected effectivenesses. The effectivenesses were corrected only in the first measuring section since already in the second section the correction was much smaller. As can be seen from these figures, the correction decreases the slopes of the sections of growth of the effectiveness and the destructive drop.

However, the fact that the corrected effectivenesses never exceed the limiting reduction of friction (dashed lines) is of greatest interest. This expands substantially the range of validity of Virk's law for the limiting reduction of friction.

It is likely that neglect of changes in the kinetic energy of the flow explains the overestimation of the limiting reduction of friction that was reported in [9]. Unfortunately, the authors of that article did not study the dynamics of reduction of friction, but from the shape of the curves of $\psi(\mathrm{Re})$ it is possible to infer that ψ changes quite noticeably along the length of the tube and, consequently, the neglected contribution must be substantial. In [10] a sharp change in the effectiveness was observed in the initial length of the channel. This can explain the extremely large reduction of friction ($\psi = 95\%$) obtained in this section.

In Fig. 3 one can see a plot of the relative effectiveness (normalized on the limiting reduction of friction) in the initial, middle, and final lengths of the tube. In general, it can be stated that for each of the measuring sections, depending on the Reynolds number, there is an "optimum" molecular weight at which the effectiveness is maximum. In the initial length, as the Reynolds number grows, the relative effectiveness increases, and in the two others it decreases. This is caused by breakdown of supermolecular structures [11] and destruction of the solution. The solution of PEO with $M_w = 0.3 \cdot 10^6$ has a low relative effectiveness under all conditions. As can be seen from Fig. 3c, in long tubes at high Reynolds numbers polymers with a higher molecular weight are more effective.

It should be noted that in a flow a polymer changes its molecular weight toward a decrease [12]. But in that article, only initial values of M_w are given. Moreover, reduction of friction depends on the molecular-weight distribution [13], and high-molecular-weight fractions operate most effectively (i.e., a specified reduction of friction is attained at lower concentrations).

Thus, the present measurements and analysis show the importance of account for the dynamics of reduction of friction resistance in a flow of commercial-PEO solutions. The maximum effectiveness of reduction of friction is close to the limiting value in the studied range $0.8 < M_w \cdot 10^{-6} < 3.25$ and is decreased in the range $0.3 < M_w \cdot 10^{-6} < 0.8$. The present results on the behavior of the effectiveness of polymer solutions in a flow change somewhat the generally recognized idea of manifestation of Thoms's effect. In particular, it can be stated that for any concentration (from a rather wide range that requires subsequent refinement), there is a section of the tube where reduction of friction attains a limiting value. It depends only on the Reynolds number and, consequently, it is unnecessary to determine the effectiveness of various grades of polyethylene oxide in the conventional sense. The various PEO grades should be characterized by the slope of the section of growth of the effectiveness, the duration of its maximum value, and the intensity of the drop. It seems promising to study methods of affecting the dynamics of Thoms's effect [11] that decrease the section of growth and increase the duration of maximum effectiveness, which increases the effectiveness of using this method of reduction of friction.

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NOTATION

ψ, magnitude of reduction of friction resistance; M_w, molecular weight; c, concentration of the solution; $[\eta]$, characteristic viscosity; Re, Reynolds number; l, length of the measuring section of the tube; R, radius of the tube; D, diameter of the tube; ρ, density of the liquid; U, mean flow velocity; S, cross-sectional area of the tube; x, longitudinal coordinate of the tube.

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