# RELATION BETWEEN MOLECULAR STRUCTURE OF POLYETHYLENE OXIDE SOLUTIONS AND DRAG REDUCTION

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The results of an experimental investigation of the special features of laminar and turbulent flows of aqueous solutions of polyethlene oxides are given.

The existence of aggregates (associations) of macromolecules in the region of concentrations where effective drag reduction occurs is still a controversial question [1-5], which indicates the existing uncertainty of the model of the medium in which this effect is manifested. An elucidation of the molecular aspects of turbulent drag reduction will help to resolve this uncertainty. This necessitates a consideration of the molecular structure of polymer solutions in the absence and presence of a velocity gradient and a comparison with the special features of their turbulent flow. In this way we can obtain a model of the medium and a basis for precise concepts that will allow an approach to an understanding of the physical nature of drag reduction and, hence, the construction of a foundation for a theory of the effect.

The aim of the present work was to solve the first part of the posed problem: to elucidate the main properties of a medium exhibiting reduced turbulent friction, as exemplified by an investigation of aqueous solutions of polyethylene oxides (PEO) with molecular masses (M) $6 \cdot 10^5$, $1 \cdot 10^6$, $3 \cdot 10^6$, and $8 \cdot 10^6$. We investigated the hydrodynamic and rheological characteristics in a wide range of Reynolds numbers (Re), shear stress ($\tau$), and concentration (C).

The drag was measured on an apparatus (Fig. 1) consisting of a pressure system 1 for the creation of the required pressure drop, a thermostat 2, which contained the working volume 3 with the polymer solution, a channel 4, an electronic thermoregulator 5, and a device 6 for determination of the liquid outflow time. The main quantity measured in this method is the time for outflow of a prescribed volume of liquid. For its measurement we used an electronic circuit consisting of inductance pickups, an amplifier, discriminator, trigger, two cathode followers, two differentiating networks, and an F 599 electronic timer. The voltage differences produced in the transducers by the passage of a steel ball mounted on a hollow rod connected to a float were converted by the electronic circuit and controlled the operation of the F 599 timer. The apparatus had the following technical specifications: range of Reynolds numbers $10^2$-$10^5$; range of working temperatures (T) 50-150°C, accuracy of maintaining prescribed temperature 0.1°C; working volume $5 \cdot 10^{-4}$ m$^3$; channel length 1.9 m; channel diameter varying from $0.2 \cdot 10^{-3}$ to $6.5 \cdot 10^{-3}$ m (a channel of diameter $2.68 \cdot 10^{-3}$ m was used).

The actual pressure drop on the ends of the channel was determined by the method described in [6]. The drag coefficient of the PEO solutions was calculated from the formula [7, 8]

$$\Lambda = \frac{\Pi^2 d^5 t^2 \Delta P}{8 l \rho V^2}, \tag{1}$$

where d is the diameter of the channel; $l$, its length; $\rho$ and V, density and volume of the liquid, respectively; $\Delta P$, pressure drop on the ends of the channel; t, outflow time for a prescribed volume of liquid. The drag reduction was expressed as a percentage:

$$\frac{\Lambda_w - \Lambda_s}{\Lambda_w} = \frac{\Delta\Lambda}{\Lambda} = \left[1 - \frac{\Delta P_s}{\Delta P_w}\left(\frac{t_s}{t_w}\right)^2\right] 100\,\%. \tag{2}$$

In this expression the subscript w refers to the solvent, and s to the solution. The error in measurement of the drag reduction was 1%.

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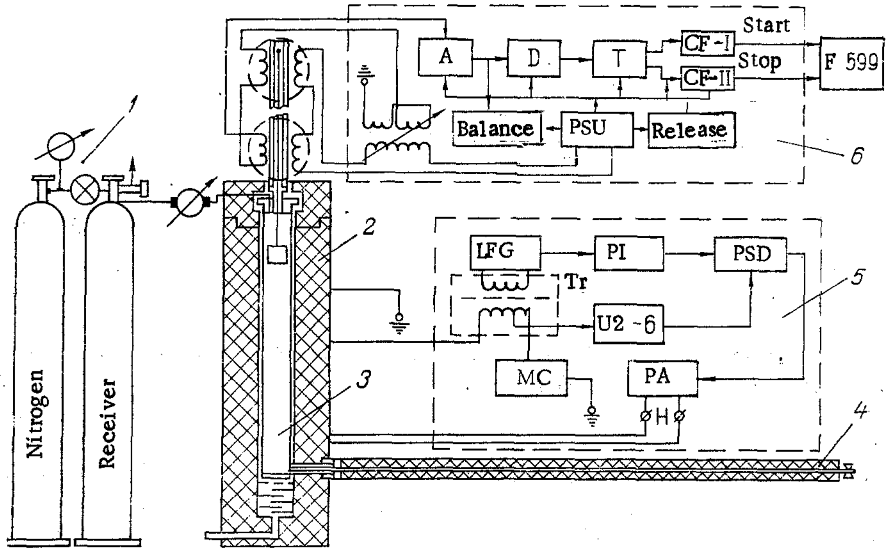

Fig. 1. Diagram of apparatus for drag measurement.

The coefficient of viscosity was measured on a capillary viscometer with a device for the production of different pressures (corresponding to those at which the liquid flowed out). The diameter of the capillaries varied in the range $2 \cdot 10^{-4}$–$5 \cdot 10^{-4}$ m. All the required constants (the diameters of the capillaries, their lengths, the working volume of the viscometer, conversion factors, etc.) were determined directly by means of a measuring microscope, weighing, etc. or by calibration against reference liquids. The correction for the difference between the pressure gauge readings and the pressure at the entrance to the capillary was taken into account in the same way as in measurement of the drag factor. Since viscosity is very sensitive to change in temperature and temperature gradient in the sample, particular attention was paid to the temperature stabilization system. For this we used a thermostat similar to that described in [9] and an electronic circuit 5 (Fig. 1) consisting of a generator, phase inverter, differential transformer with an alternating voltage bridge, phase sensitive detector, and power amplifier [10]. The temperature in the temperature range investigated was maintained at the prescribed level to within 0.05°C. The error of viscosity measurement was 1%.

The solutions were prepared with distilled water at room temperature. We first investigated the mechanical degradation and aging of the PEOs. We selected optimal conditions for preparation of the solutions, at which there was hardly any degradation or aging. The molecular masses of the PEOs were checked by viscometry. Before the measurements the solutions were held for about 24 h. We used PEO preparations of the firms BDH Chemicals Ltd. (England) and Union Carbide (U.S.A.). These PEO preparations required no further purification [11].

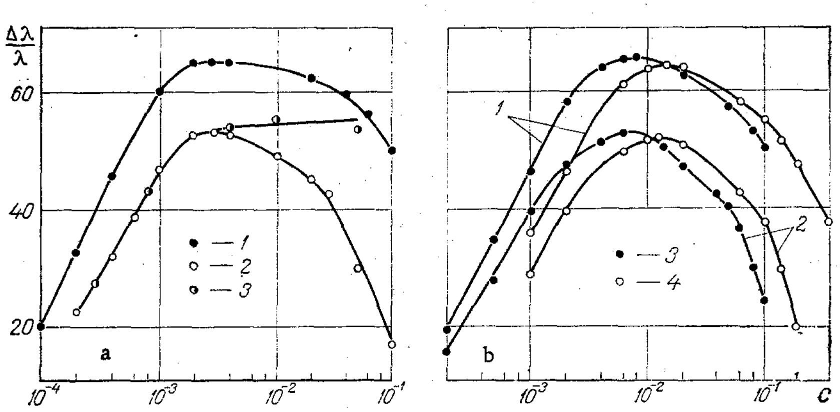

Fig. 2. Reduction of drag of aqueous PEO solutions as function of concentration at 20°C. a: 1) $Re = 2\bar{U}R_\rho/\eta_w = 20{,}000$; 2) $Re = 2\bar{U}R_\rho/\eta_w = 6000$; 3) $Re = 2\bar{U}R_\rho/\eta_{L.N} = 6000$. b: 1) $Re = 20{,}000$; 2) $Re = 6000$; 3) $M_{PEO} = 10^6$; 4) $M_{PEO} = 6 \cdot 10^5$.

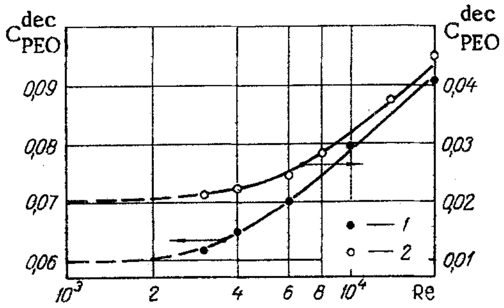

Fig. 3. $C_{PEO}^{dec}$ as function of Reynolds number in aqueous PEO solutions: 1) $M_{PEO} = 10^6$; 2) $M_{PEO} = 3 \cdot 10^6$. $C_{PEO}^{dec}$, %.

The effect of PEOs with molecular masses $3 \cdot 10^6$, $10^6$, and $6 \cdot 10^5$ on drag reduction in the case of turbulent flow of aqueous solutions of different concentrations is shown in Fig. 2a, b. It is apparent that the concentration dependence of the turbulent friction reduction passes through a maximum at concentrations $C_{PEO}^{op} = 0.003$, 0.009, and 0.015%, and then, beginning at $C_{PEO}^{dec} = 0.025$, 0.07, and 11%, respectively, of the considered molecular masses of the PEO, the effect sharply decreases. We can postulate that the fairly sharp decline in turbulent friction reduction with increase in concentration is due to molecular interaction of the polymer molecules.

It was shown in [12-14] that intense interactions of PEO molecules in solution become apparent when the inequality

$$\frac{MC_{PEO}^{tr}}{100\%} \geqslant 600 \tag{3}$$

is fulfilled. The number 600 characterizes the transition from the region with individual uncorrelated movements of the molecules (in this region there is no aggregation of macromolecules) to the region with interdependent correlated movements of the molecules associated with the formation of a fluctuational polymer network in the solution. For PEOs of molecular masses $3 \cdot 10^6$, $10^6$, and $6 \cdot 10^5$ the values of the "transition" concentrations, from Eq. (3), are 0.02, 0.06, and 0.1%, respectively.

Comparing these data with the concentration dependences of drag reduction we can conclude that the concentrations at which the effect is greatest correspond to the region in which intermolecular interactions of PEO molecules can be neglected; with the onset of cooperative motion of the macromolecules in the polymer solutions, the drag reduction sharply decreases. This is indicated by the correspondence between the "transiton" concentrations ($C_{PEO}^{tr}$) and the concentrations $C_{PEO}^{dec}$ above which the drag reduction sharply decreases. It should be noted that with reduction of the Reynolds number $C_{PEO}^{dec}$ decreases and approaches the value of the "transition" concentration (Fig. 3). This is due to the fact that in the case of large velocity gradients the external field has a significant effect on the molecular structure of the polymer solutions. While $C_{PEO}^{dec}$ depends on the Reynolds number, the optimal concentration corresponding to the maximum of the effect is practically constant in the whole investigated range of Reynolds numbers. Data characterizing the value of $C_{PEO}^{op}$ for different molecular masses of the PEOs and Reynolds numbers at 20°C are given in Table 1. Table 1 also indicates that between $C_{PEO}^{op}$ and the molecular mass of the PEO there is a definite correlation:

$$\frac{MC_{PEO}^{op}}{100\%} \simeq 90. \tag{4}$$

As the conducted rheological experiment showed, all the investigated solutions of PEOs (of high molecular masses) exhibited non-Newtonian properties. Typical results are given in Fig. 4. These and similar graphs indicate that the shear dependence of the viscosity is still a feature of solutions of PEOs of high molecular mass down to the lowest concentrations and becomes more pronounced with increase in concentration and molecular mass of the polymer. These data are in good agreement with the results of investigation of the viscosity of dilute polymer solutions in the non-Newtonian region, summed up in the monograph [15], and with the results of measurement of the viscosity of aqueous PEO solutions cited in [4, 16, 17]. At the same time it has been asserted [18, 19] that the viscosity of dilute aqueous PEO solutions is constant in a wide range of velocity gradients. This raises the question of whether the viscosity reduction that we obtained might have been due to mechanical degradation of the PEO in the flowing solution. To settle this point we made repeated measurements of the viscosity of the same aqueous solution of PEO of molecular mass $3 \cdot 10^6$ and concentration 0.003% at dif-

TABLE 1. Concentration ($C_{PEO}^{op}$, %) Corresponding to Maximum Drag Reduction

| $M_{PEO}$ | Re | | |
|---|---|---|---|
| | $3 \cdot 10^2$ | $1 \cdot 10^2$ | $3 \cdot 10^4$ |
| $6 \cdot 10^6$ | 0,010 | 0,015 | 0,015 |
| $10^6$ | 0,008 | 0,009 | 0,009 |
| $3 \cdot 10^6$ | 0,003 | 0,0025 | 0,003 |
| $8 \cdot 10^6$ | 0,0015 | 0,0015 | 0,0015 |

ferent shear rates and found that the viscosity reduction could not be attributed to mechanical degradation of the PEO. We can infer that dilute aqueous PEO solutions are non-Newtonian fluids. Non-Newtonian flow of dilute flexible-chain linear polymers (particularly PEO) is due, as is known [15, 20, 21], to orientation and periodical deformation of the individual molecular chains. In these conditions the viscosity, like several other properties, is anisotropic. i.e., the flow of polymer solutions is similar to the flow of liquid crystals [22]. The anisotropy of the viscosity means that if in a flow of solution with highly oriented macromolecules secondary flow arises due, say, to turbulent velocity fluctuations, the viscosity associated with transverse shear will be greater than that associated with longitudinal shear, i.e., the resistance to the irreversible motion of the secondary flow units in different directions is different.

To discover the relation between drag reduction and the viscous properties of the polymer solutions we compared the concentration dependence of drag reduction with those of the lowest Newtonian viscosity of aqueous PEO solutions. Figure 5 shows a plot of the lowest Newtonian viscosity ($\eta_{L.N}$) of aqueous solutions of molecular mass $3 \cdot 10^6$ against concentration at 20°C. It is apparent that until the lowest Newtonian viscosity of the PEO solutions becomes practically equal to the viscosity of the solvent (water), the drag reduction increases with increase in concentration. Beginning at concentrations at which $\eta_{L.N}$ exceeds the viscosity of water the effect begins to decrease. From the moment of formation of the fluctuational polymer network in the solutions $\eta_{L.N}$ increases more sharply with increase in concentration than is indicated by the magnitude of the effect. If we consider the drag reduction not in relation to the solvent, but in relation to a fluid with viscosity $\eta_{L.N}$ at constant Reynolds number (for not too large shear stresses), its concentration dependence will be of a nonmonotomic nature, and will tend to some limit. The correctness of this hypothesis is confirmed by the data in Fig. 2 (curve 3). We can then also understand why $C_{PEO}^{op}$ is almost independent of the Reynolds number. It is presumably due to the fact that at concentrations less than $C_{PEO}^{tr}$ structural factors play a minor role (since intermolecular interactions are absent) and, hence, have no effect on drag reduction, and the increase in the lower Newtonian viscosity of the solution is due only to an increase in the rate of energy dissipation, which depends on the volume occupied by the polymer molecules and depends weakly on the Reynolds number.

The rheological data account for the presence in large-diameter tubes of threshold Reynolds numbers ($Re_{th}$) at which drag reduction begins to appear. Table 2 gives the values of $Re_{th}$, the threshold shear stress $\tau_{th}$, and the shear stress $\tau_N$ at which the viscosity of the system becomes practically constant, for aqueous solutions of PEO of molecular mass $3 \cdot 10^6$ and concentration 0.003% flowing in tubes of different diameter. Table 2 indicates that the onset of drag reduction is associated with the attainment of some equilibrium orientation of the macromolecules, i.e., with the appearance of viscosity anisotropy in the solution. For the same liquid, larger Reynolds numbers correspond to the same shear stresses when the tube diameter increases. Hence, the onset of drag reduction corresponds to some threshold shear stress, which is independent of the tube diameter. In tubes of small diameter the stresses $\tau_N$ required for complete orientation of macromolecules with the flow arise in laminar flow of the solutions and, hence, reduction of turbulent friction appears at the critical Reynolds number.

Another important result should be noted: If polymer (PEO) solutions do not possess non-Newtonian properties, there is no drag reduction.

Thus, as a result of correlation of experimental data on the molecular structure and flow of aqueous PEO solutions we can infer that the main property of a medium in which reduction of turbulent friction is effectively manifested is the anisotropy of the viscosity that is produced in dilute polymer solutions by orientation of the flexible noninteracting

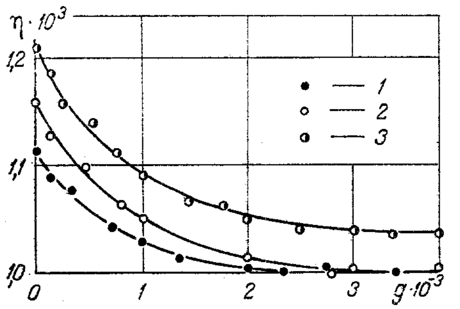

Fig. 4

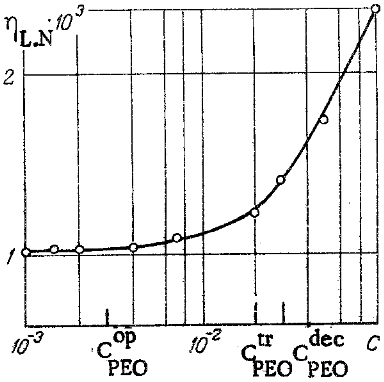

Fig. 5

Fig. 4. Viscosity of aqueous solutions of PEO of molecular mass $3 \cdot 10^6$ of different concentration as a function of shear rate at 20°C: 1) 0.0005%; 2) 0.0025%; 3) 0.005%. $\eta$, Pa•sec; g, $\sec^{-1}$.

Fig. 5. Lowest Newtonian viscosity of aqueous solutions of PEO of molecular mass $3 \cdot 10^6$ as function of concentration at 20°C. $\eta_{L.N}$, Pa·sec; C, %.

TABLE 2. Effect of Tube Diameter on $\mathrm{Re}_{th}$, $\tau_{th}$, and $\tau_N$ ($C_{PEO}$ = 0.003%; $M_{PEO} = 3 \cdot 10^6$)

| d, mm | $\mathrm{Re}_{th}$ | $\tau_{th}$, Pa | $\tau_N$, Pa |
|---|---|---|---|
| 0,2 | 2300 | 40,3 | 2,5 |
| 0,34 | 2300 | 23,7 | 2,5 |
| 0,56 | 2300 | 20,5 | 2,5 |
| 2,68 | 2300 | 5,7 | — |
| 6,15 | 3500 | 1,6 | — |
| 6,7* | 3500 | 1,4 | — |
| 8,5* | 4500 | 1,4 | — |
| 11,3* | 6000 | 1,4 | — |
| 10,0† | 6500 | 1,7 | — |

*Data from [23].
†Data from [24].

macromolecules in the shear field and, in the case of concentrated solutions (the effect is considered in relation to a Newtonian fluid with viscosity equal to the lowest Newtonian viscosity of the solution), by degradation of the structure mainly in the direction of the velocity gradient and orientation of structural formations with the flow.

The development of a theory of drag reduction due to additions of polymers on the basis of the information obtained was not the aim of the present work. It is probably best to regard these results as additional data for verification of the numerous working hypotheses advanced by different investigators in studies of the mechanism of drag reduction. Nevertheless, the obtained data allow us to put forward some ideas on the nature of drag reduction: Drag reduction in polymer solutions is due to the viscosity anisotropy arising in the viscous sublayer and the transition layer due to distortion and orientation of the macromolecules with the flow, i.e., to different resistance to the movement and development of turbulent eddies in different directions. The increase in viscosity associated with shear perpendicular to the flow gives rise to additional resistance to the development of pulsational motion and this reduces the general level of mixing of the liquid in the flow. Hence, in polymer solutions the frequency of occurrence of pulsations becomes less than in the solvent at the same Reynolds numbers. The flow of polymer solutions becomes more stable, which reduces the generation of turbulence and lowers the level of turbulent dissipation in the flow.

The postulated mechanism of turbulent friction reduction can be extended to solutions of micelle-forming surface-active substances (SAS), which also exhibit reduced drag. In SAS solutions the viscosity anisotropy is probably due to degradation of the structure mainly in the direction of the velocity gradient and to orientation of the structural formations (micelles) with the flow.

## NOTATION

M, molecular mass; Re, Reynolds number; $\tau$, shear stress; C, concentration; T, temperature; $\Lambda$, drag coefficient; d, diameter; t, time; $\Delta P$, pressure drop; $l$, length; $\rho$, density; V, volume; $\eta$, viscosity; q, velocity gradient; $\overline{U}$, mean flow rate.

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