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THE SCALE EFFECT IN THE LAMINAR FLOW OF DILUTE SOLUTIONS  
OF POLYMERS IN TUBES

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UDC 532.517.2:532.135

This paper describes the variation of the viscosity of polyoxyethylene solutions as a function of tube diameter. We investigate the effect of molecular weight and concentration of the polymer on viscosity anomalies.

1. Dilute solutions of some high-molecular-weight polymers have properties which make their hydrodynamic behavior different from that of ordinary liquids. The most striking difference is found in turbulent flow, when the hydrodynamic friction of the polymer solutions is only a fraction of the friction of the solvent. This effect was discovered by Toms in connection with the flow of solutions of polymethylmethacrylate in monochlorobenzene [1]. The phenomenon of reduced turbulent friction resistance attracted the attention of many researchers, and a large number of studies on this subject have already been published.

Subsequently Toms established an anomaly in the laminar flow of polymer solutions [2]. It was found that in the laminar flow of solutions in tubes the value of the viscosity depends on the tube diameter. Toms regarded this as proof of the existence of effective slip-page along the wall, to which Oldroyd [3] attributed the reduced-resistance effect. The scale anomalies discovered in this connection did not attract any special attention on the part of investigators. The only study worth mentioning is [4], the authors of which, in particular, noted difficulties in explaining the results on the basis of slippage along the wall.

In the mid-1960s it was found that high-molecular-weight polymers such as polyhydroxyethylene and polyacrylamide were capable of reducing turbulent friction at solution concentrations of a few parts per million. Unlike the liquid used in Toms' experiments, the viscosity of solutions at such concentrations differs by only a few percent from the viscosity of the solvent. Apparently this is why no more interest was shown in the anomalies of laminar viscosimetric flows. In investigations of the reduced resistance, researchers confined their attention to measurements of the viscosity of solutions using ordinary viscosimeters with thin capillaries, assuming that dilute polymer solutions in laminar flow behave like Newtonian liquids. Even when differences were again observed in the values of the viscosity at different diameters of the measuring segments of the viscosimeters, no importance was attached to this fact, on the assumption of possible degradation of the solutions in thin tubes or of errors in measurement [5].

This disregard of the anomalies observed in viscosity measurements did not introduce any substantial distortion into the data on turbulent resistance but led to erroneous conclusions concerning the effect of polymer additives on the stability of circular Couette flow. In a number of published reports it was asserted that polymer additives increase the value of the critical Taylor number [6-10]. As was explained in [11], this conclusion was due to the fact that in determining the Taylor number, researchers used solution viscosity values measured by means of thin capillary viscosimeters. It was shown that if the viscosity values used are those obtained by means of viscosimeters with fairly large diameters in the measuring segments, the critical values of the Taylor number for dilute polymer solutions coincide with those of Newtonian liquids. Thus, it became clear that the viscosimetric anomalies should no longer be ignored, since that might lead to further errors.

Institute of Problems in Mechanics, Academy of Sciences of the USSR, Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 34, No. 4, pp. 614-621, April, 1978. Original article submitted April 19, 1977.

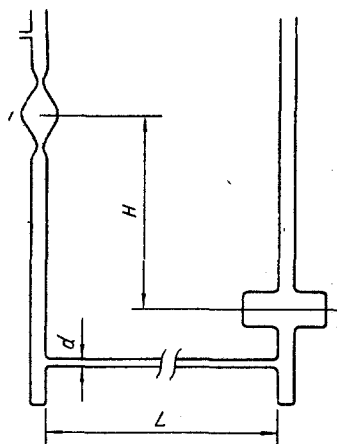


Fig. 1. Diagram of glass viscosimeters with horizontal capillary.

As the concentration of the polymer solutions increases, it is possible to observe a variation of the viscosity with the gradient of the velocity (the shear rate). This complicates the detection of the scale anomalies in viscosity. Thus, it may be assumed that lower viscosity values obtained by the use of standard capillary viscosimeters are due to the high shear rates in them.

In [12] we investigated the variation of the viscosity as a function of the velocity gradient for solutions of Polyox WSR-301 polyhydroxyethylene, using tube viscosimeters with diameters of 4.2 and 8.0 mm for shear rates  $\dot{\gamma}$  at the wall ranging up to  $350 \text{ sec}^{-1}$ . The viscosity of the solutions was found to be independent of the velocity gradient up to a weight concentration of  $2 \cdot 10^{-4}$  of the polymer and was higher than the viscosity measured with capillary viscosimeters, in which the shear rate was over  $500 \text{ sec}^{-1}$ . As the concentration was increased further, the viscosity was found to be dependent on the gradient; in the concentration range from  $2 \cdot 10^{-4}$  to  $10^{-3}$  the transition from the first Newtonian viscosity to the second took place at  $\dot{\gamma} < 350 \text{ sec}^{-1}$ . These data gave some reason to believe that the reduction in viscosity in capillary viscosimeters is not due to variation with shear rate. Otherwise it would be necessary to assume that the solutions investigated have a further interval of decreasing viscosity lying in the region  $\dot{\gamma} > 350 \text{ sec}^{-1}$ . However, further investigations were required for a final explanation.

2. In the present study we give data on the investigation of scale anomalies in viscosimetric flows of dilute solutions of polyhydroxyethylene. The tube viscosimeters used in the experiments may be divided into three groups. The first consisted of Ostwald glass viscosimeters, in which the inner diameter of the capillaries ranged from 0.20 to 1.16 mm. The second group consisted of specially made viscosimeters with a horizontal working segment (Fig. 1). Such a design of the viscosimeters made it possible to select the height of the liquid discharge  $H$  and the length  $L$  independently of each other. Unlike the first group, the viscosimeters in the second group had  $H < L$ , and the value of  $H$  was so chosen that for the flow of liquids with the same viscosity the shear rate at the wall was the same in all the viscosimeters of the group; in particular, when  $\nu = 1 \text{ cSt}$ , we had  $\dot{\gamma} \approx 300 \text{ sec}^{-1}$ . This was done in order to eliminate possible changes in viscosity caused by changes in the velocity gradient when we changed from viscosimeters with one diameter to viscosimeters with a different diameter and to investigate the effect of the diameter change in the pure form. The inner diameters of the second group of viscosimeters varied from 0.39 to 3.2 mm, and the length of their working segments was considerably greater than that of the capillaries in the viscosimeters of the first group.

In using the viscosimeters of the first and second groups, we determined the viscosity on the basis of the time  $T$  required for the flow through the working segment of a fixed volume of liquid  $V: \nu = \eta/\rho = AT - B/T$ . The second term represents the correction made to take account of the effect of the capillary tube ends. The main contribution to this correction is made by the change in the velocity profile at the inlet to the capillary. As is known, the constants  $A$  and  $B$  are related to the geometric characteristics of the viscosimeters by the formulas

TABLE 1. Characteristics of the Viscosimeters

Group of viscosimeters	d, mm	L, mm	H, mm	Re <sub>c</sub>	$\dot{\gamma}_0$ , sec <sup>-1</sup>
I	0,20	90	92	2,5	500
	0,56	90	132	78	2000
	0,73	90	163	205	3000
	0,86	90	130	262	2800
	1,16	90	128	547	3250
II	0,39	500	159	5,7	300
	0,65	500	95	16	300
	0,78	500	85	24	320
	1,50	500	41	85	300
	2,03	500	31	153	300
	3,20	1800	75	370	290
III	4,2	15500	—	10—900	5—400
	8,0	40000	—	1—50	0,1—6

$$A = \pi g H d^4 / 128 L V \text{ and } B = \zeta V / 16 \pi L,$$

where L and d are the length and diameter of the capillary; H is the average height of discharge; V is the volume of discharged liquid;  $\zeta$  is a constant which is close to 2 for straight circular capillaries. The values of A and B were determined experimentally by calibration using standard liquids with sharply differing viscosities.

The third group of viscosimeters consisted of two apparatuses used for measuring the viscosities in [11, 12]. The inner diameters of the measuring segments of these apparatuses were 4.2 and 8.0 mm. The lengths of the segments between the pressure-sampling points were 15.5 and 40 m. The pressure sampling points were situated about 300 calibers from the inlet and outlet of the tubes. The pressure drop in the measuring segment was determined in the tube with d = 4.2 mm from piezometer readings, and in the tube with d = 8.0 mm with the aid of a differential manometer which used monochlorobenzene with a density of 1.107 g/cm<sup>3</sup> as the working liquid. This meant that in the manometer we had a considerable difference in the levels of the menisci separating the monochlorobenzene and the water or aqueous solution of polymer for low pressure drops. The flow rate was determined by the volumetric method.

The viscosimeter tubes and head volumes were thermostated. The tube with d = 8.0 mm was twisted into a coil approximately 1 m in diameter and, together with the head volume, was placed in a bath at constant temperature. The tube with d = 4.2 mm was thermostated by placing it in a tube of larger diameter and pumping a thermostating liquid through the latter.

The range of shear rates at the wall was 5–400 sec<sup>-1</sup> in the tube with d = 4.2 mm and 0.1–6 sec<sup>-1</sup> in the tube with d = 8.0 mm. The lower bounds depend on the accuracy of measurement of the pressure drops. The upper bounds for the viscosimeter with d = 4.2 mm were determined by the condition Re < 1200, in order to exclude the possibility of so-called early turbulence, which is often found in polymer solutions. The upper bounds for the second viscosimeter were associated with the curvilinear nature of its measuring segment and the need to satisfy the condition Di = Re√d/D < 5, since for larger values of the Dean number, secondary flows develop in curvilinear tubes with a radius of curvature D/2.

The characteristics of all the tube viscosimeters used in the experiments, as well as the values of the Reynolds numbers and shear rates at the wall for the flow of water at a temperature of 20°C in the tubes are shown in Table 1.

In addition to the tube viscosimeters, we also made viscosity measurements by means of the apparatus for determining the stability of Couette flow between coaxial cylinders, described in [11]. The diameter of the inner rotating cylinder was 90.8 mm, the radial gap between the cylinders was 3.1 mm, and the velocity gradient at the time when the Taylor vortices appeared in water at 20°C was 17.5 sec<sup>-1</sup>. Determining the time of appearance of the Taylor vortices by using a dye and measuring the rate of rotation, we can find the viscosity on the solution, relying on the invariance of the critical Taylor number for low polymer concentrations, from the relation  $v = v_0 \omega / \omega_0$ . Here  $\omega$  is the angular velocity of rotation of the rotor at which the Taylor vortices appear in the polymer solution;  $\omega_0$  is the angular velocity for the appearance of vortices in water;  $v_0$  is the viscosity of water.

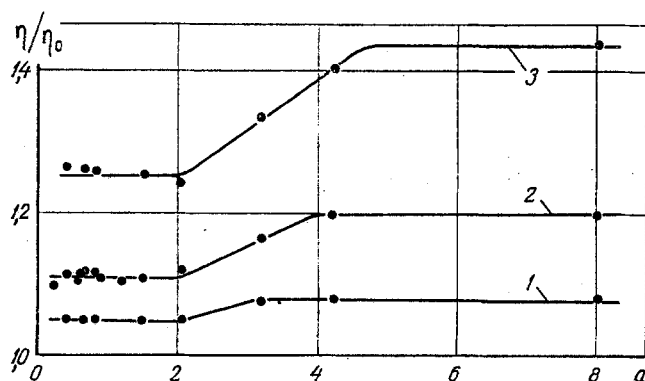


Fig. 2. Relative viscosity of aqueous solutions of polyhydroxyethylene,  $\eta/\eta_0$ , at 20°C as a function of the inner diameter of the viscosimeter tube,  $d$ , in mm: 1, 2, and 3 correspond to the different weight concentrations of the polymer in the solution:  $c = 5 \cdot 10^{-5}$ ,  $10^{-4}$ , and  $2 \cdot 10^{-4}$ .

In addition to the viscosity, we measured the velocity profiles in thin capillaries by means of the DISA 55L laser anemometer. One of the capillaries had a circular cross section with a diameter of 1.6 mm, while the other had a square cross section 1.16 mm on a side. The length of the capillaries was about 150 mm. The capillaries were fastened to the rod of an IZV-2 vertical optical height meter, by means of which we shifted them with respect to the intersection of the laser beams and determined the position of the measuring point. In the experiment we achieved a spatial resolution and coordinate specification accuracy of 50  $\mu$ m. The accuracy of the velocity measurement was about 1%. The measurements were carried out in the middle part of the capillary, where there was no inlet effect.

3. Our experiments confirmed the existence of scale anomalies in viscosity. Figure 2 shows the data on the variation of viscosity as a function of the inner diameter of the viscosimeter tube. The data relate to the flow of aqueous solutions of Polyox WSR-301 polyhydroxyethylene from the same batch as was used in the experiments of [11, 12]. The concentration of the solution did not exceed  $2 \cdot 10^{-4}$ , and for these concentrations the viscosity of the solutions is independent of the velocity gradient at least up to  $\dot{\gamma} \approx 350 \text{ sec}^{-1}$  [12].

As can be seen from the curves, in viscosimeters with capillary diameters less than 2 mm we obtain viscosity values which are practically independent of the diameter. From our measurements in viscosimeters with larger-diameter tubes we found that the viscosity values begin to increase with increasing  $d$  until they reach a new constant value. As the polymer concentration in the solution increases, there is an increase in the diameter value at which the maximum viscosity is attained. The viscosity values obtained in experiments to determine the stability of circular Couette flow coincided with the maximum viscosity values found by means of tube viscosimeters.

The observed differences between the maximum and minimum values of the viscosity for the investigated concentrations are high and considerably exceed the measurement error. This difference cannot be explained by irreversible changes (degradations) in the solutions when they flow through thin capillaries, since when the same batch of solution was poured through the tubes time after time, the initially measured value of the viscosity was satisfactorily reproducible. Furthermore, there was no degradation resulting from the first passage through the capillary. This was established by the following experiment.

One portion of the prepared solution was passed through a viscosimeter capillary with an inner diameter of 0.56 mm at a flow rate corresponding to the flow rate used in measuring the viscosity by means of this viscosimeter. After this the viscosities of the initial solution and the solution passed through the capillary were measured on the basis of the stability of circular Couette flow. The values coincided.

The functional relationship found to exist between the viscosity and the diameter is not related to gradient changes, since it is also observed in the case of constant shear rate in tubes with different diameters.

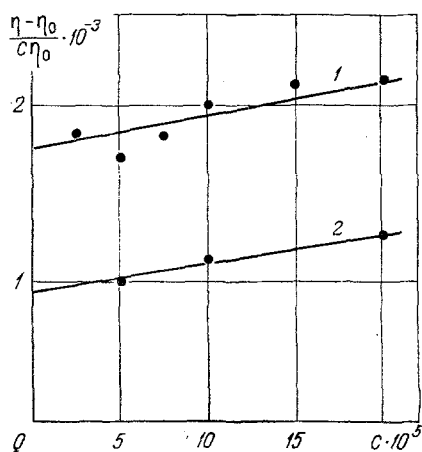


Fig. 3

Fig. 3. The value of  $(\eta - \eta_0)/c\eta_0$  as a function of the concentration  $c$  for maximum (curve 1) and minimum (curve 2) viscosity of aqueous solutions of polyhydroxyethylene at  $20^\circ\text{C}$ .

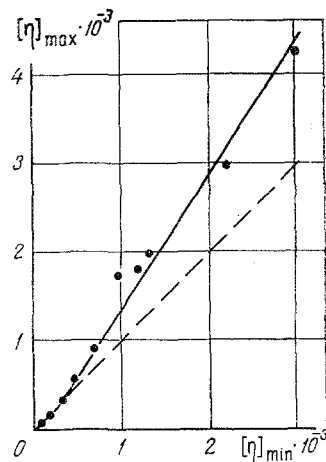


Fig. 4

Fig. 4. Relation between maximum  $[\eta]_{\max}$  and minimum  $[\eta]_{\min}$  values of the characteristic viscosity of aqueous solutions of polyhydroxyethylenes of different molecular weight at  $20^\circ\text{C}$  (the dashed line shows the case  $[\eta]_{\max} = [\eta]_{\min}$ ).

The viscosity values of polymer solutions measured with thin viscosimeters were calculated with the aid of a correction term with the same constant  $B$  as in the case of Newtonian liquids. The data in Fig. 2 show that these calculations were correct. In the diameter range from 0.2 to 2.03 mm we used 10 viscosimeters for measuring the viscosity of a solution with a concentration of  $10^{-4}$ ; these 10 included pairs with diameters which were close to each other but with widely differing lengths. The measurements made with these viscosimeters yielded practically the same viscosity value. This indicates that in the flow of the polymer solution, even if there is a change in the coefficient of the correction term, the change is not very significant.

The measurements made with the laser anemometer showed that the viscosimetric flow of the polymer solution in thin capillaries is stationary and the velocity profile agrees with the Poiseuille profile to a high degree of accuracy.

The scale effect discussed here cannot be explained by assuming the polyhydroxyethylene solutions to be a uniform continuum. In particular, the effect cannot be described within the framework of the model of a uniform viscoelastic liquid. The results cited here prove the suspension nature of the solutions.

In the flow of suspensions (for example, blood [13]) the scale effect in the viscosity is observed when the dimension of the particles is commensurable with the diameter of the tube or is smaller than the diameter by one or two orders of magnitude but no more. It is therefore difficult to suppose that the anomalies in the viscosity of polyhydroxyethylene solutions are related to individual macromolecular coils measuring no more than fractions of a micrometer [15]. Apparently we must assume that these solutions are not true solutions and contain aggregates of macromolecules.

The scale effect cannot be explained by the effective slippage resulting from the forcing of small aggregates (small in comparison with the capillary diameter) away from the wall layer, since this would have led to considerable deviations from the Poiseuille velocity profile. The most probable assumption is that the aggregates are commensurable in size with the diameters of the tubes in which these anomalies are observed. Apparently in the large-diameter tubes the aggregates can move about without any reduction in size, whereas when they enter thin tubes, there is a reversible disaggregation or restructuring of the supermolecular formations, with liberation of some of the immobilized solvent, which leads to a decrease in viscosity. This explanation is supported by the threshold character of the variation of the viscosity with tube diameter.

If we adopt this interpretation of the experiments, we find that the aggregates of macromolecules in the polyhydroxyethylene solutions attain dimensions of several millimeters. This is in good agreement with independent estimates obtained from other experiments, in particular from experiments with Pitot tubes [14].

4. In the description of polymer solutions we often encounter the quantity

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta - \eta_0}{c\eta_0},$$

which is called the characteristic viscosity. This value is used for estimating the molecular weight of a polymer related to the characteristic viscosity by the Mark-Kuhn-Hauvink formula  $[\eta] = KM^\alpha$ . The values of  $K$  and  $\alpha$ , as a rule, are found by prior determination of the molecular weight by other means, for example, by the method of light scattering.

The scale effect introduces an ambiguity into the value of the characteristic viscosity, which in this case, like the viscosity itself, depends on the diameter of the viscosimeter. Figure 3 shows the values of  $(\eta - \eta_0)/c\eta_0$  as a function of the concentration of the investigated polyhydroxyethylene in the water. The value of  $(\eta - \eta_0)/c\eta_0$  is given both for the maximum and for the minimum value of the viscosity. It is noteworthy that the straight lines have approximately the same slope. As can be seen from Fig. 3, the difference between the maximum and minimum values of the characteristic viscosity is quite large:  $[\eta]_{\min} = 940$ ,  $[\eta]_{\max} = 1750$ .

The measurements of the characteristic viscosity are usually made by means of thin capillary viscosimeters. Therefore, as a rule, in the relation  $[\eta] = KM^\alpha$  the value of the characteristic viscosity used is apparently the minimum value. For polyhydroxyethylenes in this case  $K = 1.25 \cdot 10^{-2}$ ,  $\alpha = 0.78$  [15].

We investigated the variation of the anomalies in the viscosimetric flows of solutions as functions of the molecular weight of polyhydroxyethylene in the range  $M = 5 \cdot 10^4 - 8 \cdot 10^6$ . Figure 4 shows the values of the maximum and minimum characteristic viscosity for aqueous solutions at 20°C. The measurement of the minimum viscosity was made by means of a capillary viscosimeter with  $d = 0.56$  mm, while for the maximum we used the apparatus for determining the stability of Couette flow between cylinders.

The data of Fig. 4 show that scale anomalies in viscosity occur at a particular molecular weight. Apparently low-molecular-weight polyhydroxyethylenes do not form large aggregates in the solution.

#### NOTATION

Geometric characteristics of the viscosimeters:  $d$ , inner diameter of tube;  $L$ , length of tube;  $H$ , height of discharge;  $V$ , volume of discharged liquid;  $D/2$ , radius of curvature of the tube;  $\nu$ ,  $\eta$ , kinematic and dynamic viscosities;  $\rho$ , density;  $g$ , acceleration of gravity;  $\dot{\gamma}$ , shear rate;  $\omega$ , angular velocity;  $Re$ , Reynolds number;  $Di$ , Dean number;  $[\eta]$ , characteristic viscosity;  $c$ , concentration;  $M$ , molecular weight. The subscript 0 indicates values characteristic of the solvent.

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RHEOLOGICAL EQUATIONS OF STATE OF A DILUTE SUSPENSION  
OF DIPOLE DUMBBELLS IN A POWER-LAW LIQUID

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UDC 532.135:541.182

We obtain the rheological equations of state of dilute suspensions of dipole dumbbells in a power-law liquid. As an example, we consider simple shear flow of such a medium in an electric field.

In the present paper we consider a dilute suspension of rigid axially symmetric particles in a power-law liquid whose rheological equation of state has the form

$$\tau_{ij} = -p\delta_{ij} + 2m|2d_{nm}d_{mk}|^{\frac{n-1}{2}} d_{ij}. \quad (1)$$

For  $n < 1$  this model describes pseudoplastic liquids, while for  $n > 1$  it describes dilatant liquids. The case  $n = 1$  corresponds to Newtonian behavior.

We assume that the dispersion medium interacts with the suspended particles which have zero buoyancy as with hydrodynamic bodies. As a hydrodynamic model of the suspended particles, we consider the model of a rigid point dumbbell: At a distance  $L$  equal to the length of the real axially symmetric suspended particle there are point centers of hydrodynamic interaction of the model with the surrounding liquid. As for suspensions in Newtonian liquids, we assume that the ends of the dumbbell interact with a power-law dispersion medium like spheres of radius  $a$ .

We consider the Stokes approximation for flow past suspended particles. It is known that the coefficient of frictional resistance of a sphere of radius  $a$  moving with a translational velocity  $U$  is given in the Stokes approximation by the formula [1]:

$$\zeta = 4\pi \left( \frac{12}{n^2} \right)^{\frac{n+1}{2}} F(n) m U^{n-1} a^{2-n}. \quad (2)$$

The function  $F(n)$  has been tabulated in [2]; in particular, for  $n = 1$  (a Newtonian liquid),  $\zeta = 6\pi\eta a$ .

The suspended axially symmetric particles may have a constant dipole moment  $p_c = qn$  or an induced dipole moment  $p_e = \kappa n(E \cdot n)$ . The interaction between the electric fields of the suspended particles, like the hydrodynamic interaction between the particles, is disregarded.

Since the hydrodynamic model of the particles is so simple, the determining equation for the vector  $n$  characterizing the orientation of the dumbbell can be determined by using a structural approach.

Suppose that the length of the suspended dumbbells is such that the velocity of the dispersion medium within the limits of a particle is a homogeneous function of the coordinates. Then by the first Helmholtz theorem [3], the velocity of the liquid at the point where the

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