

Drag Reduction by Dilute Polymer Solutions in Turbulent Flow

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ABSTRACT

The mechanism by which water-soluble polymers reduce hydrodynamic drag on solid surfaces has been investigated by measurements of flow birefringence and of turbulent flow in pipes. Flow birefringence and flow field orientation of Polyox polymers in the molecular weight range from 200,000 to 6,000,000 have shown that Polyox macromolecules continue to deform with increasing velocity gradient even after alignment with the flow field (at gradients in excess of 2000 sec^{-1}). Power law plots of flow data for Polyox solutions were used to determine the viscous characteristics over a shear stress range comparable to that used in the pipe flow work. All solutions used were found to be Newtonian, with the exception of the Acrysol A-5 solutions. The flow data for Polyox solutions in a Pyrex pipe were examined in terms of Meyer's fluid property parameter and Elata's relaxation time hypothesis for the initiation of drag reduction. It was found that drag reduction in the Pyrex pipe was initiated at a value of the order of one-fifth that predicted by Elata's theory. Moreover, added salt (the solution being 0.3 molar in K_2SO_4) had no effect on the flow of Polyox Coagulant solutions even though the intrinsic viscosity (upon which Rouse relaxation times depend) was cut to slightly more than one-third of its value in the pure solvent. The unusually high values of Meyer's fluid property parameter observed at low concentrations suggests that adsorption on the Pyrex pipe walls may be playing a role in drag reduction. A mechanism based on a quasi-BET adsorption model is suggested as a possible explanation for the apparent enhancement of drag reduction observed.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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DRAG REDUCTION BY DILUTE POLYMER SOLUTIONS IN TURBULENT FLOW

INTRODUCTION

Drag reduction may be defined as that effect which takes place when the rate of flow of a fluid at constant pressure gradient is increased upon addition of a colloidal additive (generally in amounts insufficient to cause large changes in the viscosity of the fluid). This effect is also known as the "Toms phenomenon" in recognition of Toms pioneering work (1). Although drag reduction effects have been observed with systems of fibers or beads in water (2-4) and solid particles suspended in gases (5-7), the most impressive drag reduction effects have been obtained through the addition of small amounts of soluble, high-molecular-weight linear polymers to fluids (8-14).

Various theories have been proposed to explain the drag reduction effects observed for polymer solutions (15,16), but these theories emphasize the non-Newtonian character of the solutions. The recent results of Hoyt and Fabula (13) and Shin (17) have shown that significant drag reduction effects may be obtained with Newtonian fluids containing additives in concentrations as low as five parts per million.

The drag reducing ability of one family of additives — the linear high molecular weight polyoxyethylene condensates, designated by the producer as Polyox compounds — has been shown to be a function of polymer molecular weight (18). Recently the view has been put forward that drag reducing effects for the high-molecular-weight additives so far studied nearly always coincide with a decrease in the magnitude of the universal constant k used in the Karman-Prandtl mixing length hypotheses (14). This view has been shown to be in error by Ernst (19), who determined velocity profiles of flowing polymer solutions and demonstrated that the mixing length constant was not affected by the presence of polymer molecules.

Meyer (20) has analyzed Ernst's results and has suggested the following equation to describe the flow behavior of dilute polymer solutions in pipes:

$$\frac{1}{\sqrt{C_f}} = \left(4 + \frac{\alpha}{\sqrt{2}}\right) \log Re \sqrt{C_f} - \frac{\alpha}{\sqrt{2}} \log \left(\sqrt{2} U_{*cr} \frac{D}{V_w}\right) - 0.4$$

where C_f is a friction factor, Re is the Reynolds number, D is the diameter of the pipe, V_w is the viscosity at the pipe wall, α is the fluid property parameter, and U_{*cr} is the critical friction velocity for drag reduction. This equation avoids the description of drag reducing effects as resulting from changes in the universal constant. The equation suffers from the addition of a vaguely defined parameter (α) to the basic turbulent flow law from which it is derived. The quantity α does appear to provide a numerical index by which the turbulent flow properties of polymer solutions can be characterized. The turbulent flow properties of dilute polymer solutions are necessarily related to at least two variables; (a) the concentration of the polymer and (b) some dimensional characteristic of the polymer.

A recent report by Elata et al. (21) proposes an equation similar to that of Meyer. The equation has the added virtue of predicting the critical value of $Re \sqrt{C_f}$ at which drag reduction is initiated, in addition to describing the flow properties of dilute polymer solutions if the relaxation time of the polymer molecule is known. The equation is

$$\frac{1}{\sqrt{C_f}} = \left(\frac{\alpha}{\sqrt{2}} + 4 \right) \log Re \sqrt{C_f} + \frac{\alpha}{\sqrt{2}} \log \left(\frac{T_1 V_w}{D^2} \right) - 0.4$$

where the variables are defined as before in Meyer's equation and T_1 is the maximum relaxation time of the polymer molecule as calculated from Rouse's theory (22).

The purpose of the study reported here was to examine the drag reducing behavior of a homologous series of linear polymeric compounds, the so-called Polyox Series, and to determine if changes in polymer dimensions and concentration can be correlated with changes in Meyer's fluid property parameter α . In addition, it was of interest to determine whether or not surface phenomena are important factors in drag reduction by these high-molecular-weight polymers, since they promote coagulation of both inorganic and organic dispersions in water (23).

The measurements reported include observations of birefringence in sheared polymer solutions, of the flow behavior of dilute solutions, and of polymer adsorption on glass surfaces.

EXPERIMENTAL

Materials

Special samples of Polyox Coagulant and of Polyoxes WSR-301, WSR-205, and WSR-35 were obtained from Union Carbide Corporation. Acrysol A-5 was supplied by the manufacturer, Rohm and Haas, as a 25% solution. It is considered by the manufacturer to be a polyacrylic acid in the molecular weight range of 250,000 to 300,000.

Determination of the intrinsic viscosities of the Polyox solutions showed that their molecular weight characteristics conformed closely to the expected values. The physical properties of the polymers which are relevant to this report are listed in Table 1.

Table 1
Physical Properties of Selected Polymers

Compound	$[\eta]$	M.W.	C_s^*	T_1^\dagger (sec)
Polyox WSR-35	2.81	4.8×10^5	2450	2.6×10^{-5}
Polyox WSR-205	4.43	9.0×10^5	1500	7.7×10^{-5}
Polyox WSR-301	18.5	5.9×10^6	330	2.1×10^{-3}
Polyox Coagulant	22.6	7.0×10^6	262	3.0×10^{-3}
Acrysol A-5	5.2	3×10^5	—	3×10^{-5}

*Estimated from $[\eta]$ using data of Ref. 17.

†At infinite dilution from Rouse theory (22).

All solutions were made up in freshly distilled water and were measured immediately after solution had taken place.

Treatment of Solutions

Solutions of Polyox compounds decrease in apparent molecular weight on standing. For example, a 0.01-wt-% Polyox Coagulant solution which had been standing quietly for a period of one month was found to have lost a significant proportion of its drag reducing properties. Examination of the degraded solution by a biochemist at this Laboratory showed that significant quantities of bacteria were present in the solution. Because of this possibility of bacterial attack, measurements were made only on freshly prepared solutions.

The method of mixing solutions is extremely important. The method of mixing initially used was Berger and Thayer's "Dissolving Method No. 1" (20). It is the author's opinion that all but the very gentlest agitation causes variations in solution properties. Accordingly, it was decided that all solutions would be prepared by sprinkling the additives over a large surface of the fluid to prevent clumping and allowing solution to take place through the processes of Brownian movement and diffusion. No more than two days of standing were required to prepare the most concentrated solutions used in this study. At the end of this time a very gentle stirring of the solution insured uniform distribution of the additive. With this procedure good precision in the measurements resulted.

Streaming Birefringence Measurements

Streaming birefringence studies were made using the Rao streaming birefringence apparatus. This instrument is similar in most respects to the apparatus used by Edsall et al. (24). The radius of the rotor used was 1.220 cm and the gap width to the inner stationary cylinder was 0.05 cm. The critical velocity gradient for the cell at 25°C was calculated as $1.0 \times 10^4 \text{ sec}^{-1}$ in pure water (25,26), and this limit was not exceeded in the experiments. A 1:40 Bentonite dispersion was used both for calibration purposes and for alignment of the apparatus.

Viscosity Measurements

A pressure-driven Cannon-Fenske viscometer was used to determine the viscosity characteristics of the fluids. The experimental arrangement was quite similar to that described by Van Wager et al. (27). Measurements were made at $30.08^\circ \pm 0.04^\circ\text{C}$. Flow times were determined to within 0.1 sec with a stopwatch. Plots of log shear stress at the wall vs log apparent shear rate at the wall were made to determine if the solutions were Newtonian. The pertinent relations used were

$$\tau_w = \left(\frac{4V}{\pi R^3} \right) \left(K_a \rho + \zeta H - \frac{K_b \rho}{\theta^3} \right)$$

and

$$\left(\frac{du}{dr} \right)_w = \frac{4V}{\theta \pi R^3}$$

where τ_w is the shear stress at the wall, V is the volume of efflux bulb of viscometer, R is the radius of viscometer capillary, K_a is the viscometer constant, ρ is the density of fluid, ζ is the applied pressure constant, K_b is the kinetic term constant, H is the applied pressure, $(du/dr)_w$ is the apparent shear rate at the wall, θ is time, u is velocity, and r is the distance perpendicular to the wall. Plots of $\log \tau_w$ vs $\log (du/dr)_w$ yield values of the slope n' , the power law exponent which serves as an index of non-Newtonian character ($n' = 1$ for Newtonian fluids), and of K' , the consistency index. ($K' =$ viscosity if the fluid is Newtonian.) The power law equation is $\tau_w = K' (du/dr)_w^{n'}$.

Pipe Flow Measurements

Pipe flow measurements were made in a precision bore glass tube having an internal diameter of 0.9525 ± 0.0005 cm. The first pressure tap was placed 70 diameters downstream from the tube entrance, and the second tap was placed 100 diameters from the first one. A constant-head device was constructed so that the fluid was gravity-fed into the pipe test section. Rate of flow through the pipe was determined by measuring the volume of fluid expelled from the open end of the pipe during a measured time interval. Measurements of the friction factor could be made up to a Reynolds number of 30,000 with the apparatus. The manometer fluids used were mercury and Halocarbon 437 (Halocarbon Products Corp.) to which a trace of Fat Ponceau (Coleman and Bell) had been added to improve readability. It is believed that avoidance of pumps in the flow system eliminates a major source of polymer degradation. Viscosities of polymer solutions were measured before and after the test runs; no change in viscosity due to polymer degradation was observed.

Adsorption Measurements

The adsorbents used were sized glass microbeads supplied by the Cataphoto Corporation. The glass beads were cleaned in a hot, oxidizing mixture of nitric and sulfuric acids. The beads were then washed with successive portions of hot distilled water until all traces of acid were removed, as determined by pH measurements of the washings. They were then dried to constant weight at 100°C .

The polymer solutions were equilibrated with the adsorbent for 3 hours, employing a very gentle stirring technique. The amount of polymer adsorbed was determined by measuring the change in concentration of the supernatant liquid. This analysis was performed by measuring the viscosity of the supernatant liquid and then determining its concentration from a viscosity-concentration calibration curve. The data indicated adsorption to be complete within an hour or less. The adsorption experiments were performed at 28°C . The BET surface area, determined by krypton adsorption, was found to be $0.089 \text{ m}^2/\text{g}$.* Prior to the BET determination the sample was outgassed at 200°C .

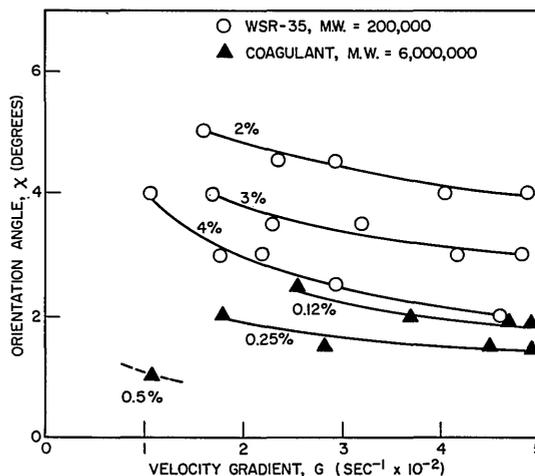
RESULTS

Streaming Birefringence

The streaming birefringence of aqueous solutions of Polyox water soluble resins, ranging in molecular weight from 200,000 to 6,000,000, was studied. Figure 1 reports the experimental results for the molecular weight extremes of the compounds studied. The orientation angle χ shows qualitatively the expected dependence on velocity gradient and concentration. Observations in the Rao streaming birefringence apparatus were complicated by the Weissenberg effect at higher concentrations ($> 4\%$ for WSR-35; $> 0.25\%$ for Coagulant) and by decreased visibility of the cross of isocline at slightly lower concentrations ($< 2\%$ for WSR-35; $< 0.12\%$ for Coagulant). In general, it appears that a velocity gradient of the order of 1000 sec^{-1} is necessary before the cross of isocline becomes sufficiently well-defined to allow meaningful measurement. These experimental difficulties make it hard to justify the application of theoretical flow birefringence relations, developed for infinitely dilute solutions, to the raw data. Even so, these results appear typical of flexible linear macromolecules which form tangled random coils in quiescent solutions but which apparently require a threshold hydrodynamic field to develop sufficient deformation of the coil to cause orientation with streamlines of flow.

*Kindly performed by Dr. V. R. Deitz of this Laboratory.

Fig. 1 - The effect of concentration, velocity gradient, and molecular weight on the orientation angle of Polyox molecules, at 25°C



Evidence for the deformation of molecules of the same two Polyox compounds is provided by a comparison of Fig. 1 and Fig. 2 (in which the magnitude of the birefringence is plotted against the velocity gradient). In those cases where the birefringence Δn continues to increase with increases in velocity gradient G while the orientation angle χ is almost nonvariant at a level near zero, the molecule is considered to be undergoing progressive deformation with increasing shear gradient (28). Concavity of the plot of Δn vs G with respect to the abscissa may also be considered as evidence for a large internal viscosity according to the treatment of Kuhn and Kuhn (29).

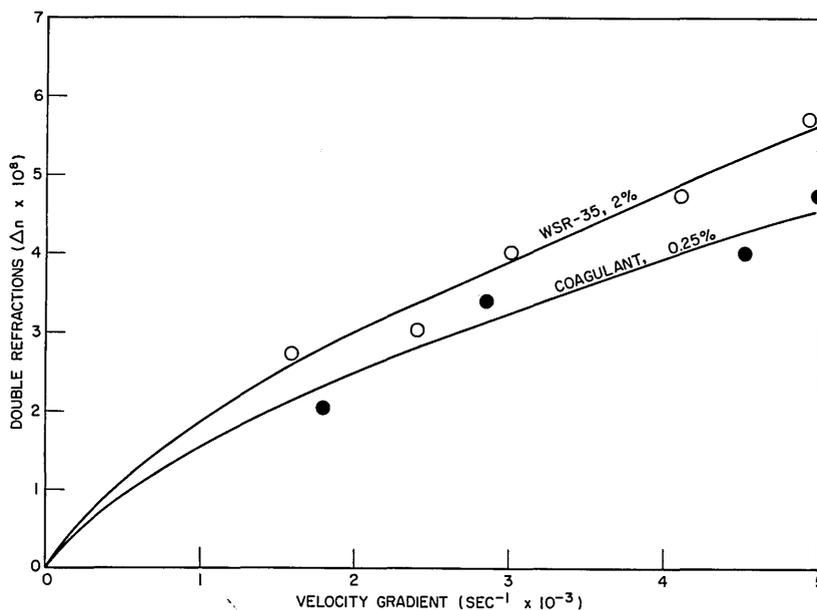


Fig. 2 - The dependence of double refraction on velocity gradient for Polyox solutions

Viscosity of Solutions

Power-law plots of the viscosity data indicated that all Polyox solutions used in this study exhibited Newtonian behavior. The viscosity data provided, in addition, other needed information: (a) a check on possible pipe flow degradation of the solutions, (b) the determination of the intrinsic viscosity of the polymer needed for determinations of the critical concentration, and (c) production of a calibration curve of viscosity vs concentration for use in the adsorption studies.

Power-law plots of the 0.1-wt-% polyacrylic acid solutions at two different pH values revealed the non-Newtonian character of these solutions, as shown in Fig. 3. In addition, the much greater intrinsic viscosity of the partially neutralized solution (with KOH) is considered to reflect the extension of the polymer coils into rods because of mutual repulsion of the charged carboxyl groups on the polymer chain (30).

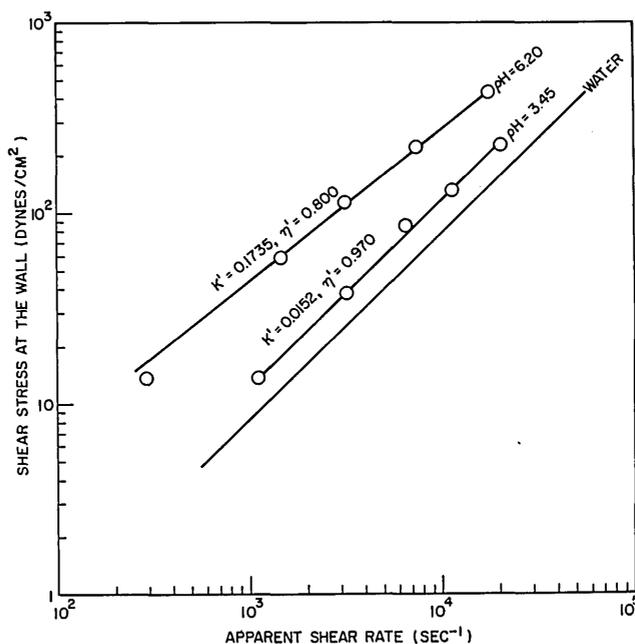


Fig. 3 - Power-law plots for 0.1% acrysol A-5 solutions, at 30.05°C

Friction Factor Data

Typical friction factor data for selected solutions of acrysol A-5 and Polyox compounds are shown in Fig. 4. The results illustrate, in general, the precision of the flow system data and the transition zone for turbulent flow. Moreover, the influence of pH on the flow properties of Acrysol A-5 may be noted. In addition, Fig. 4 illustrates the expected increase in drag-reducing ability in the Polyox family as the molecular weight of polymer is increased. It is of interest to observe that frictional drag reduction for solutions of WSR-205 and WSR-35 are initiated in the fully developed turbulence regime. However, data for many solutions of Coagulant and WSR-301 (not shown) interact with turbulence eddies well within the transition zone. The same effect — namely interaction with turbulence in the transition zone — is shown by guar gum solutions containing 3000 ppm of guar gum or more. That is, a polymer molecule will appear to interact with

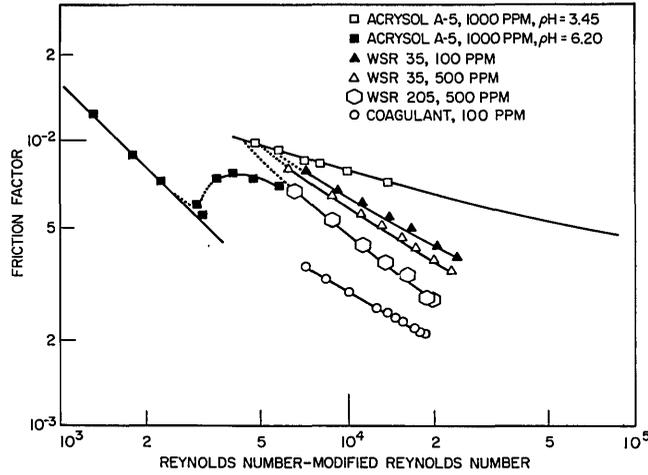


Fig. 4 - Friction factor vs Reynolds number plots for selected flow data for polymer solutions

turbulence eddies in the transition zone to a degree dependent on its molecular dimensions and its concentration in solution.

Adsorption

Polyox compounds adsorb readily on glass surfaces from aqueous solution, as shown by Fig. 5. The shape of the isotherm suggests Langmuir-type adsorption. It is of interest to note that adsorption appears to terminate when the critical concentration for the touching of random coils in the bulk solution is reached. There is insufficient evidence

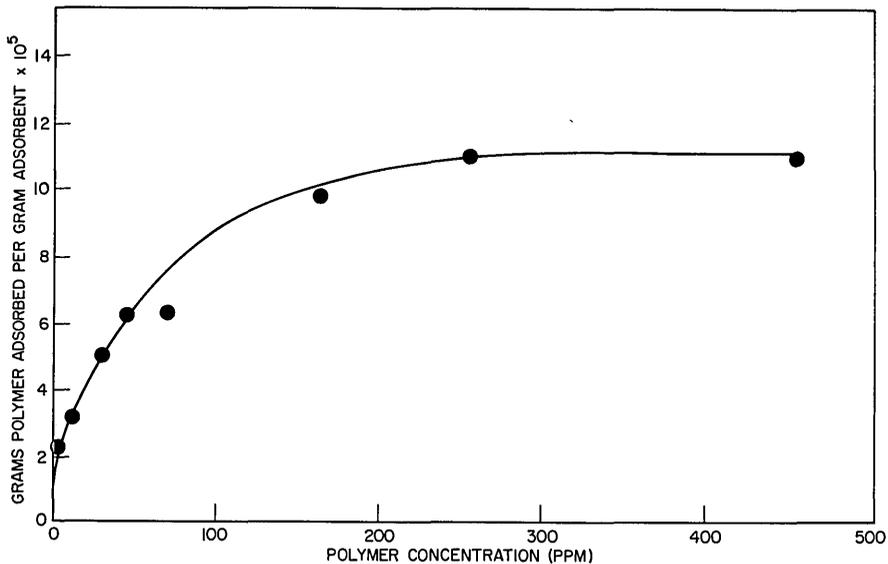


Fig. 5 - The adsorption of Polyox Coagulant on 30-micron glass beads, at 28°C

at this time to determine whether or not this is fortuitous. This type of adsorption isotherm is in accord with the view of La Mer and his coworkers (31-34), who have studied the adsorption of high-molecular-weight polymers on colloidal particles dispersed in aqueous media and also found Langmuir-type adsorption. La Mer and his coworkers consider the individual polymer segment rather than the whole molecule to be in competition with solvent molecules for surface sites. They suggest that the segments operative in the adsorption process are separated by loops of unattached segments extending into the liquid phase and that the adsorbed operative segments in adsorption behave as separate small molecules, independent of other adsorbed clusters of segments along the polymer molecule.

A Langmuir plot of the data (see Fig. 6) yielded a value of $\sigma = 1.9 \text{ g} \times 10^{-4} \text{ g}$ of polymer per gram of glass beads corresponding to monolayer coverage. Since the surface area of the glass beads was determined by krypton adsorption to be $0.089 \text{ m}^2/\text{g}$, the cross-sectional area per molecule on the surface was computed to be $9 \times 10^5 \text{ \AA}^2$ per molecule. By contrast, the cross-sectional area/molecule in the solution random coil state is $2 \times 10^7 \text{ \AA}^2$. Thus, the adsorbed polymer molecule, at monolayer coverage, occupies less surface area than would be taken by randomly coiled molecules randomly applied to the surface. However, it occupies more surface area than would be required for a densely coiled spherical macromolecule containing no solvent ($6 \times 10^4 \text{ \AA}^2$).

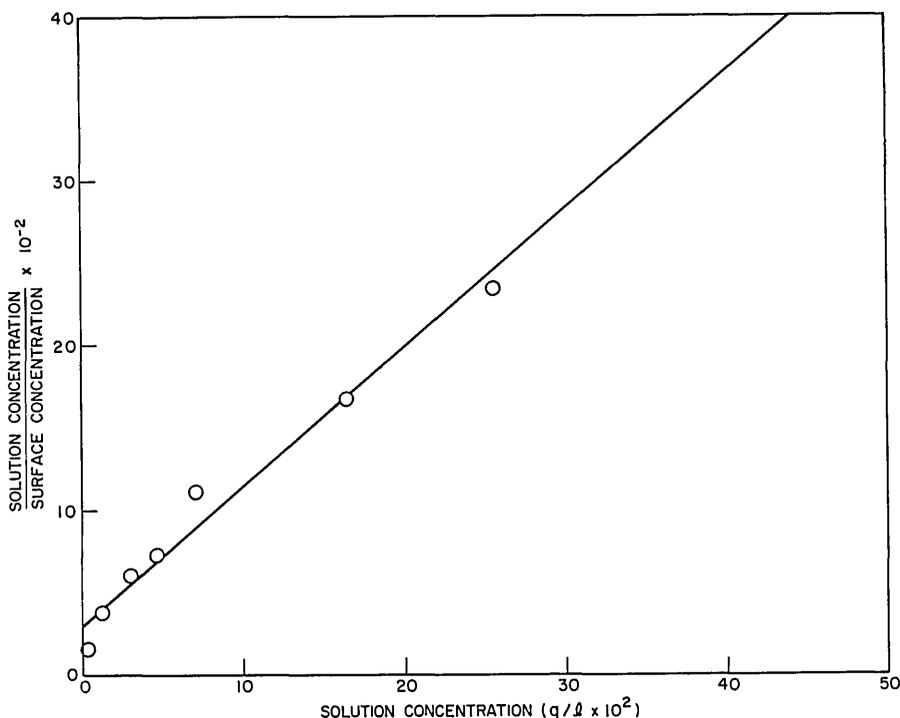


Fig. 6 - Langmuir plot of Polyox Coagulant adsorption data

DISCUSSION

The flow zones of a fluid in turbulent flow past a wall or surface may be roughly classified into three regions: (a) an inner viscous sublayer next to the surface, (b) an intermediate or transition zone, and (c) a turbulent zone extending outward beyond the two thin zones at the wall. In the intermediate transition region the flow is neither

viscous nor turbulent but rather combines the attributes of both types of flow. In recent years it has been determined also that the viscous sublayer is not laminar as was formerly assumed; it is, rather, modified by the turbulence to a degree (35). However, the turbulent motions which penetrate into the viscous sublayer to the wall itself are of a strictly viscous nature. But the viscous sublayer is not merely passive in nature. In addition to the disturbances brought about by external turbulent motions, it is found that the space and time variations of the velocity at the wall create adverse pressure gradients. These pressure gradients cooperate with turbulent motions outside of the sublayer to produce local instabilities at the wall itself. The viscous sublayer itself is, therefore, a generator of turbulent motions (34).

Relaxation Time Hypothesis

Saffman (6) has analyzed the drag reduction effect observed with dusty air in Couette flow (5). He has theorized that when the time scale (equal to the disturbance length divided by its velocity) of the disturbance is less than the relaxation time of the dust particles (considered by Saffman to be a measure of the time for the dust to adjust to changes in the velocity of the fluid) then the stability of the flow is increased. When the dust particles are small, their relaxation times are short and the dust moves with the disturbance. If the dust particles are coarse, their relaxation times become longer than that of the time scale of the disturbance and the disturbance must flow around the particle. As the disturbance flows around the particle, energy is dissipated and the kinetic energy of the disturbance is reduced. Stabilization of the disturbance and reduction of the turbulence intensity decreases the Reynolds stresses; therefore the force required to maintain a given flow rate will be reduced. Alternatively, to maintain the same Reynolds stresses the flow rate will have to be increased. When the time scale of the disturbances exceeds the relaxation time of the particles, interaction is no longer possible and the larger scale turbulence is therefore not affected by the presence of the particles. Since the smaller high-energy eddies are found near the wall and the larger eddies in the outer portion of the boundary layer, one would expect a thicker viscous sublayer to be developed when drag-reducing particles are present.

Elata's equation permits the estimation of the onset of turbulence if the relaxation time of the particles is known. The pertinent formula is $(Re \sqrt{C_f})_r = D \sqrt{2/T_1 V_w}$. Table 2 compares the experimental results with those predicted from Elata's equation for flowing Polyox solutions. The agreement is rather poor; a relaxation time 25 times larger than that indicated for WSR-35 (Table 1) and 9 times larger for WSR-205 would be needed to make theory and experiment agree. Elata (21) suggests that the linear Rouse theory may not apply to the calculation of relaxation times of polymer molecules under high shear rates. Possibly the disagreement of Elata's theory with the experimental results represents the inadequacies of the Rouse theory when applied to polymer molecules under high shear.

Table 2
Comparison of the Experimental Values of $(Re \sqrt{C_f})_r$ with Those Predicted From Elata's Equation

Compound	Predicted Values	Experimental Values
WSR-35	2900	600
WSR-205	1500	460

To examine the relaxation time hypothesis more closely the effect of ionic strength on the flow properties of a 0.01-wt-% Polyox Coagulant solution was observed. The intrinsic viscosity of this Polyox Coagulant sample was 19.0 in pure water and 7.5 in 0.3-molar K_2SO_4 . The intrinsic viscosity in the latter case is only slightly more than one-third the value in pure water. Since Rouse theory relaxation times are proportional to reduced viscosities (or intrinsic viscosities if the solution is sufficiently dilute as in the present case) one would expect a distinct difference in the flow properties of the two

solutions. Figure 7 shows a plot of flow rate vs shear stress at the wall for the two polymer solutions. Their flow properties are identical — within experimental error. The values for the critical value of $(Re \sqrt{U_f})_c$ for drag reduction would be virtually the same, since the actual solution viscosities are not sufficiently different to affect the results. This indicates that relaxation times computed by Rouse theory cannot be applied to polymer molecules under high shear. The fact that flow properties of the two solutions are virtually the same indicates that the computation of the relaxation time of polymer molecules under high shear will have to await new theoretical developments. It appears experimentally that the time difference between the initial and final states of the interacting polymer molecules undergoing relaxation must be the same, under turbulent flow conditions, whether the polymer molecules are in a salt solution or in pure water under the turbulent high shear conditions occurring in the present flow system.

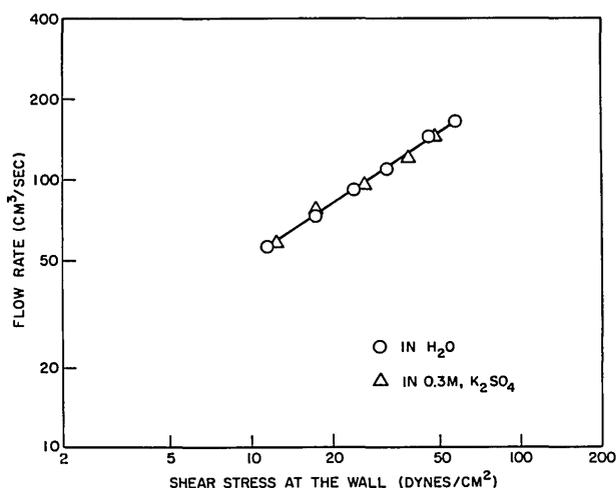


Fig. 7 - Turbulent flow of 0.01-wt-% Polyox Coagulant in water and in 0.3-molar K_2SO_4

It is of interest to note, finally, that some information on the relative merits of rod vs coil type molecules may be gained from observations on Acrysol A-5 solutions. Acrysol A-5 solution (pH = 6.20, almost completely neutralized with KOH, with a concentration of 1000 ppm) appears to be a drag-reducing agent (see Fig. 4) when compared with another fluid having the same consistency index in the same flow range. (The ionized polyacrylic polymer molecule is considered to be an extended rod.) However, its drag-reducing properties, when compared with the base solvent, are virtually wiped out when the comparison is made on the basis of a flow rate vs pressure gradient (see Fig. 8).

Drag Reduction and Critical Concentration

Recent data obtained by Hoyt and Soli (18) have been examined because of the large range of molecular weights experimentally covered. These authors have collected a large number of data for a number of concentrations and have measured the drag reduction in percent (defined as $100 [1 - (\Delta P_t / \Delta P_w)]$, where ΔP_t = pressure difference between pressure taps for the pure fluid and ΔP_w = pressure difference with the polymer solution) at a constant Reynolds number of 14,000.

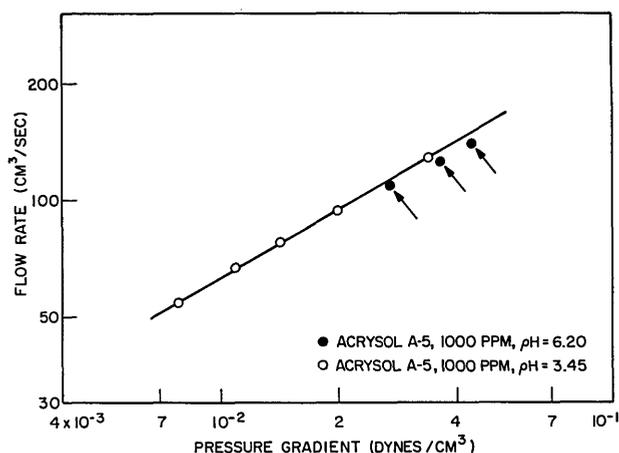


Fig. 8 - Flow characteristics of Acrysol A-5 solutions at two pH values

Table 3 was generated from their graphical data. From their graph we have determined the concentration of polymer needed to produce a 40% drag reduction (this percentage was chosen because of the more complete spread of data available). If one then divides this concentration by the critical concentration for the touching of random coils (determined from the data of Shin's thesis (17)), it is found that the same ratio of concentration for 40% drag reduction to critical concentration (c/c_s) is obtained regardless of variations in molecular weight. In other words, Polyox compounds appear to produce similar drag reduction effects when compared at the same fraction of their critical concentrations — at least in tubes of small diameter (an I.D. of 1.09 mm was used by the author). These results appear to establish the importance of the critical concentration in reducing the drag reduction data for compounds of a homologous series to a common basis.

Table 3
Relation of Critical Concentration for Polymer Interaction to Drag Reduction (From Ref. 18)

Molecular Weight of Polyox Compound	Conc. for 40% Drag Reduction (ppm)	Critical Conc. (ppm)	Conc. for 40% Drag Reduction (fraction of critical conc.)
6×10^6	3	300	0.01
5×10^6	3.5	360	0.01
4×10^6	4	450	0.009
3×10^6	5	560	0.009
2×10^6	7	780	0.009
1×10^6	14	1500	0.009
5×10^5	25	2500	0.01

Adsorption as a Possible Factor in Drag Reduction

Although turbulence damping by linear high-molecular-weight additives does not seem to require the presence of a wall or surface — as evidenced by the jet experiments of Gadd (36) — it is conceivable that the presence of an adsorbed layer on the wall or surface may additionally influence the nature of the flow. Figure 9 shows the dependence of

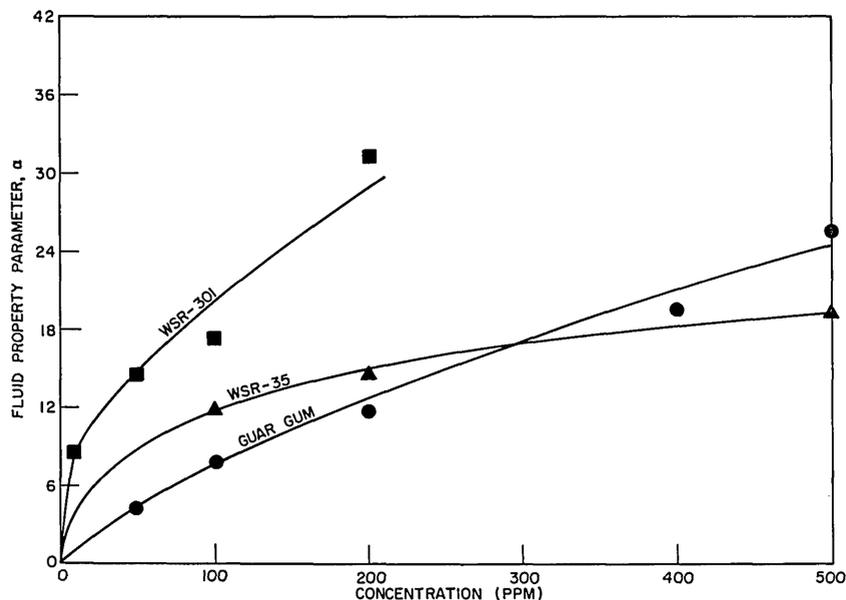


Fig. 9 - Dependence of Meyer's fluid property parameter on concentration

Meyer's fluid property parameter on the concentration of polymer. The Polyox compounds are two for which data were obtained at this Laboratory, while the guar gum data is that of Elata and Tirosh (14) using Lucite pipes. The initial curvature of the plots is much greater for the Polyox compounds than for guar gum. Of particular interest are the data for WSR-35 and guar gum. The Polyox compound appears to be more effective initially but drops below the guar gum curve at about 300 ppm. The observation that the first additions of polymer appear to produce disproportionately large increases in drag reduction might possibly be linked to a surface effect which occurs to a greater extent in the Pyrex pipe than in the Lucite pipe. The adsorption of Coagulant on glass beads has been demonstrated earlier in this report. WSR-35 also adsorbs on glass beads but to a lesser extent; these data are not reported here because of their incompleteness. A Lucite surface (having a much lower surface energy) could be expected to adsorb much less of a given polymer than a glass surface would. The differences in performance of the WSR-35 and guar gum solutions can therefore be rationalized on the basis of differences in adsorption abilities of the two pipe wall materials.

A Quasi-BET Model to Account for Enhanced Drag Reduction at Low Concentrations

A model can be proposed to account for the observed curvature of the $\alpha - C$ plots for solutions of Polyox compounds flowing through glass pipes. The analysis is borrowed from the BET theory of multilayer adsorption (37). In this quasi-BET approach, α is considered to be a function of the fraction θ of the wall covered by polymer molecules under the given flow conditions. Although in this case we undoubtedly have a Langmuir-type adsorption rather than multilayer adsorption, other molecules in successive flow layers within the laminar sublayer are also "counted" or rather add their effect to the observed α value. It should be noted here that polymer adsorption under quiescent conditions (such as the glass bead experiments) may not be in a one-to-one correspondence with polymer adsorption under flow conditions, since in the first case the adsorbed

polymer coils tend to be spherical, whereas in the latter case they are elongated and somewhat aligned with the hydrodynamic field.

The BET equation may be written

$$\frac{C}{\theta(Q-C)} = \frac{1}{K_c} + \frac{(K_c - 1)}{K_c} \frac{C}{Q}$$

where C is the concentration of additive, θ is the fraction of monolayer covered, K_c is the constant, and Q is some reference concentration. It was found that an appropriate reference concentration for the collected data on flowing guar gum solutions was the quantity C_s , where C_s is the critical concentration for coil interaction as previously defined. The major assumption was that of taking $\alpha = K_d \theta^2$. Other functions were tried, but only the above relation gave a linear BET plot over the experimental range of concentrations. Making the appropriate substitutions a quasi-BET plot was made by plotting $K_d C / \alpha^{1/2} (C_s - C)$ vs C/C_s as in Fig. 10. The slope and the intercept of the plot allowed an estimate of the two constants K_c and K_d . It was found that $K_c = 42.1$ corresponding to a heat of adsorption of 2.2 kcal per mole and $K_d = 11.8$. The value of 2.2 kcal per mole for a net heat of adsorption of the polymer from aqueous solution to the glass surface is not an unreasonable value, but it may be pushing an already strained analogy too far to read such an interpretation out of the plot. Since many polymer segments are operative in adsorption, the energy of adsorption per polymer segment need be only slightly higher than that of the solvent molecules for significant adsorption to take place; i.e., if there are 220 segments per molecule involved, on the average, in the adsorption process, each segment need have an adsorption energy of only 10 calories per "mole" of segment above that of the solvent to account for the postulated net heat of adsorption. Also included in Fig. 10 are some limited WSR-35 data. In this case $K_d = 13.4$ and $K_c = 228$, corresponding to a net heat of adsorption of 3.2 kcal per mole. The postulated higher heat of adsorption of WSR-35 over guar gum would be in keeping with its stronger adsorption on the glass surface. It is noted that the same function, $\alpha = K_d \theta^2$, holds for both guar gum and

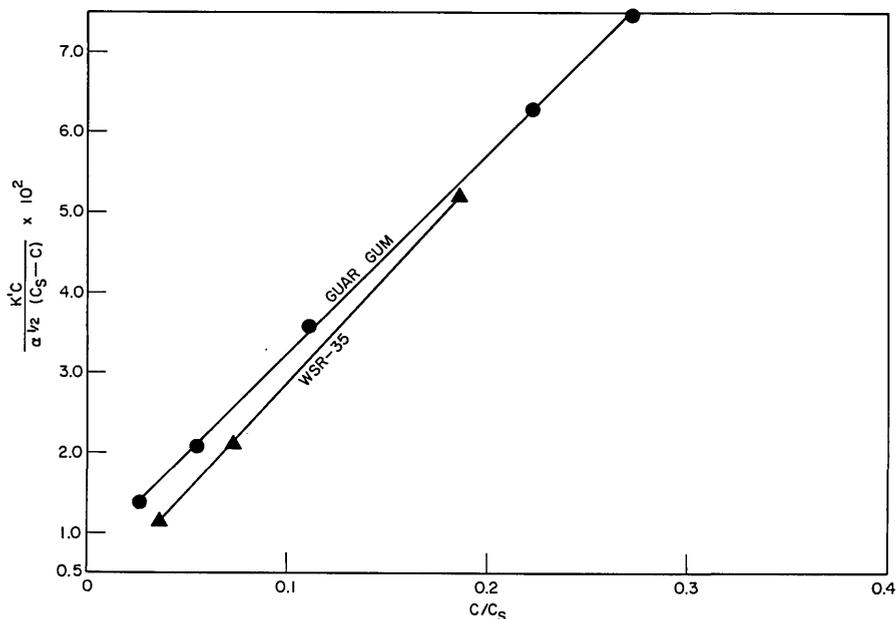


Fig. 10 - Quasi-BET plot for guar gum and WSR-35 data

WSR-35, although the values for K_d are slightly different in each case. K_d is probably a function of the polymer family.

Finally, it is of interest to note that a composite BET plot can be made from all of the Polyox data collected if, instead of C_s , the quantity $C_s + 240$ is used for the reference concentration. Figure 11 shows that the α data for the four Polyox compounds indicated are apparently reduced to a single linear relation when this adjustment is made. α is now expressed in terms of two variables alone, i.e.,

$$\alpha = \left[\frac{834 (C_s + 240) C}{(C_s + 240 - C)(C_s + 240 + 227C)} \right]^2$$

over a concentration range to approximately one-third of the critical concentration for the Polyox compounds.

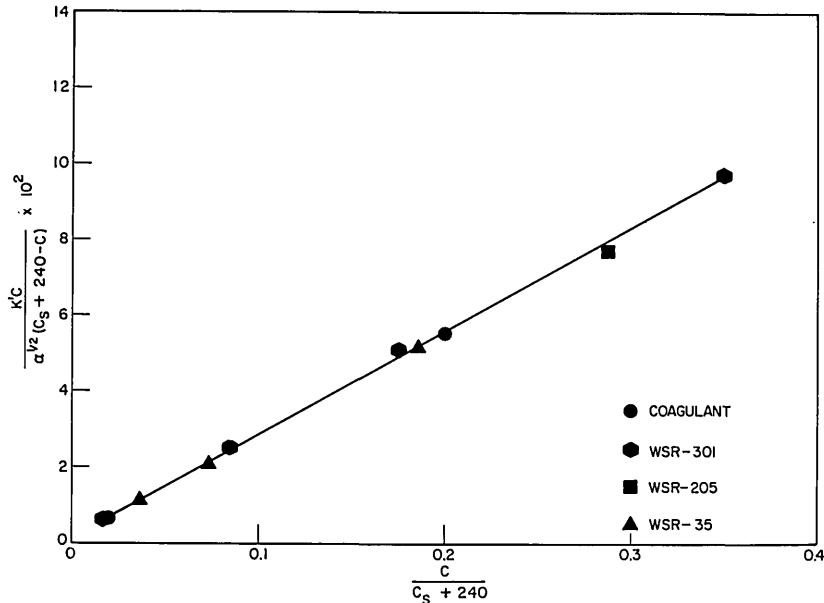


Fig. 11 - Composite quasi-BET plot for the indicated Polyox compounds assuming $\alpha = K'\theta^2$ and adding an arbitrary constant to the concentration terms

Concluding Remarks

The analysis which relates polymer adsorption to drag reduction is admittedly speculative. It would be useful to study other polymer families and to include more members of a given family. At present, it is strongly suspected that adsorbed molecules are involved in drag reduction effects, particularly in view of the fact that more and more evidence has been accumulated which indicates that drag reduction effects apparently occur in the laminar sublayer of the flow (19-21). One of the main effects of this report, then, is to demonstrate that adsorption effects are at least not inconsistent with what appears to be a relatively large drag reducing effect at very low concentrations of additive. The primary application of the postulated adsorption effect would be in putting the drag reduction additive precisely at the point where it would do the most good — at the interface of the wall and the flowing liquid.

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13. ABSTRACT The mechanism by which water-soluble polymers reduce hydrodynamic drag on solid surfaces has been investigated by measurements of flow birefringence and of turbulent flow in pipes. Flow birefringence and flow field orientation of Polyox polymers in the molecular weight range from 200,000 to 6,000,000 have shown that Polyox macromolecules continue to deform with increasing velocity gradient even after alignment with the flow field (at gradients in excess of 2000 sec ⁻¹). Power law plots of flow data for Polyox solutions were used to determine the viscous characteristics over a shear stress range comparable to that used in the pipe flow work. All solutions used were found to be Newtonian, with the exception of the Acrysol A-5 solutions. The flow data for Polyox solutions in a Pyrex pipe were examined in terms of Meyer's fluid property parameter and Elata's relaxation time hypothesis for the initiation of drag reduction. It was found that drag reduction in the Pyrex pipe was initiated at a value of the order of one-fifth that predicted by Elata's theory. Moreover, added salt (the solution being 0.3 molar in K ₂ SO ₄) had no effect on the flow of Polyox Coagulant solutions even though the intrinsic viscosity (upon which Rouse relaxation times depend) was cut to slightly more than one-third of its value in the pure solvent. The unusually high values of Meyer's			

(over)

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Drag reduction Adsorption Polymers Flow fields Viscosity Birefringence						

fluid property parameter observed at low concentrations suggests that adsorption on the Pyrex pipe walls may be playing a role in drag reduction. A mechanism based on a quasi-BET adsorption model is suggested as a possible explanation for the apparent enhancement of drag reduction observed.