An Observation of the Effect of Integral Scale on Drag Reduction

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Drag reduction pipe flow experiments using random coiling polymers have been dominated by the small scales of turbulence. An experiment is reported using polyelectrolytes DNA and collagen, which have extended conformations in solution that shows a relationship between the large scales and drag reduction. Turbulent or molecular interactions can explain the observed increase in drag reduction with an increase in pipe diameter.

SCOPE

Most drag reduction studies in turbulent pipe flow have used solutions which are not dilute in the sense that spheres circumscribing the elongated molecules would more than fill the volume. The length-to-diameter ratio of the molecules is very large as a result of uncoiling in the high strain rate of the turbulence. This mean strain rate appears to be the only parameter needed to describe drag reduction. An effect of the time of exposure to the relatively rotation free strain field necessary to stretch the molecules is not usually observed. Apparently, the molecules elongate all they can and align in the flow until they are limited by other molecules.

Experiments designed to find the influence of the turbulence integral scale are reported in this work. Some care is taken to examine degradation, the difference between uncoiling and alignment, and the change in the integral scale. The study uses DNA and collagen dilute solutions which give observable drag reduction for molecules which either exist normally in solution in completely (collagen) or partially elongated (DNA) conformations. These molecules have a much larger diameter than linear polymers typically used in drag reduction studies, so that the circumscribed volume is about the same as the total volume. These experiments involve molecules approaching the dilute range, where single isolated molecular behavior can be studied. Observations of the interaction of individual molecules with turbulence are important in finding the mechanism of drag reduction and in improving our understanding of turbulent flow and mixing.

CONCLUSIONS AND SIGNIFICANCE

An effect of Lagrangian integral time scale D/u_τ is not observed for polyethylene oxide even if narrow fractions are examined in solutions of less than 0.1 p.p.m. (Berman, 1977*a*). The polyethylene oxide molecules have a large length-to-diameter ratio when stretched completely so that the volume required for free rotation of all the molecules is at least 100 times the solution volume. In this work, DNA and collagen solutions were set up so that the necessary free rotation volume for the molecules and the actual solution volume were about equal if the molecules were fully expanded.

Both the rate of strain and the persistence time of strain should be important in the uncoiling and alignment of macromolecules in turbulent flows, but the scales are related if experiments are conducted in a single-diameter pipe. An increase in the Reynolds number leads to an increase in the strain rate and a decrease in the time scale. Then the elongation reaches a constant level for a given solution and pipe diameter when no other limits are present. When the pipe diameter is increased, this level is increased because the molecules have a longer time to expand. Therefore, drag reduction should increase with pipe diameter when measurements are made at constant mean strain rates, unless the molecules are inhibited from expansion by interactions with other molecules.

Under some conditions, polyelectrolytes expanded by the lack of counter ions in solution have shown an increase in drag reduction when pipe diameter is increased (Berman, 1977*b*). In this work, calf thymus DNA solutions also showed this trend, but calf skin collagen solutions did not.

Degradation appeared to have only minor effects on the amount of observed drag reduction for 200 p.p.m. solutions of calf skin collagen or 20 and 50 p.p.m. solutions of calf thymus DNA. No change in drag reduction was observed for the DNA solutions when solvent viscosity was changed. DNA is coiled and capable of increased expansion, while collagen is not when the molecules are in solution at rest. These observations suggest that the time the coiled DNA molecule spends in the high strain, low vorticity areas of turbulent flow was significant in extending the molecule and increasing drag reduction.

The results also raise the question of whether high levels of drag reduction can be obtained without intermolecular interactions. Significant observations of drag reduction have always required sufficient concentrations, so that the expanded molecules overlap, and this condition could only be reached when the DNA molecules were expanded.

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0001-1541/78/9910-0124/$00.95

The phenomenon of drag reduction by macromolecular additives is well known and has been discussed extensively in recent reviews by Virk (1975), Little et al. (1975), and Lumley (1973). One difficulty in the interpretation of drag reduction is whether or not experiments show the effects of single molecules or groups of molecules. Patterson and Abernathy (1970) show a tendency for drag reduction to approach a linear dependence on concentration for concentrations below 0.1 p.p.m. This result predicts an intrinsic drag reduction in the limit as concentration approaches zero. However, the correlation was made for constant Reynolds number and for commercial polydisperse samples of polyethylene oxide (Polyox grades). The actual concentration and molecular weight of the molecules which contribute to the drag reduction are unknown and, more importantly, not constant. A way to avoid that part of the problem relating to concentration is utilized by Virk. He correlates the difference in slope between a drag reduction trajectory and the Newtonian turbulent line (the slope increment δ) on Prandtl-von Karman ($1/\sqrt{f}$ vs. $Re\sqrt{f}$) coordinates to obtain

$$\delta \alpha c^{1/2} M \tag{1}$$

The concentration dependence is reasonable for the relatively high concentrations used by Virk, but again the polydispersity colors the molecular weight relationship. Berman (1977*a*), for example, shows that for Polyox N-80, which gives an average molecular weight of 2×10^5 from viscosity measurements, only 2% of the sample with molecular weights greater than 1×10^6 are responsible for the observed drag reduction in a 5.54 mm pipe. Virk's result does not extrapolate to an individual molecule limit.

The concept of molecular stretching in the relatively rotation free high strain rate areas of turbulent flow has been linked to drag reduction by many investigators. Berman and George (1974) present an indirect proof that onset of drag reduction and molecular terminal relaxation time are related when the appropriate flow time is a measure of the strain rate u_τ^2/ν. Berman (1977*b*) also has shown that the persistence time of the large eddies, which should be related to the length of time the molecules are stretched, does not influence onset or slope increment for polydisperse Polyox or other random coiling macromolecules in solution. Lumley (1976) and Little et al. (1975) recognized the possibility that for individual molecules the stretching time should be a parameter. North and Champion (1974) found that degradation of DNA depended on both the shear rate and the time of shear. The absence of any effect of persistence time of the strain field in drag reduction experiments and Virk's correlation with $c^{1/2}$ leads to the suspicion that molecules are not acting individually in drag reduction experiments and that molecular interactions are important.

In order to interpret experiments, we must find the correlation between drag reduction and very low concentration of polymers with narrow molecular weight distributions. Berman and Yuen (1977) find that polyethylene oxide fractions yield

$$\delta \alpha c^{2/3} [\eta] \tag{2}$$

Concentrations as low as 0.07 p.p.m. by weight are represented, and, again, an individual molecule effect is not found. Even at this low concentration, the molecules could not expand as much as possible in the turbulent strain field of the laboratory flow. Another experiment to observe single-molecule behavior is the drag reduction by expanded polyelectrolytes in different pipe sizes. Berman (1977*b*) found that in a larger pipe, where the persistence time of the strain field is higher, drag reduction increased, compared to a smaller pipe diameter. The molecular sizes were unknown in these solutions, but the commercially available proteins, calf skin collagen, and calf thymus DNA have been well characterized. These molecules have approximately the same intrinsic viscosity in salt solutions, and their effective dimensions are similar. The DNA, however, can expand, while collagen is always completely extended.

Previous studies using DNA were conducted by Hoyt (1966), Hand and Williams (1970), and Parker and Hedley (1974). These experiments in capillary tubes observed only small changes in drag reduction as functions of pipe diameter. The shear rates were high enough so that behavior similar to the random coils with onset dominated these experiments. No experiments using pipe sizes in the range 5 to 15 mm diameter were used, and no attempts to examine the effect of solution viscosity or degradation were noted in these previous experiments.

MATERIALS AND EQUIPMENT

The DNA used was the sodium salt from calf thymus obtained from Sigma Chemical Company (Cat. No. D 1501). This material has been recently characterized by Sakamoto et al. (1976). It is necessary to dissolve the fibers in very pure water to prevent degradation. We dissolved the DNA in 0.01 M sodium chloride solution with 0.0017 M sodium citrate as a buffer to a concentration of 500 p.p.m. Approximately 36 hr were allowed to complete the solution at room temperature. Then, after dilution to 100 p.p.m., the solution was left for an additional 24 hr before the final dilution, and the pipe tests were made. Specific viscosities were measured with a Cannon-Fenske number 50 viscometer at 30°C. For the 50 p.p.m. test, the specific viscosity divided by concentration was 2260 cm^3/g, which is representative of all batches used in this work. Sakamoto et al. were able to obtain 3000 cm^3/g in 0.2 M sodium chloride and 7 000 cm^3/g in 10^{-3} M by using water stored under nitrogen and solution at 3°C. Their results indicate an average molecular weight of 4×10^6, a root mean square end to end length for a coil of twenty two segments of 0.42 μm. The extended or contour length would be 2 μm when the segments are about 0.09 μm in length. Since the intrinsic viscosity showed only a small variation with salt concentration down to 10^{-3} M, the DNA exists in a coiled form in the 10^{-2} M salt solution of this work. Sakamoto et al. based their conformation conclusions on light scattering and dielectric relaxation measurements in addition to viscosity. For concentrations under 100 p.p.m., the coiled polymers also did not show evidence of entanglements, although a 500 p.p.m. solution did. Although DNA molecules consist of a double helix structure, the chain length for a molecular weight over 10^6 is much longer than the persistence length of the double helix. Then the conformation in solution is a stiff coil intermediate between a rod extended to the contour length and a random coil (Morawetz, 1975, or Steiner and Millar, 1970).

Calf skin collagen was also obtained from Sigma (Cat. No. C 3511). Walton and Blackwell (1973) list the molecules as 0.28 μm long by 1.4 nm in diameter flexible rods with a molecular weight of 3×10^5. The collagen was dissolved in 0.01 M acetic acid over a 48 hr period at room temperature. The 200 p.p.m. solution used in the pipe flow studies has a specific viscosity divided by concentration of 2 580 cm^3/g. When another solution was measured at different concentrations, a Huggins constant of 0.47 was obtained for concentrations greater than 50 p.p.m. Based on a comparison with the DNA solutions of 200 p.p.m., collagen solutions of similar concentration would also not show entanglements. The elongated molecular conformation, however, leads to a solution viscosity 50% higher than the solvent viscosity. Random coils of a similar molecular weight would give much lower increases in solution viscosity for similar concentrations.

Studies of degradation were done using small amounts of solution and a Brookfield counterrotating mixer rotating at 2 240 ± 20 rev/min for collagen and 3 600 rev/min for DNA.

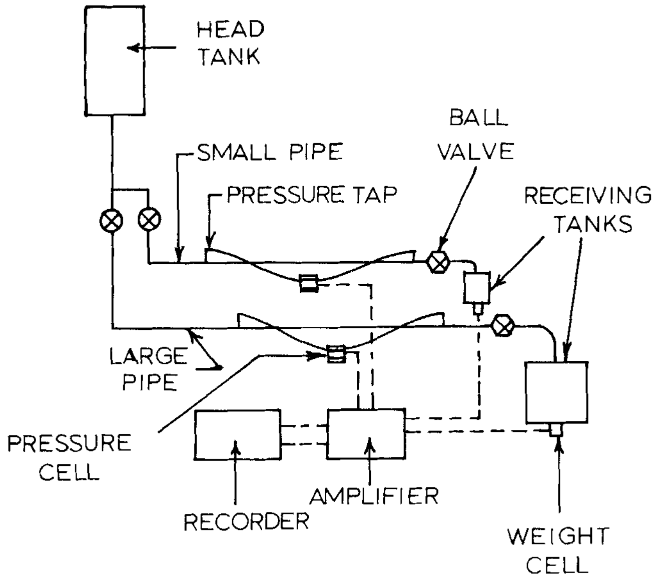

Fig. 1. Schematic diagram of the pipe flow apparatus.

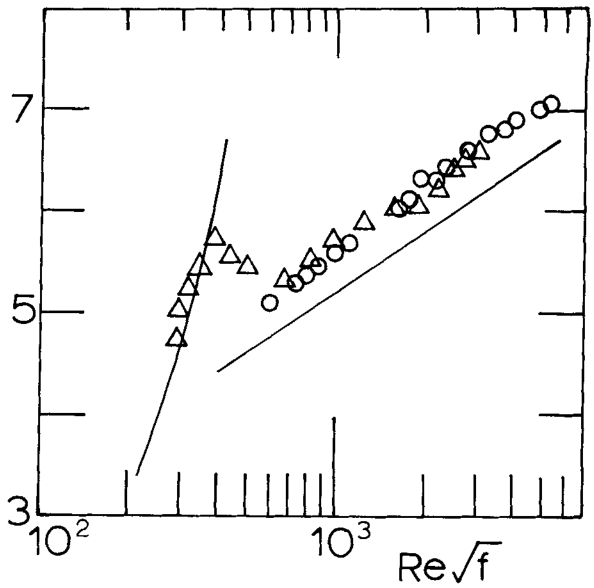

Fig. 2. Viscosity effect on drag reduction for 20 ppm DNA in the 5.54 mm tube. Data are for water as the solvent ○ and 30% glycerol △.

Viscosities were measured after several minutes of violent stirring and the process repeated.

Pipe flow pressure drop and flow rates were measured in an unsteady apparatus similar to that previously described by George et al. (1975). Only 5 l of solution are necessary to measure the friction factor Reynolds number curve over the range of Reynolds numbers needed to examine drag reduction in a 5 mm tube and 18 l for a 15 mm tube.

Figure 1 shows a schematic diagram of the equipment. It consisted of a steel head tank of approximately 30 l in capacity, two stainless steel pipes of internal diameters 0.554 and 1.494 cm, and containers of capacity 4 and 25 l, respectively, connected to the end of each of the pipes by flexible plastic tubing. Pressure taps were connected to a Statham Instrument Incorporation Model PM280TC ± 25 lb/in.^{2} differential pressure transducer by plastic tygon tubing. The first pressure tap was placed approximately 103 diam downstream from the entrance for the smaller pipe and 50 diam for the larger pipe, while the second pressure tap was 154.9 cm downstream from the first pressure tap for the small pipe and 152.4 cm for the large one. The flow rate was measured by monitoring the weight of the containers continuously with Statham Model UC3 strain gauge weight transducers on which the containers were freely rested.

Both the pressure drop and the weight signals were amplified by a Honeywell Accudata 11MDC amplifier and recorded on a chart with a Leeds and Northrup dual pen amplifier recorder. A steel cross was present at the entrance of the large pipe, and the pipe surface near the entrance was roughened to ensure fully developed turbulent flow before the first pressure tap was reached. Both pipes were mounted rigidly on a wall.

The head tank was initially pressurized and the run begun by closing off the system and opening the valve at the end of the pipe leading to the containers. When the system had come to equilibrium with pressures equal throughout, the head tank was isolated and the other tank drained. Several runs were necessary at different head tank pressures to fill in an entire Reynolds number friction factor curve. Flow rates were found from the weight vs. time charts using 2 s averages for the small pipe in turbulent flow and 1 s averages for the larger pipe. Longer times were used for low Reynolds number laminar flows with restrictions in the inlet lines necessary to limit the

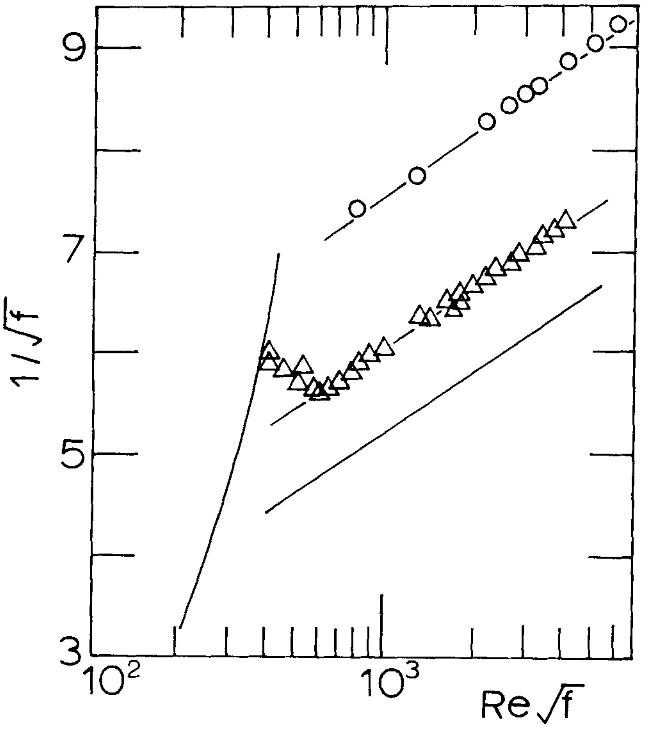

Fig. 3. Drag reduction trajectories for 50 ppm solution of DNA in 5.54 mm tube △ and 14.94 mm tube ○.

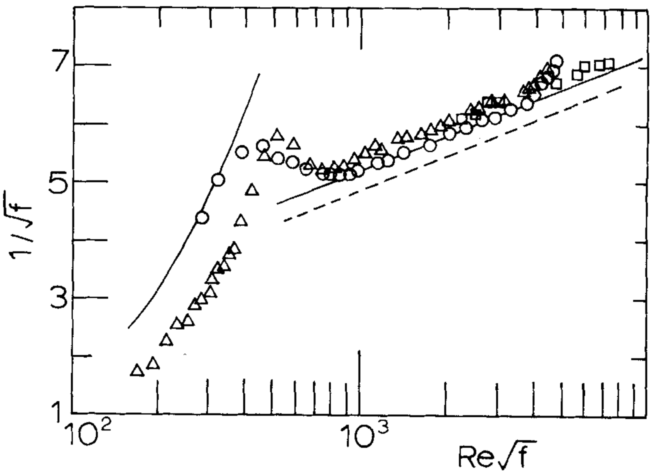

Fig. 4. Drag reduction of 200 ppm collagen in 0.01 M acetic acid. Data corresponding to the list in Table 1 are for run 1, △; runs 2 and 3, □; and run 4, ○. The points are based on the viscosity of the solvent. The dashed line represents Newtonian turbulent flow at the viscosity of the solution for run 1 points.

Table 1. Summary of Viscosities for Collagen Experiments With Initial Concentration of 200 p.p.m.

Run	Pipe diam (mm)	η_{sp}/c before (cm^3/g)	η_{sp}/c after (cm^3/g)	Representative shear rate (s^{-1} × 10^{-3})
1*a*	5.54	2 580	2 030	25
1*bcd*	5.54	2 580	2 170	2.5
1*e*	5.54	2 580	1 980	70
2	14.94	1 980	1 810	20
3	14.94	1 810	1 690	4
4*	5.54	452	—	—

* This sample was heated to degrade.

flow. Temperature measurements were taken before and after the runs, and no significant changes were found.

EXPERIMENTAL RESULTS

Drag reduction results are shown in Figures 2 and 3 for DNA solutions and in Figure 4 for collagen. The solvent viscosity was used to calculate the Reynolds number in all cases. Fresh DNA solutions were used for all runs, but the collagen had to be reused. Table 1 shows the specific viscosity divided by concentration of the collagen solutions before and after each run, along with a representative shear rate corresponding to the average flow rate. For run 4, the solution was heated to approximately 50°C to degrade the collagen and then cooled for the test. Over the shear rate range of all the data, the viscosity of the collagen solution was most likely constant at 1.35 centipoise at 25°C. Measurements were made with collagen at shear rates from 60 to 600 s^{-1} in laminar flow showing essentially a constant viscosity. Another similar polyelectrolyte was measured at higher shear rates with no non-Newtonian tendencies in steady flow observed.

Comparisons of two different polymers are sometimes difficult to interpret when degradation is present. Most random coil polymers used in drag reduction are commercial samples with high molecular weight tails. Degradation can be significant, even though viscosity measurements on solutions of low concentrations have only slight changes as in Paterson and Abernathy (1970). After the pipe flow tests, collagen showed some measurable change in viscosity as given in Table 1, but no change was found for DNA. The turbulent pipe flow apparatus does not give constant degradation conditions, and the numbers of molecules active in drag reduction for the extended polyelectrolytes would be much higher than in the case of random coiling nonelectrolytes, where the largest molecules become effective at lower shear rates (Berman, 1977*a*).

Several experiments were run with a Brookfield stirrer so that DNA and collagen flow degradation could be compared. A first-order kinetic mechanism was assumed to govern the degradation as found in a high shear, laminar flow study of DNA by North and Champion (1974).

Assume that the original solution contains no undegraded molecules and that the degraded molecules do not contribute to the viscosity of the solution. Also, the mixing rate is fast enough to ignore the statistics of the interaction which breaks the molecules. Then

$$\eta - \eta_s = \frac{c}{c_o}(\eta_o - \eta_s) \qquad (3)$$

$$d\left[\frac{(\eta - \eta_s)}{c_o}\right] = \frac{\eta_o - \eta_s}{c_o}\frac{dc}{c_o}$$

$$d[\eta] = [\eta_o]\frac{dc}{c_o} \qquad (4)$$

For a first-order system

$$\frac{dc}{dt} = -kc \quad \text{or} \quad \frac{d[\eta]}{dt} = -k[\eta] \qquad (5)$$

Also

$$k = A\exp(-E_a/RT) \qquad (6)$$

The rate constant can be found from slopes of plots of log $[\eta]$ vs. time. We used η_{sp}/c instead of the intrinsic viscosity. The activation energy was found by measuring the rate constant at several temperatures between 278° and 301°K for collagen and at 297° and 303°K for the DNA solution.

The results are 20 kcal/mole for collagen and 31 kcal/mole for DNA. The stirrer rate of rotation was set to give an appreciable range of data in 2 to 4 hr at the lowest temperature. Only the linear parts of the data were used to obtain the rate constants. The data show that collagen degrades more rapidly at lower shear rates than DNA and has a lower activation energy for degradation.

The drag reduction curves in Figures 2 through 4 show the following:

1. Both DNA and undegraded collagen show a constant drag reduction for the turbulent conditions of the experimental apparatus with no onset. Heat degraded collagen shows no drag reduction until a well-defined onset point is reached. Some of the collagen in the undegraded sample is actually present as random coils characteristic of the heat degraded collagen, and these molecules do have an onset. The upward trend of the points in Figure 4 beyond Re$f^{1/2}$ of 3 000 is an indication of this random coil behavior. The transition from laminar to turbulent flow is accompanied by a decrease in $f^{-1/2}$ beyond Re$f^{1/2}$ of 400 in all cases, even for pure solvent, and is not due to degradation.

2. Drag reduction for DNA is independent of solution viscosity, as shown in Figure 2. Random coiling polymers show a pronounced change when solution viscosity is altered (Berman, 1977*a*).

3. Tube diameter does not influence the collagen drag reduction, but the drag reduction of DNA solutions increases with an increase in tube diameter for the diameters used in this work.

In other experiments using Separan NP-10 and AP-30 dissolved in distilled water, the increase in drag reduction with pipe diameter is found only for low Reynolds numbers when the molecules are not stretched by the strain rate of the turbulent flow. The higher molecular weight AP-30 shows the same behavior as reported by Berman (1977*b*), except the curves are shifted to lower Reynolds numbers. A diagram of the results is shown in Figure 5.

DISCUSSION AND CONCLUSIONS

Analysis of Degradation

The activation energies found using this method are in the same range as weak chemical bonds or several hydrogen bonds. Bowman and Davidson (1972) find an activation energy for DNA of 37 kcal/mole at temperatures between 25° and 35°C. The activation energy is somewhat high to indicate a large amount of degradation under the laboratory flow conditions. Although collagen degrades in the pipe, the differences given in Table 1 indicate that degradation cannot by itself explain the pipe diameter effect. Some decrease in drag reduc-

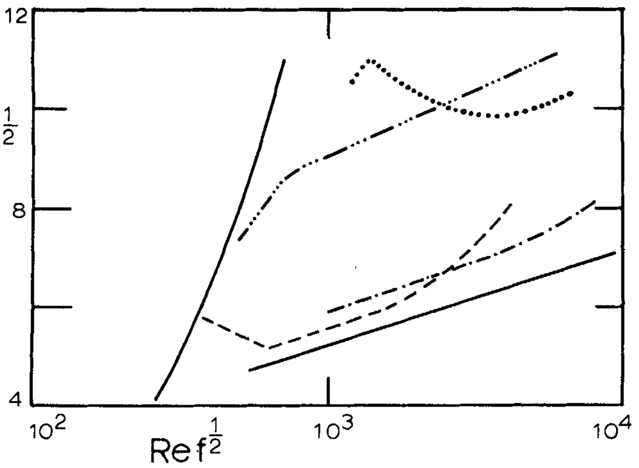

Fig. 5. Drag reduction trajectories for two different molecular weight Separan samples in distilled water. The solid curves represent Newtonian behavior; – – – is for 20 ppm of Separan NP-10 in the 5.54 mm tube, and —·— for the same solution in the 14.94 mm tube; —···— is for 10 ppm of Separan AP-30 in the 5.54 mm tube, and ···· for the same solution in the 14.94 mm tube. The molecular weight of AP-30 is higher than NP-10.

tion is observed in the larger pipe for collagen corresponding to the 20% reduction in viscosity. There appears to be no change at all attributable to the increase in pipe diameter.

North and Champion (1974) present some data that can be used to evaluate the extent of flow degradation. For a shear rate of 10^5 s^{-1} and a time of exposure of 0.25 s representative of the worst case in this work, the degradation of a DNA sample is negligible. Degradation should increase for the larger pipe when observations are taken at constant mean shear rates. Such a result is not observed for DNA, and we conclude that degradation does not influence the results.

Onset Analysis

Heating collagen above 40°C leads to unwinding of the triple stranded helix and formation of random coils. The intrinsic viscosity is representative of random coils and not flexible rods. In turbulent flow, there is no drag reduction until the molecules can uncoil. For random coiling molecules, Berman and George (1974) find that drag reduction trajectories are drastically changed when glycerine water solutions are used as the solvent compared to water alone. The change is in the direction expected if the terminal relaxation time were related to the onset flow strain rate. The DNA solution, however, is not sensitive to solvent viscosity. Also, no onset is observed. Therefore, the molecules must retain the same conformation over the experimental range of Reynolds numbers when the diameter is constant.

Diameter Effect

Drag reduction can be increased when pipe diameter is increased if the persistence time of the large eddies which is proportional to D/u_τ is important. We note that viscosity is not a parameter in the Lagrangian internal time scale. Since collagen does not show this diameter effect, and in solution the molecule is a rod, the large eddies may have no influence unless molecular stretching is possible. Another possibility is that the effect is dependent on the length of the rod. A completely elongated DNA molecule would be over seven times as long as a collagen molecule. Partially elongated Separan molecules (Berman, 1977*b*) show a similar diameter trend, suggesting that the elongation explanation is correct. Direct confirmation of the molecular behavior would require light scattering measurements in the process of drag reduction. Other explanations would be the expansion of the molecules in the entrance, or an increase in drag reduction when molecular interactions are involved.

The interaction of turbulence with a long chain, random coiling macromolecule is discussed by Lumley (1976). A single molecule is subjected to random rotation and strain rates in a turbulent flow, but the possibility of expansion in a relatively rotation free strain field is high. Both the magnitude of the strain and the length of time the dominance of the strain field exists would be expected to influence the elongation processes. The result of Lumley's (1972) analysis shows that the criterion for expansion is

$$u_\tau^2 T_1/\nu \gtrsim b \tag{7}$$

where b is weakly dependent on Reynolds number if the persistence of the strain field is important. This model is a bead-spring type, giving an infinite expansion when stretched. Hassager (1974) treats a bead rod model in pure strain, which leads to a finite deformation. The asymptotic expression for the increase in elongational viscosity of the stretched bead rod at high strain rates is

$$\frac{\eta_e - \eta_o}{\eta_o} = c[\eta]N\{1 - 0.8/T_1\bar{k} - \ldots\} \tag{8}$$

The rapid increase in elongational viscosity begins at essentially the same strain rate u_τ^2/ν or $\bar{k}$ in Lumley's and Hassager's analyses. Berman and Yuen (1977) point out that the concentration and molecular weight dependence of Equation (8) is not observed, although the form of the strain rate dependence is. The molecules must not uncoil completely because they do not have room in the solution to uncoil and line up with the direction of the greatest rate of extension.

Batchelor (1971) in his discussion of the increase in elongational viscosity for nondilute suspensions gives a relationship for the definition of a dilute suspension. The particle length l divided by the average distance between particles h must be small to be dilute. In this work, the ratio is near unity. A typical very dilute polyethylene oxide solution containing 0.1 p.p.m. with molecular weight above 10^6 would give a ratio of 100 if the molecules are fully elongated. Such solutions of narrow fractions were used by Berman and Yuen (1977), and no effects of pipe diameter were found. The major differences in this work are the much larger molecular diameter and the much smaller l/h ratio. The DNA must almost expand entirely to give the l/h equal to unity. Collagen molecules are short enough so that there is no tendency to coil up. The DNA concentration dependence of the drag reduction level for the small pipe from Figures 3 and 4 is greater than the two thirds power, but not the first power. These results are consistent with the situation intermediate between the dilute and nondilute cases described by Batchelor for both the collagen and DNA solutions. Hinch has also indicated that there is a relationship between the elongational viscosity and drag reduction for molecules with large l/h (Landahl, 1973).

Expansion of the molecules in the turbulent flow is very complex and must be related to statistics of the vorticity, strain rate, and time of strain fields. If the molecules are already expanded or for fibers, they appear to align in the flow and reach a constant drag reduction level as collagen shows in Figure 4. The DNA solution has the same behavior, so an increase in strain rate, which would align and stretch the molecules, and a corresponding decrease in Lagrangian integral time scale, which would shorten the exposure time to vorticity free high strain rates, would cancel out along a drag reduction trajectory. The strain rate is proportional to u_τ^2/ν, while the integral scale is proportional to D/u_τ. There is, perhaps, a weak residual effect of Reynolds number, as shown in Figure 2. The DNA in water solution shows a slight increase in drag reduction with Reynolds number, but the glycerol-water solvent does not, especially at lower Reynolds numbers. This can be explained by the change in time scale for the molecules in the two solvents and a small amount of additional expansion. For a single pipe size and solvent, u_τ^2/ν and D/u_τ only have the variable u_τ as a parameter, so it is not surprising that no integral scale dependence can be found. The change in pipe diameter by a factor of 2.7 does give a larger integral scale for the same u_τ, so that the molecules on the average would spend 2.7 times as long with a similar relationship between strain rate and vorticity. The result is more elongation or more time to interact.

The experiment suggests that molecular flexibility and interactions are necessary for significant drag reduction. Just elongated conformations or rigid rods seem to give only small amounts of drag reduction.

The experimental result also has some significance for the correlation of turbulent bursting times $\overline{T}_B$ with flow parameters. Our observation that drag reduction can be independent of viscosity but dependent on pipe diameter suggests that the average time for turbulent production or bursting period would scale with D/u_τ. We assume that Tiederman et al. (1977) are correct in their observation that drag reduction and turbulent bursts are related and that there is some universal correlation between flow parameters and the bursting rate.

Laufer and Narayanan (1971) showed that Newtonian fluids gave $\overline{T}_B$ proportional to D/U. For drag reducing fluids with trajectories on von Karman coordinates of the form

$$1/\sqrt{f} = a \log Re\sqrt{f} + b \qquad (9)$$

the bursting period for the same Reynolds number as the Newtonian fluid should increase. Mizushina and Usui (1976) were able to show this experimentally for random coiling molecules and derive the correlation

$$\overline{T}_B u_\tau^2/\nu = 0.112\, Re^{0.93} \qquad (10)$$

Other Newtonian results by Tiederman et al. (1977) and Achia and Thompson (1974) will also fit this equation. Most data, however, have been measured in pipes or channels with almost the same length scale (generally 25 mm). The drag reducing data of Donohue et al. (1972) and Tiederman et al. show that the bursting period is always the same when measured at constant wall shear stress. In each case, the length scale was held constant.

Consider the DNA results, where we may approximate the friction factor—Reynolds number relationship by

$$f = BRe^{-1/4} \qquad (11)$$

where B is a function of concentration and pipe diameter or drag reduction. Then, Laufer and Narayanan's analysis gives

$$(U\overline{T}_B/D)_{\mathrm{D.R.}} > (U\overline{T}_B/D)_{\mathrm{Newtonian}} \qquad (12)$$

as observed by Donohue and Tiederman. If $\overline{T}_B u_\tau^2/\nu$ is proportional to Reynolds number, we obtain

$$\overline{T}_B \sim G(D/u_\tau) \qquad (13)$$

where G is a function of drag reduction related to B in Equation (11).

Equation (13) is not a universal relation independent of drag reduction. Another possibility is that $\overline{T}_B u_\tau^2/\nu$ is proportional to $\mathrm{Re}f^{1/2}$, $(u_\tau D/\nu)$. Then

$$\overline{T}_B \sim C(D/u_\tau) \qquad (14)$$

where C is a constant independent of drag reduction. If we use the actual DNA data and assume drag reduction and $\overline{T}_B$ are related, we get

$$\overline{T}_B u_\tau^2/\nu = C(\mathrm{Re}f^{1/2})^{\beta} \qquad (15)$$

where β is 1.2. Further tests of this relationship should be made because it provides another indication that the Lagrangian integral time scale is a parameter in the interaction between macromolecules and turbulence.

Finally, it is interesting that experimentally, in order to observe high amounts of drag reduction, we have always had to have enough molecules present so that when stretched, the mean distance between two molecules is less than the size of an elongated molecule. It is still not clear if this is a necessary condition for drag reduction. If fully elongated molecules can indeed produce increased drag reduction, the effect should be observed for much lower concentrations than have been reported. In order to expand the buffer layer toward the pipe center, as suggested by Lumley (1973), there is a change in the turbulent dynamics which must require an increased concentration of polymer to proceed. The net result becomes complex but should be examined to find out if the high levels of drag reduction found in laboratory flows are dependent on molecular interactions.

ACKNOWLEDGMENT

The authors acknowledge the support of the National Science Foundation grants ENG 75-19550 and SMI 76-02988 and the Donors of the Petroleum Research Fund administered by the American Chemical Society.

NOTATION

A = constant in Equation (6)
a = constant in Equation (9)
B = constant in Equation (11)
b = constant in Equation (9)
C = constant in Equations (14) and (15)
c = concentration
c_0 = initial concentration
D = pipe diameter
E_a = Arrhenius activation energy
f = friction factor, $f = 8u_\tau^2/U^2$
G = constant in Equation (13)
h = average distance between molecules, $h = (c\mathbf{N}l/M)^{-1/2}$
k = rate constant
$\overline{k}$ = elongational rate
l = molecular length
L = pipe length
M = molecular weight
N = number of mass points in the bead rod model
$\mathbf{N}$ = Avagadro number
P = pressure, ΔP pressure difference
R = gas constant
Re = Reynolds number DU/ν
t = time
T = temperature
T_1 = Rouse Relaxation time, $T_1 = (\eta - \eta_s)M/4cRT$
$\overline{T}_B$ = average turbulence bursting time
U = mean velocity
u_τ = friction velocity, $u_\tau = \sqrt{\tau_0/\rho}$

Greek Letters

β = constant exponent Equation (15)
δ = slope increment
η = viscosity
$[\eta]$ = intrinsic viscosity $[\eta] = (\eta - \eta_s)/c\eta_s$, limit as c and shear rate approach zero
η_e = elongational viscosity
η_o = initial viscosity of undegraded solution
η_s = solvent viscosity
η_{sp} = specific viscosity, $(\eta - \eta_s)/\eta_s$
ν = kinematic viscosity, $\nu = \eta/\rho$
ρ = density
τ = shear stress
τ_o = wall shear stress, $(-\Delta P)D/4L$

LITERATURE CITED

Achia, B. U., and D. W. Thompson, "Laser Holographic Measurement of Wall-Turbulence Structures in Drag Reducing Pipe Flow," *Proc. Inten. Conf. Drag Reduction St. John's Coll. Cambridge*, N. G. Coles, ed., BHRA Fluid Engineering, Bedford, England (1974).

Batchelor, G. P., "The Stress Generated in a Non-Dilute Suspension of Elongated Particles by Pure Straining Motion," *J. Fluid Mech.*, **46**, 813 (1971).

Berman, N. S., "Drag Reduction of the Highest Molecular Weight Fractions of Polyethylene Oxide," *Phys. Fluids*, **20**, 715 (1977*a*).

———, "Flow Time Scales and Drag Reduction," *Phys. Fluids* supplement, IUTAM Symposium on Structure of Turbulence and Drag Reduction, to be published (1977*b*).

———, and W. K. George, "Onset of Drag Reduction in Dilute Polymer Solutions," *Phys. Fluids*, **17**, 250 (1974).

———, and J. Yuen, "The Study of Drag Reduction Using Narrow Fractions of Polyox," Second International Conference on Drag Reduction (1977).

Bowman, R. B., and N. D. Davidson, "Hydrodynamic Shear Breakage of DNA," *Biopolymers*, **11**, 2601 (1972).

Donohue, G. L., W. G. Tiederman, and M. M. Reischman, "Flow Visualization of the Near-Wall Region in a Drag Reducing Channel Flow," *J. Fluid Mech.*, **56**, 559 (1972).

George, W. K., G. B. Gurney, and N. S. Berman, "Technique for Rapid Friction Factor Fluid Characterization," *J. Hydronautics*, 9, 3b (1975).

Hand, J. H., and M. C. Williams, "DNA and Structural Effects in Turbulent Drag Reduction," *Nature*, **227**, 369 (1970).

Hassager, O., 'Kinetic Theory and Rheology of Bead Rod Models for Macromolecular Solutions. 1. Equilibrium and Steady Flow Properties," *J. Chem. Phys.*, **60**, 2111 (1974).

Hoyt, J. W., "Turbulent-flow Properties of Deoxyribonucleic Acid Solutions," *Nature*, **211**, 170 (1966).

Landahl, M. T., "Drag Reduction by Polymer Addition," *Proceedings Thirteenth International Congress Applied Mechanics*, E. Becker and G. K. Mikhailov, ed., Springer-Verlag, Berlin (1973).

Laufer, J., and M. A. Badri Narayanan, "Mean Period of the Turbulent Production Mechanism in a Boundary Layer," *Phys. Fluids*, **14**, 182 (1971).

Little, R. C., R. J. Hansen, D. L. Hunston, O. Kim, R. L. Patterson, and R. Y. Ting, "The Drag Reduction Phenomenon: Observed Characteristics, Improved Agents, and Proposed Mechanisms," *Ind. Eng. Chem. Fundamentals*, **14**, 283 (1975).

Lumley, J. L., "On the Solution of Equations Describing Small Scale Deformation," *Symposia Mathematica*, 9, 315 (1972).

———, "Drag Reduction in Turbulent Flow by Polymer Additives," *J. Polymer Sci., Macromol. Rev.*, **1**, 263 (1973).

———, "Two-Phase and Non-Newtonian Flows," in *Turbulence*, P. Bradshaw, ed., pp. 290-324, Springer Verlag, New York (1976).

Mizushina, T., and H. Usui, "Reduction of Eddy Diffusion for Momentum and Heat in Viscoelastic Fluid Flow in a Circular Tube," paper presented at IUTAM Symposium on Structure of Turbulence and Drag Reduction, Washington, D.C. (1976).

Morawetz, H., *Macromolecules in Solution*, 2 ed., Wiley, New York (1975).

North, P. F., and J. V. Champion, "Hydrodynamic Degradation of DNA," *J. Chem. Phys.*, **71**, 1282 (1974).

Parker, C. A., and A. H. Hedley, "A Structural Basis for Drag-Reducing Agents," *J. Appl. Polymer Sci.*, **18**, 3403 (1974).

Paterson, R. W., and F. H. Abernathy, "Turbulent Flow Drag Reduction and Degradation with Dilute Polymer Solutions," *J. Fluid Mech.*, 43, 689 (1970).

Sakamoto, M., H. Kanda, R. Hayakawa, and Y. Wada, "Dielectric Relaxation of DNA in Aqueous Solutions," *Biopolymers*, **15**, 879 (1976).

Steiner, R., and D. B. S. Millar, "The Nucleic Acids," in *Biological Polyelectrolytes*, A. Veis, ed., Marcel Dekker, New York (1970).

Tiederman, W. G., A. J. Smith, and D. K. Oldaker, "Structure of the Viscous Sublayer in Drag Reducing Flows," *Turbulence in Liquids: Proceedings of the Fourth Biennial Symposium 1975*, J. L. Zakin and G. K. Patterson ed., Science Press, N. J. (1977).

Virk, P. S., "Drag Reduction Fundamentals," *AIChE J.*, **21**, 625 (1975).

Walton, A. G., and J. Blackwell, *Biopolymers*, Academic Press, New York (1973).

Manuscript received August 12, 1977, and accepted October 12, 1977.

Mass Transfer Characterization of Donnan Dialysis

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Donnan dialysis is a relatively new ion exchange process using ion exchange membranes to permit continuous operation. Potential applications exist in many areas where traditional columnar ion exchange, requiring a regeneration cycle, is currently used. A mathematical model was developed. Mass transfer parameters for the model were determined from laboratory data and correlated with the system operating variables.

SCOPE

Donnan dialysis is a continuous ion exchange membrane process based on the Donnan equilibrium equation (Donnan, 1924) applied to permselective membranes. These membranes have fixed charges incorporated into their structure and are permeable to ions of the opposite charge (counterions) while excluding ions of the same charge (coions). The significant aspect of the Donnan relationship is that concentration ratios are the important factors in

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0001-1541/78/7793-0130/$01.05 © 1978, American Institute of Chemical Engineers.