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The Influence of Polymer Conformation on Turbulent Drag Reduction

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In recent years the search for more efficient turbulent drag reducers has motivated a number of interesting studies on molecular conformation and flexibility (Balakrishnan and Gordon, 1975; Banijamili et al., 1974; Frommer et al., 1974; Hand and Williams, 1970; Kim et al., 1973; Liaw et al., 1971; Parker and Hedley, 1972). Many of these studies have utilized polyelectrolytes, for which conformational changes may easily be induced by variations in solution *p*H or addition of electrolyte. It has been shown that procedures which increase molecular expansion, as reflected, for example, by an increased solution viscosity, generally lead to enhanced drag reducing ability (Balakrishnan and Gordon 1975; Banijamili et al., 1974; Frommer et al., 1974; Kim et al., 1973; Parker and Hedley, 1972). Here we present additional experimental evidence supporting this concept and discuss the complicating effect of elevations in solution viscosity for highly extended molecules. The data also suggest the intriguing possibility that drag reduction experiments may be utilized to infer the presence of intramolecular hydrogen bonding in solution.

EXPERIMENTAL

Aqueous solutions of two commercially available polyelectrolytes were studied: Separan AP273 (Dow Chemical), a polyacrylamide which has undergone approximately 30% hydrolysis, and Versicol S25 (Allied Colloids), a polyacrylic acid. The solution concentrations were 10 and 20 p.p.m. by weight, respectively. According to the manufacturers, both polymers have extremely large molecular weights, about 10^7.

Pressure drop and flow rate measurements were made with a once-through flow system containing a Moyno pump (Robbins and Myers) and a 1.092 cm I.D. stainless steel tube [data for 0.457 and 2.146 cm I.D. tubes are also available (White, 1975)]. Pressures were determined manometrically, and flow rates were obtained by collecting the fluid over a given time interval. Fluid temperatures were approximately 22° to 23°C. Data on water agreed within 3% with accepted friction factor–Reynolds number correlations for smooth tubes.

Solution viscosities were measured with a Wells-Brookfield semimicro viscometer (Brookfield Engineering), at a polymer concentration of 200 p.p.m. by weight and a shear rate of $115 s^{-1}$. Viscosity values at the concentrations utilized in the drag reduction experiments could not be obtained with the Wells-Brookfield viscometer due to the presence of undissolved gellike particles nor could these values be calculated from the friction factor data, since these did not extend far enough into the laminar region.

RESULTS AND DISCUSSION

The polymer solution viscosities are presented in Table 1 for deionized water, high and low *p*H, and with added salt. Although these data are for 200 p.p.m. by weight, it is anticipated that they also reflect conformational changes occurring at the lower concentration levels of interest in drag reduction. Similar findings with regard to the influence of *p*H on viscosity for polyacrylic acid, but at much lower concentration levels, have been reported by Kim et al. (1973). Both polymers exhibit maximum viscosities at intermediate pH levels, where pendant —COO^- groups would be expected to show greatest ionization. At high *p*H values, obtained with sodium hydroxide addition, the excess electrolyte is believed to shield the carboxyl groups from one another, ultimately reducing coil expansion. Viscosity reduction at low *p*H (hydrochloric acid addition) occurs through suppression of COOH ionization. Some work with polyacrylic acid also suggests

TABLE 1. SUMMARY OF POLYMER SOLUTION VISCOSITY DATA

Polymer	Solution	Viscosity @ 200 p.p.m. by weight and 25°C, shear rate $= 115 s^{-1}$
Separan AP273	Deionized water (*p*H ~ 8.6)	0.0086 Ns/m^2
	High *p*H (*p*H = 11.5)	0.0058
	0.1 M NaCl	0.0020
	Low *p*H (*p*H = 3.5)	0.0025
Versicol S25	Deionized water (*p*H ~ 8.1)	0.0105 Ns/m^2
	High *p*H (*p*H = 11.5)	0.0070
	0.1 M NaCl	0.0025
	Low *p*H (*p*H = 3.5)	0.0013

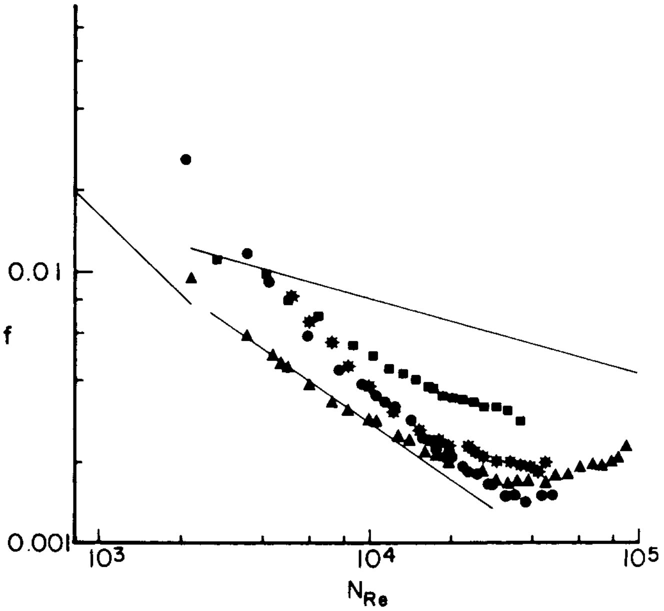

Fig. 1. Friction factor vs. Reynolds number for Separan AP273 in 1.09 cm tube. ● = deionized water solution (pH ~ 8.6); ■ = low pH solution (pH = 3.5); * = salt solution (0.1M sodium chloride); ▲ = high pH solution (pH = 11.5). Polymer concentration, 10 p.p.m. by weight.

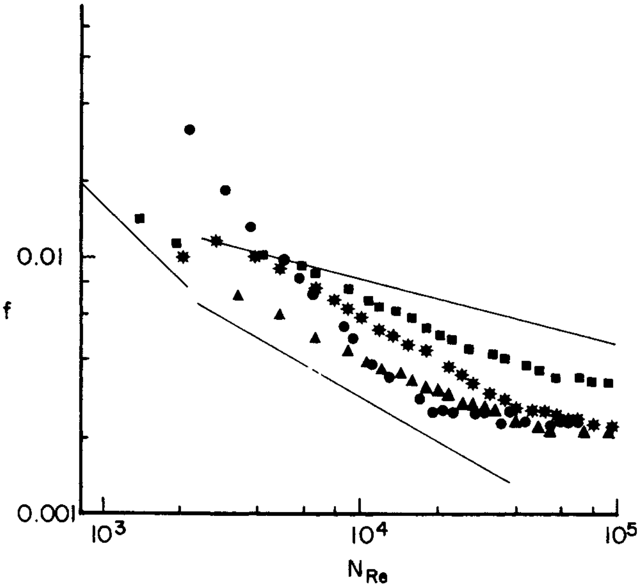

Fig. 2. Friction factor vs. Reynolds number for Versicol S25 in 1.09 cm tube. ● = deionized water solution (pH ~8.1); ■ = low pH solution (pH = 3.5); * = salt solution (0.1M sodium chloride); ▲ = high pH solution (pH = 11.5). Polymer concentration, 20 p.p.m. by weight.

the possibility of a helical coil transition at low *p*H levels (Hand and Williams, 1969; Mathieson and McLaren, 1965). This would necessarily imply the presence of intramolecular H bonding, consistent with the results reported below.

The measured friction factor-Reynolds number data for each polymer, in four different solutions, are presented in Figures 1 and 2. In each figure, the three solid lines correspond to:

(i) laminar flow

$$f = 16/N_{Re}$$

(ii) turbulent flow (Newtonian fluids)

$$\frac{1}{\sqrt{f}} = 4.0 \log_{10} N_{Re} \sqrt{f} - 0.4$$

and

(iii) Virk's maximum drag reduction asymptote (Virk, 1971)

$$\frac{1}{\sqrt{f}} = 19.0 \log_{10} N_{Re} \sqrt{f} - 32.4$$

In all cases, the Reynolds number is calculated by using the solvent viscosity in order to portray the true drag reducing ability of the various solutions.

Figure 1 indicates that for $2\,000 \leq N_{Re} \leq 20\,000$, drag reduction with polyacrylamide is greatest in the high *p*H solution. For larger Reynolds numbers, the data for the salt solution, the high *p*H solution, and the deionized water solution tend to bunch together, with the deionized water solution showing slightly greater drag reduction than the high *p*H solution, which in turn is slightly superior to the salt solution. At low Reynolds numbers, from about 4 000 to 6 000, the data for the salt, low *p*H, and deionized water solutions fall together, but for $N_{Re} > 7\,000$ to 8 000, the low *p*H data diverge upward, leading to significantly poorer drag reduction at higher N_{Re}.

The viscosity data in Table 1 indicate that Separan AP273 is most extended in the deionized water and high *p*H solutions and is collapsed to approximately the same extent in the salt or low *p*H solutions. Hence, the former solutions should yield greatest drag reduction, if indeed extension of the coil is the controlling factor. This statement must be qualified somewhat due to the pronounced viscosity increase of the polymer in deionized water. This may be seen more clearly by considering the simplified model of turbulent drag reduction recently presented by Katsibas and Gordon (1974). Using a modification of the Einstein and Li penetration model (1956) gave the following expression for the friction factor:

$$f = \frac{4}{u_b} \sqrt{\frac{\nu}{\pi\theta}}$$

Here, u_b is the bulk fluid velocity, ν the kinematic viscosity, and θ the average time between turbulent bursts. The action of the polymer is simply to increase the contact time, or the time between bursts θ. For the current situation, we obtain at constant solvent Reynolds number

$$\frac{f_p}{f} = \sqrt{\frac{\nu_p \theta}{\nu\, \theta_p}}$$

where f_p is the friction factor of the polymer solution. The factor $(\nu_p/\nu)^{1/2}$ is a constant, while $(\theta/\theta_p)^{1/2}$ decreases continuously with increasing N_{Re}. [For maximum drag reduction, $(\theta/\theta_p)^{1/2} \sim N_{Re}^{-0.30}$ (Katsibas and Gordon, 1974).] At low N_{Re}, if ν_p/ν is sufficiently large, it may offset the modest reduction in θ/θ_p, leading to low or insignificant levels of drag reduction. At sufficiently large N_{Re}, however, pronounced drag reduction can still occur.

Figure 1 appears to be consistent with these ideas. Thus, the partially extended polymer in high *p*H solution shows optimum drag reduction at lower Reynolds numbers since the viscosity increase is small. The high viscosity of the deionized water solution offsets any drag reduction at low N_{Re}, but at high N_{Re} the solution exhibits drag reducing ability equivalent (and actually slightly superior) to the high *p*H solution. Use of a generalized Reynolds number (Metzner and Reed, 1955) will, of course, reduce all the data to a single curve in the laminar flow region, but this procedure masks the amount of actual drag reduction, relative to the pure solvent, which occurs.

The salt and low *p*H solutions show low levels of drag reduction at small Reynolds number due to their collapsed conformations. At high Reynolds numbers, however, coil expansion should occur, with solution behavior approaching that of the deionized water or high *p*H solutions. This clearly is the case for the salt solution, and the fact that it does not occur with the low *p*H solution implies the presence of storing intramolecular interactions between nonadjacent sections of the polymer coil, most probably in the form of hydrogen bonds.

Turning now to Figure 2 for Versicol S25, we see that this is very similar to Figure 1 for Separan AP273, although the actual percentage drag reduction obtained is not as great. Here again, the high *p*H solution shows maximum drag reduction at low N_{Re}, while as the Reynolds number increases, the data for the salt, deionized water, and high *p*H solutions all merge together. The low *p*H solution gives significantly poorer drag reduction, especially as N_{Re} is increased.

These findings may be explained in exactly the same fashion as for the case of Separan AP273. In deionized water at low N_{Re}, the chain is overextended, the increase in solution viscosity offsetting the increased contact time (or time between turbulent bursts). The partially extended coil in the high *p*H solution, offering a compromise between extension and viscosity, yields optimal drag reduction. The salt and low *p*H solutions both show poor drag reduction initially, but as N_{Re} increases, the coil in the salt solution expands to a greater extent than in the low *p*H solution, giving greater friction reduction. At high Reynolds numbers, the polymer coil is maximally extended in the salt, high *p*H, and deionized water solutions, which yield identical drag reduction. The smaller extension of the polyacrylic acid molecule in the low *p*H solution is consistent with the postulate that the molecule assumes a partially helical structure in an acidic medium.

CONCLUSIONS

The experimental results in this study support the concept that increased polymer extension in solution leads to better drag reduction. The elevated solution viscosities of highly extended conformations may, however, offset any drag reduction enhancement at low Reynolds numbers and must be carefully accounted for.

The friction factor data for polyacrylamide or polyacrylic acid in deionized water, in high *p*H solution, and in 0.1M sodium chloride solution tend to merge together at high values of N_{Re}, suggesting that in each solution the polymer coils approach the same degree of extension. The much higher value of the friction factor in low *p*H solution implies that the polymer coils have become stiffened, suggesting the presence of strong intramolecular bonding, most probably in the form of hydrogen bonds.

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Optimal Batch Reactor Temperature Policy for Reactions with Concentration Dependent Catalyst Decay

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Catalyst deactivation is an important practical problem that has generated considerable interest in recent years. Early work in catalyst deactivation usually involved empirical methods specific for a particular reaction. However, more recently, fundamental approaches, involving direct gradient search techniques or indirect variational methods, have been used to model catalyst deactivation

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