

Influence of Molecular Conformation and Intermolecular Interactions on Turbulent Drag Reduction

Although turbulent drag reduction has been extensively studied in recent years, there are still many aspects of this phenomenon which are not well understood. In this note, we are concerned with two specific problems dealing with (i) the optimum molecular conformation for maximum drag reduction, and (ii) the mechanism whereby the drag-reducing ability of a given polymer begins to decrease as the concentration is raised above a certain value, C_{max} .

OPTIMUM MOLECULAR CONFORMATION FOR DRAG REDUCTION

The characteristics of a polymer most desirable for drag reduction have been discussed by many authors.¹⁻⁶ Liaw, Zakin, and Patterson have suggested that chain flexibility is an important parameter,¹ while Parker and Hedley have stressed the need for a highly extended and presumably "stiff" chain.⁴ All workers seem to agree that increasing molecular weight has a beneficial effect.

In an interesting study, Hand and Williams⁵ measured the drag-reducing ability of an aqueous solution of poly(acrylic acid) (PAA) at 25 wppm in a 0.12-cm tube, at different pH levels. These authors concluded that poly(acrylic acid) is most effective at pH values between about 2 and 1, where the molecule assumes a very compact structure, "suspected to be helical." On the other hand, Parker and Hedley,⁴ using a different sample of poly(acrylic acid), found the extended coil conformation which occurs at higher pH values to lead to the best drag reduction; and similar results were reported by Kim, Little, and Ting.⁶

We have also studied this problem, both with poly(acrylic acid) (Versicol S25 Allied Colloids) and a partially hydrolyzed polyacrylamide (PAM) (Separan AP 273, Dow Chemical Company), in order to see if these different findings could be reconciled. Figure 1 is a plot of the viscosity of aqueous solutions of these polymers measured at 200 wppm in a cone-and-plate viscometer. The viscosity curves suggest that both molecules are maximally extended in the pH range from about 7 to 9. The decrease in viscosity at higher pH values is probably due to the increased counterion concentration, which tends to shield the ionized carboxyl groups along the polymer backbone from one another. The abrupt decrease in viscosity of the PAA at low pH values is

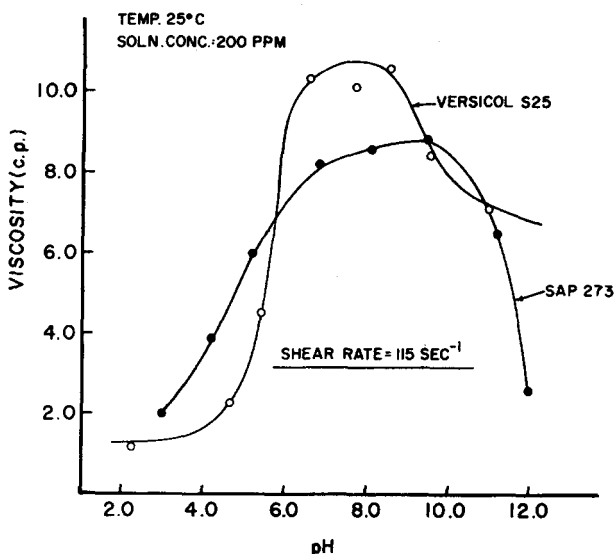


Fig. 1. Viscosity of Versicol S25 (PAA) and SAP 273 (PAM) vs. pH.

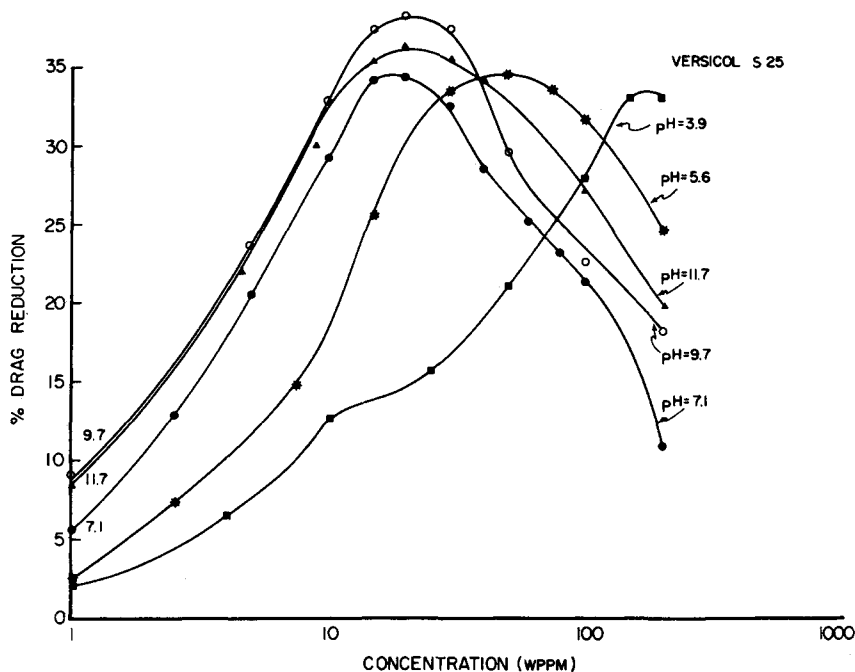


Fig. 2. Per cent drag reduction vs. concentration for Versicol S25 at different pH levels.

thought to be due to a second-order phase transition from a highly extended rigid rod to a more compact helical structure.^{5,7} The viscosity decrease of the PAM solution at low pH values is probably due to a combination of increased counterion concentration and a degree of second-order phase transition (Separan AP273 contains approximately 30% COO groups⁸). Results similar to Figure 1 for PAA have been reported by Kim, Little, and Ting.⁶

Figures 2 and 3 illustrate the drag-reduction behavior of these polymers as a function of pH. The data have been obtained in a gravity flow apparatus described previously.⁹ This consisted of a cylindrical Plexiglas tank to which was attached a stainless steel tube 0.45 cm in diameter and 185 cm long. Reynolds numbers of up to 14,500 were obtained, depending on the polymer. Considering first the pH curves of 3.9, 5.6, and 7.1 for the PAA, we see that these order with the viscosity values at 200 wppm, suggesting that the highly extended conformation is the most effective one. This result is in agreement with the findings of Parker and Hedley⁴ and Kim, Little, and Ting.⁶ On the other hand, at the higher pH values of 9.7 and 11.7 where the solution viscosity is again decreased, the drag reduction curve is increased slightly above that at pH 7.1. The PAM data show similar trends, with the higher pH values yielding the best drag reduction. If the conformation of PAA or PAM is as suggested above, i.e.,

low pH → intermediate pH, → high pH,
 compact, partially highly extended, rigid compact, flexible,
 helical, difficult easily extended
 to extend

then these results imply that the flexible, random coil conformation is the most effective for turbulent drag reduction.

In an earlier publication,⁹ we indicated that C_{VI} , the concentration required for vortex inhibition, correlated extremely well with drag-reducing ability. It was therefore of interest to measure this quantity for the PAA and PAM solutions at various pH levels. The results of this study are listed in Table I, where it is evident that C_{VI} also correlates closely with the drag-reducing ability of these systems. A comparison of Figure 1 and Table I further indicates particularly in the case of the PAM solutions, the lack of correlation between C_{VI} and solution viscosity.

TABLE I
Vortex Inhibition Concentration^a C_{VI} Versus pH for Polyacrylamide and Poly(acrylic Acid)

	pH	C_{VI}		pH	C_{VI}
PAM	2.1	40	PAA	3.9	200
	3.75	5		5.6	10
	5	3		7.1	3
	7	3		9.7	3
	12	1.5		11.7	5

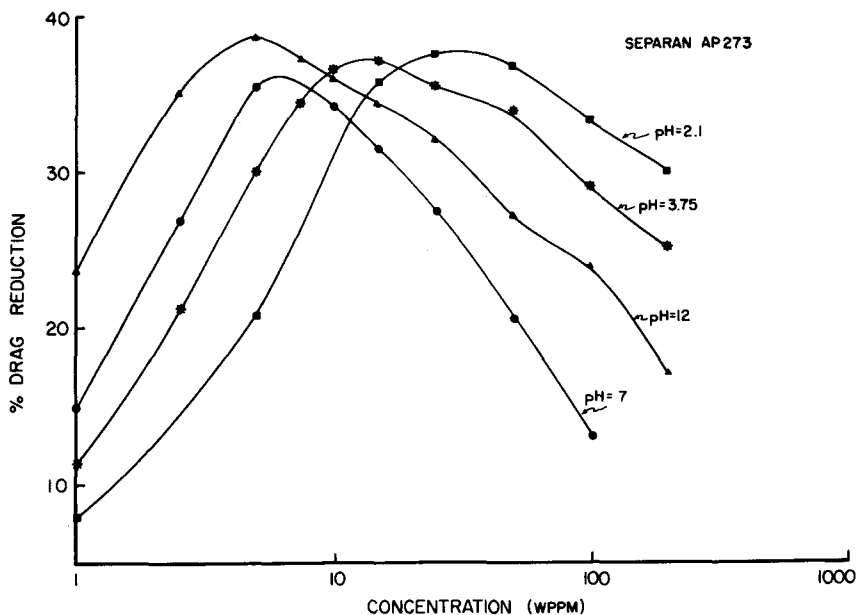


Fig. 3. Per cent drag reduction vs. concentration for Separan AP 273 at different pH levels.

In an experiment where a single concentration of polymer is utilized, Figures 2 and 3 imply that the concentration chosen can significantly alter the findings with regard to the "optimum pH." Thus, for PAA, if studies of the friction factor versus the Reynolds number are made at a concentration of 10 wppm, then clearly from Figure 2 the higher pH values would be associated with better drag reduction. Alternatively, if a concentration greater than 100 wppm is used (the exact concentration level being dependent, of course, on both polymer molecular weight and tube diameter), then the low pH conformation would appear to have the best drag-reducing properties. These remarks may explain the anomalous results of the Hand and Williams study.

INTERMOLECULAR INTERACTIONS

As we just observed, the conclusions reached concerning the effects of pH on drag reduction are dependent on which side of the drag reduction concentration curve we are on, i.e., to the right or left of the maximum. The question naturally arises as to the reason for this maximum and whether or not the existence of such a maximum can yield insight into the mechanism of friction reduction.

Figure 4 is a plot of per cent drag reduction versus concentration for WSR301, degraded WSR301 (degraded in a high shear mixer), and WSRN 3000 (WSR 301 and WSRN 3000 are high molecular weight water-soluble polyethylene oxide samples manufactured by Union Carbide.) These curves are from left to right, in order of decreasing molecular weight, and in

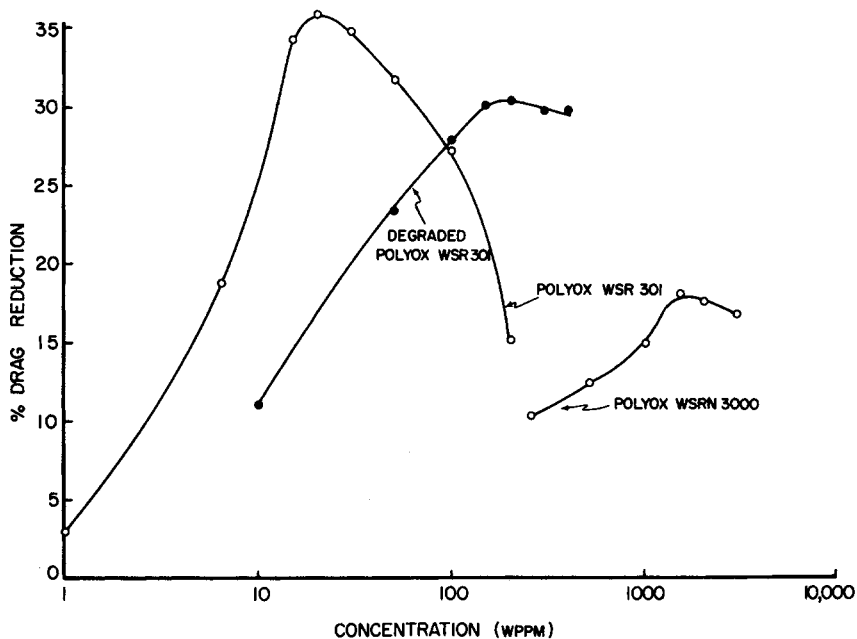


Fig. 4. Per cent drag reduction vs. concentration for three solutions of poly(ethylene oxide).

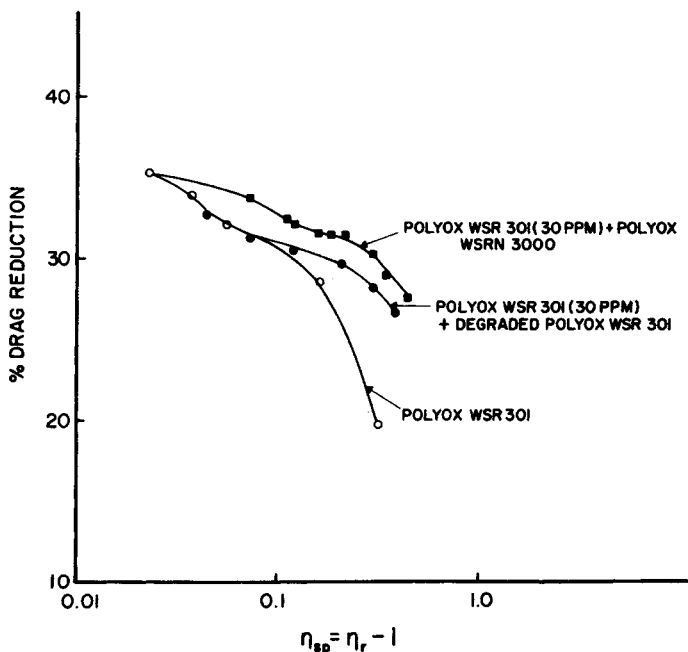


Fig. 5. Per cent drag reduction vs. specific viscosity, for various poly(ethylene oxide) solutions (see text).

particular we see that WSRN 3000 is a very inefficient drag reducer, with a limited "high molecular weight" tail.^{2,9,10} It is generally believed that the maximum in these drag reduction curves occurs as a result of the increase in solution viscosity which ultimately overwhelms the friction reduction ability of the polymer. To test this hypothesis, we have plotted per cent drag reduction for WSR 301 versus specific viscosity in Figure 5. There are three curves here,

one for fresh WSR 301, one for WSR 301 where degraded WSR 301 (Fig. 4) was substituted for fresh WSR 301 once the concentration C_{\max} was reached, and one where WSRN 3000 was added to the WSR 301 once C_{\max} was reached. In light of the fact that the highest molecular weight species (HMWS) are preferentially degraded in a shear field, with little change in solution viscosity, and furthermore that these HMWS are primarily responsible for drag reduction,^{9,10} Figure 5 suggests the following picture: for concentrations below C_{\max} , the HMWS act independently of one another, leading to high levels of drag reduction; above C_{\max} , however there is an excess of HMWS, which entangle and interfere with one another, reducing overall drag reduction efficiency. As Figure 5 indicates, eliminating some of these HMWS through degradation for $C > C_{\max}$ may actually increase the drag reduction exhibited by the solution.

CONCLUSIONS

1. Both poly(acrylic acid) and polyacrylamide are most effective as drag reducers at high pH levels, where the polymers assume compact but flexible and easily extended conformations. The highly extended "stiff" conformation, which occurs at intermediate pH values, is only slightly less effective. At low pH levels, where the polymers are presumably in helical or partially helical conformations, the drag-reducing ability is significantly less, particularly for poly(acrylic acid).

2. The maximum in a plot of per cent drag reduction versus concentration appears to occur as a consequence of as yet ill-defined intermolecular interactions between the highest molecular weight species in a given polymer sample, rather than being due to viscosity effects.

3. The vortex inhibition concentration of PAA and PAM as a function of pH was found to vary precisely as the drag-reducing ability of these solutions, offering further evidence that vortex inhibition and turbulent drag reduction are due to the same viscoelastic mechanism.

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