

## NOTES

*Effect of Secondary Polymer Structure on the Drag-Reducing Phenomenon*

The reduction of turbulent drag by the addition of high molecular weight polymer molecules to a solvent has been a subject of much research interest since Fabula<sup>1</sup> called attention to the published results of Toms<sup>2</sup> on the flow of moderately concentrated solutions of poly(methyl methacrylate) in monochlorobenzene. Subsequent work (e.g., White<sup>3</sup>) has shown that even extremely dilute solutions, as low as 0.5 wppm, are effective in reducing turbulent friction. As a consequence, this phenomenon is of considerable engineering interest.

Correlations of drag reduction behavior have been proposed by Elata et al.,<sup>4</sup> Metzner and Seyer,<sup>5</sup> Wells,<sup>6</sup> and others.<sup>7</sup> Molecular arguments, predicting the onset of drag reduction, have been advanced by Astarita,<sup>8</sup> Hershey and Zakin,<sup>9</sup> Patterson and Zakin,<sup>10</sup> Walsh,<sup>11</sup> and Virk et al.<sup>12</sup> These arguments are based on molecular theories which are strictly applicable only under theta conditions, where there are no preferential interactions among solution species. Experimental investigations have, however, disclosed an effect due to solvent. Some polymers are found to be better drag reducers in "good" solvents, where the chain is highly solvated and extended, than in "poor" solvents, where the molecule tends to collapse to a small domain volume.<sup>9,13</sup> Liaw<sup>14</sup> has demonstrated the importance of chain flexibility, showing that the more flexible polymers tend to be better drag reducers.

To date, little attention has been paid to the effects of secondary molecular structure on the drag-reducing phenomenon. This note reports the results of an experimental study of the system poly(acrylic acid)-water which is known to undergo a second-order phase transition upon variation in solvent environment.

## MATERIALS AND EXPERIMENTAL PROCEDURE

Poly(acrylic acid) was obtained from the Dow Chemical Co. (Experimental product NC 1183.1). Viscosity-average molecular weight, determined in 2.0M NaOH, was found to be  $4.6 \times 10^6$ , using the relation<sup>15</sup>:

$$[\eta] = (4.22 \times 10^{-4}) \bar{M}_v^{0.64}. \quad (1)$$

The polymer was used unfractionated, as received.

The basic apparatus is a single-pass, gas-driven capillary flow device. Polymer solution is mixed to the desired concentration and pH in the holding tank. The pH is measured with a Beckman pH meter. The tank is then sealed and pressurized with nitrogen to a desired value in the range 0-160 psig. Pressure at the entrance to the capillary is measured with Bourdon tube pressure gauges, while the exit pressure is atmospheric. The method of data analysis neglects inlet and exit pressure losses, which can be shown to be small. Polymer solution flows through a stainless steel capillary tube with internal diameter 0.0460 in. and length 50 in., is collected, and the time required to pass 1 liter of solution is measured with a phototransistor system.

Data are presented in the usual engineering fashion as a plot of the logarithm of the dimensionless friction factor,  $f$ , defined as

$$f = (2D(\Delta P/L))/\rho \bar{v}^2 \quad (2)$$

where  $D$  = capillary diameter,  $\Delta P$  = pressure difference between the ends of the capillary,  $L$  = capillary length,  $\rho$  = solution density, and  $\bar{v}$  = average solution velocity, against the logarithm of the Reynolds number,  $Re$ , defined as

$$Re = D\bar{v}\rho/\mu \quad (3)$$

where  $\mu$  = solution viscosity.

In all cases reported here, polymer concentration was 25 wppm. The properties  $\rho$  and  $\mu$  of the solutions are assumed to be those of the solvent (1.00 g/cc and 0.89 cp at test conditions of 25°C). In this case, any deviation of the  $f(Re)$  curves below that for pure solvent implies a reduction of pumping requirement.

## RESULTS AND DISCUSSION

**Calibration.** The system is first calibrated with distilled water. Results, shown in Figure 1 for a number of capillary tubes of different diameter, indicate excellent agreement with the relationships

$$f = 64/Re; \quad 0 < Re \lesssim 2400 \quad (4)$$

which is exact for laminar flow, and

$$f = 0.0056 + 0.5/Re^{0.32}; \quad 2400 \lesssim Re \quad (5)$$

which is a turbulent flow correlation for smooth tubes presented by Foust et al.<sup>16</sup> Transition from laminar to turbulent flow occurs at a Reynolds number of about 2400. The data can be reproduced to within  $\pm 5\%$ , except at very low Reynolds number ( $Re < 1000$ ) where pressure regulation is a problem.

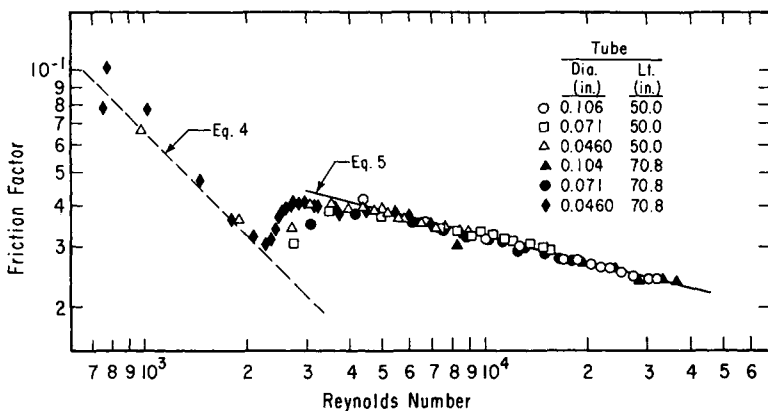


Fig. 1. Calibration of experimental apparatus with distilled water.

**Poly(acrylic acid).** Results for the PAA-water system are shown in Figures 2a and 2b as a function of pH. At 25 wppm, the untreated solution has a pH of 5.01. A small amount of drag reduction is observed at this pH, as the data fall slightly below the curve for distilled water. Transition to turbulence is observed to begin at a Reynolds number of 2100, below the value for distilled water.

The pH is raised by the addition of concentrated NaOH solution until a pH of 9.00 is reached. In such a basic solution, the polymer is completely ionized and highly extended and behaves as a rigid rod.<sup>17</sup> A slight increase in drag reduction is observed, contrary to previously reported results on this system.<sup>18</sup> Transition from the laminar regime is observed at a Reynolds number of 2500.

As the pH is lowered below 5 by the addition of concentrated HCl solution, the material abruptly becomes an effective drag reducer between pH 3 and pH 2.8. Mathieson and McLaren<sup>19</sup> have shown that near this pH, PAA undergoes a second-order phase

transition from extended rod to a more compact structure, suspected to be helical. We therefore infer that this second structure of PAA is an effective drag reducer.

Data at pH 2.77 and pH 2.90 (Fig. 2b) indicate that transition is delayed to a Reynolds number of 3000, at which a normal transition appears to begin but is never fully accomplished. A region of drag reduction develops at slightly higher Reynolds num-

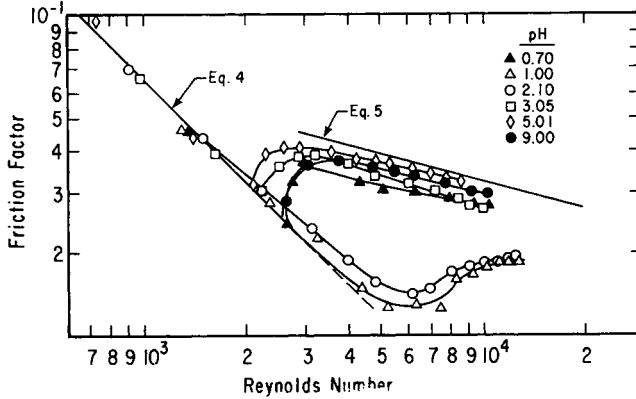


Fig. 2a. Limiting drag reduction behavior at low and high pH.

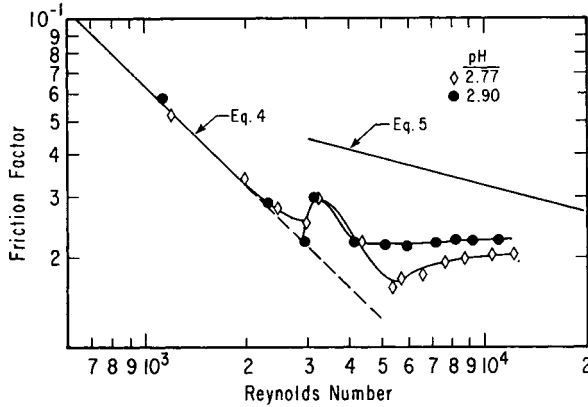


Fig. 2b. Drag reduction at intermediate pH.

bers, leading to a highly unusual  $f(Re)$  curve with a dramatic maximum-minimum character.

As pH is lowered further, the normal turbulent transition disappears completely and is replaced by a gradual departure from the laminar flow line. In pH 1 solution, the flow is still effectively laminar at a Reynolds number of 5500.

Hershey and Zakin<sup>9</sup> have shown the existence of two types of drag reduction curves. In one case, a normal transition to turbulence appears, followed by an onset of turbulence suppression. In the other case, laminar flow is maintained to a high Reynolds number, followed by a return to turbulence. This study shows the existence of both types of drag reduction with the "same" material and serves to demonstrate the sensitivity of the phenomenon to details of polymer secondary structure.

When the hydrogen ion concentration is increased still further, the material ceases to be a highly effective drag reducer near  $[H^+] = 0.2M$ .

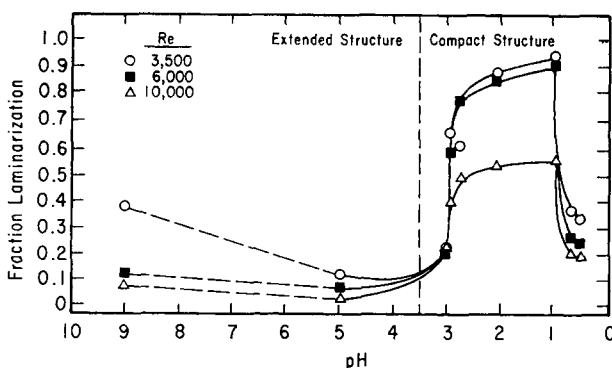


Fig. 3. Influence of pH on the fraction laminarization at various Reynolds numbers.

A more graphic illustration of the behavior of this system may be seen in Figure 3 where the fraction laminarization, defined as

$$F.L.(Re) = \frac{f_{\text{turbulent}} - f}{f_{\text{turbulent}} - f_{\text{laminar}}}, \quad (6)$$

is plotted as a function of pH, with Reynolds number as a parameter. Here,  $f$  is determined experimentally, and  $f_{\text{lam}}$  and  $f_{\text{turb}}$  are given by eqs. 4 and 5, respectively.

Mathieson and McLaren<sup>9</sup> suggest that PAA precipitates in the region of pH 2. To test if this phenomenon is influencing the measurements of this study, we have observed the flow behavior, at constant pressure drop, of a solution adjusted to pH 2. Over a period of 36 hr, no observable changes in the drag-reducing properties of the solution were detected. Furthermore, no visible evidence of precipitation could be detected.

This does not preclude the possibility of formation of a stable dispersion of gel-like polymer particles. The system dynamics would then resemble, qualitatively, the flow of dusty gases as discussed by Saffman,<sup>20</sup> in which an increased stability of the laminar regime is noted. The theoretical analysis of the gas-solid particle problem would probably have to be reformulated to account for elasticity of the suspended polymeric solids and the relatively small density difference between solution and solid.

## CONCLUSION

We believe the evidence presented in this study clearly indicates the importance of the secondary structure of the polymer molecule in determining the effectiveness of a drag-reducing material. Work is continuing on further analysis of this phenomenon toward the goal of molecular engineering of an optimum additive.

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