

## The Effect of Added Salt on the Flow of Highly Dilute Solutions of Poly(ethylene Oxide) Polymers

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### Synopsis

Early transition, early turbulence, and drag reduction were detected in flowing solutions of high molecular weight poly(ethylene oxide) condensates. Progressive addition of salt (magnesium sulfate) increased the onset point characterizing deviations from Newtonian flow for 1 ppm Polyox Coagulant solutions and eliminated early transition in the 10 ppm WSR-35 solutions. No further drag reduction was observed when the salt molarity reached the 0.65 level. In the Coagulant solutions the onset wall shear stress characterizing the flow deviation was an inverse function of the intrinsic viscosity of the polymer in the salt solution.

### INTRODUCTION

Recent experiments with flowing solutions of a high molecular weight poly(ethylene oxide) polymer ( $MW = 7.0 \times 10^6$ ) have demonstrated the existence of early turbulence below the natural laminar-to-turbulent transition point in a 0.1575-cm capillary flow tube.<sup>1</sup> An attempt was made in the cited report to connect the effects of the flow disturbances detected in the laminar regime with the drag reduction effect observed in the turbulent regime. A reasonable connection was found when it was observed that the flow line initiated in the laminar flow zone as a result of flow disturbances proceeded with virtually no change in slope well into the turbulent flow regime. It was then conjectured that the same polymer segmental motions or oscillations responsible for the generation of early turbulence in the apparatus were also operative in drag reduction (defined here as a lowering of the wall shear stress at constant flow rate upon addition of polymer).

In order to further test the thesis that the early turbulence generation observed in the laminar regime and the turbulence damping phenomenon observed in the turbulent regime were closely related phenomena, it was decided to observe the effect of added salt on the flow of poly(ethylene oxide) solutions. Such experiments would affect the configuration of poly(ethylene oxide) molecules in that the end-to-end distance of these polymer molecules would be decreased with progressive addition of salt. Decreases in end-to-end distance would obviously diminish the supposed tendency of the molecules to aggregate under flow conditions<sup>2</sup> and also decrease the viscoelastic properties of the polymer solution. While the literature contains

some evidence that the presence of salts has virtually no effect on the degree of drag reduction observed,<sup>3,4</sup> the intrinsic viscosity of a given polymer solution is known to change quite drastically with added salt.<sup>5</sup> It may therefore be instructive to carefully catalog the effect of added salt on highly dilute poly(ethylene oxide) solutions in order to resolve this apparent flow anomaly.

### EXPERIMENTAL

Samples of Polyox Coagulant and WSR-35 were obtained from the Union Carbide Corporation. Their intrinsic viscosities were previously determined<sup>2</sup> as 22.6 and 2.81, respectively, corresponding to molecular weights of  $7.0 \times 10^6$  and  $4.8 \times 10^5$  using the intrinsic viscosity-molecular weight relationship of Shin.<sup>4</sup> The magnesium sulfate used was of reagent-grade quality (Baker Chemical Co.). The preparation and treatment of solutions together with their use in the specially constructed turbulent flow rheometer is described elsewhere.<sup>1,6</sup> In brief, however, the flow apparatus was completely automated in design and operation. The flow pipe used was a 0.1575-cm Pyrex capillary tube, the first tap being located 200 diameters from the entrance and the second tap, 100 diameters from the first. Solutions were prepared with a minimum of agitation, stored at 6°C, and used as soon as practicable, usually within four days of preparation.

### RESULTS

The influence of magnesium sulfate molarity is shown graphically in Figures 1 to 4 for 1-ppm solutions of Polyox Coagulant. The onset point for early turbulence progressively increases from 80 dynes/cm<sup>2</sup> in pure water to 160 dynes/cm<sup>2</sup> in 0.4M MgSO<sub>4</sub>. In the 0.5M salt solution, the onset point is advanced to the laminar-to-turbulent transition region. Progressive addition of salt even increases the onset point into the fully turbulent region where the flow deviation is manifested as a drag reduction

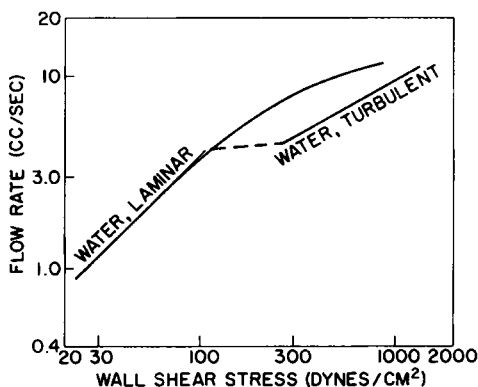


Fig. 1. Flow of 1 ppm coagulant in water.

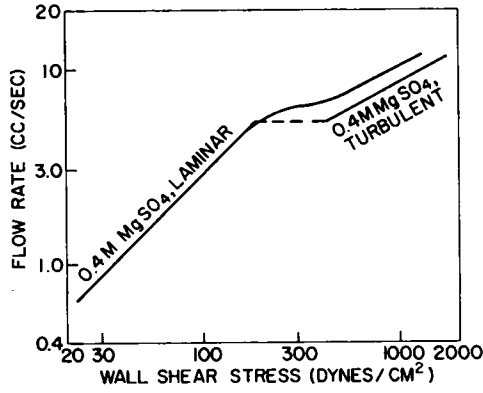


Fig. 2. Flow of 1 ppm coagulant in 0.4M magnesium sulfate.

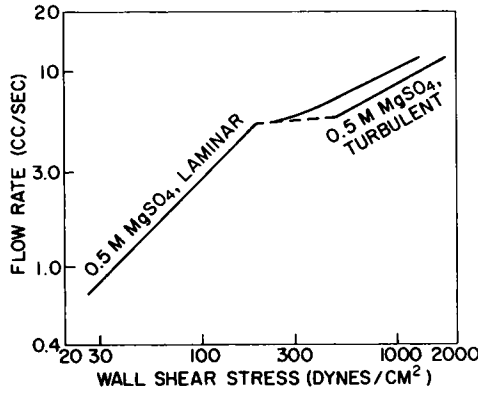


Fig. 3. Flow of 1 ppm coagulant in 0.5M magnesium sulfate.

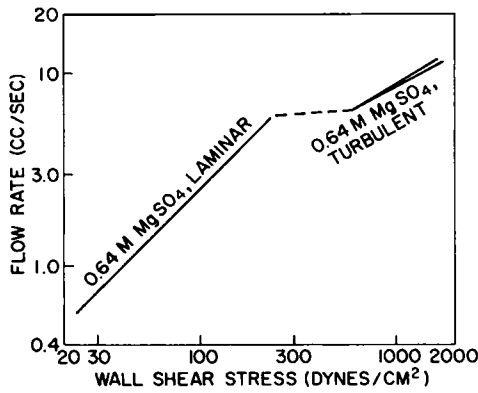


Fig. 4. Flow of 1 ppm coagulant in 0.64M magnesium sulfate.

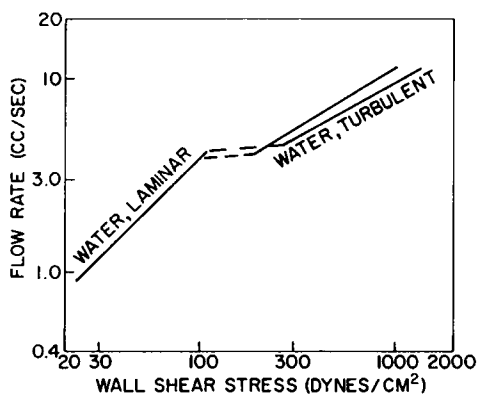


Fig. 5. Flow of 10 ppm WSR-35 in water.

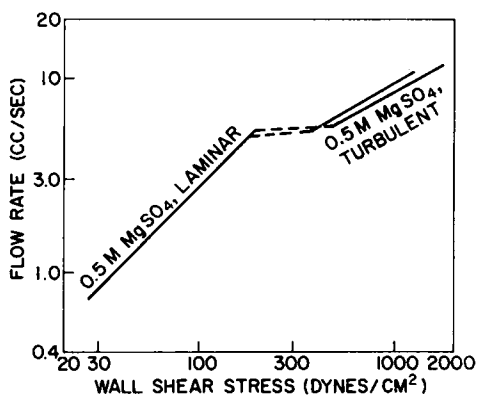


Fig. 6. Flow of 10 ppm WSR-35 in 0.5M magnesium sulfate.

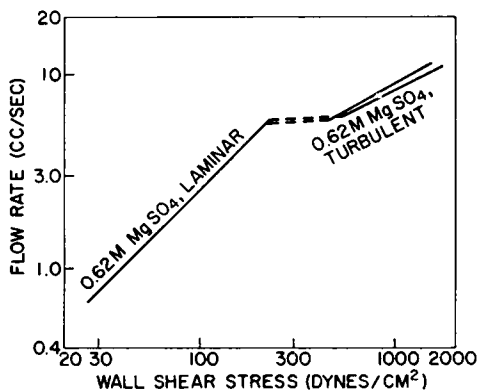


Fig. 7. Flow of 10 ppm WSR-35 in 0.62M magnesium sulfate.

effect. Further additions of salt beyond the 0.64*M* level, however, completely nullify the drag reduction effect within the experimental range of the apparatus (although drag reduction may perhaps persist at flow rates above 16 cc/sec ( $N_R = 13,000$ ) level, the present limit of observation).

Figures 5 to 7 show a somewhat different effect for 10 ppm WSR-35 in a similar series of salt solutions. These solutions do not show early turbulence (although concentrations of 25 ppm or greater do). They do, however, manifest an early transition which is decreasingly depressed below that for the solvent as the salt molarity increases. As the salt concentration continues to increase, the extent of drag reduction also decreases as evidenced by the closer drawing together of solution and solvent flow lines in the turbulent region. Finally, at a salt concentration of 0.65*M* MgSO<sub>4</sub>, no further drag reduction is observed within the experimental range of the apparatus.

## DISCUSSION

### Early Transition

While WSR-35 solutions do not show early turbulence effects in the capillary flow apparatus at the 10-ppm level as do the more dilute Coagulant solutions, they do, nonetheless, display a slightly earlier transition than that observed for the solvent as previously stated. Early transition has, however, also been observed for flowing WSR-301 solutions in larger tubes.<sup>7</sup> In this case, through the use of smooth nozzle entry and the minimizing of inlet tank disturbances, it was possible to observe a critical transition Reynolds number for distilled water in the range of 8,000 to 11,000 in a 1/4-in. tube. For the 50 ppm WSR-301 solution, on the other hand, transition consistently occurred at a Reynolds number between 2,900 and 3,300. In the present case, although less dramatically than in the cited literature work, transition occurred at Reynolds numbers of 2,700, 2,800, 2,900, and 3,000, corresponding to 10 ppm WSR-35 solutions in distilled water and 0.5*M*, 0.62*M*, and 0.65*M* MgSO<sub>4</sub>, respectively. These data compare with the natural Reynolds transition number of 3,000 for the capillary tube using distilled water. The increase in Reynolds number with increasing salt molarity reflects the decreased ability of the polymer molecules to influence the flow as their end-to-end distances decrease. The present data and those of Paterson<sup>7</sup> are therefore in opposition to Virk's results<sup>8</sup> where Polyox solutions appeared to undergo transition at higher Reynolds numbers than those observed for distilled water. Virk's tests, however, were conducted with high inlet disturbance conditions. Additionally, Virk noted that the sensitivity of the pressure-measuring apparatus used made it difficult to rigorously confirm his observations.

### Early Turbulence

The behavior of drag-reducing polymer solutions in laminar flows around circular cylinders having diameters of 0.005 and 0.006 in. has been reported

by James.<sup>9</sup> He observed increased drag at a particular Reynolds number above that observed for a Newtonian fluid at the same Reynolds number when using dilute aqueous solutions of WSR-301. He further observed that the critical Reynolds number for the increased drag decreased as the polymer concentration and molecular weight increased. This last observation bears a striking similarity to the structural turbulence results reported by Ram and Tamir<sup>10</sup> for polyisobutylene solutions in kerosene and mineral oils, where the critical Reynolds number for the observation of structural turbulence in capillary tubes also decreased as the polymer concentration and molecular weight increased. James observed in his experiments that, above the critical Reynolds number, the region of the flow field influenced by the cylinder was two to three times larger for the polymer solutions than for the Newtonian fluid (water). Below the critical Reynolds number, the cylinder flows of both polymer solution and solvent were similar.

The reported ability of dilute polymer solutions to stretch the flow field normal to the direction of shear in the vicinity of a disturbance under laminar flow conditions may have some significance in the development of early (structural) turbulence. The term "early turbulence" in the present case is to be preferred to "structural turbulence" since the former would suggest all contributory effects to laminar flow deviations, i.e., those arising from both fluid and system, while the latter would refer strictly to flow deviations arising out of fluid properties alone. Of particular interest, then, are the recent data of Ram and Tamir.<sup>10</sup> In their early turbulence experiments, using their special capillary viscometer equipped with stainless steel capillaries of varying radius,<sup>11</sup> they reported Reynolds turbulence in the Reynolds number range of 1400 to 1950 for pure kerosene. These unusually low transition Reynolds numbers—well below the value of 2,100 normally observed for Newtonian fluids—may be suggestive of flow disturbances originating within the viscometer, most probably within the stainless steel capillary tubing used. This writer has examined stainless steel hypodermic tubing down to 27 gauge (0.2 mm O.D., 0.1 mm I.D.). In all cases, spiral striations were noted on the inner walls of the tubing. Since stainless steel capillary tubing is, in general, drawn from bored tubing stock of larger diameter, it is evident that striations occurrent in the larger tube will persist into the drawn daughter tubing.

In the light of James's work,<sup>9</sup> it would appear that surface irregularities on the wall might possibly trigger early early turbulence effects within the laminar flow regime. It is not intended to harshly criticize prior work, particularly that of Ram and Tamir, but to merely point out the strong possibility that early turbulence in general may be a cooperative phenomenon involving both wall irregularities (or asperities) and the viscoelastic effects arising out of resultant changes in polymer configurations under flow. In any event, this is a subject for future research since the remarks presented here do border to some extent on the speculative side.

### Early Turbulence and Drag Reduction as Influenced by Salt Concentration

Figures 1 to 4 previously cited indicate how the onset of early turbulence or drag reduction varies with the molarity of the salt solution used. Additional data supplementing these curves demonstrate that a precise relationship apparently exists between the onset points for the flow deviations and the  $\text{MgSO}_4$  molarity, as shown in Figure 8. Here it was found that the

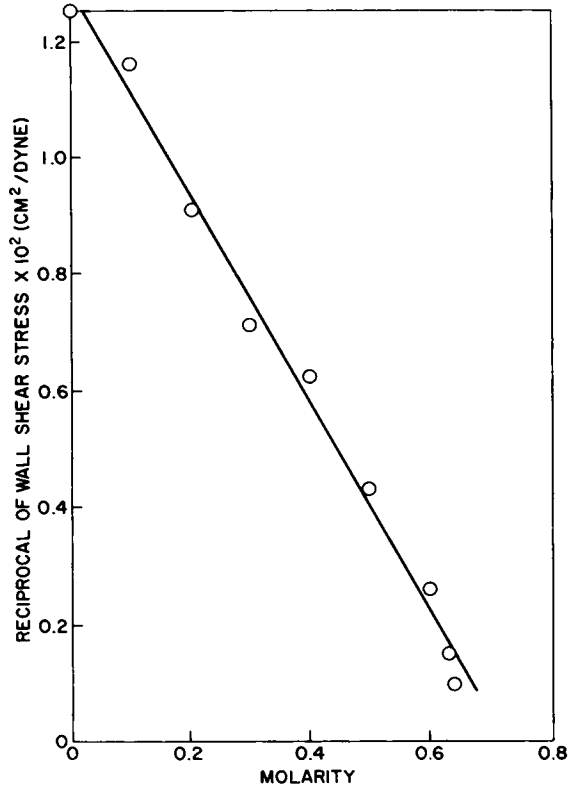


Fig. 8. Early turbulence and drag reduction onset points vs. magnesium sulfate molarity for 1 ppm Polyox Coagulant solutions.

onset wall shear stress,  $\tau_w$ , was an inverse function of the molarity, being described by the empirical relation

$$\frac{1}{\tau_w} = -1.76 \times 10^{-2}M + 1.27 \times 10^{-2}, \quad (1)$$

where  $\tau_w$  = wall shear stress and  $M$  = molarity. The increase in onset point is a function of the decreasing end-to-end distance of the polymer

molecules as the salt concentration is increased. Any tendency of polymer molecules to form aggregates under flow conditions suggested in the literature,<sup>12</sup> or most certainly the viscoelastic nature of the solution, will be diminished by the effect of salt. The effect of salt on the intrinsic viscosity of poly(ethylene oxide) solutions is well documented in the literature,<sup>5</sup> the intrinsic viscosity of these solutions decreasing linearly with increasing salt molarity. A relation between the intrinsic viscosity of the Polyox Coagulant presently used and the  $\text{MgSO}_4$  molarity may therefore be described by the relation

$$[\eta] = -31.6M + 22.6. \quad (2)$$

If one combines the two relations, the onset wall shear stress for the deviation from Newtonian behavior—be it early turbulence or drag reduction in the present case—is expressed as a function of the intrinsic viscosity of the given Polyox Coagulant–salt solution system, i.e.,

$$\tau_\omega \times [\eta] = 1780. \quad (3)$$

It is of interest to note that Fabula, Lumley, and Taylor<sup>13</sup> have recently proposed a molecular viscoelasticity hypothesis for drag reduction by appropriate combination of narrow-band deformation frequency considerations of tumbling macromolecules in the viscous sublayer and the relaxation time of polymer molecules from Rouse-Zimm theory. They obtained the relation

$$\tau_\omega = \frac{RT}{100a_1[\eta]m} \times \frac{\eta}{\eta_s} \quad (4)$$

where  $R$  = gas constant,  $T$  = absolute temperature,  $a_1$  = constant =  $1/2$ ,  $[\eta]$  = intrinsic viscosity,  $\eta$  = solution viscosity,  $\eta_s$  = solvent viscosity, and  $m$  = molecular weight. For dilute solutions, as in the present case,  $\eta/\eta_s = 1$ . Evaluation of their relation for the Polyox Coagulant–water system leads to the simple numerical relation

$$\tau_\omega \times [\eta] = 83. \quad (5)$$

Assuming a degree of equivalency in the onset data for early turbulence and drag reduction in the experimental relation, suggested both by the present data and the literature,<sup>1,13</sup> it is possible to compare eqs. (3) and (5). Comparison indicates a difference somewhat in excess of one order of magnitude in the two numerical constants. Again, using a somewhat different path, that is, through use of a single polymer with a series of solvents ranging from good to poor rather than a homologous series of polymers, a separate demonstration of the failure of molecular theories<sup>14,15</sup> to account for the observed drag reduction effect in terms of a molecular relaxation time hypothesis is noted. Fabula et al.<sup>13</sup> reported that their relation failed to follow the experimental plot of onset wall shear stress versus molecular properties (radius of gyration in this case) but appeared to give an approximate order of magnitude value for the onset point in some cases.



However, it should be pointed out that their relation<sup>13</sup> deviates nearly an order of magnitude from the observed data for a compound with a radius of gyration equal to that of the present coagulant sample ( $R_G = 2600 \text{ \AA}$  using Shin's relation<sup>4</sup>). This deviation rapidly increases with increasing molecular weight (or  $R_G$ ). One must therefore conclude, as have others, that either a molecular entanglement mechanism<sup>13</sup> or an elongational viscosity effect<sup>16</sup> is the most probable operative factor in the drag reduction phenomenon.

### References

1. R. C. Little and M. Wiegard, *J. Appl. Polym. Sci.*, **14**, 409 (1970).
2. R. J. Hansen and R. C. Little, *A.I.Ch.E. Symp. Series, Drag Reduction*, **67**, 93 (1971).
3. W. D. White, in *Viscous Drag Reduction*, C. S. Wells, Ed., Plenum Press, New York, 1969, p. 173.
4. H. Shin, Sc.D. Thesis, Massachusetts Institute of Technology, 1965.
5. F. E. Bailey, Jr., and R. W. Callard, *J. Appl. Polym. Sci.*, **1**, 56 (1959).
6. H. R. Baker, R. N. Bolster, P. B. Leach, and R. C. Little, *Ind. Eng. Chem., Prod. Res. Develop.*, **9**, 541 (1970).
7. R. W. Paterson, Ph.D. Thesis, Harvard, 1969.
8. P. S. Virk, E. W. Merrill, H. S. Mickley, K. A. Smith, and E. L. Mollo-Christensen, *J. Fluid Mech.*, **30**, 305 (1967).
9. D. F. James, Ph.D. Thesis, California Institute of Technology, 1967.
10. A. Ram and A. Tamir, *J. Appl. Polym. Sci.*, **8**, 2751 (1964).
11. A. Ram and A. Tamir, *Ind. Eng. Chem.*, **56**, 47 (1964).
12. A. G. Fabula, Ph.D. Thesis, Pennsylvania State University, 1966.
13. A. G. Fabula, J. L. Lumley, and W. D. Taylor, in *Modern Developments in the Mechanics of Continua*, Academic Press, New York, 1966, p. 145.
14. P. E. Rouse and K. Sittel, *J. Appl. Phys.*, **24**, 690 (1953).
15. B. H. Zimm, *J. Chem. Phys.*, **24**, 690 (1953).
16. A. B. Metzner, A.I.Ch.E. Symp. Drag Reduction (Invited Lecture), Atlanta, Ga., February 1970.

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