# Turbulent Friction Reduction by Aqueous Poly(ethylene Oxide) Polymer Solutions as a Function of Salt Concentration

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## Synopsis

Turbulent friction reduction by high molecular weight poly(ethylene oxide) polymers has been examined in a series of salt solutions ranging from pure water to nearly theta solvent conditions. The effects of polymer homology and solvent character have been successfully analyzed under these conditions and relationships are proposed for the observed effects. The reduction in turbulent friction (drag reduction) has been catalogued through evaluation of the polymer intrinsic concentration—an index of drag reduction effectiveness. Plots of the reciprocal of the polymer intrinsic concentration versus salt molarity are approximately linear and are similar to the plots of intrinsic viscosity versus molarity reported by other workers. An attempt is made to graphically and numerically combine these results. The suggestion is advanced that those solvent properties which bring about decided conformational changes in these polymer molecules (as indexed by intrinsic viscosity effects) also affect, in an apparently analogous fashion, the turbulent friction reduction efficiencies of these molecules. The decreases in turbulent friction reduction resulting from the increasingly collapsed state of the polymer coil suggest the possibility of correlating friction reduction with changes in the polymer expansion factor $\alpha$. On the basis of the limited data available, the suggestion is also made that drag reduction studies might best be made under theta solvent conditions where different polymer families might be more meaningfully compared in the absence of solvent effects.

## INTRODUCTION

Turbulent friction reduction (drag reduction) may be defined as that effect which takes place when the rate of flow of a fluid at constant pressure is increased upon the addition of a polymeric or colloidal additive (generally in amounts insufficient to cause large changes in the viscosity of the fluid). While the mechanism underlying the drag reduction phenomenon is not completely understood, it is well known that the most efficient additives have been soluble, linear, high molecular weight polymers. Solvent power was also shown to be an important factor in the observed drag reduction in earlier studies of Hershey and Zakin[1] who observed 40% less drag reduction for polyisobutylene in a poor solvent (benzene) than in a good solvent (cyclohexane). The per cent drag reduction of polystyrene was also observed in a variety of nonpolar liquids of varying solvent power, where it was again found that drag reduction was better in good solvents than in poor ones.[2]

The effect of salt concentration on the drag reduction of aqueous solutions of nonionic polymers such as the poly(ethylene oxides) has been briefly discussed in the literature,[3,4] and it has been generally concluded that the presence of salt has little or no effect on the observed drag reduction. While this may be true for salt concentrations such as those occurring in sea water, it cannot be true for higher salt concentrations or for salts such as potassium carbonate or sulfate, which are known to have strongly depressant effects on the intrinsic viscosity and the precipitation temperature of poly(ethylene oxide).[5] The nonsolvent effect of salt can therefore be expected to reduce the drag reduction effect just as in the case of the nonaqueous systems.

The only extensive work done on the effect of a salt upon the drag reduction of high molecular weight polymers appears to be that of Pruitt, Rosen, and Crawford.[6] These authors attempted to analyze their drag reduction data by devising a correlation in terms of the exponent a in the Mark-Houwink relation $[\eta] = KM^a$. The drag reduction $(DR)$ of three poly-(ethylene oxide) polymers was examined in water and five potassium sulfate solutions ranging from 0.1 molar to 0.8 molar. In specific, they proposed the relation

$$\frac{DR}{(DR)_w} = \frac{a - 0.5}{a_w - 0.5}$$

(where the subscript $w$ refers to water) to account for the observed effect. Thus by noting the observed drag reduction in water and evaluating the exponent by intrinsic viscosity determinations of the family in a given salt solution, one could compute the drag reduction in the salt solution. However, there are several quite relevant criticisms apropos to their analysis. First of all, they assumed that $K$ in the Mark-Houwink equation was a constant, whereas it actually varies from $1.25 \times 10^{-4}$ in water to $1.3 \times 10^{-3}$ under theta conditions. Thus, the values of the exponent $a$ as calculated are incorrect. Secondly, while these authors determined intrinsic viscosities in distilled water at 30° C, they performed their drag reduction tests on solutions made up with tap water. Thirdly, the mixing methods used in solution preparation were poorly defined. The use of tap water and poorly defined mixing methods has been shown to greatly reduce the validity of the drag reduction results, particularly for dilute polymer solutions.[7,8] Thus, while the reported results are qualitatively correct, the drag reduction information should be considered somewhat suspect.

The effect of salt ($K_2CO_3$) concentration on the observed drag reduction of a poly(ethylene oxide) polymer of approximately 740,000 molecular weight has been reported in a recent article.[9] Specifically, a relationship between the intrinsic concentration of the polymer and the salt molarity was proposed. The intrinsic concentration may be thought of as an effective drag reduction index. Low values indicate highly effective agents while high values are indicative of less efficient agents. It is the purpose of the present report to amplify these recent results with additional data and to explore the effect of salt on other poly(ethylene oxide) homologs.

## EXPERIMENTAL

### Materials

The poly(ethylene oxide) polymers were obtained from the Union Carbide Corporation and were used as received. Freshly distilled water was used exclusively in preparing all solutions. Since irreproducible mixing techniques can cause large variations in solution properties, all solutions were prepared carefully by the following procedures. The additives in powder form were sprinkled uniformly over a large surface of distilled water to avoid clumping of particles. Solution was allowed to take place through diffusion at 6° C for a period of several days. Occasional gentle stirring with a glass rod ensured adequate dispersion of solute. In order to obtain the desired concentration of polymer, a stock solution of reagent-grade potassium carbonate was slowly added with gentle stirring to the required amount of polymer solution. Stock solutions of polymer were always stored at 6°C and were discarded after a two-week period.

### Methods

**Intrinsic Viscosity Determination.** The viscosity measurements were made with a Cannon 50-S400 multiple-bulb viscometer at 25°C, and the intrinsic viscosity was calculated at a shear rate of 15 sec$^{-1}$. The molecular weight $M_v$, determined from Shin's intrinsic viscosity–molecular weight relation at the same shear rate,[4] was employed to calculate the intrinsic viscosity at theta conditions using the relation of Bailey et al.,[5] i.e., $[\eta]_\theta = 1.3 \times 10^{-3} M_v^{0.5}$.

**Drag Reduction Measurements.** The apparatus used has been previously described in some detail.[10] Essentially, it was an automated version of a type previously described by Hoyt.[11] The flow pipe, however, was a Pyrex capillary tube with the first tap 200 diameters from the entrance, and the second tap 100 diameters from the first and 54 diameters from the tube exit. The tube diameter was 0.1575 cm. The pressure transducer output and the d.c. generator output (which monitored the flow rate) were converted to logarithmic signals and fed to an x–y recorder.

## RESULTS AND DISCUSSION

Figure 1 reports the drag reduction results obtained for these polymers in distilled water flowing through the system at a Reynolds number of 9,000. The results are quite similar to those previously obtained[8] and lucidly illustrate the growth of drag reduction with increasing concentration within the region below the drag reduction saturation point, i.e., that point where the maximum drag reduction asymptote is reached.[12] This region of rapid drag reduction growth is of particular importance since it allows the evaluation of the intrinsic concentration [C] of the polymer, a parameter first devised by Virk in his universal drag reduction relation.[12] Virk's relation,
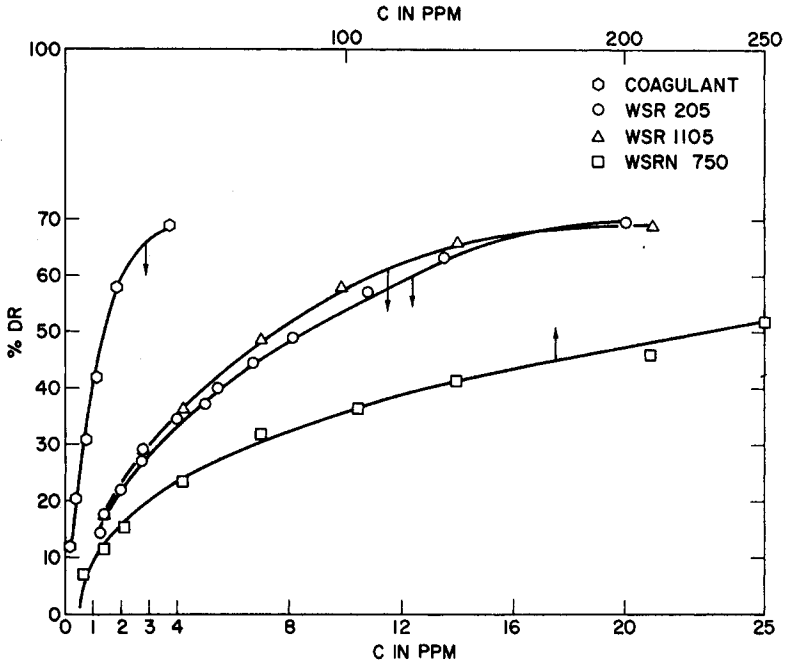
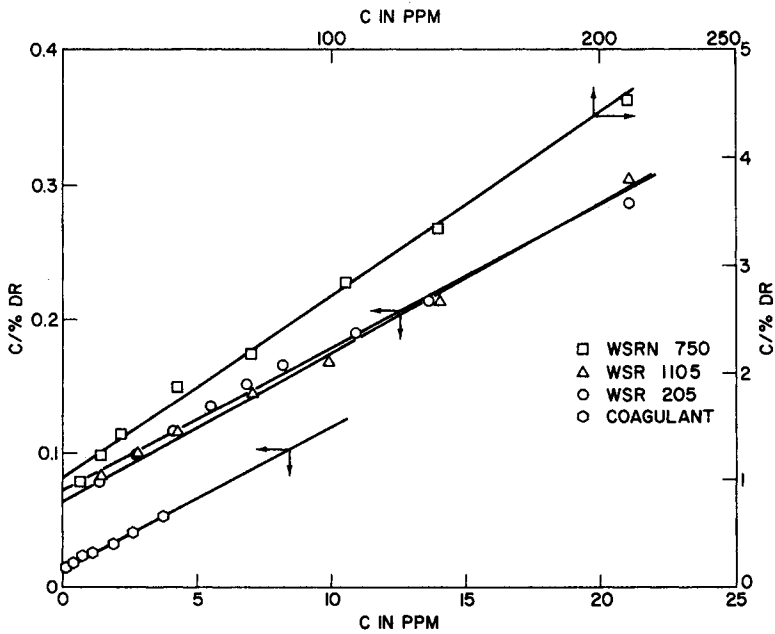Fig. 1. Per cent drag reduction vs. concentration for Polyox compounds in water.



Fig. 2. Test for conformity to eq. (1) for Polyox compounds in water.

TABLE I
Experimental Values of [C] and $DR_{max}$ in Water and Salt Solutions

| Polyox polymer | $K_2CO_3$ molarity | [C] | $DR_{max}$ |
|---|---|---|---|
| WSRN-750 | 0 | 61.7 | 60.4 |
| | 0.1 | 94.5 | 69.2 |
| | 0.3 | 126.0 | 66.7 |
| | 0.5 | 139.1 | 57.8 |
| WSR-205 | 0 | 6.89 | 91.1 |
| | 0.1 | 8.11 | 95.6 |
| | 0.3 | 10.5 | 88.5 |
| | 0.4 | 12.96 | 80.0 |
| | 0.5 | 18.53 | 89.2 |
| WSR-1105 | 0 | 6.01 | 90.5 |
| | 0.1 | 7.07 | 97.9 |
| | 0.3 | 10.04 | 99.0 |
| | 0.5 | 17.55 | 106.4 |
| Coagulant | 0 | 1.67 | 106.3 |
| | 0.1 | 1.78 | 104.0 |
| | 0.3 | 3.19 | 120.0 |
| | 0.4 | 3.05 | 109.6 |
| | 0.5 | 3.37 | 81.3 |

however, can be more meaningfully arranged in a form which is somewhat more useful for the analysis of experimental data,[8] as follows:

$$\frac{DR}{DR_{max}} = \frac{C}{[C] + C} \tag{1}$$

where $DR$ is the observed drag reduction, $DR_{max}$ is the maximum drag reduction obtainable at the specified flow rate, $C$ is the concentration in ppm, and $[C]$ is the intrinsic concentration.  Plots of $C/DR$ versus $C$ are linear if eq. (1) is obeyed.  The reciprocal of the slope provides a value for $DR_{max}$, while the intrinsic concentration is obtained from the intercept divided by the slope.

An appropriate test of this equation is provided by Figure 2.  Here, the drag reduction data for all four compounds have been plotted in this manner by the method of least squares.  In each case, conformity to the equation is excellent.  However, such plots may also be used for those same polymers in salt solutions of increasing strength.  Figure 3 shows the results obtained for WSR 205 in water, 0.1, 0.3, 0.4, and 0.5 molar potassium carbonate solution.  Again, agreement is excellent; Table I is a collection of the determined constants.  It is obvious from Table I that increasing salt concentrations cause increases in the value of the intrinsic concentration; this is indicative of less efficient drag reduction behavior.

Figure 4 summarizes all of the intrinsic concentration data for the four compounds on a single graph.  It was found that the reciprocal of the intrinsic concentration was virtually a linear function of the salt molarity.

TABLE II
Experimental Constants for Equations (2) and (3)

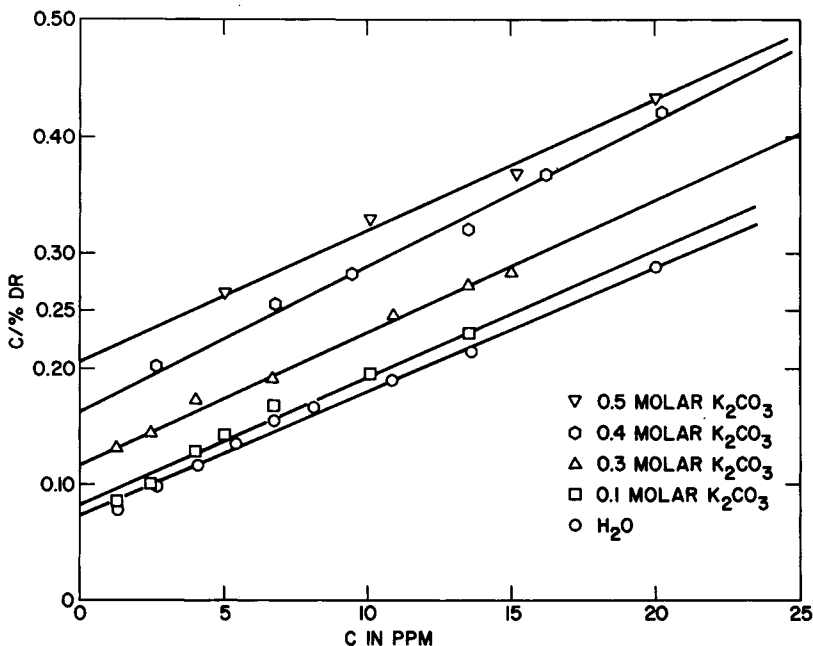| Polymer | $[C]_{H_2O}$, ppm | $M'$, m/l. | $[\eta]_{H_2O}$, dl/g | $M''$, m/l. |
|---|---|---|---|---|
| WSRN-750 | 65.8 | 0.752 | 3.69 | 0.735 |
| WSR-205 | 6.94 | 0.832 | 3.90 | 0.730 |
| WSR-1105 | 6.06 | 0.764 | 4.30 | 0.719 |
| Coagulant | 1.68 | 0.881 | 12.5 | 0.640 |



Fig. 3. Test of eq. (1) for WSR-205 in a series of salt solutions.

Simple analysis revealed that these relations could be easily summarized by an equation of the type

$$\frac{1}{[C]} = \frac{1}{[C]_{H_2O}} \left( 1 - \frac{M}{M'} \right) \tag{2}$$

where $[C]_{H_2O}$ refers to the water value, $[C]$ is the value in a salt solution of molarity $M$, and $M'$ is the molarity at $[C] = \infty$, an analytical convenience. Literature data obtained for the poly(ethylene oxide) family suggest that the effect of salts on the intrinsic viscosity data of these polymers may also be conveniently expressed as a linear function of salt molarity. In the present work, the expression

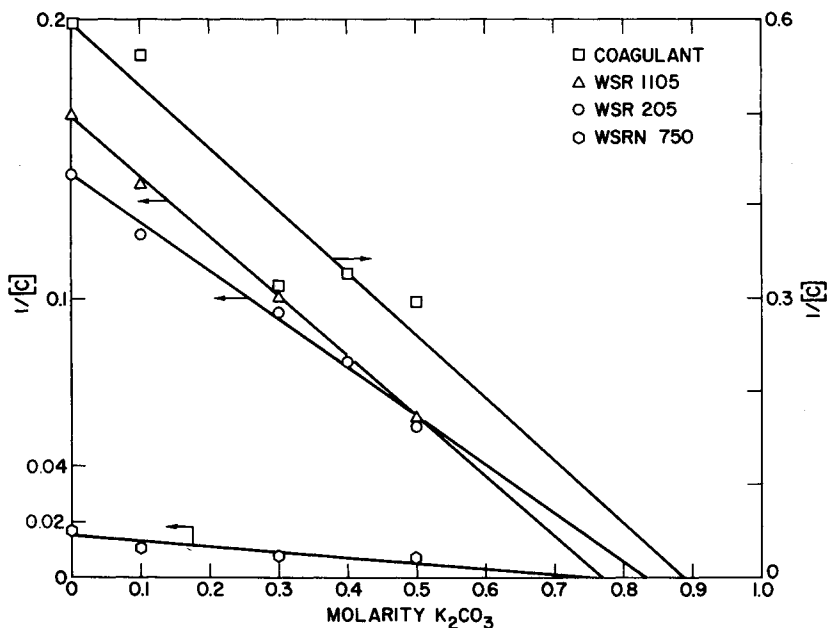$$[\eta] = [\eta]_{H_2O} \left( 1 - \frac{M}{M''} \right) \tag{3}$$

Fig. 4. Reciprocal of intrinsic concentration vs. salt molarity for Polyox compounds.

successfully describes the trend where $M''$ is the molarity at which $[\eta] = 0$ (an analytical convenience as before). The resemblance of this equation to the prior one is obvious. Table II summarizes the data which were obtained for each polymer in terms of constants of these analytic expressions.

Equations (2) and (3) may be easily combined in an attempt to express $[C]$ as a function of $[\eta]$ as follows:

$$([\eta] + A)[C] = B \tag{4}$$

where

$$A = \frac{(M' - M'')[\eta]_{\mathrm{H_2O}}}{M''}$$

and

$$B = \frac{M'}{M''}\,[\eta]_{\mathrm{H_2O}}[C]_{\mathrm{H_2O}}.$$

It is clear that when $M' = M''$, the relation simply reduces to

$$[\eta][C] = [\eta]_{\mathrm{H_2O}}[C]_{\mathrm{H_2O}}. \tag{5}$$

This relation suggests an interesting new avenue in the characterization of drag-reducing polymers in various solvent systems; that is, if

$$[\eta]_\theta[C]_\theta = [\eta][C]$$

then

$$[C] = [C]_\theta\,\frac{[\eta]_\theta}{[\eta]} = \alpha^{-3}[C]_\theta \tag{6}$$

TABLE III
Comparison of Equations (4) and (5)

| Compound | $A$ | $B^a$ | $[\eta]_{H_2O}[C]_{H_2O}$ | $[C]_\theta$ eq. (4) | $[C]_\theta$ eq. (5) |
|---|---|---|---|---|---|
| WSRN-750 | 0.085 | 248 | 243 | 214 | 225 |
| WSR-205 | 0.550 | 30.9 | 27.1 | 18.5 | 24.2 |
| WSR-1105 | 0.268 | 27.7 | 26.1 | 19.0 | 21.9 |
| Coagulant | 4.83 | 28.9 | 20.8 | 40.0 | 8.81 |

$^a$ $B$ values are in mixed units of dl/g $\times$ ppm. They may be made dimensionless by multiplying by $10^{-4}$, assuming density of water is 1 in order to convert ppm to g/dl.

where $\alpha$ is the polymer expansion factor. This would then imply that one need only characterize a given polymer under theta solvent conditions. Drag reduction research in other solvent systems might, in principle, merely be accomplished through use of a viscometer. Such a relationship would also suggest the apparent importance of the volume occupied by the polymer molecule in solution as a distinct factor in the drag reduction effect which was proposed in earlier work.[7,8]

In general, eq. (4) was obeyed rather than eq. (5) proposed in earlier preliminary work.[9] However, the WSR 1105 and the WSRN-750 data come fairly close to following the latter equation, since in this case $M' \cong M''$ (see Table II). Table III summarizes the predicted values for theta solvent conditions using the experimental relation, eq. (4), and eq. (5). Theta solvent condition, of course, represents the greatest mismatch between results estimated from experiment and the prediction of eq. (5). Except for the case of coagulant, the agreement is somewhat tolerable. It appears certain that shear degradation effects become important in the capillary tube equipment at Re = 9,000, since shear stresses of the order of 400 to 1300 dynes/cm$^2$ are involved dependent upon the degree of drag reduction. In the case of molecular weights in excess of several million, degradation effects might be substantial.[13] The plots of intrinsic viscosity and intrinsic concentration versus salt molarity appear to be consistent with this view, since a higher intercept value was noted in the intrinsic concentration data than in the intrinsic viscosity data, as shown in Table II.

The intrinsic concentration data may also be plotted as a function of $[\eta]/[\eta]_\theta$ as shown in Figure 5 for the WSR-205 data. The log–log plot of the data is reasonably linear, and from it an empirical equation of the form

$$[C] = [C]_\theta \left(\frac{[\eta]}{[\eta]_\theta}\right)^n$$

is easily devised. This is, of course, a patched-up version of eq. (5), but with the redeeming virtue of expressing the mismatch in terms of the exponent; that is, if eq. (5) is obeyed by the data, the exponent is of course $-1$. Exponent values for the four compounds investigated are as follows: WSRN-750, $-0.960$; WSR-205, $-0.772$; WSR-1105, $-0.884$; coagulant, $-0.64$. All of the plots were linear over the entire range from water to
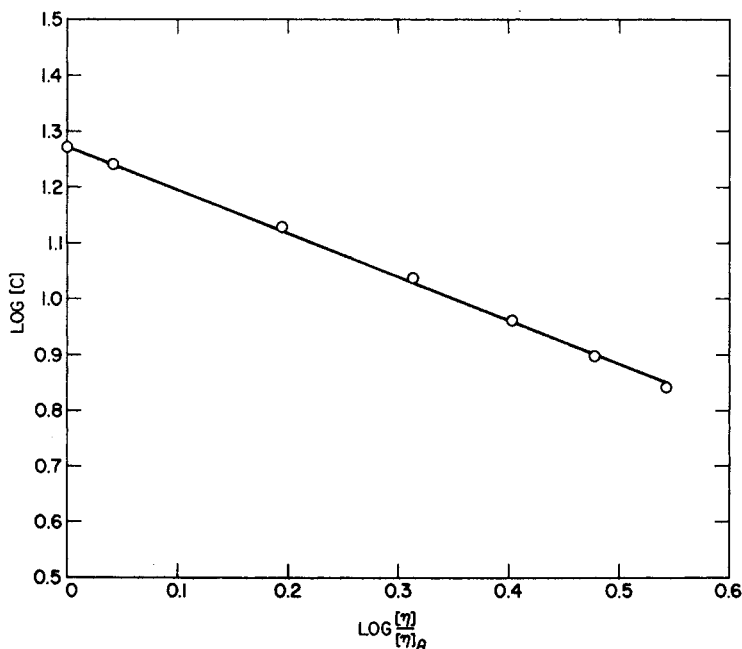
Fig. 5. Log $[C]$ vs. log $[\eta]/[\eta]_\theta$ for WSR-205.

theta solvent conditions, except for the coagulant data where the relation began to deviate from the experimental data above the 0.4 molar level. If the polymer expansion factor $\alpha$ is substituted as the independent variable as in eq. (6), the exponents are of course multiplied by 3, provided the usual definition $\alpha_\eta^3 = [\eta]/[\eta]_\theta$ is accepted, i.e., $[C] = [C]_\theta \alpha^{-3n}$. As a convenience measure, the values of $[C]$ have been tabulated in ppm, since most drag reduction data express polymer concentration as such. However, $[C]$ may also be expressed as g/dl and the appropriate data of Tables II and III converted through multiplication by $10^{-4}$. Constant $B$ of eq. (4) and the products of eq. (5) are then dimensionless numbers.

In order to possibly minimize the effects of mechanical degradation and to eliminate specific polymer–solvent interactions, it may be appropriate to make drag reduction measurements in theta solvents so that a more meaningful comparison may be made between not only homologs but also between different polymer families.

It is difficult to see how a polymer molecule can influence a flow domain which is two to three orders of magnitude greater in size than its own dimensions. Volume elements influenced by greatly elongated polymer molecules do not appear to be the answer, since the experiments of Cottrell suggest that polymer molecules are far less elongated than theory would predict.[14] Even discounting somewhat Cottrell's experiments, molecular deformation under conditions of simple shear definitely is not excessive since the molecule sees a rotating strain field.

On the other hand, in turbulent flow, turbulent bursts of fluid are periodically ejected from the viscous sublayer.[15] Such bursts produce an axisymmetric strain in that the direction of principal strain rate remains fixed relative to the molecule. Such extensions could be extreme, particularly if the strain rate is greater than the reciprocal of twice the relaxation time.[16] In such a case, the elongational viscosity might well be relevant to the mechanism of drag reduction since a high elongational viscosity could possibly surpress the growth of turbulent vortices in the sublayer during the bursting process. Ting[17] has shown through use of more complete constitutive equations that the elongational viscosity appears to be the only macroscopic effect of suitable magnitude which can be correlated with the drag reduction effect at such high dilutions. He also showed in the same study that viscoelastic effects on transient shear flows are negligibly small. According to Lumley, the elongational intrinsic viscosity for a 50-ppm solution of poly(ethylene oxide) of molecular weight $6 \times 10^5$ could be $2.7 \times 10^6$ dl/g. (The polymer was in this case producing a drag reduction of 38%.)

However, definitive elongational viscosity measurements on polymers of drag reduction rank must be made to lend credence to this view. In the present work, the WSR 205 and WSR 1105 samples correspond closely in molecular weight to the compound cited by Lumley; these samples showed a volume ratio of the order of $2^{1}/_{2}$ magnitudes for the comparison of $1/[C]$ with $[\eta]$. Such a ratio seems consistent with the concept of an elongational viscosity effect. It is of interest to note that the intrinsic elongational viscosity corresponding to extension of a thread is three times that for simple shear at zero shear rate conditions. As the strain rate exceeds the inverse of twice the terminal relaxation time of the molecule, the ratio of the intrinsic elongational viscosity to its zero shear rate value roughly equals the number of monomer units.[18] The elongational viscosity at some high fixed shear rate would therefore be proportional to the simple shear intrinsic viscosity. This again seems to be consistent with the relations observed in this report. Nonetheless, the need remains for the appropriate elongational viscosity measurements to be made although the experimental problems appear formidable in the case of highly dilute solutions.

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