

The Drag Reduction of Dilute Polymer Solutions as a Function of Solvent Power, Viscosity, and Temperature

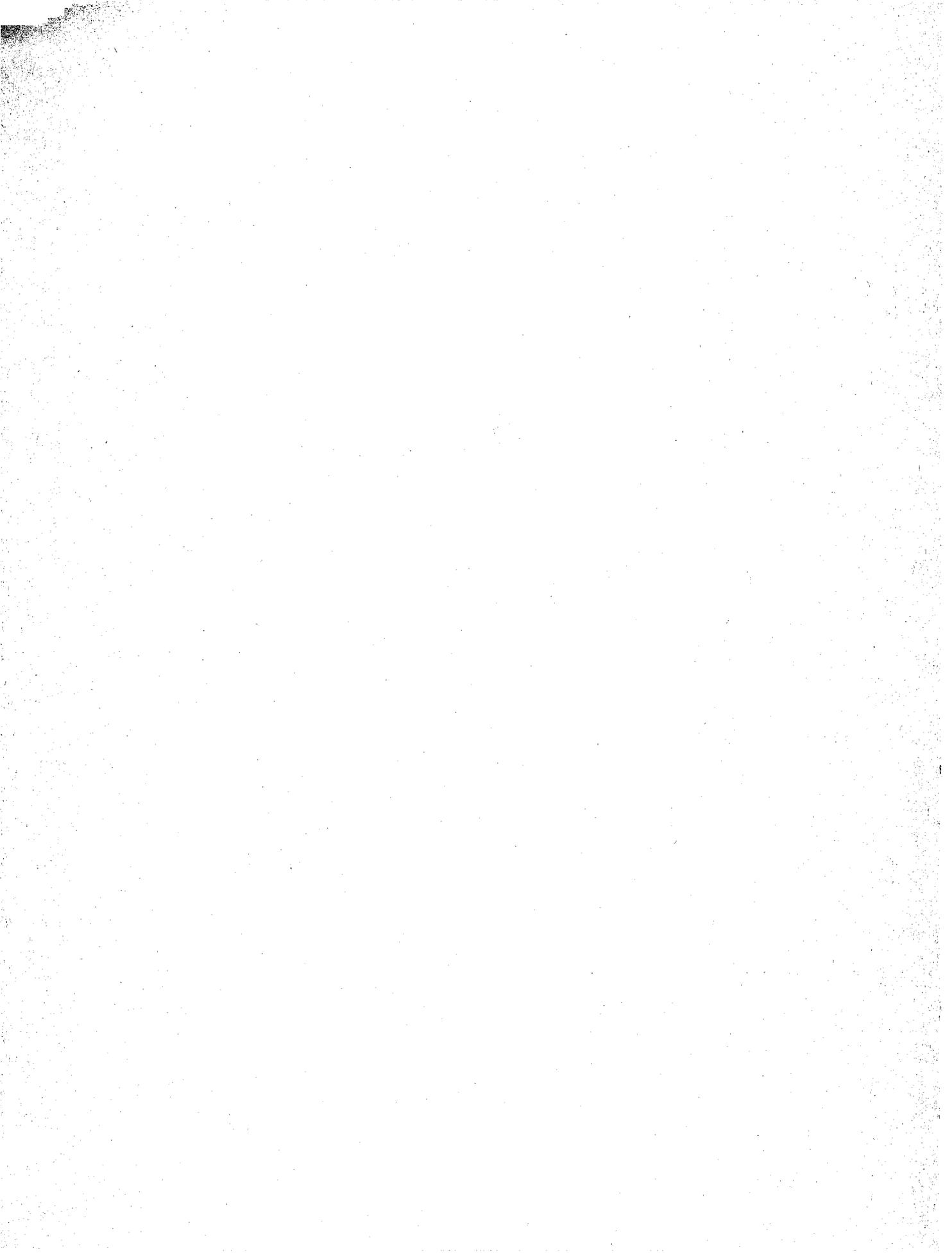
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ABSTRACT

The frictional drag reduction of high-molecular-weight polyethylene oxide and polystyrene solutions under turbulent flow conditions has been studied as a function of temperature, solvent power, and solvent viscosity. A rotating disk apparatus was used to make the drag reduction measurements. For aqueous polyethylene oxide solutions, at concentrations well above that needed to produce maximum drag reduction, all drag reduction data reduced to a common curve when percent drag reduction was plotted against the Reynolds number for the flow. However, for polyethylene oxide solutions below this optimum concentration the drag reduction-versus-Reynolds number curves showed decreasing drag reduction with increasing temperature. The data are explained primarily in terms of the inverse temperature solubility characteristics of polyethylene oxide in water.

The percent drag reduction of polystyrene in nonaqueous liquids was found to be greater in good solvents than in poor ones. It was also found that increases in solvent viscosity and decreases in temperature increased the percent drag reduction. The results are discussed in relation to the current drag reduction theories and are shown to be in opposition to Virk's theory. It is concluded from the data that drag reduction is very likely a function of a relaxation time phenomenon involving the polymer molecules and the flow system. The results also emphasize the importance of considering solvent power, viscosity, and temperature in the design of an efficient drag reduction system.

PROBLEM STATUS

This is an interim report; work on the problem is continuing

AUTHORIZATION

NRL Problem C02-20
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THE DRAG REDUCTION OF DILUTE POLYMER SOLUTIONS AS A FUNCTION OF SOLVENT POWER, VISCOSITY, AND TEMPERATURE

UNCLASSIFIED

INTRODUCTION

Parts per million quantities of certain additives have the ability to reduce the frictional drag in a fluid under turbulent flow. The mechanism underlying the drag reduction (DR) phenomenon is not well understood. The most efficient additives reported have been soluble, high-molecular-weight, linear polymers. Most DR research has been restricted to studies of such polymers at one temperature and in one solvent. White (1), however, measured the DR of polyethylene oxide at 4°C, room temperature, and 37°C, and reported that DR was independent of temperature when the data were compared at the same Reynolds number. A survey by Hoyt and Fabula (2) indicated that the best drag-reducing polymers in water are also the most soluble ones that exhibit the greater solvent-polymer interactions. From this survey they concluded that for a given polymer DR will be greater in the better thermodynamic solvent. Hershey and Zakin (3) found 40% less DR for polyisobutylene in benzene, a poor solvent, than in cyclohexane, a good solvent. No additional information is available concerning the effect of solvent power, temperature, and viscosity on the extent of DR. This report explores the effect of these variables on the degree of DR and suggests how the results relate to the DR mechanism.

EXPERIMENTAL PROCEDURE

Apparatus

A Cole-Parmer constant-speed control unit (Model 4420) was used to rotate a Teflon-coated stainless-steel disk at speeds of 0 to 3000 rpm. The output (mV) of the linear torque sensing device in the instrument was displayed on a Mosley Model 680 recorder. The disk and its shaft were placed in an all Pyrex container (Fig. 1), which was then immersed in a water bath controlled to $\pm 0.01^\circ\text{C}$.

Chemicals and Polymer Characterization

Relevant properties of polyethylene oxide (PEO), obtained from Union Carbide, and polystyrene (PS), obtained from Pressure Chemical Co., are listed in Table 1. The intrinsic viscosities of Polyox FRA in water and PS in toluene were measured at $30^\circ\text{C} \pm 0.01$ in a four-bulb Ubbelohde viscometer (Cannon 50) and the results extrapolated to zero shear. The intrinsic viscosity of Polyox FRA in water was also measured in a Beckman low shear viscometer at 30° , 40° , and 70°C (Ref. 4).

Distilled water was used to prepare all aqueous solutions. The toluene used was Baker reagent grade. Certified-grade cyclohexane, 1,4-dioxane, and purified-grade tetralin were obtained from the Fisher Co.; trans-decalin, 99% pure, was obtained from the Peninsular Chemical Research Co.

Viscosity Measurements

Intrinsic viscosities of polymer solutions are defined by:

$$\frac{\eta_r - 1}{C} = [\eta] + [\eta]^2 kC, \quad (1)$$

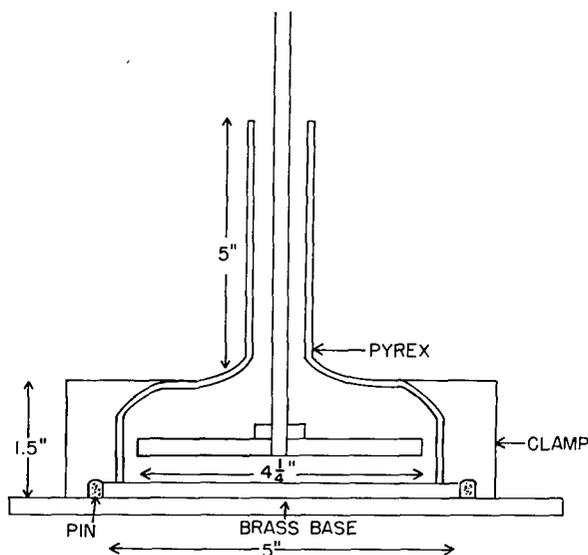


Fig. 1 - Teflon-coated rotating disk in a Pyrex container

Table 1
Physical Properties of Polyethylene Oxide and Polystyrene

Polymer	Manufacturer's Designation	Viscosity-Average Molecular Weight	Intrinsic Viscosity at 30°C in H ₂ O	Mw/Mn
PEO	FRA	7.1×10^6 (a)	27.5	Broad
PEO	WSR-35	4.8×10^5 (b)	2.81	Broad
PS	None	1.8×10^6 (c)	See Table 4	1.2 (c)

(a) Measured in a four-bulb Ubelohde viscometer and extrapolated to zero shear.

(b) From Ref. 29.

(c) Manufacturer's specifications.

where

$[\eta]$ = intrinsic viscosity,

η_r = relative viscosity,

C = concentration in g/100 g,

and

k = Huggins constant.

The viscosity-average mol wt of Polyox FRA was calculated from an equation given by Bailey (5). Using this mol wt the intrinsic viscosities at 35° and 45°C were calculated (Fig. 2) from two other equations given by Bailey (6). The 97°C point was estimated from the precipitation temperature of this mol wt polymer (6) and the equation given by Bailey (6) for the intrinsic viscosity of the polymer near precipitation (θ) conditions.

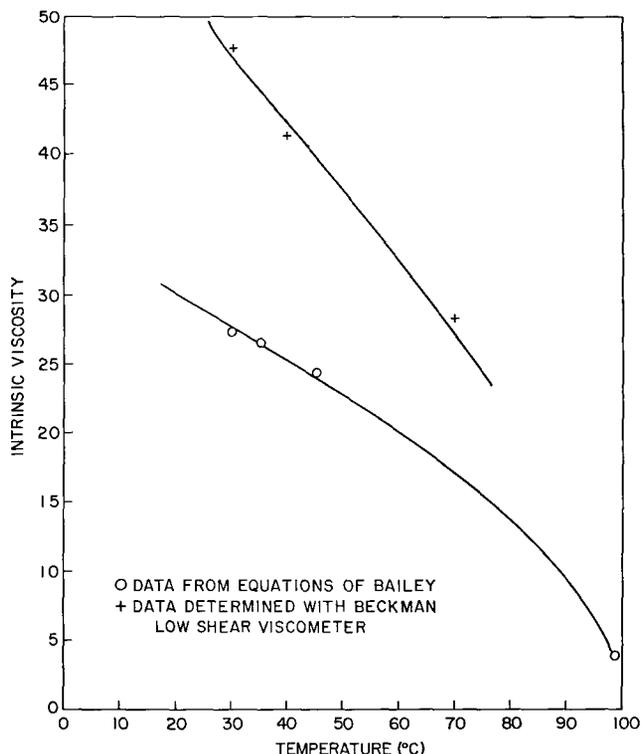


Fig. 2 - Intrinsic viscosity of Polyox FRA as a function of temperature. Rate of shear at 30°C = 2.1 sec⁻¹, at 40°C = 2.8 sec⁻¹, and at 70°C = 2.0 sec⁻¹.

Also included in Fig. 2, but not used in our subsequent calculations, are very low shear intrinsic viscosity values determined from measurements made with a Beckman low shear viscometer at 30°, 40°, and 70°C.

The intrinsic viscosity of PS in toluene at 30°C was determined experimentally and the intrinsic viscosity of PS in cyclohexane at 34°C was supplied by the manufacturer. The intrinsic viscosities of PS in toluene, dioxane, and cyclohexane at the required temperatures were calculated from the Fox-Flory theoretical relationships (7,8) using the literature values of the theta temperature and the variable ψ . The intrinsic viscosity of PS in tetralin was interpolated between the calculated values for toluene and dioxane (9). The intrinsic viscosity of PS in trans-decalin was obtained by plotting the data of Ref. (10) as a function of mol wt and temperature and then estimating the intrinsic viscosities from the graphs. In a similar manner the values of the Huggins constant k were measured or estimated from the literature. In general $[\eta]$ and η_r were believed to be accurate to within $\pm 5\%$.

The kinematic viscosities of dioxane at the required temperatures were determined experimentally. All other necessary solvent densities and viscosities were obtained from the literature (11-17) or by extrapolation of literature values to intermediate values.

Drag Reduction Measurements

The rotating disk cell was filled with solvent and allowed to come to thermal equilibrium. The disk was then rotated at a series of constant rpm's, recording the resultant

torque as a function of time. The solvent was then replaced with polymer solution and the procedure repeated. Ten to fifteen seconds were required to adjust the rpm to the desired value. For Polyox solutions the DR decreased with time of rotation, presumably due to shear degradation of the polymer. The observed torques were therefore extrapolated to zero time. Degradation of the polymer appeared to increase with increasing Reynolds number and decreasing concentration. Fresh solutions of Polyox were used for each run. The preparation and handling of Polyox solutions have been previously described (18). For PS solutions, however, no detectable change in DR was found with time of rotation. The percent DR was defined as

$$\% \text{ DR} = \left[1 - \frac{(\text{mV})_p}{(\text{mV})_s} \right] \times 100, \quad (2)$$

where $(\text{mV})_p$ = millivolt output for polymer solution and $(\text{mV})_s$ = millivolt output for solvent (corrected for solution viscosity). Comparisons of % DR were made at the same Reynolds number,

$$\text{Reynolds number} = R_e = \frac{r^2 w}{\nu}, \quad (3)$$

where

r = radius of disk in cm,

w = speed of rotation in rad/sec,

and

ν = kinematic viscosity.

Except for Polyox FRA, the kinematic viscosities of the polymer solutions differed significantly from those of the solvents. Therefore, to calculate % DR, the measured values of $(\text{mV})_s$ were corrected to correspond to those of solvents whose viscosities were equal to those of the polymer solutions at low shear rates. The solution viscosity was used to calculate R_e . Since the torque on the disk in the turbulent regime was found to be proportional to the 0.13 power of the kinematic viscosity, slight uncertainties in the kinematic viscosity did not seriously affect the accuracy of the % DR data.

RESULTS AND DISCUSSION

Polyox-Water System

Figure 3 shows that for 31 ppm Polyox FRA, DR at various temperatures can be represented by a master plot of % DR vs R_e , except for an indication of a decrease in DR at 90°C. The same behavior was observed for 571 ppm Polyox WSR 35 (Fig. 4). In contrast, a decreased DR at the high temperatures was found for 125 ppm Polyox WSR 35 (Fig. 5). Table 2 lists the % DR of Polyox WSR 35 as a function of concentration at 40°C and suggests that maximum DR would occur at concentrations of 200 ppm or greater. (Maximum DR was estimated to be reached at about 10 ppm for Polyox FRA.) A plot of DR vs R_e similar to Figs. 3 and 4 was obtained by Hoyt and Fabula (2) when they varied R_e by varying the radius of the disk and the rpm, rather than by varying the kinematic viscosity (via the temperature) and the rpm, as in the present investigation. The results in Figs. 3 and 4 also confirm those of White (1) who found no temperature effect on DR.

It would appear that % DR is more sensitive to temperature when the polymer concentration is near or below the value needed to achieve maximum DR. Since the solvent-power of water for Polyox becomes less at higher temperatures, the lower values of DR

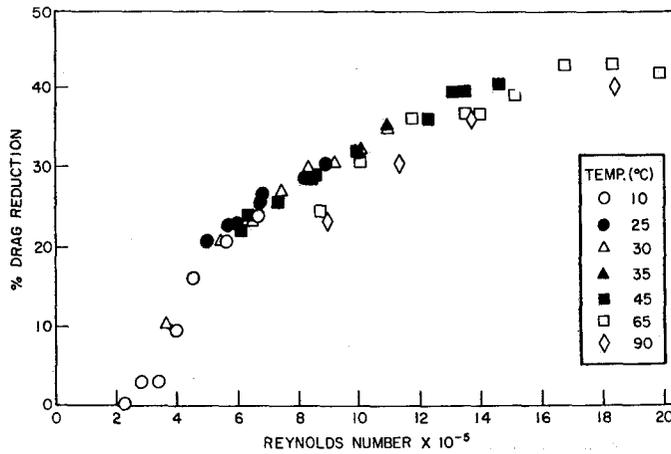


Fig. 3 - Percent drag reduction of aqueous Polyox FRA solutions, 31 ppm, as a function of Reynolds number at various temperatures

Fig. 4 - Percent drag reduction of aqueous Polyox WSR 35 solutions, 571 ppm, as a function of Reynolds number at various temperatures

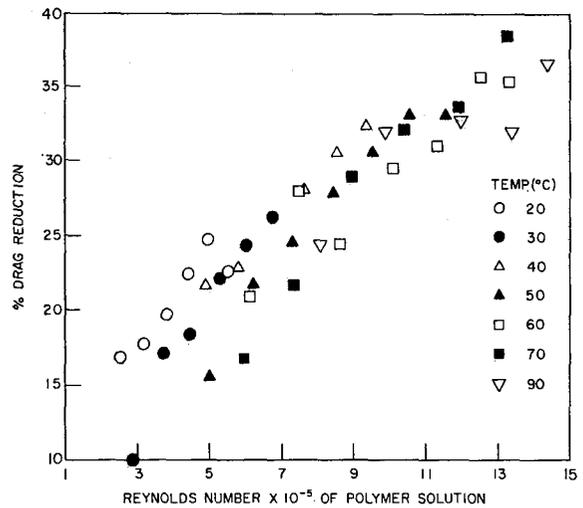


Fig. 5 - Percent drag reduction of aqueous Polyox WSR 35 solutions, 125 ppm, as a function of Reynolds number at various temperatures

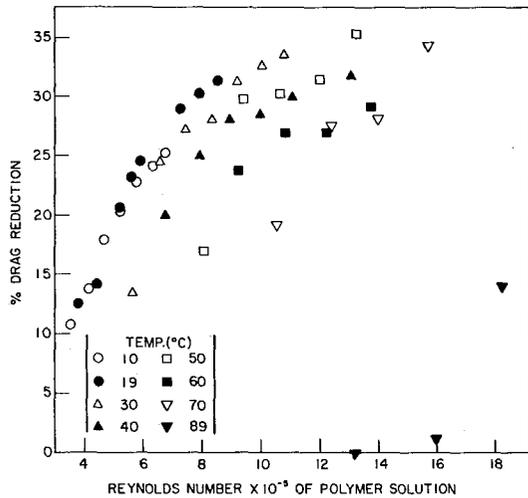


Table 2
Percent Drag Reduction of Polyox WSR 35
as a Function of Concentration at 40°C

% Drag Reduction	Concentration (ppm)	Reynolds Number of Polymer Solution $\times 10^{-5}$
37.3	657	10.88
38.2	330	11.99
37.9	195	12.37
36.3	109	12.67
31.2	25	13.06

observed above 40°C are simply explained by the previous observations that DR is greater in the thermodynamically better solvent. On the other hand, with polymer concentrations above that needed to achieve maximum DR, the decrease in DR efficiency with increasing temperature was masked by the effect of the excess DR agent. A similar masking of DR efficiency would occur at a high enough Reynolds number, even at low concentration. Hence, even at the low concentration used for Fig. 5, DR at high temperature begins to approach that of lower temperatures at high Re . (The viscosity effect discussed in the next section provides additional explanation of these results.)

Since White (19) has suggested that under conditions of turbulent shear strain a polymer may be oxidized and degraded, it is conceivable that certain of the experimental results were due to degradation, although under static conditions no polymer degradation was observed for a time equivalent to that of an experimental run. However, similar results were obtained for PS in organic solvents, where no sign of shear degradation was detected. To further test White's explanation of an oxidative shear degradation process, 2% isopropanol was added as an antioxidant (20) to one sample of a normally shear degradable Polyox solution. No decreased degradation or increased DR effect was observed for this sample as compared to the normally prepared Polyox solutions.

PS-Organic Solvent Systems

The dependence of DR on PS concentration in toluene, from 10° to 70°C is shown in Table 3. For this case, maximum DR was obtained at ≈ 0.20 g/100 ml. Hence, DR measurements were made at roughly this concentration so that solvent, viscosity, and temperature effects would not be masked. The data are shown in Figs. 6 to 8. Table 4 lists some of the pertinent rheological parameters. Based on the intrinsic viscosity data, toluene is the best solvent for PS followed closely by tetralin and dioxane. Tetralin is the most viscous of the good solvents followed by dioxane and then toluene. Cyclohexane and trans-decalin are poor solvents for PS with decalin being the more viscous. From Figs. 6 to 8 and Table 4 the following generalizations are obtained:

1. DR is significantly greater in good solvents.
2. In any one solvent, at a given temperature, % DR increases with increasing Re .
3. In any one solvent, DR increases as the temperature decreases.
4. % DR is greatest in the most viscous solvent when comparisons are made at similar Re and solvent power.

Table 3
Percent Drag Reduction of Polystyrene, MW 1.8×10^6 ,
in Toluene as a Function of Concentration and Temperature

Temperature °C	Concentration g/100 ml	% Drag Reduction	Reynolds Number of Polymer Solution $\times 10^{-5}$
A) 10	0.038	11.42	9.90
	0.057	14.43	9.22
	0.085	18.04	8.33
	0.092	20.65	8.18
	0.143	21.64	6.84
	0.150	17.9	5.69
	0.150	21.63	6.68
	0.150	19.0	6.21
	0.241	24.25	5.04
	0.413	23.25	2.91
B) 20	0.039	7.44	11.15
	0.039	6.22	10.39
	0.091	18.99	9.28
	0.148	19.97	7.59
	0.148	19.40	7.05
	0.410	23.0	3.30
C) 30	0.039	6.45	12.46
	0.039	3.82	11.57
	0.090	18.78	10.37
	0.147	20.54	8.50
	0.147	20.65	7.90
	0.406	20.66	3.72
D) 40	0.038	2.74	13.80
	0.038	0	12.82
	0.089	17.18	11.52
	0.145	20.16	9.46
	0.145	19.58	8.79
	0.401	21.01	4.18
E) 50	0.038	0.70	15.19
	0.038	0.77	14.11
	0.088	16.03	12.70
	0.144	18.21	10.45
	0.144	15.71	9.71
	0.397	19.76	4.64
F) 60	0.038	0.83	16.57
	0.038	0.57	15.39
	0.087	15.24	13.89
	0.142	16.87	11.46
	0.142	17.32	10.65
	0.393	17.81	5.13
G) 70	0.037	0	18.01
	0.037	0	16.73
	0.087	15.24	15.12
	0.140	15.25	12.51
	0.140	16.09	11.62
	0.388	16.37	5.63

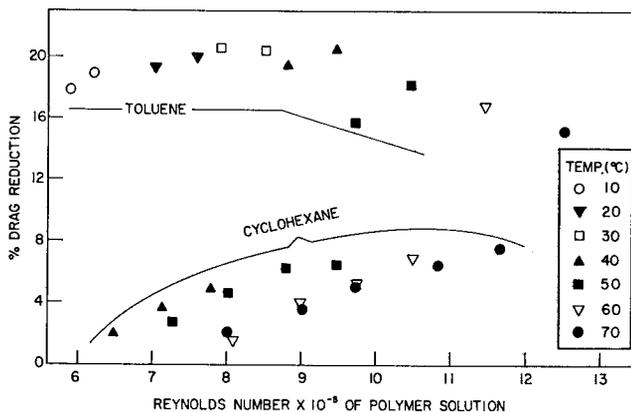


Fig. 6 - Percent drag reduction of polystyrene in toluene (0.17 g/100 g) and cyclohexane (0.11 g/100 g) as a function of Reynolds number at various temperatures

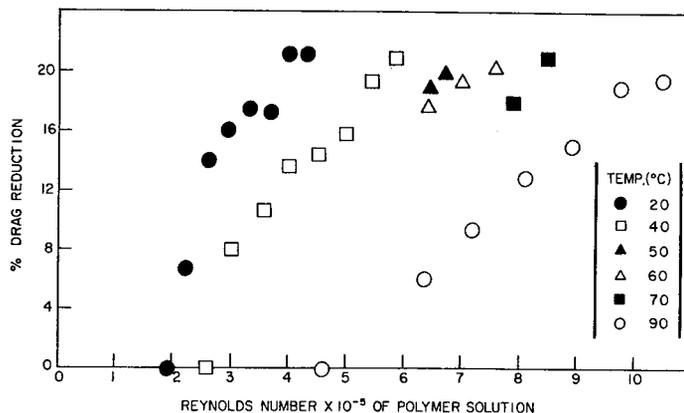


Fig. 7 - Percent drag reduction of polystyrene in dioxane (0.15 g/100 g) as a function of Reynolds number at various temperatures

Items 3 and 4 are novel and cannot be explained by the same arguments used for the Polyox-water system.

Data Relation to Current DR Theories

The experimental results may be analyzed in terms of the three current DR theories. The first theory due to Virk (21) correlates the "onset" of DR with a dimensionless ratio of the length of the individual polymer molecule in solution to the fine scale of the turbulent shear flow; namely,

$$R_g \cdot \frac{(\rho \tau_{wc})^{1/2}}{\eta_0} = K, \quad (4)$$

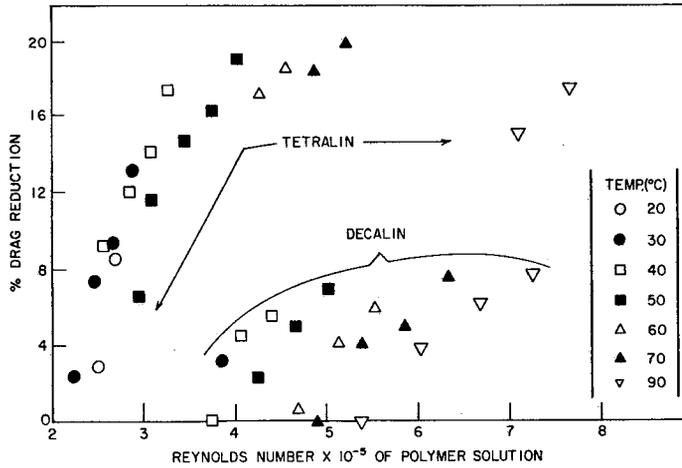


Fig. 8 - Percent drag reduction of polystyrene in tetralin (0.15 g/100 g) and trans-decalin (0.10 g/100 g) as a function of Reynolds number at various temperatures

Table 4
Viscosity and Intrinsic Viscosity of Polystyrene in Various Solvents

Solvent	Solvent Viscosity (cp) at		Intrinsic Viscosity at	
	40°C	70°C	40°C	70°C
Toluene	0.465	0.346	3.62	3.62
Dioxane	0.921	0.638	3.36	3.43
Tetralin	1.58	0.986	3.41	3.47
Cyclohexane	0.704	0.464	1.38	2.13
Trans-decalin	1.493	0.978	1.58	2.05

where

R_g = radius of gyration,

ρ = density,

η_0 = viscosity of solvent,

τ_{wc} = critical wall shear stress = wall shear stress at onset of DR,

and

K = universal constant.

D. A. White (22) has shown by the methods of dimensional analysis that Virk's onset correlation implies the more general formulation

$$\% DR = f\left(\frac{\tau_w}{\tau_{wc}}, Re\right) = f\left[\frac{\tau_w(R_g)^2 \rho}{K^2 \eta_0^2}, Re\right], \tag{5}$$

where

%DR = percent drag reduction,

$f(\)$ = monotonically increasing function of,

τ_w = wall shear stress,

Re = Reynolds number,

and

$\rho, \eta_0, \tau_{wc}, K$ = as before.

Equation (5) may be used to discuss solvent and temperature effects at a fixed polymer concentration. In the good solvents, toluene, dioxane, and tetralin, R_g changes little as the solvent and temperature are varied. Also, in the turbulent regime, τ_w does not increase greatly with increasing viscosity. Hence, Eq. (5) would predict greatest DR in the lowest viscosity medium - in direct opposition to the present experimental results.

The second theory, developed by Elata (23), relates DR with a dimensionless ratio of a characteristic relaxation time of the dissolved polymer molecule to that of the flow system (a Deborah number, De):

$$t_p \cdot \frac{\tau_{wc}}{\eta_r \eta_0} = De, \quad (6)$$

where $t_p = \frac{S\eta_0 (\eta_r - 1)}{T_K C} M$, in which

t_p = Zimm-Rouse relaxation time,

S = constant,

c = concentration (g/100 g),

M = molecular weight,

T_K = Kelvin temperature,

and

other symbols are as before.

In a manner similar to Eq. (5) Elata's specific flow equation in the case of a particular polymer concentration may be generalized to

$$\% DR = f\left(t_p \cdot \frac{\tau_w}{\eta_r \eta_0}, Re\right) = f(De, Re). \quad (7)$$

This formulation of the Deborah number predicts a small increase of DR with increasing solvent viscosity (increasing τ_w) for the good solvents. However, other characteristic times of the flow system could be considered. For example, Patterson, Zakin, and Rodriguez (24) formulate a De for pipe flow whose viscosity dependence would be in good qualitative agreement with our results. Namely

$$t_p \cdot \frac{\eta_r \eta_0}{D^2 \rho} = De, \quad (8)$$

where D = diameter of tube. (The Deborah number De was not dimensionless in Ref. 24 because $D^{1.2}$ was used instead of D^2 .) For a rotating disk a natural choice for De would be

$$t_p (\text{rpm}) = De. \quad (9)$$

Later this De will be used to correlate the data.

The third theory, due to Metzner (25), also employs a Deborah number in a manner similar to Eqs. (6) and (7). The relaxation time of the polymer solution, however, is related to a measured difference of normal shear stress of the solution. One can show (26,27) that Metzner's relaxation θ is related to t_p as follows:

$$\theta = S' t_p \frac{(\eta_r - 1)}{\eta_r}, \quad (10)$$

where S' is a constant and $\theta < t_p$.

In the good organic solvents of the present work, η_r varied from 1.5 to 1.7; hence, $(\eta_r - 1)/\eta_r$ did not change significantly. For present purposes then, Metzner's theory will not be considered as different from that of Elata.

The shear dependence of the polymer solutions viscosity has so far been ignored. Theoretical treatments given in Ref. 28 relate this dependence as follows:

$$[\eta]_G = [\eta]_0 (1 - A\beta^2 + \text{higher terms with even powers of } \beta) \quad (11)$$

where

G = shear rate

$[\eta]_G$ = intrinsic viscosity at G

$[\eta]_0$ = intrinsic viscosity at G equals zero,

A = a factor which differs from theory to theory (Ref. 28 found A to be independent of solvent viscosity for PS),

$\beta = (M[\eta]_0 \eta_0 / RT_K)G = \text{a Deborah number}$

and

R = gas constant.

It can be seen that the average extension of a polymer molecule being sheared (increasing with increasing $[\eta]_G$ in the relation for β) is, in a complicated way, a function of the Deborah number. From this point of view the length hypothesis of Virk (21) has not been eliminated by the present results. In calculating the relaxation time of the polymer molecule t_p the zero shear relative viscosity should be used. The data of Patterson (29) and that of Fig. 2 show that very-high-molecular-weight Polyox has a much higher solution viscosity at very low shear rates than at moderately low shear rates. No extrapolation to zero shear rate is possible from the available data. (This difficulty may explain the better, although poor, correlation that Virk found for the length-based onset hypothesis as compared to the time-based hypothesis (20).)

The η_r needed to calculate the Re and the % DR of a measurement almost certainly should be determined at a shear rate equal to that of the experiment. Only for PS in toluene at 30°C is relative viscosity data (30) available for polymer solutions at shear rates comparable to those of the present measurements ($\approx 50,000 \text{ sec}^{-1}$). For this case

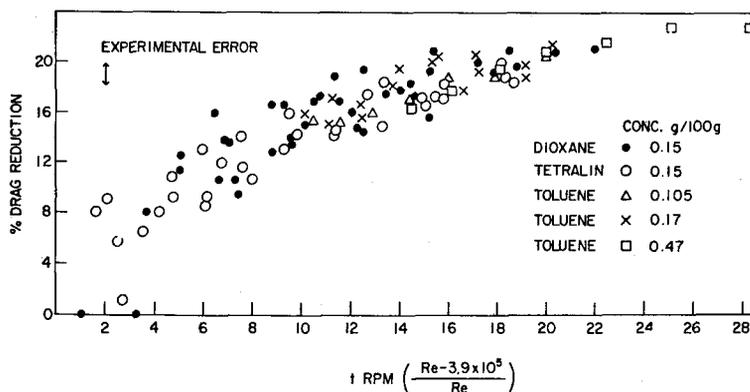


Fig. 9 - Correlation function

(0.1 g/100 g) a Re of 1.1×10^5 and a % DR of 18.3 for the refined calculation is estimated as compared to a Re of 1.0×10^5 and a % DR of 18.8 for the calculation based on the low-shear-rate viscosity. The use of relative viscosities determined at shear rates much lower than those prevailing in the rotating disk experiment seems to result in only a small error in the calculation of % DR and Re . These errors are small when compared to the general trend of the experimental results presented here.

A Time-Based Correlation

Based on the above considerations the following correlation was developed:

$$\% DR = K(\text{rpm}) \frac{\eta_0 (\eta_r - 1)}{T_K C} \frac{(Re - 3.9 \times 10^5)}{Re}, \quad (12)$$

where K = constant. The rationale behind the Reynolds number factor is that for a given polymer, temperature, and solvent type, one can plot % DR vs Re on a master curve. That is, DR is initiated at a critical Re , rises with increasing values of Re , and finally levels off at high Re . The Re part of this correlation function has these properties since it goes to zero for $Re = 3.9 \times 10^5$ and approaches unity for $Re \gg 3.9 \times 10^5$.

The correlation function in Eq. (12) is of a limited scope and would be expected to break down at low % DR. Its main purpose is to demonstrate the possible relevance of De to the DR mechanism. The inclusion of additional parameters while perhaps improving the correlation would have contributed little to an understanding of the DR mechanism. The correlation shown in Fig. 9 includes several concentrations of PS in toluene where the effect of concentration is taken into account by the function $(\eta_r - 1)/C$. The function fitted the data very well considering the experimental error of the DR measurement and the uncertainties involved in calculating t_p . The poor-solvent data (not shown) tended to fall slightly below the good-solvent points.

Aggregation

So far the results have been discussed only in terms of an isolated polymer molecule. However, many suggestions of polymer aggregation due to shear flow can be found in the literature (31-36). Of particular relevance is the work of Munk and Peterlin (36) who found, when the value of β in Eq. (11) was greater than 10, a streaming birefringence for

PS in Aroclor that decreased with time. They explained their results in terms of the entanglement of polystyrene molecules under shear flow to form larger, crosslinked, more spherical macromolecules. Since for the present experiments β is one to two orders of magnitude greater than 10, the possibility that the PS molecule was aggregated must be considered. However, the decrease in birefringence due to shear, suggesting the formation of a nonlinear macropolymer, does not fit well into the concept of increased DR with increased linearity of the drag-reducing polymer. It may be that under conditions of very high shear a linear type of macropolymer is formed. Unfortunately, experimental data as to the effect of shear rate, viscosity, and temperature on aggregate formation are not available. Moreover, if aggregates do form, a relaxation time based on the individual polymer molecule would be improper.

CONCLUSIONS

Despite uncertainties as to what particular relaxation time is of importance, the data do present strong evidence that a relaxation time is involved in the mechanism of drag reduction. In addition, it should also be pointed out that solvent power, viscosity, and temperature are important factors to be considered in the design of efficient drag reduction systems.

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