Literature Cited

(1) Easteal, A. J., Angell, C. A., *J. Phys. Chem.*, **74**, 3987 (1970).
(2) Morgan, D. P., MS Thesis, Bowling Green State University, Bowling Green, Ohio, 1972.
(3) Newman, D. S., Rohr, W., Kirklin, D., Frame, H. D., *J. Electrochem. Soc.*, **119**, 797 (1972).
(4) Rerat, P. C., *Acta Crystallogr.*, **15**, 427 (1962).
(5) Rozdhestvenskii, M. S., Brode, L. M., *J. Appl. Chem. USSR*, **10**, 722 (1937).
(6) "Handbook of Chemistry and Physics", 47th ed, Chemical Rubber Company, Cleveland, Ohio, 1966, p C-517.
(7) "Handbuch der Organischen Chemie", *Beilstein*, **20**, Suppl II, p 103.
(8) Wallace, R. A., Bruins, P. F., *J. Electrochem. Soc.*, **114**, 209 (1967).

Received for review October 30, 1975. Accepted February 13, 1976. The authors wish to thank the National Science Foundation Summer Institute at Bowling Green State University as well as the Faculty Research Committee at Bowling Green State University for providing support for this research.

Characterization of the Drag Reducing Properties of Poly(ethylene oxide) and Poly(acrylamide) Solutions in External Flows

Ralph C. Little, Robert L. Patterson, and Robert Y. Ting*
Naval Research Laboratory, Washington, D.C. 20375

The drag reduction characteristics of aqueous solutions of high molecular weight poly(ethylene oxide) and poly(acrylamide) and its related polymers were studied in a rotating disk apparatus. Intrinsic viscosity measurements were also made in a multibulb capillary viscometer. The concentration dependence of the percent drag reduction was found to obey the universal drag reduction relationship. The drag reduction efficiency for each compound was determined and compared with those obtained from two pipe flow systems. The data show that characterizations in the three different apparatus are consistent in rating the drag reduction efficiency. It also demonstrated the usefulness of the universal drag reduction equation in laboratory characterization of the drag reducing properties of dilute polymer solutions in both internal and external flows.

The ability of very high molecular weight polymeric additives to reduce frictional drag in the turbulent flow of Newtonian fluids is well known. Many investigators have verified this drag reduction phenomenon, in pipe flows as well as in rotating disk flows, using various combinations of polymer–solvent systems (*1*). Extensive research in recent years has indicated that the factors contributing to the effectiveness of drag reducing polymers include molecular flexibility, high molecular weight, and good solubility, but little has been achieved in the development of techniques for quantitative characterization of polymer drag reduction effectiveness. Different graphic presentations or proposed slope parameters by different authors seemed to have so far caused more confusion than leading to a unified basic understanding of the phenomenon. Therefore, it is highly desirable to develop even an empirical function to relate drag reduction to relevant solution properties, particularly one which would quantitatively characterize the drag reduction effectiveness and greatly reduce the amount of time spent in evaluation procedures.

The most striking feature of the drag reduction phenomenon is the low concentration involved in causing a substantial effect. For instance, a 60% drag reduction can easily be achieved in a turbulent pipe flow by the addition of as little as 5 ppm of polymers such as poly(ethylene oxide). A compound may be considered more effective than a given reference sample if it produces a higher percent drag reduction for a fixed concentration. Alternatively, a more effective agent may be considered as one which requires a lower concentration to achieve a certain percent drag reduction. Therefore, it seems reasonable to relate the effectiveness of a compound to its concentration dependence of the drag reduction effect.

Little (*5*) recently modified Virk's universal drag reduction equation (*3*) to account for the concentration dependence of drag reduction in capillary tubes. The equation, for a given Reynolds number or flow rate, takes the form

$$\frac{\mathrm{DR}}{\mathrm{DR_m}} = \frac{c}{c + [c]} \tag{1}$$

where DR is the percent drag reduction, c is the polymer concentration, $\mathrm{DR_m}$ is the maximum drag reduction, and $[c]$ is the intrinsic concentration. It has been shown that the parameter $[c]$ was useful in superposing all the experimental data onto a single universal drag reduction curve (*5, 10*). The drag reduction equation, empirical in nature, involves two adjustable constants $[c]$ and $\mathrm{DR_m}$. These parameters, being constants characteristic of a given polymer compound, may serve as a measure of the drag reduction effectiveness and thus be useful tools for laboratory characterization of drag-reducing polymers. The physical significance of these parameters becomes very clear if the limit of (DR/c) at zero concentration is examined. According to eq 1,

$$\lim_{c\to 0} \frac{\mathrm{DR}}{c} = \lim_{c\to 0} \frac{\mathrm{DR_m}}{c + [c]} = \frac{\mathrm{DR_m}}{[c]} \tag{2}$$

The parameter, $\mathrm{DR_m}/[c]$, therefore is a measure of the "efficiency" of the polymer additives on a unit concentration basis at infinite dilution. It may be obtained by plotting the drag reduction data in terms of c/DR vs. c. Equation 1 may be rearranged as

$$\frac{c}{\mathrm{DR}} = \frac{c}{\mathrm{DR_m}} + \frac{[c]}{\mathrm{DR_m}} \tag{3}$$

i.e., a linear relationship exists between c/DR and c. Such a plot, if linear, shows the validity of eq 1. The intercept at $c = 0$ yields the value of $[c]/\mathrm{DR_m}$, the inverse of which is the drag reduction efficiency. The intercept at $c/\mathrm{DR} = 0$ gives the intrinsic concentration $[c]$, which is the concentration required to reach half of $\mathrm{DR_m}$ at the given flow rate.

The validity of the drag reduction equation has been established for data obtained in internal flows of different tube diameters (*5, 9*) using many different polymer–solvent combinations

Table I. Drag Reduction Efficiency and Intrinsic Viscosity

	Pipe[a]		Capillary[a]		Disk[b]			
Compound	[c] (ppm)	DR$_m$/[c] (%/ppm)	[c]	DR$_m$/[c]	[c]	DR$_m$/[c]	[η] (dl/g)	$10^{-6} M_w$
Polyox-1	1.7	44.4	2.88	42.0	0.65	57.1	23.9	7.56[c]
Polyox-2	2.1	36.4	4.23	33.3	0.75	50.0	14.4	3.95[c]
Polyacrylamide	2.3	33.3	3.88	30.9	0.6	45.5	20.0	7.52[d]
Calgon TRO-375	4.5	17.1	7.22	15.6	2.85	17.9	. . .	8 ~ 10[e]
Polyacrylic acid	4.45	16.4	8.60	14.7	6.0	11.5	3.59	3.70[f]

[a] At Reynolds number = 9000. [b] At 2250 rpm. [c] $[\eta] = 1.03 \times 10^{-4} M_w^{0.78}$ (dl/g) in H_2O at 25 °C. [d] $[\eta] = 6.31 \times 10^{-5} M_w^{0.80}$ (dl/g) in H_2O at 25 °C. [e] As claimed by the manufacturer. [f] $[\eta] = 5.39 \times 10^{-3} M_w^{0.43}$ (dl/g) in 2 N NaOH at 30 °C.

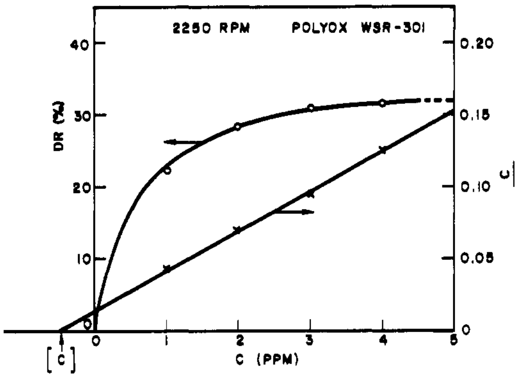

Figure 1. Percent drag reduction and c/DR as a function of the concentration of Polyox.

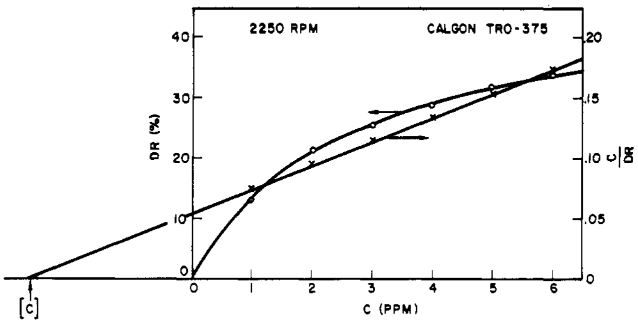

Figure 2. Percent drag reduction and c/DR as a function of the concentration of Calgon poly(acrylamide).

(*3, 6, 8*). However, such a validity has not yet been demonstrated in external flows, where polymer drag reduction was also reported (*2, 4, 7*). In this report, the concentration effect in such flows is examined in aqueous solutions of poly(ethylene oxide), poly(acrylamide), hydrolyzed poly(acrylamide), and poly(acrylic acid) using a rotating disk apparatus.

Experimental Section

Material. Poly(acrylamide) was polymerized by using 12% (by weight) of acrylamide monomer (Eastman Organic Chemicals) in aqueous solution with ammonium persulfate as the initiator to yield a high molecular weight compound. Acrylic acid (also from Eastman Organic Chemicals) was polymerized after distillation under diminished pressure. Polymerization of the monomer (10% aqueous solution) was carried out with ammonium persulfate as catalyst under nitrogen atmosphere at 35° overnight. The polymer was then diluted with water and completely neutralized with sodium hydroxide to produce a poly(acrylic acid) sodium salt. Two high molecular weight poly(ethylene oxide) samples of the Polyox-series were obtained from Union Carbide Corporation and were used as received. Intrinsic viscosities of these compounds were determined in a multibulb viscometer. The results and the derived average-molecular weights were tabulated in Table I. One hydrolyzed poly(acrylamide) sample was also used as received from Calgon Corporation (TRO-375). Intrinsic viscosity was not measured on this sample because of its electrolyte nature. The average-molecular weight for this compound, as given in Table I, was the manufacturer's estimate. Solution preparation was an important integral part of the drag reduction experiments, and was carefully carried out following the previously reported preparation technique (*5*).

Apparatus. The rotating disk system consisted of a Lucite container, 9 in. in diameter and 5 in. in height, in which a 4.25-in. diameter Teflon-coated stainless steel disk rotated. The disk was driven by a dc electric motor equipped with a constant-speed control unit (Cole Palmer Model 4425). The rates of rotation of the disk were such that turbulent flow existed over a major portion of the disk. The rotation speed of the disk was measured using a strobe lamp. The output of a linear torque-sensing meter built in the speed control unit was recorded continuously on a recorder. In this case, most of the measured torque was near the outer edge of the disk. The reduction in torque was proportional to the reduction in shear stress on the disk surface.

Two turbulent pipe flow rheometers were also used to test the compounds for comparing results with those obtained in the rotating disk system. The details of such systems have been described elsewhere (*3*). The tube diameters were 0.1575 and 0.62 cm, and are designated in Table I as "capillary" and "pipe", respectively.

The percent drag reduction in these systems was computed by using the following relationship:

$$\mathrm{DR}\% = \left[1 - \frac{\tau\text{w-polymer}}{\tau\text{w-water}}\right] \times 100\% \qquad (4)$$

where τw is the wall shear stress.

Result and Discussion

The drag reduction data obtained in the rotating disk system show that percent drag reduction increases very rapidly with polymer concentration and reaches a saturation level at only a few parts per million. The concentration dependence of drag reduction in this external flow condition was also found to follow eq 1 very well. This was examined by plotting the data in terms of c/DR vs. c. The plots normally give a linear correlation, which for a least-squares fit has a correlation coefficient of 0.983 or better. Figures 1 and 2 are typical plots for poly(ethylene oxide) and poly(acrylamide) solutions, respectively. The disk rotation speed was at 2250 rpm.

The fact that a universal drag reduction relationship exists for both the pipe flow and the disk flow is of some interest. First of all, it suggests that the interaction of polymers with turbulence

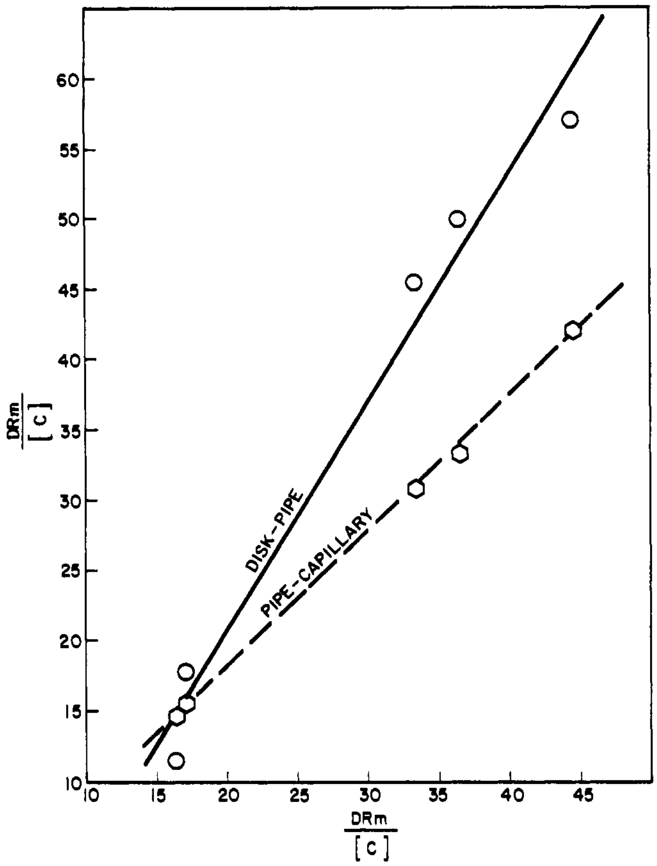

Figure 3. Comparison of the drag reduction ratings from different flow systems.

field in reducing the frictional drag is similar in both internal and external flows. Specifically, it shows that polymer affects the turbulence in the wall layer adjacent to the solid surface. This rules out the possibility of the formation of plug flows in pipe systems at these dilute polymer concentrations. The drag reduction effect, as readily seen from eq 1, increases on a unit concentration basis as the concentration decreases, and eventually for $c/[c] \leq 0.01$ it approaches a constant value of $DR_m/[c]$, the designated "efficiency". This seems to indicate that in drag reduction the interaction of single polymer molecules with the solvent system perhaps dominates the effect of polymer–polymer interaction. It also suggests, as pointed out earlier (*9*), that eq 1 only accounts for dilute solution behavior and predicts drag reduction results up to concentrations below that needed to produce a saturation drag reduction effect. The maximum drag reduction, DR_m, is the theoretical DR value as $c \rightarrow \infty$; therefore it is not really attainable in the experiments. In fact, at higher solution concentrations substantial increase in solution viscosity is observable and often causes a decrease in the drag reduction ability of the solutions.

The drag reduction efficiency, $DR_m/[c]$, of each compound in the rotating disk system was therefore derived as described above. The intrinsic concentration $[c]$ was also obtained, for the inverse of which may be considered as a measure of the influence of single macromolecules on turbulent flow, just as the intrinsic viscosity $[\eta]$ is for laminar flows. These results are given in Table I. Similar results obtained from data in the pipe and the capillary systems are also presented for comparison. For reference purposes the viscosity-average molecular weight for each compound is also included.

One may estimate the shear rates involved in each of the three flow systems. For the disk system a rotation speed of 2250 rpm leads to a shear rate of the order of 236 s^{-1}. For the pipe and capillary tube systems at 9000 Reynolds number, the shear rates (approximated by the ratio flow velocity/tube radius) are 468 and 7230 s^{-1}, respectively. Although this represents a wide range of shear rates, it is interesting to note that the ratings of drag reduction efficiencies are totally consistent among the three laboratory systems used. This consistency is demonstrated in Figure 3, where $DR_m/[c]$ obtained in one system is plotted against $DR_m/[c]$ in another. Least-squares fits of the data seem to indicate that the drag reduction efficiency follows a linear scaling relationship from one system to another. The correlation of the disk and the pipe results has a slope of 1.63 in this plot. The correlation between the disk and the capillary data has a similar slope of 1.69, for the slope of the pipe-capillary tube data correlation is nearly unity. These correlations show the usefulness of the universal drag reduction equation in laboratory characterizations of the polymer drag reduction effect. Thus, whether an internal or external flow system is used, meaningful drag reduction indices may still be evolved and the efficiencies of various drag reducing materials thereby routinely cataloged.

Literature Cited

(1) Gadd, G. E., *Encycl. Polym. Sci. Technol.*, **15**, 224–253 (1971).
(2) Gold, P. I., Amar, P. K., Swaidan, B. E., *J. Appl. Polm. Sci.*, **17**, 333 (1973).
(3) Kim, O. K., Little, R. C., Ting, R. Y., *J. Colloid Interface Sci.*, **47**, 530 (1974).
(4) Lang, T. G., Patrick, H. V. L., ASME Paper No. 66-WA/FE-33, Fluid Engineering Division, ASME Annual Meeting, New York, N.Y., Dec 1966.
(5) Little, R. C., *J. Colloid Interface Sci.*, **37**, 811 (1971).
(6) Little, R. C., Patterson, R. L., *J. Appl. Polym. Sci.*, **18**, 1529 (1974).
(7) Mashelkar, R. A., *AIChE J.*, **19**, 382 (1973).
(8) Patterson, R. L., Hunston, D. L., Ting, R. Y., Little, R. C., *J. Chem. Eng. Data*, **20**, 381 (1975).
(9) Ting, R. Y., Little, R. C., *J. Appl. Polym. Sci.*, **17**, 3345 (1973).
(10) Virk, P. S., Sc. D. Dissertation, MIT, Cambridge, Mass., 1966.

Received for review November 26, 1975. Accepted March 29, 1976.