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Universal Characteristics of Drag Reducing Polyisobutylene in Kerosene

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NOTES

UNIVERSAL CHARACTERISTICS OF DRAG REDUCING POLYISOBUTYLENE IN KEROSENE

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ABSTRACT

A homologous series of oil-soluble polyisobutylene (PIB) in kerosene was investigated to study the drag reduction in a turbulent flow with a rotating disk apparatus (RDA). The drag reduction data were plotted to observe the universal characteristics of PIB-kerosene systems. Intrinsic concentration [C] was found to be extremely useful quantity in normalizing the drag reduction data for different molecular weights of PIB and concentrations similar to poly(ethylene oxide) (PEO) in water. An explanation of the drag reduction phenomenon by an individual molecule was obtained by the plot of intrinsic drag reduction vs. [C].

INTRODUCTION

Turbulent drag reduction by minute amounts of polymer additives has been the subject of intensive theoretical and experimental research because of its wide range of applications [1]. Although the use of polymers as drag reducing agents in water-based systems is well known and has been extensively explored, very little has been reported for comparable additives for hydrocarbon-based fluids. Among oil-soluble polymers, PIB homopolymer is commonly used [2], and in this paper, we present empirical correlations among molecular parameters of PIB in RDA.

Drag reduction is known to be strongly influenced by the molecular parameters of the dissolved polymer. Improving Virk's drag reduction equation, Little and other investigators [3, 4] studied the concentration dependence of drag reduction and found that a linear relationship exists between the characteristic parameters, $DR_{max}/[C]$ [Note : [C] is the intrinsic concentration and will be defined later.] and polymer molecular weight. Furthermore, it is suggested that the critical

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concentration of polymer might be used to normalize the drag reduction data since the critical concentration appeared to produce the degree of drag reduction, irrespective of the polymer molecular weight [3]. In order to characterize the effectiveness of PIB on drag reduction, Dschagarowa and Mennig [5] also studied the concentration and flow rate dependence for PIB, with different moleclar weights in pipe flow and obtained the universal drag reduction curve for [C] and intrinsic drag reduction. Our purpose in this paper is to observe the effects of polymer concentration on drag reduction and to characterize an oil-soluble PIB drag reducer using an RDA [6-8]. Recently, we characterized the concentration dependence on drag reduction for a homologous series of PEO covering a wide range of molecular weights in an RDA and found a relationship between the polymer concentration, drag reduction index, and viscosity-average molecular weight (M_V) [7]. In addition, [C] was found to be extremely useful quantity in normalizing the drag reduction data of different molecular weight compounds in a homologous series of PEO. Therefore, we investigate with a PIB-kerosene solution in an RDA and compare the data with a PIB-toluene solution flowing through a pipe.

EXPERIMENTAL

Four different grades of PIB (L-80, L-100, L-120 and L-140) based on molecular weight, obtained from Exxon Chemical Americas, are used as drag reducing additives. M_V's, which are used for our analysis, are 9.9×10^5 for L-80, 1.2×10^6 for L-100, 1.6×10^6 for L-120 and 2.1×10^6 for L-140. Other molecular characteristics of these polymers such as M_n, M_W and M_W/M_n can be found in ref. [9]. A 5%-stock solution of PIB in kerosene as a solvent was prepared, and then carefully syringed in a turbulent flow. RDA consists of a stainless steel disk whose dimensions are 10.1 cm in diameter x 0.32 cm in thickness, enclosed in a cylindrical, thermostatically controlled container, which is made of stainless steel and whose dimensions are 16.3 cm inner diameter x 5.5 cm height. The volume of solution required to fill the entire container is 1020 cm^3. When the constant rotational velocity of the disk using the speed controller (Cole Parmer Master Servodyne Unit) and DC varying speed motor was sustained, the variable torque was measured by a multimeter. The temperature of the system was maintained at $(25 \pm 0.5)^\circ C$ by a contant temperature circulating apparatus and the rotational velocity of the disk was measured by a digital tachometer.

Drag reduction efficiency was obtained first by measuring the torque required to rotate the disk at a given speed in pure kerosene (T_O). The percent drag reduction (DR) is then estimated by measuring the corresponding torque required at the same speed in the kerosene with a polymer added (T_P) : $DR = (T_O - T_P)/T_O \times 100$. All data were taken at a fixed rotational speed of 1600 rpm, corresponding to a kerosene-based Reynolds number, N_{Re} of 4.59×10^5. In addition, Ubbelohde viscometer was used to measure the intrinsic viscosity $[\eta]$ at $(30 \pm 0.5)^\circ C$ in toluene (reagent grade). M_V's of PIB were estimated using the Mark-Houwink equation, $[\eta] = 0.02 \times M_v^{0.67}$, at $30.0^\circ C$.

RESULTS AND DISCUSSION

Since the drag reduction is caused by a sum of contributions from individual polymer molecules, the concentration of a polymer solution has effect on the increment of drag reduction. Thereby, the concentrations having the maximum drag reduction at each different molecular weight are determined, and the values of the maximum drag reduction for different molecular weights of PIB are used in the analysis. To find an empirical formula which relates drag reduction to polymer solution properties, Virk et al. [10] experimentally studied the drag reduction caused by dilute PEO solutions in a turbulent pipe flow and found that the extent of drag reduction induced by a homologous series of polymers is a universal function of concentration, flow rate, and molecular weight for a given flow geometry. Furthermore, Little et al. [4] suggested using a simplifed Virk's universal function to account for the concentration dependence of drag reduction in pipe flows, which takes the form,

$$\frac{DR/C}{[DR]} = \frac{1}{1 + C/[C]} \quad . \tag{1}$$

For experimental purposes, two important quantities in Eq.(1), previously reported by Little [3], are intrinsic drag reduction [DR] and [C] defined as $\lim_{C \to 0} DR/C = [DR]$ and $[C] = DR_{max}/[DR]$, where DR_{max} is the maximum percent drag reduction for a given polymer solution, and C is the polymer concentration expressed in wppm. The drag reductions involve only a few parts per million of polymer additives; therefore, one can hypothesize that polymer-solvent interactions play a very important role. From Eq. (1) and the definition of [C], we obtain

$$\frac{C}{DR} = \frac{[C]}{DR_{max}} + \frac{C}{DR_{max}} \quad . \tag{2}$$

Equation (2) shows that there is a linear relationship between C/DR and C. This is valid for most drag reducing polymers for both pipe flow [3, 4] and rotating disk flow [7, 11]. Recently Mumick et al. [11] analyzed structure and solvation effects of polyampholytes in drag reduction. They found that good drag reducers exhibit low values of [C] and polymer-solvent interaction has a large effect on the [C] using Eq. (2).

The effect of concentration on the drag reduction was investigated and demonstrated that the existence of a critical concentration at which the drag reduction was maximized. As the concentration of a drag reduction agent increases from very low values, the degree of drag reduction increases at first, passes through a maximum, and then decreases at very high concentrations of the polymer [6]. Values of maximum drag reduction of different molecular weights of PIB are obtained from the experiment and further analyzed. As shown in Table 1, it clearly indicates that the concentration required for maximum drag reduction decreases with increasing molecular weight. The linear relationship between C/DR and polymer concentration for four different molecular weights in a range of conditions close to the maximum

TABLE 1

Intrinsic drag reductions, maximum drag reductions, and intrinsic concentrations for various molecular weights.

	L-80	L-100	L-120	L-140
[DR]	21.87	53.85	90.70	100.8
DR_{max} (%)	17.03	16.64	17.57	17.89
[C]	0.7787	0.3091	0.1937	0.1788

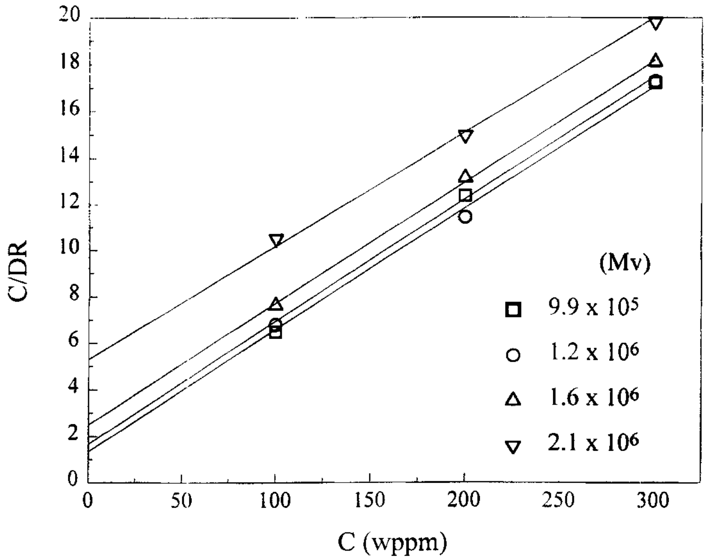

Fig. 1. Concentration dependence of drag reduction for PIB.

drag reduction is illustrated in Fig. 1, showing that Eq. (2) can also be applied to drag reducing polymer-solvent systems for different geometries (e.g., an RDA). For the dilute solution limit, Little et al. [4] explained that Henry's law is applicable in this range, in which C/[C] values approach 0.01.

The parameter $DR_{max}/[C]$, the Henry's law constant, shown in Eq. (3) defines the efficiency of the polymer additives on a unit concentration basis at infinite dilution:

$$\lim_{C\to 0}\frac{DR}{C} = \lim_{C\to 0}\frac{DR_{max}}{C+[C]} = \frac{DR_{max}}{[C]} \tag{3}$$

Only at these intermolecular distances, the percent drag reduction is a linear function of polymer concentration. Near the maximum DR condition, the polymer molecules are only a few diameters apart and virtually touch. Equation (3) is valid

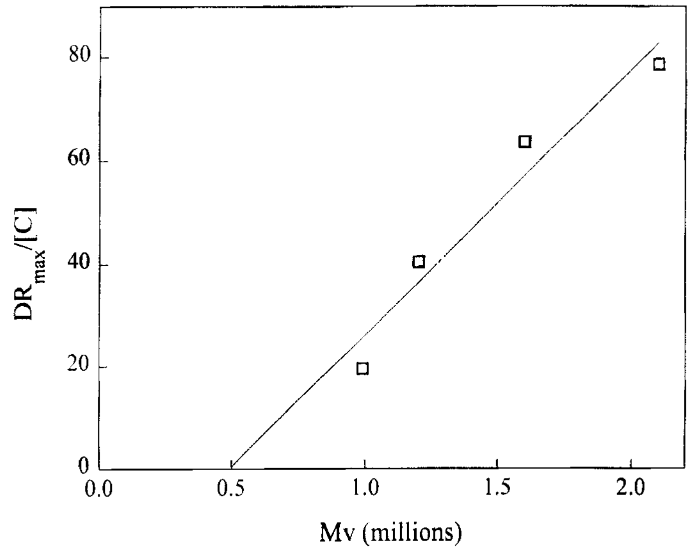

Fig. 2. Plot of $DR_{max}/[C]$ versus viscosity-average molecular weight for PIB.

not only in a turbulent pipe flow system but also in a turbulent rotating disk flow system. The intercept value at C/DR = 0 yields [C] and this quantity divided by the intercept at C = 0 permits the evaluation of DR_{max}. Figure 2 shows a correlation between [DR] in Eq. (3) and M_V for the homologous series of PIB. The plot is linear and the intercept value of $M_V = 5.0 \times 10^5$ is obtained from a least squares fit, to give a cut off point in molecular weight, below which no drag reduction takes place at the Reynolds number for 1600 rpm.

In addition, when we normalize the drag reduction data of four PIB compounds using [C], we find that the reciprocal of [C] is a linear function of M_V as shown in Fig. 3. The linear relationship is also represented by the following equation: $M_V \times 10^{-6} = 34.96/[C] + 0.5$. M_V/DR_{max} is also correlated with M_V as shown in Fig. 3. DR_{max} can be approximated as $DR_{max} = 17.39M_V/(M_V + 3.69 \times 10^5)$. Furthermore, [C] was found to be extremely useful in normalizing the drag reduction data of different molecular weight compounds in a homologous series. It demonstrates that [C] can be used to normalize data obtained from an RDA. Defining (DR/C)/[DR] as β and C/[C] as α, Eq. (1) becomes $\beta = 1/(\alpha + 1)$. Figure 4 also infers that a universal equation for the PIB family fits well for the rotating disk system. However, for a PIB-toluene solution, Dschagarowa and Mennig [5] obtained $\beta = 1/(\alpha + 0.4)$ for pipe flow. From the similar behavior observed for both water-PEO and toluene-PIB for pipe flow, they proposed a universal curve with a single parameter which depends on polymer/solvent system as $\beta = 1/(\alpha + K)$.

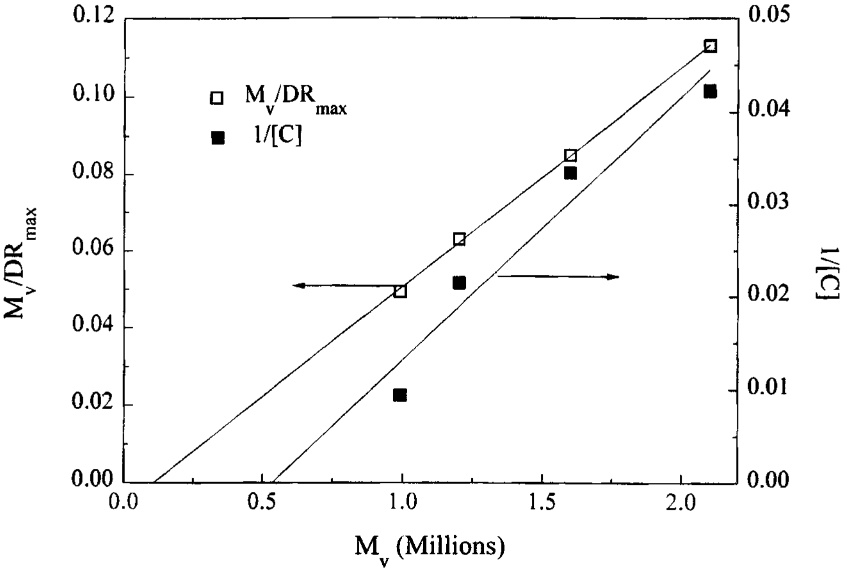

Fig. 3. Plot of both M_v/DR_{max} and 1/[C] versus viscosity-average molecular weight for PIB.(The open square is M_v/DR_{max} and the solid square is 1/[C].)

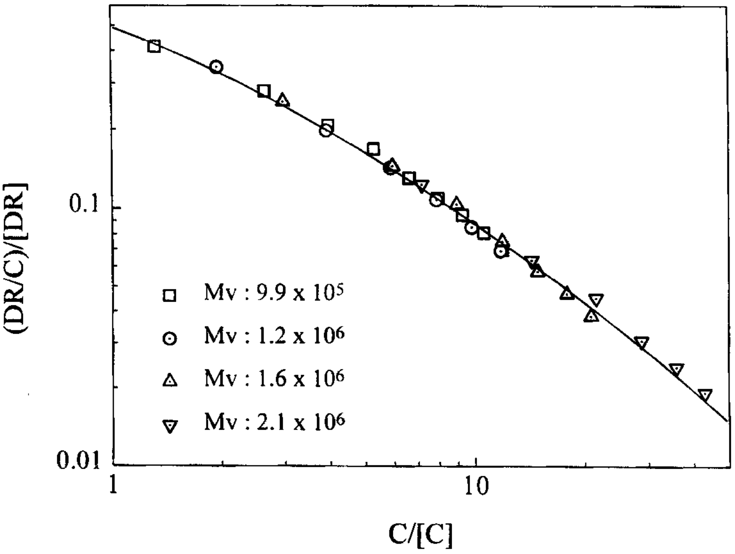

Fig. 4. Universal drag reduction curve; (DR/C)/[DR] vs. C/[C].

The constant K depends on the molecular characteristics of a polymer in a given solvent and does not depend on the molecular weight or flow geometry. K is 1 for water-PEO in a pipe-flow [10]. On the other hand, for toluene-PIB and kerosene-PIB [5], K is observed to be 0.4 as shown in Fig. 4. From this study, we thus conclude that the empirical equations to relate drag reduction to the physical properties of a solution would reduce the amount of time spent in evaluation procedures of the efficiency of drag reduction. The polymer concentration was used to normalize the drag reduction data since the same fraction of critical concentration appeared to produce the same degree of drag reduction, irrespective of polymer molecular weight. The universality of drag reduction of PIB solution was obtained from [DR] and [C], and the universal drag reduction curve of kerosene-PIB in an RDA agreed well with that of toluene-PIB in a pipe system. That means that the universality of a polymer is the same regardless of flow geometries and of solutions.

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