Effects of Molecular Characteristics of Polymers on Drag Reduction

GIN-CHAIN LIAW, JACQUES L. ZAKIN, and GARY K. PATTERSON

University of Missouri, Rolla, Missouri

Turbulent measurements in capillary tubes and in pipes were made on nonpolar solutions of seven polymer species, three at more than one molecular weight, over wide concentration ranges.

A critical concentration, C_c, was taken as the minimum concentration for disappearance of the turbulence transition region. Above this concentration, friction factor-generalized Reynolds number data show only a gradual deviation from extension of the laminar line. C_c increases with tube diameter and decreases with molecular weight. The critical dimensionless volume friction $C_c\,[\eta]$ is less dependent on molecular weight.

The levels of $C_c\,[\eta]$ for different polymer species in a given tube show marked differences which are related to β, the molecular rigidity parameter. Low β values, or high flexibility, are associated with low $C_c\,[\eta]$ values. Available data for $C_c\,[\eta]$ in good and in poor solvents show little solvency effect.

Polymer samples of low m', the ratio of the polymer molecular weight to the critical entanglement molecular weight of the polymer, give solutions with little or no drag-reducing capacity, even those with low β values. Samples must have m' values of 50 or more to show significant drag reduction. This allows prediction of the minimum useful molecular weights for drag reduction for any polymer species.

For solutions above C_c, all of these data and literature data (for aqueous and nonaqueous systems with a wide range of n' values) fit a single f/f_{pv} versus generalized Reynolds number relationship.

Drag reduction has been defined as the decrease in pressure loss at constant flow rate in turbulent conduit flow caused by the addition of small amounts of additives to the carrier fluid. The phenomenon has been observed in tubes and also in other types of solid boundary turbulent flows with polymer solutions, soap solutions, and solid suspensions in liquids and in gases.

High polymer additives are particularly effective drag-reducing agents, even at low concentrations, and many drag reduction studies have been made with polymer additives. However, these studies generally covered either a limited number of polymer-solvent systems or a limited range of concentrations. No broad study aimed at learning the effect of variations in polymer structure on their effectiveness as drag reducers has been made. Also, most investigators studied either dilute or concentrated polymer solutions, often drawing contradictory conclusions because the significance of the concentration region studied was not recognized.

Thus, examination of the polymer solution drag reduction literature shows that the effects of concentration, molecular weight, and polymer structure are still not fully understood. It is the purpose of this paper to describe some experimental results which clarify the effects of these variables.

Specifically, the drag-reducing characteristics of several polymers of various molecular structures were studied in nonpolar solvents over a wide range of concentrations (*1*). In a few cases the effects of molecular weight on drag reduction were examined.

Literature Review

A recent review paper (*2*) has covered most of the pertinent background literature and only those papers of special importance to this work will be cited here.

Shin (*3, 4*) performed a series of turbulence experiments using a Couette type viscometer with polyethylene oxide (PEO) in water and polyisobutylene (PIB) in cyclohexane. He varied concentration and molecular weight for both polymers and observed that an optimum concentration for minimum torque C^* could be found at his flow conditions. C^* decreased with molecular weight. At higher concentrations the additive was less effective in reducing drag as viscosity began to increase rapidly. Shin also estimated a critical concentration, $C_{c,s} = 0.493/[\eta]\gamma^3$, as the concentration for a hypothetically fully packed solution (26% void volume), assuming each polymer has an effective spherical diameter which is of the order of magnitude of its root-mean-square end-to-end distance. Solutions were considered dilute for concentrations below $C_{c,s}$.

Walsh (*5*) also considered dilute polymer solutions in a similar way. He defined dilute as concentrations for which $C[\eta] < 0.025$. In earlier polymer solution viscosity studies (*6*), $C[\eta]$ was shown to be close to a hypothetical pervaded volume fraction. At $C[\eta] = 1.08$, the onset of the concentrated region, overlap of polymer chains became important.

Shin's data for conditions of maximum drag reduction showed a gradual deviation from an extension of the laminar line when plotted on a $T/\rho N^2$ versus N/γ plot in the region of N/γ values where Newtonian solvents showed a definite transition to turbulent flow behavior.[†] The minimum concentration for which the extension of the laminar line occurred C_t was compared to $C_{c,s}$ values. Values of $C_t/C_{c,s}$ for PEO were considerably lower than for PIB when compared at equal molecular weights or equal number of atoms in the main chain.

Shin also examined β, the molecular rigidity factor.[‡]

Gin-Chain Liaw is with the A. E. Staley Company, Decatur, Illinois.

[†] In some cases the concentration C_t to reach the gradually deviating curve exceeded C^*.

[‡] $\beta = \left(\dfrac{r_0^2}{r_{0f}^2}\right)^{1/2}$ where r_0^2 = mean square end-to-end distance of polymer molecules at theta conditions, and r_{0f}^2 = mean square end-to-end distance for freely rotating molecules.

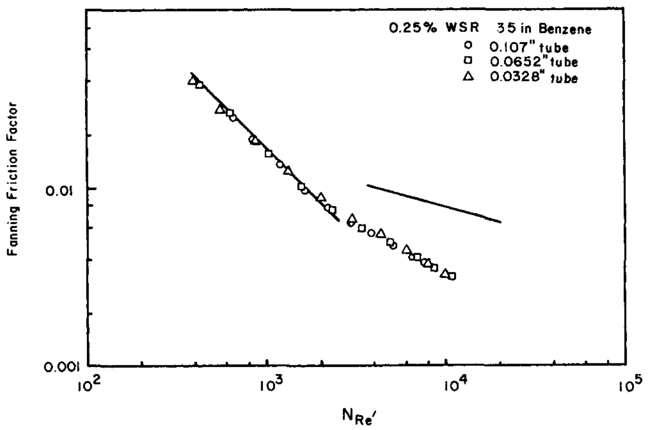

Fig. 1. Friction factor versus Reynolds number for 0.25% WSR 35 in benzene.

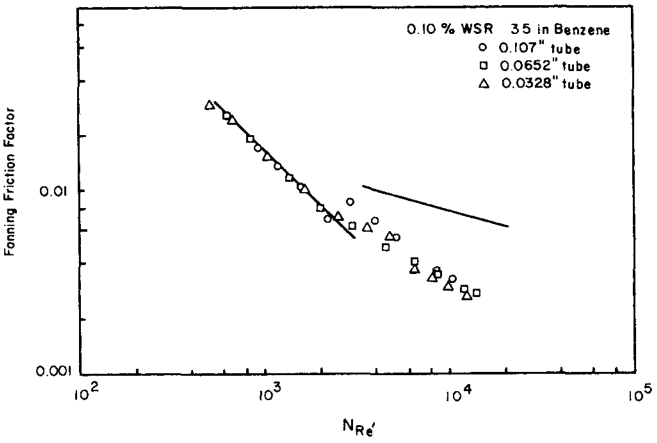

Fig. 2. Friction factor versus Reynolds number for 0.10% WSR 35 in benzene.

He noted that values of β are 1.36[†] for PEO and 1.80 for PIB, and suggested that drag reduction correlates with this parameter, drag-reducing effectiveness decreasing with increasing β.

Lee (*7*) examined another random-coiled polymer, polyacrylamide (PAM), in the same apparatus used by Shin. Comparison of C^* values on the basis of number of atoms in the main chain showed PAM to be more efficient than PEO or PIB, even though its β value, according to Lee, is about 2.7. Comparison of C^* values at equal molecular weights showed PAM to be between PEO and PIB. He concluded that there was no simple relationship between β and effectiveness. However, he did not compare $C^*/C_{c,s}$ at equal molecular weights. Examination of his data indicates that on this basis PAM is less effective than the other two polymers.

Virk (*8*, *9*) also studied the effect of concentration and molecular weight on drag reduction in the polyethylene-oxide water system in pipe flow experiments. He noted increasing effectiveness of drag reduction with increasing concentration until the increased viscosity overwhelms the drag reduction. At a high molecular weight he observed a limiting drag reduction asymptote for his 0.115- and 1.26-in. tube data which was characterized by the equation

$$f = 0.42\ N_{Re}^{-0.55}$$

This is nearly the same slope on a log-log plot as that reported by Shin (0.5) for a log-log plot of $T/\rho N^2$ versus (N/ν) for his points of maximum drag reduction. However since all of Virk's solutions were Newtonian[‡] (with maximum relative viscosities near 2), his relationship is not generally applicable.

Pruitt and Crawford (*10*) studied the effect of molecular weight and segmental constitution on the drag reduction of water-soluble polymers in capillary tubes. The polymers tested in their study were polyethylene oxide (four different molecular weight samples), polyacrylamide (three different molecular weight samples), carboxymethyl cellulose (six different molecular weight samples), and guar gum. Generally, measurements were made at four concentrations (2, 10, 50, and 250 p.p.m.). They observed that drag reduction increased as the number of main-chain segments (molecular weight) increased and as the size of the segmental side-chain decreased.

Pruitt, Rosen, and Crawford (*11*) observed that the drag-reducing ability of PEO-water solutions decreased as theta solvent conditions were approached (that is, by addition of electrolyte). Hershey (*12*, *13*) observed a large decrease in the drag-reducing ability of a PIB sample when dissolved in benzene at 24°C., a theta solvent, compared with a cyclohexane solution (good solvent) of the same polymer at equal concentrations.

Merrill et al. (*4*) reported that for a theta solvent the concentration of one PEO sample had to be increased by a factor of about 4 to reach C^* (or C_t). Lee (*7*) observed

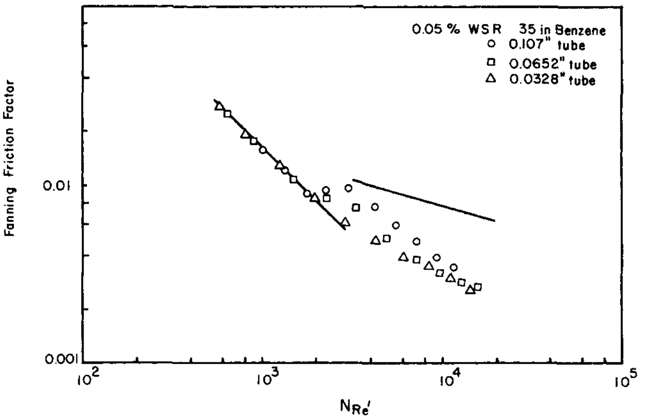

Fig. 3. Friction factor versus Reynolds number for 0.05% WSR 35 in benzene.

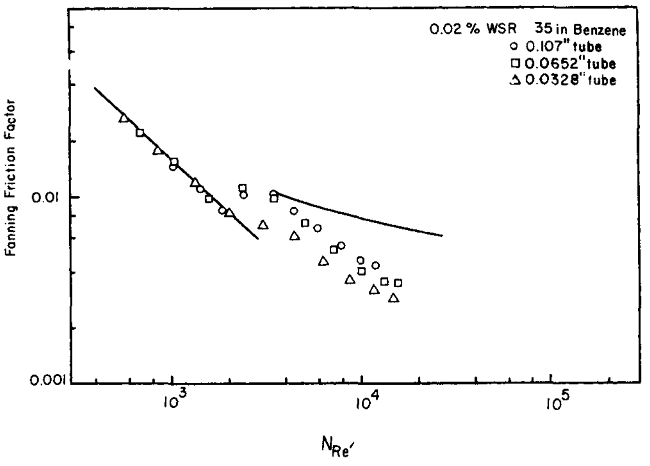

Fig. 4. Friction factor versus Reynolds number for 0.02% WSR 35 in benzene.

[†] Reference *15* gives β = 1.38 for PEO.

[‡] Newtonian refers here to fluids with n' = 1.0.

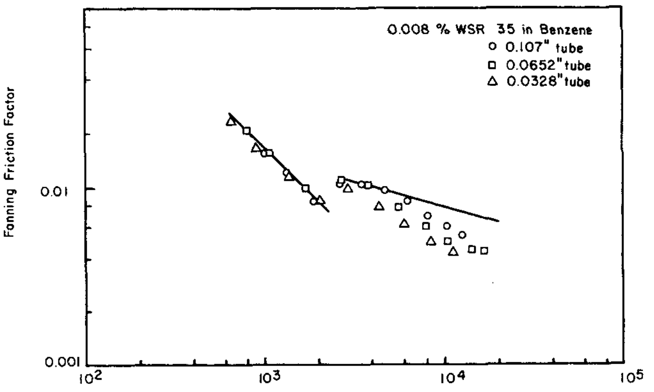

Fig. 5. Friction factor versus Reynolds number for 0.008% WSR 35 in benzene.

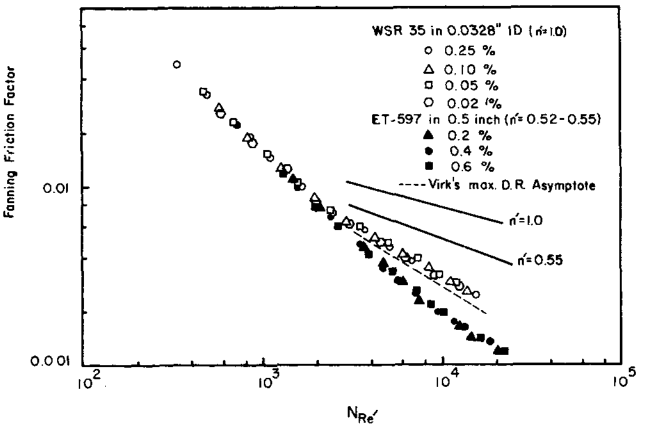

Fig. 6. Friction factor versus Reynolds number for concentrated solutions of WSR 35 in benzene and ET-597 in water.

a three- to fourfold increase in C^* for polyisobutylene in benzene at 25°C. (a poor solvent) compared with cyclohexane. Thus at equal concentrations the more expanded polymer conformations result in more effective drag reduction.

EXPERIMENT

Laminar and turbulent region friction factor versus Reynolds number data for the polymer solutions studied were obtained in a recirculating capillary tube apparatus. The capillary tubes were 0.0328, 0.0652, and 0.107 in. in I.D. with length-to-diameter ratios greater than 500. Entrance corrections were made. Temperature of the recirculating fluid was 25.0 ± 0.1°C.

The apparatus and procedure were similar to those described previously (*12* to *14*). The molecular weights of the polymers were estimated by means of intrinsic viscosity measurements in dilute solutions at low shear rates and literature correlations (*1*). The polymers studied are listed in Table 1.

The effects of degradation and solvent evaporation were minimized by minimizing the observation times. Spot checks of degradation and changes in concentration after the measurements were completed showed only minor effects (*1*).

RESULTS AND DISCUSSION

Concentration, Molecular Weight, and Molecular Structure Effects

Friction factor-Reynolds number plots for five concentrations of polyethylene oxide WSR 205 in benzene in three capillary tubes are shown in Figures 1 to 5. At the highest concentration, 0.25% by weight, the data for all three tubes show a gradual deviation from an extension of the laminar line but no transition is observed. At 0.1% the data for both the 0.0652- and 0.0328-in. tubes show the same behavior but a transition is observed for the 0.107-in. tube. At 0.05% the 0.0652-in. tube also shows a transition. Only when concentration was reduced to 0.02% does the 0.0328-in. tube show a transition region. At 0.008% it shows a more pronounced transition. Data for the other polymer solutions studied followed the same trends. If we consider transition behavior to be a characteristic of dilute solutions and the absence of a transition as defining concentrated solution behavior, we can define a critical concentration C_c for each tube which separates the two concentration regions. This critical concentration increases with tube diameter.

A summary of the data for each of the polymers listed in Table 1 and of the data of Hershey (*12*) and Rodriguez (*14*), all in the 0.0328-in. tube, is given in Table 2. Values of C_c increased with decreasing molecular weight. Values of $C_c[\eta]$, the critical volume fraction, are generally less sensitive to molecular weight variations (the cases of SE 30 and WSRN 10 will be discussed later) but also increase with decreasing molecular weight. The details of this trend cannot be determined from these data, as generally concentration changes were taken by factors of two or two and one-half in these experiments.

TABLE 1. POLYMERS STUDIED

Polymers	Designation	Source	Solvent	Temperature, °C.	Intrinsic viscosity $[\eta]$, dl./g.	Estimated molecular weight
Polydimethyl siloxane	SR 130	General Electric Co.	Toluene	25	8.0	11×10^6
Polydimethyl siloxane	SR 54	General Electric Co.	Toluene	25	5.3	5.6×10^6
Polydimethyl siloxane	SE 30	General Electric Co.	Toluene	25	0.83	3.0×10^5
Polyethylene oxide	PEO Coag	Union Carbide Co.	Water	30	13.2	2.8×10^6
Polyethylene oxide	WSR 301	Union Carbide Co.	Water	30	11.4	2.3×10^6
Polyethylene oxide	WSR 205	Union Carbide Co.	Water	30	4.95	7.8×10^5
Polyethylene oxide	WSR 35	Union Carbide Co.	Water	30	2.95	4.0×10^5
Polyethylene oxide	WSRN 10	Union Carbide Co.	Water	30	0.80	7.8×10^4
trans-Polyisoprene	trans-PIP 60	Polymer Corp.	Benzene	32	2.5	6.0×10^5
cis-Polybutadiene	PBD	B. F. Goodrich Co.	Toluene	30	3.6	3.5×10^5
cis-Polyisoprene	cis-PIP 280	Shell Chemical Co.	Toluene	25	8.5	2.7×10^6
cis-Polyisoprene	cis-PIP 70	B. F. Goodrich Co.	Toluene	25	4.0	7.1×10^5
Ethyl (cellulose)	ECN	Hercules Powder Co.	Benzene	25	3.1	1×10^5
1:1 Copolymer of epichlorohydrin and ethylene oxide	Hydrin 200	B. F. Goodrich Co.	Toluene	25	3.1	$2 \times 10^{6*}$

* Molecular weight estimated supplier.

TABLE 2. CRITICAL CONCENTRATIONS IN 0.03-IN. TUBE

Polymer	Solvent	C_c, wt. %	$[\eta]$ dl./g.	$C_c\,[\eta]$*	β
SR 130	Toluene	≈ 0.001	8.0	≈ 0.007	1.30
SR 54	Toluene	≈ 0.003	5.3	≈ 0.014	1.30
SE 30	Toluene	0.7-1.5	0.87	$\gg 0.45$	1.30
PEO Coag.	Benzene	0.001-0.003	13.5	<0.035; >0.012	1.38
WSR 301	Benzene	<0.003	12.7	<0.034	1.38
WSR 205	Benzene	0.008-0.02	4.5	0.03-0.08	1.38
WSR 35	Benzene	0.02-0.05	2.5	0.04-0.11	1.38
WSR N 10	Benzene	$\gg 0.4$	0.78	$\gg 0.27$	1.38
Hydrin	Toluene	<0.1	3.1	<0.27	—
trans-PIP 60	Toluene	≈ 0.2	2.5	≈ 0.43	1.50
cis-PBD	Toluene	>0.2	3.6	$>.62$	1.61
cis-PIP-280	Toluene	<0.02; >0.008	8.4	0.058-0.15	1.70
cis-PIP-70	Toluene	0.15-0.30	4.0	0.52-1.04	1.70
PIB L-200‡	Toluene	0.1-0.4	4.2	0.35-1.40	1.80
PIB L-200‡	Cyclohexane	0.05-0.20	6.6	0.28-1.14	1.80
PIB L-80†	Cyclohexane	0.1-0.3	3.5	0.30-0.91	1.80
PIB L-80†	Benzene (24°C.)	>0.9	0.82	>0.64	1.80
ECN	Toluene	$\gg 0.25$	2.5	$\gg 0.54$	2.0
PMMA§	Toluene	>0.9	1.7	>1.3	2.10
Polystyrene¶	Toluene	$\gg 0.94$	1.03	$\gg 0.80$	≈ 2.2

* C_c in g./dl.
† Polyisobutylene (*12*).
‡ Polyisobutylene (*14*).
§ Polymethyl methacrylate (*12*).
¶ Reference (*12*).

Not enough precise values of C_c in different tubes are available to determine the diameter dependency of $C_c[\eta]$. The few data available in the 0.03- and 0.1-in. tubes suggest a proportionality to D^2. This suggests that addition of another dimensionless length term such as (r^2/D^2) would give a constant product $C_c[\eta](r^2/D^2)$, independent of diameter and molecular weight for defining the critical concentration for each polymer. If so, in a given tube $C_c[\eta]$ should vary with intrinsic viscosity with a dependency of $[\eta]^{-(2+2a)/3a}$ or an exponent of about $-(1.5$ to $1.7)$ for a values of 0.8 to 0.65. The limited data for different molecular weights for polydimethyl siloxane and PEO solutions indicate a slope (log-log) greater than unity and less than two. More precise values of C_c are needed to describe quantitatively the effect of molecular weight on $C_c[\eta]$. Shin's $C^*[\eta]$ values for polyethylene oxide-water and polyisobutylene-cyclohexane solutions show a greater decrease with molecular weight than this.

The levels of $C_c[\eta]$ values are very sensitive to molecular structure differences. Values of β, the rigidity factor (*15*), are tabulated in the last column of Table 2. It can be seen that the low values of β (1.30 for polydimethylsiloxane and 1.38 for polyethylene oxide) are associated with low values of $C_c[\eta]$ and high values of β (1.80 for polyisobutylene and 2.10 for polymethyl methacrylate) are associated with high values of $C_c[\eta]$. Of particular interest is the comparison of trans-polyisoprene (trans-PIP 60) with cis-polyisoprene (cis-PIP 70), both of about the same molecular weight. The more flexible trans-polyisoprene ($\beta = 1.50$) with a slightly lower molecular weight ($\approx 600{,}000$) has a slightly lower value of $C_c[\eta]$ than the cis-polyisoprene ($\beta = 1.70$ and molecular weight $\approx$ 700,000).

Effect of Solvent

Since the theta solvent results of Hershey (benzene at 24°C.) for PIB L-80 did not extend to a concentration equal to C_c, it is not clear if $C_c[\eta]$ is also dependent on polymer-solvent interactions. Lee observed a three- to fourfold increase in C^* for polyisobutylene in benzene at 25°C. compared with polyisobutylene in cyclohexane (a good solvent). If this were also approximately the ratio for PIB L-80, C_c in benzene at 24°C. would be between 0.9 and 1.2% and $C_c[\eta]$ 0.63 to 0.85, close to the 0.91 value for PIB L-80 in the good solvent cyclohexane. Values of $C_c[\eta]$ for PIB L-200 in toluene and cyclohexane are about the same but toluene is also a fairly good solvent for polyisobutylene.

TABLE 3. CRITICAL CONCENTRATION FOR PEO IN 0.1-IN. TUBES

	Intrinsic viscosity $[\eta]$ dl./g.		Critical concentration C_c, %		$C_c\,[\eta]$*	
	Water	Benzene	Water (8)	Benzene (1)	Water	Benzene
WSR 301	20.0	—	0.0005-0.002	—	0.01-0.04	—
PEO Coag.	13.2	13.5	—	0.003-0.008	—	0.035-0.09
WSR 301	11.4	12.7	—	0.008-0.02	—	0.08-0.2
WSR 205	4.95	4.5	—	0.1-0.25	—	0.4-1.0
N 3000	3.9	—	0.1-0.2	—	0.4-0.8	—
N 750	3.4	—	>0.3	—	>1.0	—
WSR 35	2.95	2.5	—	0.1-0.25	—	0.2-0.5
N 80	1.8	—	>0.5	—	>0.9	—
WSRN 10	0.80	0.78	—	$\gg 0.4$	—	$\gg 0.3$
WSRN 10	0.73	—	$\gg 0.75$	—	$\gg 0.5$	—

* C_c in g./dl.

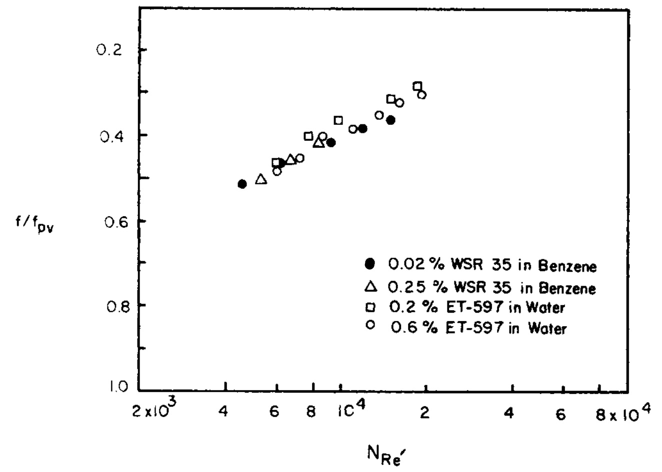

Fig. 7. Friction factor ratio versus Reynolds number for concentrated solutions of WSR 35 in benzene and ET-597 in water.

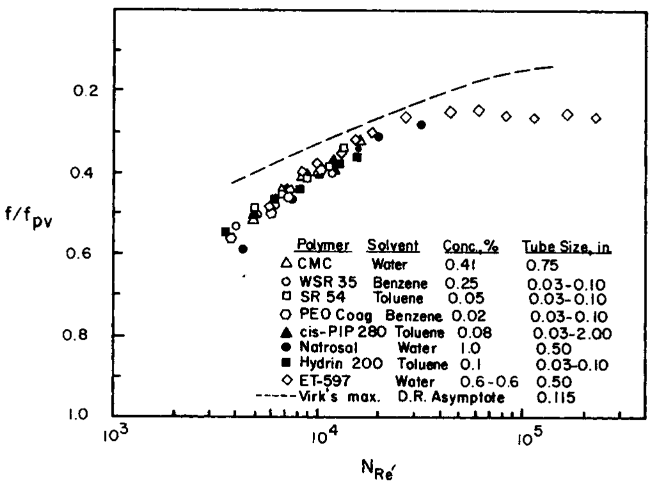

Fig. 8. Friction factor ratio versus Reynolds number correlation for eight concentrated polymer-solvent systems.

In Table 3 estimates of $C_c[\eta]$ for Liaw's data for several PEO samples in benzene in the 0.107-in. tube are given along with Virk's data on PEO samples in water in a 0.115-in. tube. For roughly equivalent molecular weights, the values of $C_c[\eta]$ in benzene solutions are of the same order or possibly a bit smaller than for the water solutions. At the highest molecular weight, $C_c[\eta]$ values in water are quite low. No sample with molecular weight as high as this was tested in benzene. Both are good solvents for PEO. Intrinsic viscosities in the two solvents are about equal, as seen in Table 3.

Molecular Weight Limits

As shown in Table 2 it was observed that two samples with low β values (SE 30 and WSRN 10) had values of $C_c[\eta]$ which were high. These polymers showed little drag reduction even at high $C[\eta]$ values. SE 30 had a molecular weight of 300,000 and WSRN 10 of 78,000. WSR 35 with a molecular weight of 400,000 had good drag-reducing characteristics and a low value of $C_c[\eta]$. Thus it appears that some minimum chain size must be exceeded before significant drag reduction occurs. Furthermore, the molecular weight required varies with the nature of the polymer.

TABLE 4. THE EFFECT OF ENTANGLEMENT CAPACITIES OF POLYMERS AND THEIR EFFECTIVENESS AS DRAG REDUCERS

Polymer	M	M_c(16)	m'	Effectiveness as drag reducers
SR 130	11.0×10^6	29,000	380	Good
SR 54	5.6×10^6	29,000	193	Good
SE 30	3.0×10^5	29,000	10	Poor
PEO Coag	2.8×10^6	6,000	458	Good
WSR 301	2.3×10^6	6,000	383	Good
WSR 205	7.8×10^5	6,000	133	Good
WSR 35	4.0×10^5	5,000	67	Good
WSRN 10	7.8×10^4	6,000	13	Poor
trans-PIP 60	6.0×10^5	——	——	Fair
cis-PBD	3.5×10^5	5,800	60	Fair
cis-PIP 280	2.8×10^6	14,000	191	Good
cis-PIP 70	7.1×10^5	14,000	50	Fair
PIB L-200	4.7×10^6	17,000	276	Good
PIB L-80	8.6×10^5	17,000	50	Fair
PIB LMMH	4.8×10^4	17,000	3	*
ECN	1.0×10^5	20,000	5	Poor
PMMA-G	1.5×10^6	36,000	42	Fair
PMMA-V 100	1.1×10^5	36,000	3	†
Polystyrene	2.4×10^5	35,000	7	*
Hydrin 200	2.0×10^6	——	——	Good

* No drag reduction (*12*).
† No drag reduction, (*14*).

The entanglement capacity of a polymer chain m' can be defined as

$$m' = M/M_c$$

where M_c is the critical chain entanglement molecular weight or the minimum chain size for molecular entanglements to occur. Polydimethyl siloxane has a large critical chain entanglement molecular weight [$M_c \approx 29{,}000$ (*16*)], while polyethylene oxide has a low value [$M_c \approx 6{,}000$ (*16*)]. Values of M_c, m', and rough classifications of relative effectiveness* as drag reducers are tabulated in Table 4.

The low entanglement capacities of WSRN 10 and SE-30 affect their ability to act as effective drag-reducing agents. This is also true for the ECN and polystyrene samples, as well as for the low molecular weight polyisobutylene and polymethyl methacrylate samples. The polymer samples with m' higher than about 50 are relatively effective drag-reducing additives, while those with m' below about 15 are poor despite low β values. This provides an estimate of the molecular weight level necessary for effective drag reduction in any polymer.

Friction Factor Correlation

Rodriguez (*14, 17*) has proposed a correlation of f/f_{pv} versus $V\tau_1/D^{0.2}$ which accounts for the effects of diameter and concentration in many dilute polymer systems.† This correlation is not suitable for concentrated solutions. Figure 6 shows the friction factor-generalized Reynolds number ($N_{Re'}$) plot for four WSR 35-benzene solutions (0.02, 0.05, 0.1, and 0.25%) in the 0.0328-in. tube and for Seyer's (*19*) ET 597-water solutions (0.2, 0.4, and 0.6%) in a 0.5-in. tube. No concentration effect is observed in

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* 50 percent drag reduction in the 0.1-in. capillary tubes in the range of flow rates studied here is good, 20% in the 0.1-in. tube is fair, and slight drag reduction in the 0.03-in. tube is poor.

† f_{pv} is the friction factor predicted by the Dodge-Metzner correlation (*18*) for purely viscous non-Newtonian flow, $1/\sqrt{f_{pv}} = (4.0/n'^{0.75})\log(N_{Re'}\, f_{pv}^{1-n'/2}) - 0.4/n'^{1.2}$. The use of f/f_{pv} allows the increased viscosity of the solutions and their non-Newtonian character to be taken into account in measuring friction factor reduction. This is particularly important for concentrated solutions. While an optimum polymer concentration for maximum drag reduction is observed at fixed turbulent flow conditions, values of f/f_{pv} generally approach some asymptotic value as concentration increases.

these two polymer-solvent systems, both of which are above C_c for the tube diameters used. The Seyer data lie well below those for the WSR 35-benzene solutions. This can be accounted for by the difference in the conventional predicted friction factors f_{pv} for the two systems. The WSR 35-benzene solutions with $n' \approx 1.0$ have much higher f_{pv} values than the ET 597-water solutions with $n' = 0.52$ to 0.55 at the same $N_{Re'}$. However, if the ratio f/f_{pv} is plotted versus $N_{Re'}$ as shown in Figure 7, the data for both systems coincide.

This correlation was tested with eight polymer-solvent systems as shown in Figure 8. The data of Shaver (*20*) for 0.41% CMC in water in a ¾-in. tube ($n' = 0.53$), of Seyer for 0.2 to 0.6% ET 597 in water in a ½-in. tube ($n' = 0.52$ to 0.55), and of Meter (*21*) for 1.0% Natrosol in water in a ½-in. tube ($n' = 0.35$ to 0.52) are included in this plot. Thus this correlation is good for both Newtonian and non-Newtonian fluids, for $N_{Re'}$ between 3.5×10^3 and 2×10^5, for both polar and nonpolar solvent solutions at all concentrations above C_c, and is independent of tube diameter.

Virk's postulated maximum drag reduction asymptote ($f = 0.42\ N_{Re}^{-0.55}$ based on his data for PEO in water solutions for Reynolds numbers of 4,000 to 150,000) is plotted in Figures 6 and 8 for comparison. In the correlation in Figure 8, the concentrated solution data approach Virk's maximum drag reduction asymptote for $10^4 < N_{Re'} < 3 \times 10^4$. Above and below that range, they lie below the asymptote. Virk's asymptote was obtained from experimental data on PEO solutions, most of which were dilute, that is, showed a definite transition region. Since these data are for concentrated solutions, they would not necessarily be expected to coincide with the asymptote.

It is of interest to note that Seyer's data for concentrated ET-597 solutions, which extend to high $N_{Re'}$, approach a value of f/f_{pv} of about 0.25 above $N_{Re'}$ of 40,000. Additional data at high values of $N_{Re'}$ are required to confirm this.

CONCLUSIONS

1. Drag-reducing polymer solutions can generally be classified as dilute or concentrated, depending on whether a critical concentration C_c is exceeded. Above C_c, friction factor-Reynolds number plots show a gradual deviation from an extension of the laminar line with no transition region. C_c increases with tube diameter approximately as D^2.
2. Values of $C_c[\eta]$ increase with decreasing molecular weight. The data are not precise enough to determine the exact molecular weight dependency. The D^2 dependency (see No. 1) suggests a dependence on $1/r^2$.
3. Data from this investigation and previous work show that $C_c[\eta]$ for equivalent molecular weights is a function of molecular structure. As the molecule becomes less flexible, β, the molecular rigidity factor, increases and $C_c[\eta]$ for a given tube size increases.
4. Comparative data in good and poor solvents indicate that solvent has little effect on values of $C_c[\eta]$.
5. Even for molecules of low β values, the ratio of molecular weight to M_c, the critical chain entanglement molecular weight, must exceed about 50 for effective drag reduction to occur.
6. For polymer solutions above C_c, all turbulent friction factor data can be correlated as a single function of f/f_{pv} versus $N_{Re'}$ over a Reynolds number range of 3×10^3 to 2×10^5. At high Reynolds numbers, f/f_{pv} approaches a value of about 0.25.

ACKNOWLEDGMENT

Acknowledgement is made to the donors of the Petroleum Research Fund, Administered by the American Chemical Society, for partial support of this research. The assistance of the suppliers of polymers used in this investigation is also appreciated. The help of J. M. Rodriguez, I. Radin, and J. Latty is also acknowledged. The suggestions of Professor A. Ram of the Technion, Israel Institute of Technology, were most helpful.

NOTATION

a = constant in Mark-Houwink equation, $[\eta] = KM^a$
C = concentration of polymer in solution
C_c = critical concentration from experimental flow data
$C_{c,s}$ = critical concentration (*3*) from $C_{c,s} = 0.493/[\eta]\gamma^3$
C^* = optimum concentration for minimum torque in Couette measurements (*3*)
C_t = minimum concentration for which extension of laminar line occurs in Couette experiments (*3*)
D = tube diameter
f = Fanning friction factor
f_{pv} = friction factor predicted from Dodge-Metzner relation (*18*)
g_c = gravitational constant
K' = consistency index defined by laminar tube equation $\tau_w = K'\ (8\ V/D)^n$
M = molecular weight
M_c = critical molecular weight for chain entanglement
m' = M/M_c
N = rotational speed of outer cylinder of Couette viscometer (*3*)
n' = flow behavior index
$N_{Re'} = \dfrac{D^{n'}\ V^{2-n'}}{g_c\ K'^{(n'-1)}}$
r^2 = mean square end-to-end distance of polymer molecules
r_0^2 = mean square end-to-end distance of polymer molecules at theta conditions
r^2_{0f} = mean square end-to-end distance for freely rotating polymer molecules
T = torque in Couette measurements (*3*)

Greek Letters

β = flexibility factor $\left(\dfrac{r_0^2}{r_{0f}^2}\right)^{1/2}$
ν = kinematic viscosity
ρ = density
$[\eta]$ = intrinsic viscosity
τ_1 = characteristic relaxation time of polymer molecule in solution
τ_w = wall shear stress in tube flow
γ = ratio of effective polymer molecular diameter to its root-mean-square end-to-end distance (*3*)

LITERATURE CITED

1. Liaw, G. C., Ph.D. thesis, Univ. Missouri, Rolla (1968).
2. Patterson, G. K., J. L. Zakin, and J. M. Rodriguez, *Ind. Eng. Chem.*, **61**, 22 (1969).
3. Shin, H., Sc.D. thesis, Massachusetts Inst. Technol., Cambridge (1965).
4. Merrill, E. W., K. A. Smith, H. Shin, and H. S. Mickley, *Trans. Soc. Rheol.*, **10** (10), 335 (1966).
5. Walsh, M. A., Sc.D. thesis, California Inst. Technol., Pasadena (1967).
6. Simha, R., and J. L. Zakin, *J. Chem. Phys.*, **31**, 1791 (1960).
7. Lee, T. S., Sc.D. thesis, Massachusetts Inst. Technol., Cambridge (1966).
8. Virk, P. S., Sc.D. thesis, Massachusetts Inst. Technol., Cambridge (1966).

9. ———, E. W. Merrill, H. S. Mickley and K. A. Smith, *J. Fluid Mech.*, **30**(2), 305 (1967).
10. Pruitt, G. T., and H. R. Crawford, *Rept. DTMB under Contract Nonr-4306(00)*, Western Co. (Apr. 1965).
11. Pruitt, G. T., B. Rosen and H. R. Crawford, *Rept. DTMB-2 under Contract Nonr-4306(00)*, Western Co. (Aug. 1966).
12. Hershey, H. C., Ph.D. thesis, Univ. Missouri, Rolla (1965).
13. ———, and J. L. Zakin, *Chem. Eng. Sci.*, **22**, 1847 (1967).
14. Rodriguez, J. M., M. S. thesis, Univ. Missouri, Rolla (1966).
15. Brandrup, J., and E. H. Immergut, "Polymer Handbook," Interscience, New York (1966).
16. Porter, R. S., and J. F. Johnson, *Chem. Rev.*, **66**, 1 (1966).
17. Rodriguez, J. M., J. L. Zakin, and G. K. Patterson, *Soc. Petrol Eng. J*, **7**, 325 (1967).
18. Dodge, D. W., and A. B. Metzner, *AIChE J.*, **1**, 434 (1955).
19. Seyer, F. A., and A. B. Metzner, *Can. J. Chem. Eng.*, **45**, 121 (1967).
20. Shaver, R. G., Sc.D. thesis, Massachusetts Inst. Technol., Cambridge (1957).
21. Meter, D. M., Ph.D. thesis, Univ. Wisconsin, Madison (1965).

Manuscript received December 1, 1969; revision received March 2, 1970; paper accepted March 5, 1970.

Blood-Gas Transfer in an Axial Flow Annular Exchanger

HSIN-KANG CHANG and LYLE F. MOCKROS

Northwestern University, Evanston, Illinois

The rates of hemoglobin saturation and carbon dioxide reduction in blood flowing in an annular-shaped membrane exchanger were studied theoretically by considering two limiting cases: the fluid-limited case and the wall-limited case. The blood is assumed to flow axially with a fully developed laminar profile. In the fluid-limited analysis the membrane wall is assumed to be infinitely permeable, so the efficiency of the oxygenator depends solely on the rate of gas transport within the blood. In the wall-limited case the blood is assumed to have infinite transport ability, thus the efficiency of the oxygenator is limited by the diffusion rate through the wall. For realistic radii ratio, the oxygenator is fluid limited, thus suggesting the need for enhanced blood mixing. In the fluid-limited case the rate of gas transport depends on the radii ratio and a dimensionless length, which is independent of the cylinder sizes. If $P_{O_2} = 715$ mm. Hg and $P_{CO_2} = 0$ mm. Hg are maintained at both walls, oxygenation is the slower process. For the same flow rate the length required for complete hemoglobin saturation in the annulus with an inner to outer radius ratio of 0.95 is 1/65 of that required in a circular tube.

Auxiliary blood-gas exchange devices, commonly (although incorrectly) known as oxygenators, are generally of three types: bubble, film, and membrane. Of these three types the membrane oxygenator is the least developed, but considered by many to be most promising (*1*). A membrane oxygenator consists of a closed, semipermeable conduit submerged in an oxygen-rich atmosphere. The blood flows in the conduit and receives oxygen and expels carbon dioxide through the conduit wall. Recently, several investigators (*2* to *6*) have studied the properties of membrane oxygenators with both experiments and mathematical analyses and have, in general, been successful in their theoretical predictions. The present paper utilizes a mathematical technique, which has been experimentally substantiated for other geometries, for the study of gas transfer in an axial flow annular exchanger. This paper, together with a subsequent paper on channel flow exchangers, is intended to supplement the previous papers on circular tube flow and provide overall guidelines for designing oxygenators.

Since the resistance to mass transfer comes from two sources, the membrane and the blood, some knowledge of the overall rate of gas exchange may be gained by considering two limiting cases. The first limiting case, referred to as the fluid-limited case, assumes that the wall flux so exceeds the flux in the blood that the wall may be neglected. The second limiting case, referred to as the wall-limited case, assumes that the lateral gas transfer in the blood phase is infinitely fast and the efficiency of the oxygenator is limited by the diffusion rate through the membrane.

In the fluid-limited analysis the gas transport process is described by two convective diffusion problems, one for oxygen and one for carbon dioxide, with generation or loss of material by instantaneous chemical reactions. Due to the Bohr and Haldane effects, these two problems are not independent of each other. The mutual dependency manifests itself at the local level. In large-scale systems, such as these auxiliary lungs, the interdependent effect is small and it is practical to treat the two diffusion processes separately, with some provisions for the Bohr and Haldane effects on each of them.

FLUID-LIMITED ANALYSIS

The analysis of the fluid-limited case for the blood gas

Hsin-kang Chang is at the State University of New York at Buffalo, Buffalo, New York.