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NOTATION

D = molecular diffusivity, cm^2/s
D_p = particle diameter, cm
J = $(k_L/U)\ (N_{Sc})^{2/3}$
k_L = mass transfer coefficient, cm/s
N_{Sc} = Schmidt number, ν/D
N_{Re} = Reynolds number, D_pU/ν
U = superficial velocity, cm/s
ϵ = porosity
ν = kinematic viscosity, cm^2/s

LITERATURE CITED

Dryden, C. E., O. A. Strang, and A. Z. Withrow, "Mass Transfer in Packed Beds at Low Reynolds Numbers," *Chem. Eng. Progr.*, **49**, 191 (1953).

Garner, F. H., and R. D. Suckling, "Mass Transfer from a Soluble Solid Sphere," *AIChE J.*, **4**, 114 (1958).

Kataoka, T., Y. Hiroyuki and U. Koresune, "Mass Transfer in the Laminar Region in the Packed Bed," *J. Chem. Eng. Japan*, **5**, 132 (1972).

Linton, W. H., Jr., and T. K. Sherwood, "Mass Transfer from Solid Shapes to Water in Streamline and Turbulent Flow," *Chem. Eng. Progr.*, **46**, 258 (1950).

McCune, L. K., and R. H. Wilhelm, "Mass and Momentum Transfer in Solid-Liquid Systems," *Ind. Eng. Chem.*, **41**, 6 (1949).

Steinberger, R. L., and R. E. Treybal, "Mass Transfer from a Solid Soluble Sphere to a Flowing Liquid Stream," *AIChE J.*, **6**, 227 (1960).

Williamson, J. E., K. E. Bazaire, and C. J. Geankoplis, "Liquid Phase Mass Transfer at Low Reynolds Numbers," *Ind. Eng. Chem. Fundamentals*, **2**, 146 (1963).

Wilson, E. J., and C. J. Geankoplis, "Liquid Mass Transfer at Very Low Reynolds Numbers in Packed Beds," *AIChE J.*, **5**, 9 (1966).

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Turbulent Drag Reduction By Polyacrylic Acid

S. H. BANIJAMALI, E. W. MERRILL, K. A. SMITH and L. H. PEEBLES, JR.

Department of Chemical Engineering
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

In this note we offer further observations on the role of polyacrylic acid in drag reduction of turbulent flows. Savins (1967) reported that polyacrylic acid in aqueous solution, at several degrees of neutralization up to and including the completely ionized sodium salt, was not drag reducing while polyacrylamide of comparable molecular weight was drag reducing. Hand and Williams (1971) later reported finding maximum drag reduction of aqueous polyacrylic acid solutions over the *p*H range 1 to 3 with insignificant drag reduction over the *p*H range 3 to 9.

More recently Kim et al. (1973) and Ting et al. (1973) restudied the effects of hydrogen ion concentration (and thus degree of salt formation) of polyacrylic acid. Their conclusions indicate that polyacrylic acid, contrary to Hand and Williams (1971), is more effective in the ionized form, at *p*H levels in the alkaline range. It is of course well recognized that a polyelectrolyte such as the sodium salt of polyacrylic acid will become extended in aqueous solutions as the ionic strength is lowered and that the drag reducing qualities become somewhat enhanced on this account. We sought to clarify the behavior of polyacrylic acid and its sodium salt in aqueous solutions by synthesizing a polymer of higher molecular weight than previously reported, characterizing it by light scattering under various *p*H conditions, and determining the drag reducing properties of the polymer as a function of *p*H and ionic strength.

EXPERIMENT

Polymerization

Acrylic acid was polymerized by ultraviolet irradiation (300 watt mercury source) of an aqueous solution of the monomer under nitrogen.

The monomer previously had been purified by redistillation at 16 mm of mercury. The temperature of reaction was 25°C. Concentration of the acrylic acid in water was 20% by volume. After one hour a transparent, nearly-gelled continuum was obtained. This was transferred into distilled water and subjected to gentle agitation for several hours to form a viscous solution. No residual gel was found after this treatment. The solution was placed in a vacuum oven at partial vacuum (35 mm mercury) at 75°C for 16 hours to volatilize the residual unreacted monomer. The final polymer concentration in the solution following monomer removal, was determined by two independent methods: (1) drying to constant weight, and (2) titration with 1 Normal NaOH. The two methods agreed to within 5%.

Characterization of Polymer

The polymer was analyzed by light-scattering at 25°C in three different solvent media:

1. 1.0 M NaCl solution adjusted to a *p*H of 10 by addition of NaOH;
2. 0.5 M NaCl solution and *p*H of 4.1;
3. distilled water adjusted to a *p*H of 2 by addition of concentrated HCl.

Correspondence concerning this note should be addressed to E. W. Merrill. L. H. Peebles is at the Office of Naval Research, Boston, Massachusetts.

Table 1. Intrinsic Viscosities and Radii of Gyration in Three Solvent Media

		Viscosity data	
Solution of PAA, $\overline{MW} \simeq 8 \times 10^6$	$[\eta]$, dl/g	$<\bar{\rho}^2>^{1/2}$ Based on Flory-Fox equation	$<\bar{\rho}^2>_z^{1/2}$ Based on light-scattering
Distilled water $pH = 2, C = 35$ ppm	6.7	1200Å	1435Å
Distilled water $pH = 4.1, C = 35$ ppm	17.0	1620Å	
Distilled water $pH = 10, C = 35$ ppm	61.0	2450Å	
0.5 Molar NaCl $pH = 4.1, C = 45$ ppm	11.3	1400Å	1680Å
1.0 Molar NaCl $pH = 7.3, C = 45$ ppm	18.0	1635Å	
1.0 Molar NaCl $pH = 10, C = 35$ ppm	23.2	1760Å	2050Å

Figures 1a through 1c show the Zimm plots obtained for the same polymer in the three media. From the ordinate intercept the weight average molecular weights were calculated to be 8.4×10^6 (as obtained by the first two solvent media) and 7.7×10^6 in the third medium. Further, the square root of the z-averaged squared radius of gyration $<\rho^{-2}>_z^{1/2}$ was found to be 2050 Å in 1.0 M NaCl solution at pH 10, 1680 Å in 0.5 M NaCl solution at pH 4.1, and 1435 Å in distilled water at pH 2. The intrinsic viscosities of this polymer in the three solvent media were also obtained and are shown in Table 1.

The simultaneous determination of the values for the intrinsic viscosities and the molecular weight allowed determination of the root mean squared radius of gyration $<\bar{\rho}^2>^{1/2}$ by utilizing the Flory-Fox equation for semipermeable random-coiling polymers:

$$[\eta] = \Phi \frac{<\bar{r}^2>^{3/2}}{M} \tag{1}$$

and the relation

$$<\bar{\rho}^2> = \frac{<\bar{r}^2>}{6} \tag{2}$$

Fluid Mechanical Studies

Equipment used for measuring drag reduction consisted of a 5-gal. blow-down tank from which the solution was forced under a constant gas pressure through a smooth stainless steel tube of 0.457-cm internal diameter. This tube had two pressure taps, the first at about 100 diameters downstream from the entrance. The pressure difference between the two taps was measured by a transducer with a precision of 1 mm of mercury and the volumetric flow rate measured directly by observation of the rate of filling of a container from the pipes.

RESULTS

Drag reduction experiments were carried out on the polyacrylic acid samples in water of varying pH (varied by addition of HCl or NaOH) to study the effect of degree of ionization of the polymer on its drag-reduction potentiality. Results are shown in Figure 2. At a pH between 4.1 and 10 the solution becomes highly drag reducing and the onset of drag reduction begins at the laminar region. At a pH of 2.0, the drag reduction is negligible, exactly the opposite of that reported by Hand and Williams (1971). These results in Figure 2 are replotted according to the method of Virk (1971) in Figure 3 to indicate the degree of approach to the maximum drag reduction asymptote.

To explore further the effect of ionic strength of the solution, we added a solution of sodium chloride to the

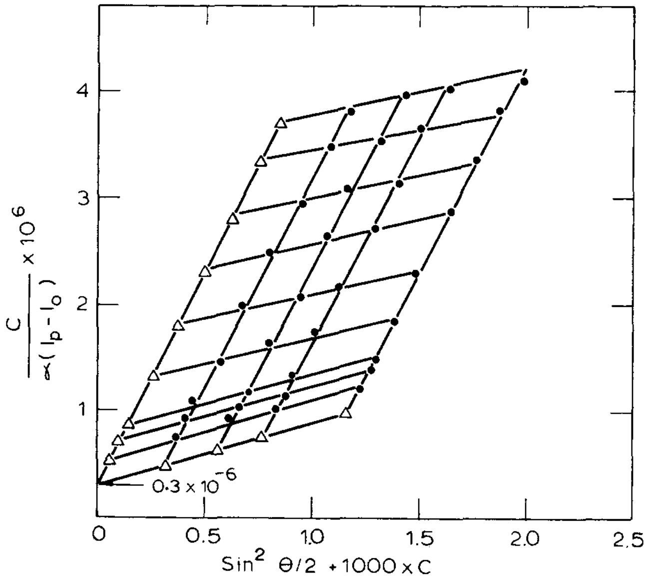

Fig. 1a. Zimm plot—Sample PAA, $\overline{M}_w = 8.4 \times 10^6$ in 1 M NaCl, pH = 10.

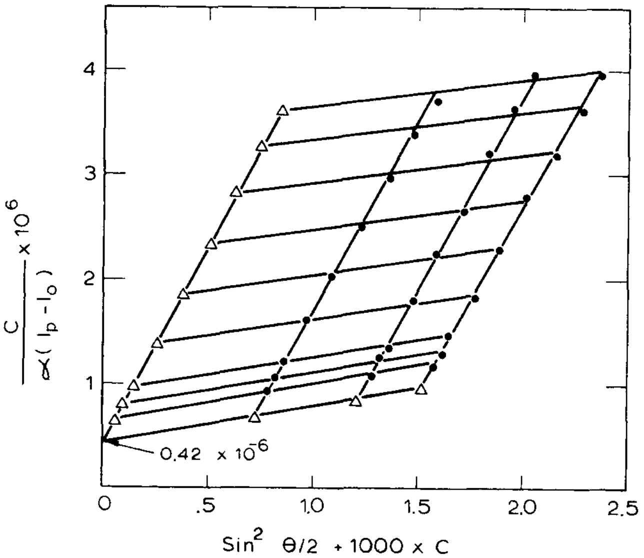

Fig. 1b. Zimm plot—Sample PAA in 0.5 M NaCl, pH = 4.

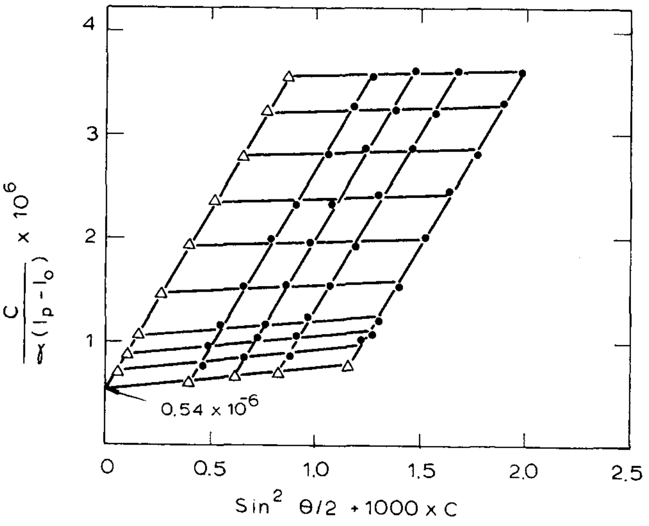

Fig. 1c. Zimm plot—Sample PAA in distilled water adjusted to pH = 2 by hydrochloric acid.

polymer to form a 0.5 M solution at *p*H 4.1, and 1.0 M solution at *p*H 7.3, and a 1.0 M solution at *p*H 10. Figure 4 shows that there is no significant effect of added salt on the already excellent drag reducing properties of the fully ionized polysalt at *p*H 7.3 and 10. At *p*H 4.1, however, the partially ionized polymer which was effective in water at low ionic strength, probably on account of self-expansion, is seen to become significantly less effective.

DISCUSSION

We believe these data are completely at variance with the report of Hand and Williams (1971) who suggested that the polyacrylic acid might have a helix conformation in solution at low *p*H so that it becomes a better drag reducer. Our data confirm in general the conclusions of Kim et al. (1973) and Ting et al. (1973). As the polymer varies from the nonionized polycarboxylic acid in the form of a compact coil at *p*H 2 to the polycarboxylate salt in the form of a very highly extended coil in solutions of low ionic strength, its effectiveness in drag reduction continuously increases. The drag reducing properties of this polymer as a polysalt are completely in accord with most previous observations reported in the literature and with extensive work previously done in our laboratories.

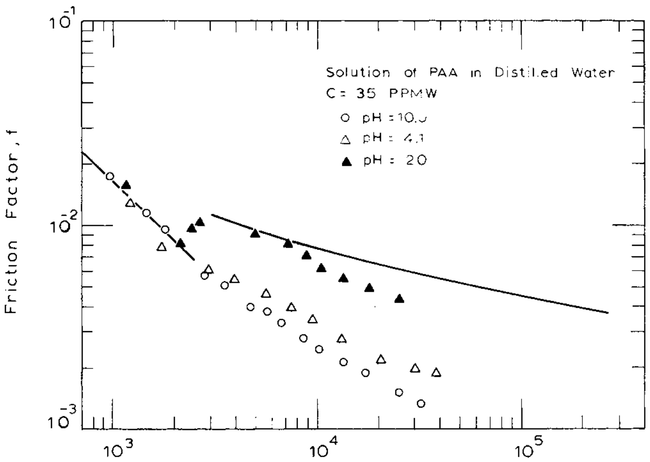

Fig. 2. Friction factor vs. Reynolds number—PAA solutions at three values of *p*H.

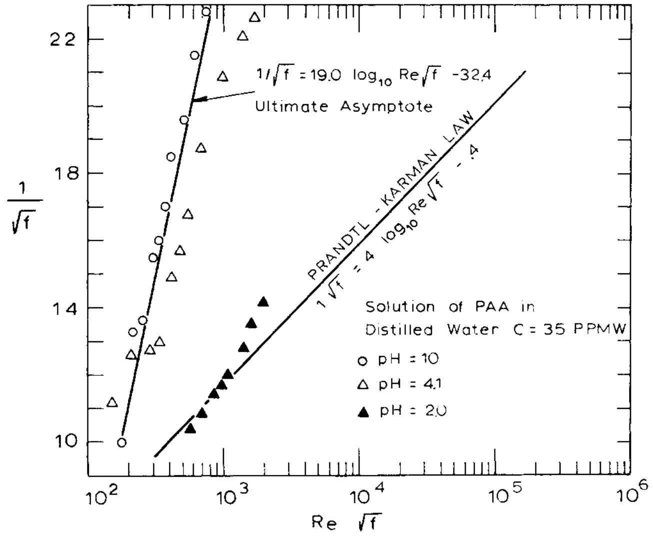

Fig. 3. Maximum drag reduction asymptote compared with Prandtl-von Karman Law.

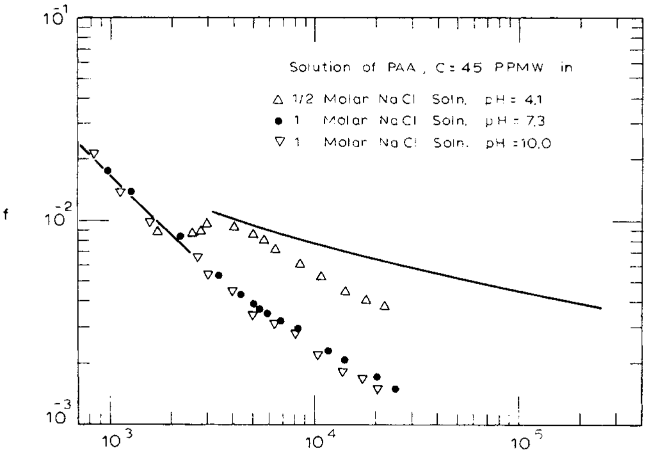

Fig. 4. Friction factor vs. Reynolds number—PAA solution at different *p*H values.

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NOTATION

f = friction factor, $f = 2D(\Delta P/L)\rho\bar{V}^2$
D = tube diameter
$\bar{V}$ = average velocity inside the tube
ΔP = pressure drop along the length L of the tube
Re = Reynolds number, $\rho\bar{V}D/\eta$
η = solution viscosity
ρ = solution density
c = polymer concentration, g/cm^3
I_P = intensity scattered by the polymer solution
I_0 = intensity scattered by the solvent
θ = observation angle
α = $\sin^2\frac{\theta}{2}/(1 + \cos^2\theta)$
$[\eta]$ = intrinsic viscosity, dl/g
Φ = universal constant, 2.66×10^{21}
$\bar{r}^2$ = squared end-to-end distance of macromolecule
$\bar{\rho}^2$ = squared radius of gyration of macromolecule

LITERATURE CITED

Clarke, W. B., Sc.D. thesis, "Polyelectrolytes in Solution—Their Conformation and Turbulent Flow Characteristics," M.I.T., Cambridge (1970).

Hand, J. H., and M. Williams, "The Role of Polymer Conformations in Drag Reduction," *Chem. Eng. Prog. Symp. Ser. No. 111,* 67, (1971).

Kim, O. K., R. C. Little, and R. Y. Ting, "Polymer Structural Effects in Drag Reduction," *AIChE Symp. Ser. No. 130,* **69,** 39 (1973).

Savins, J. G., "A Stress-Controlled Drag-Reduction Phenomenon," *Rheol. Acta.,* 6, 323 (1967).

Ting, R. Y., and O. K. Kim, "Drag reduction properties of ultra-high molecular weight polyacrylamide & related polymers," p. 151, in *Water Soluble Polymers,* N. M. Bikales, Editor, (Polymer Sci. & Technology, vol. 2), Plenum Pub., New York (1973).

Virk, P. S., Sc.D. thesis, "The TOMS Phenomenon—Turbulent Pipe Flow of Dilute Polymer Solutions," M.I.T., Cambridge (1966).

———., "An Elastic Sublayer Model for Drag Reduction by Polymer Solutions of Linear Macromolecules," *J. Fluid. Mech.,* **45,** 417 (1971).

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