

Drag Reduction and Molecular Structure. The Interaction of Polyethylenimine with Some Linear High Polymers

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Synopsis

The structure of polyethylenimine in aqueous and ethanolic solutions was investigated by measuring the fluorescence polarization of dansyl conjugates. In aqueous solutions, all polyethylenimines, whatever their molecular weight, are associated into large aggregates containing rotating units having rotary relaxation times corresponding to spherical particles of molecular weight about $3-6 \times 10^3$. The interaction of polyethylenimine with very dilute solutions of linear high polymers has been investigated by fluorescence polarization measurements and by the measurement of turbulent drag. Addition of polyethylenimine causes the solutions of anionic polymers to lose their capability of reducing turbulent drag. The results are discussed in relation to the proposed structure of the anionic-cationic complexes formed in the mixtures.

INTRODUCTION

According to one hypothesis,¹ the degree of reduction of turbulent drag in flowing liquids should be greatest with those additives whose particles assume greatly elongated forms under the conditions of shear stress concerned. Although some additives consist of nonionic linear polymers having apparently little capability of aggregation, others such as certain complex soap systems² seem to rely for their drag-reducing capability on the formation of micelles. It is therefore of interest to observe the effect of polymers capable of aggregating by hydrogen bond formation or by electrostatic attraction. The object of the present experiments was to investigate the degree of aggregation of one such polymer using fluorescence polarization measurements and to determine the effect of mixing it with dilute solutions of other polymers capable of causing drag reduction on their own.

APPLICATION OF FLUORESCENCE POLARIZATION MEASUREMENTS

The general theory of the rotary depolarization of the fluorescence of solutions has been worked out by Perrin³⁻⁵ and Weber.⁶ For solutions containing one size of rigid spherical fluorescent molecule illuminated with

vertically polarized exciting light, the degree of polarization of the fluorescence (p) is related to the rotary relaxation time of the molecules (ρ_0) and the lifetime of the fluorescence (τ) by

$$\frac{1}{p} = \frac{1}{p_0} + \left(\frac{1}{p_0} - \frac{1}{3} \right) \left(\frac{3\tau}{\rho_0} \right) \quad (1)$$

where p_0 is the maximum value of p observed in completely rigid medium, or by

$$\frac{1}{p} = \frac{1}{p_0} + \left(\frac{1}{p_0} - \frac{1}{3} \right) \left(\frac{\tau RT'}{V\eta} \right) \quad (2)$$

where V is the volume of the sphere and η is the viscosity of the solution. A plot of $1/p$ against T/η will thus give a straight line from the slope and intercept of which τ/V can be determined.

If the solution contains a mixture of spherical molecules of various volumes but all carrying the same fluorescent oscillator, and if one chooses a temperature range for which $\tau/\rho_0 \gg 1$ for all molecules except the largest, the polarization will obey the equation

$$\frac{1}{p} = \frac{1}{p_0'} + \left(\frac{1}{p_0'} - \frac{1}{3} \right) \left(\frac{3\tau}{\rho_0} \right) = \frac{1}{p_0'} + \left(\frac{1}{p_0'} - \frac{1}{3} \right) \left(\frac{\tau RT'}{V'\eta} \right) \quad (3)$$

Thus, a linear plot is still obtained, but with a larger intercept $1/p_0'$. From this plot, the value of τ/V' for the largest molecules in the mixture may be determined. The value of p_0' may be used to determine f_1 , the fraction of the total fluorescence intensity contributed by the largest species, using the equation

$$f_1 = \frac{1/p_0 - 1/3}{1/p_0' - 1/3}. \quad (4)$$

Many nonspherical molecules, whether rigid or flexible, give a linear plot over an appropriate range of T/η , from which by substituting in eq. (3) a value of V' may be determined. This value we define as the "equivalent spherical kinetic unit." This corresponds to the largest section of the complex molecule that rotates as a unit and contributes significantly to the total fluorescence intensity. The actual volume may be smaller than V' because the mean rotary relaxation time of an oblate spheroid and the larger rotary relaxation time of a prolate spheroid are both greater than that of a sphere of equal volume (by factors of approximately 4.5 and 13 for an axial ratio of 10). The size of the equivalent spherical kinetic unit is nevertheless convenient for assessing the significance of the polarization data. For example, if it is much smaller than the molecular weight, the molecule must contain many independently rotating parts. If it is much larger than the molecular weight, the material must form large rigid aggregates. Finally, it should be noted that an upward curvature of the reciprocal polarization- T/η plot indicates that intramolecular rotational dissociation takes place as the temperature is raised.

EXPERIMENTAL

Polyethylenimine (PEI). Specimens were obtained from the Dow Chemical Company having the following nominal ranges of molecular weight: 0.45–0.75, 1.05–1.35, 1.65–1.95, 40–60, and 50–100 $\times 10^3$. The materials were said to contain primary, secondary, and tertiary nitrogen atoms in the approximate ratio 1:2:1. This corresponds to a linear polymer in which one third of the nitrogen atoms have the group $C_2H_4(NH_2)$ attached. The actual structure is no doubt multibranched, but the degree of branching must be limited in order to maintain the primary/tertiary ratio near unity. The materials were provided as concentrated aqueous solutions, and the proportion of polymer was determined by titration with hydrochloric acid using bromocresol green as indicator.

Drag-Reducing Polymers. The poly(ethylene oxide) (Polyox WSR 301) was obtained from Union Carbide (UK) Ltd. The polyacrylamides and poly(acrylic acids) were provided by Allied Colloids Manufacturing Co. Ltd. The proportion of anionic groups in the polyacrylamide R155 was determined by conductometric titration and found to be 11.5% calculated as acrylic acid. The poly(acrylic acid) E21 was provided as an approximately 10% solution. Portions of this were dried to constant weight to determine the concentration of the polymer. The poly(acrylic acid) S25 was provided in partly neutralized form. The sodium and volatile matter were determined and allowed for in preparing standard solutions. The molecular weights of the poly(acrylic acids) were estimated from viscosity measurements in $2 \times 10^{-3}N$ HCl. The intrinsic viscosities $[\eta]$ were found to be 2.16 and 4.54 dl/g for E21 and S25, respectively. According to the data of Katchalsky and Eisenberg,⁷ for poly(methacrylic acid) these values correspond to molecular weights of 8.9 and 39×10^6 .

Introduction of Fluorescent Groups. To 0.5 g of polymer (11.6 mmoles of monomer) dissolved in 50 ml water was added a solution of 12 mg (0.045 mmole) 1-dimethylaminonaphthalene-5-sulfonyl chloride (dansyl chloride) dissolved in 1 ml acetone. To facilitate dispersion of the reagent, the dansyl chloride solution was added dropwise while the polymer solution was subjected to mild ultrasonic agitation. (The addition took 1–2 min, and separate experiments showed that ultrasonic agitation for 30 min had a negligible effect on the properties of the polymer.) The solution was finally kept in gentle motion overnight to allow complete reaction of the dansyl chloride. A small part of the latter was hydrolyzed to dansic acid the fluorescence of which would dilute the fluorescence polarization of the polymer conjugate. In many experiments, the dansic acid was removed by diluting the solution to a polymer concentration of 2000 ppm and passing it through a column of Amberlite IRA 410 anion exchange resin 200 mm long and 10 mm in diameter. The dansic acid was strongly adsorbed in the first few millimeters, and the column could be used for treating several batches of solution before regenerating it with 1.0*N* sodium hydroxide.

Measurement of Fluorescence Polarization. One double quartz prism monochromator was used to isolate the required wavelength of exciting

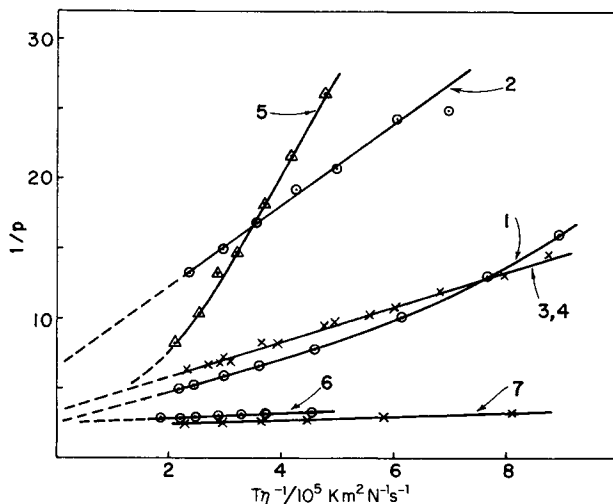


Fig. 1. Typical polarization-temperature plots of dansyl-conjugated polyethylenimine solutions. The numbers against the graphs refer to the solutions numbered in column 6 of Table I. Ordinate: $1/p$; abscissa: $T\eta^{-1}/10^5 \text{ Km}^2 \text{ N}^{-1} \text{ s}^{-1}$.

light (366 nm mercury line) and a second to isolate a band of wavelengths (25 nm half-bandwidth at 550 nm) near the maximum of the fluorescence emission spectrum. Interference by exciting light scattered by the polymer was thus negligible. The spectrofluorimeter was used in the right-angle mode and was fitted with the usual arrangement⁸ of beam splitter, quantum counter, and ratio recorder to compensate for fluctuations in the intensity of the mercury lamp. Glan-Thompson prisms were used to polarize the exciting light and analyze the polarization of the fluorescence using the method of Azumi and McGlynn⁹ to correct for polarization introduced by the optics. The solutions were maintained at the required temperature inside a Dewar vessel by means of a current of air the temperature of which was controlled by passing it through a cooled copper coil or an electrically heated tube. Reciprocal polarization- T/η plots were made using solutions containing 100 ppm of polymer ($2.3 \times 10^{-3} M$ monomer). Solvents were: water, dilute HCl, ethanol, and dilute ethanolic HCl containing 5% v/v water. Many of the plots were linear, either throughout their length or at low values of T/η , and there was no difficulty in measuring the intercept $1/p_0'$ and the slope. These were inserted in eq. (3) with the calculated fluorescence lifetime (see below), and the value of V' , the equivalent spherical kinetic unit, was calculated. Some plots curved upward throughout their lengths. These were extrapolated to an intercept $1/p_0'$ equal to 2.0 and the best estimate made of the limiting slope. In some cases, this estimate was highly subjective (e.g., curve 5 in Fig. 1), and the derived values of V' from such cases are only very approximate. These values are enclosed in square brackets in Table I. Some typical plots are shown in Figure 1. The complete set of data are summarized in Table I. Values of f_1 were calculated using eq. (4) with the assumption that $1/p_0' = 2.0$. The

TABLE I
Summary of Polarization-Temperature Data^a

| Solvent | Mol. wt. of polymer $M_r, \times 10^3$ | p_0' | $V',$ $10^{-3}m^3$ | f_1 | Shape of plot |
|--|---|--------|-----------------------|-------|---------------------|
| Water | 0.6 | 0.15 | 4.7 ^b | 0.26 | slight upward curve |
| | 1.8 | 0.26 | 3.7 ^b | 0.47 | linear |
| | 50 | 0.50 | 3.3 ^b | 1.0 | slight upward curve |
| | 75 | [0.5] | [3.5] ^b | [1.0] | slight upward curve |
| | 75 | 0.40 | 4.5 ^b | 0.77 | slight upward curve |
| 1.15 × 10 ⁻³ N HCl | 75 | 0.43 | 6.0 ^b | 0.84 | (1) upward curve |
| | 75 | 0.41 | 2.8 ^b | 0.79 | linear |
| 2.3 × 10 ⁻³ N HCl | 0.6 | 0.16 | 4.0 ^b | 0.28 | (2) linear |
| | 0.6 | 0.15 | 6.3 | 0.26 | approx. linear |
| | 1.2 | 0.27 | 2.9 ^b | 0.50 | linear |
| | 1.8 | 0.23 | 3.6 ^b | 0.42 | linear |
| | 75 | 0.42 | 2.9 ^b | 0.81 | linear |
| | 75 | 0.31 | 4.3 ^b | 0.58 | (3) linear |
| | 75 | 0.31 | 4.2 | 0.58 | (4) linear |
| 10 ⁻² N HCl | 1.8 | 0.29 | 4.0 ^b | 0.54 | slight upward curve |
| | 75 | 0.41 | 3.5 ^b | 0.79 | linear |
| | 75 | 0.40 | 3.8 ^b | 0.77 | linear |
| Ethanol | 0.6 | [0.5] | [0.8] | [1.0] | upward curve |
| | 1.8 | [0.5] | [1.4] | [1.0] | upward curve |
| | 75 | [0.5] | [5.3] | [1.0] | (5) upward curve |
| | 75 | [0.5] | [4.0] | [1.0] | upward curve |
| Ethanolic HCl 2.3 × 10 ⁻³ N | 1.2 | 0.34 | 48 | 0.64 | linear |
| | 1.8 | 0.33 | 120 | 0.62 | upward curve |
| | 50 | 0.41 | 100 | 0.79 | (6) linear |
| | 75 | 0.38 | 130 | 0.73 | linear |
| Poly(acrylic acid) (50% excess) in 0.001M NaHCO ₃ | 75 | 0.44 | 86 ^b | 0.86 | (7) linear |

^a The numbers in column 6 refer to the curves in Fig. 1.

^b Indicates that the solution of conjugated PEI had been passed through an anion exchange column.

values are thus only approximate but serve to show that the V' values refer to kinetic units contributing a large proportion of the total fluorescence intensity. Some single measurements at 20°C and some temperature plots were also made with solutions of PEI mixed with the drag-reducing polymers. The results of single measurements are summarized in Table III, and the value of V' are included in Table I. Further measurements with varying proportions of polymers are included in Figure 2.

Fluorescence Efficiency and Lifetime. The fluorescence efficiencies of the dansyl-PEI in the various solvents were measured in the usual way⁸ by comparison with quinine bisulfate in 0.1N H₂SO₄, allowance being made for the polarization of the polymer solutions. The results are given in Table II. The lifetime of the dansyl-PEI in ethanol was measured by monitor-

TABLE II
 Fluorescence Efficiencies

| Solution | Fluorescence maximum $\nu, \mu\text{m}^{-1}$ | Fluorescence efficiency | Calculated fluorescence lifetime τ, ns |
|---|---|-------------------------|---|
| PEI in water | 1.72 | 0.177 | 4.4 |
| PEI in $2.3 \times 10^{-3} N$ HCl | 1.70 | 0.095 | 2.3 |
| PEI in 95% ethanol | 1.85 | 0.457 | 11.3 ^a |
| PEI in $2.3 \times 10^{-3} N$ ethanolic HCl | 1.83 | 0.476 | 11.8 |
| PEI-PAA complex in 0.001M NaHCO ₃ | 1.78 | 0.256 | 6.3 |

^a Direct determination on this solution gave 10.6 ns (Dr. Phillip's apparatus) and 12.0 ns (author's apparatus). The indicated mean value was used for the calculation on the other solutions.

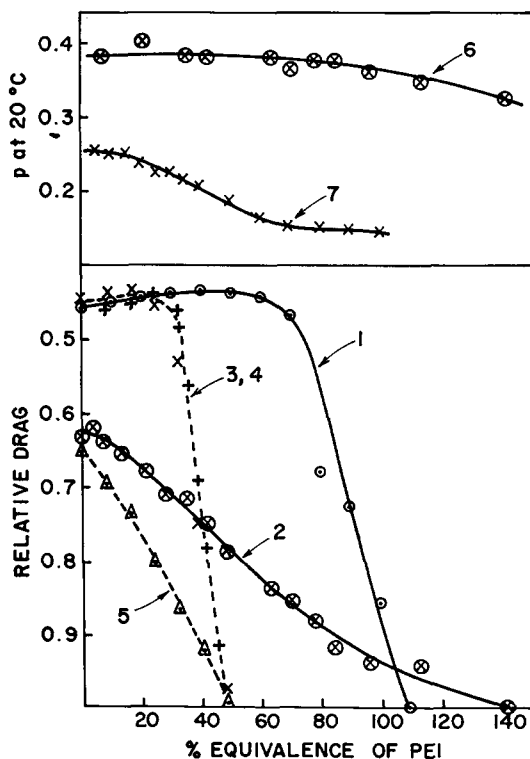


Fig. 2. Relative drag and polarization of mixed polymer solutions. Molecular weight of PEI was 75,000. All solutions contained 0.001M NaHCO₃. Relative drag values: (1) 10 ppm poly(acrylic acid) S25; (2) 30 ppm poly(acrylic acid) E21 (3 ppm S25 gave similar curve); (3) and (4) 3 and 5 ppm polyacrylamide R155; (5) 1 ppm R155. Polarization: (6) 30 ppm E21; (7) 30 ppm R155. Upper ordinate: p at 20°C; lower ordinate: relative drag; abscissa: % equivalence of PEI.

ing the fluorescence decay following excitation by a 5-ns oxygen or nitrogen spark source.¹⁰ This lifetime was used to calculate the lifetimes of the other solutions. To do this, it was assumed that the radiative lifetime was the same for all conjugates, and the actual lifetime was thus assumed to be proportional to the fluorescence efficiency. The results are shown in column 4 of Table II.

Measurement of Turbulent Drag Reduction. The effect of solute on the magnitude of the turbulent drag was determined by observing the rate of flow of solution through a cylindrical glass tube 1.09 mm in diameter and 500 mm long when driven by a constant gas pressure of approximately 0.08 MN m⁻² (12 psi). Thus, in effect, the "drag" as measured by the wall shear stress (S) was maintained constant and the increased rate of flow caused by the presence of the drag-reducing agent was determined by observing the time for a constant volume of liquid (53.5 ml) to be ejected. The electronic timer was controlled by pulses produced by the passage of the meniscus in front of illuminated phototransistors situated at positions in the reservoir separated by a volume of 53.5 ml. The Reynolds number with water was 3250, with a standard deviation of 0.3% for a single determination; and with polymer present the highest Reynolds number was about 4900. Thus, some of the measurements, viz., those corresponding to a Reynolds number of 4000 or less, were carried out under conditions in which turbulence (in water) is not fully developed. Values of "relative drag" were calculated from the square of the ratio of the time of flow with solution (t_s) to that of water (t_w). The significance of this relative drag value is as follows. For flow through a tube, Fanning's friction factor f is defined by

$$f = S/^{1/2}\delta v^2 = K(Re)^n \quad (5)$$

where δ is the density of the fluid, v is the mean velocity, and Re is the Reynolds number. For turbulent flow, K and n have the values 0.064 and -0.23 , respectively. The time of flow of a constant volume was measured at constant driving pressure, i.e., constant S , and hence (since the viscosity of the solutions was almost identical with that of water)

$$f \propto 1/v^2 \propto t^2. \quad (6)$$

Hence, the relative friction factor at constant shear stress is given by

$$(f_s/f_w)_S = (t_s/t_w)^2. \quad (7)$$

This is the parameter we call "relative drag." Except in the most concentrated solutions, it approximates the relative friction factor measured at constant Reynolds number because the viscosities of the solution were almost identical with that of water and the flow was not laminar so that the friction factor varied as a fractional power of the Reynolds number. The relative drag values observed with solutions of linear polymers alone and with equivalent concentrations of PEI are given in Table III. More detailed results obtained with the anionic polymers are plotted in Fig 2 as a function of relative proportion of PEI added calculated on the basis of monomer concentrations.

TABLE III
Interaction of Polyethylenimine with Drag-Reducing Polymers

| Polymer | Concentration <i>c</i> , ppm | Relative drag | | Polarization of mixture at 20°C |
|--------------------------------|---------------------------------|---------------|-------------|---------------------------------------|
| | | Alone | With PEI | |
| Poly(ethylene oxide) (WSR 301) | 5 | 0.48 | 0.48 | 0.167 |
| Polyacrylamide (nonionic R351) | 5 | 0.48 | 0.47 | 0.163 |
| Polyacrylamide (anionic R155) | 5 | 0.49 | 1.00 | 0.187 |
| Poly(acrylic acid) (E21) | 30 | 0.62 | 0.94 | 0.362 |
| Poly(acrylic acid) (S25) | 3 | 0.43 | 0.89 | 0.337 |
| None | — | — | 0.99 | 0.167 |

* All solutions contained 0.001*M* NaHCO₃. The amount of PEI (mol. wt. 75×10³) added was equivalent to the amount of linear polymer calculated on a monomer basis.

RESULTS AND DISCUSSION

The fluorescence depolarization of dansyl-PEI has been measured previously by Wahl¹¹ and by Teramoto et al.¹² Wahl worked with a PEI of molecular weight 30–40×10³. In water he obtained a polarization plot having an upward curvature from which he derived a value of 44×10³ for the molecular volume. He therefore concluded that the molecule rotated as one rigid unit. Teramoto et al. worked with fractionated PEI specimens in both water and salt solution. In 0.2*M* NaCl, they found the relaxation time to vary by only 30% between specimens having limiting viscosity numbers varying by a factor of 10. Our results indicate that the situation is more complicated than suggested by Wahl. In aqueous solution, whether neutral or acid, all polymers, whatever their molecular weight, gave approximately the same value of *V'*. This value is much greater than the values calculated (assuming unit density) from the molecular weights of the lower polymers, indicating that a considerable degree of molecular association occurs.

The size of the equivalent spherical kinetic unit is 10 to 20 times less than the values calculated from the molecular weights of the largest polymers and contributes more than half of their total fluorescence intensity. Units of this size contribute less than half of the fluorescence intensity of the solutions of the low molecular weight polymers, suggesting that these contain a greater proportion of loosely bound groups. The polarization temperature plots of the aqueous solutions generally show an upward curvature, indicating the occurrence of some intramolecular rotational dissociation. This is absent in the acid solutions. The results in ethanol are in marked contrast. The size of the equivalent spherical kinetic unit is now much smaller with the polymers of low molecular weight. Neutralization with HCl now causes the formation of very large aggregates with all polymers (as judged by the values of *V'*), and this is confirmed by the greatly increased light scattering from these solutions. As with the aqueous solutions, the plots became linear when acid was present.

The nonionic polymers, Polyox and polyacrylamide R351, had no effect on the fluorescence polarization of dansyl-conjugated PEI, and the latter

produced no change in the drag-reducing properties of the nonionic linear polymers (see Table III). It is concluded, therefore, that hydrogen bonding between PEI and these linear polymers must be very weak. In contrast, the addition of poly(acrylic acids) E21 or S25 caused a large increase in the fluorescence polarization, indicating the formation of rigid aggregates. These aggregates did not, however, confer drag-reducing properties on the solution. On the contrary, the drag reduction shown by the poly(acrylic acids) alone was largely destroyed by the addition of PEI. The drag reduction of the anionic polyacrylamide was completely destroyed by admixture with the equivalent concentration of high molecular weight PEI, although the polarization increased by only a small amount in this case.

The results of a more detailed investigation of the anionic-cationic systems are shown in Figure 2, in which the polarization at 20°C and the relative drag are shown plotted against the percentage equivalents of PEI added calculated on the monomers. The relative drag of dilute solutions of the poly(acrylic acids) changed approximately in proportion to the degree of "neutralization" by the PEI (for example, curve 2 in Fig. 2), and at the equivalence point the relative drag was only slightly less than unity.

With solutions containing concentrations of poly(acrylic acid) greater than the critical value corresponding to minimum relative drag, the relative drag at first remained approximately constant with increasing addition of PEI, and then increased sharply in a manner reminiscent of a titration endpoint. The polarization (Fig. 2, curve 6) remained high, almost up to the point of equivalence, and then decreased at a rate approximately equal to that calculated for a mixture of poly(acrylic acid)-PEI complex ($p = 0.38$) with PEI aggregate alone ($p = 0.16$). A polarization temperature plot (Fig. 1, curve 7) was constructed for the E21 poly(acrylic acid) solution, which had been 64% "neutralized" with PEI. The results are included in Table I, from which it will be seen that the equivalent spherical kinetic unit (which contributed 86% of the total fluorescence) had a volume equivalent to a molecular weight of 0.1×10^6 . This was still very much smaller than the size of the aggregates since these contained poly(acrylic acid) of molecular weight 9×10^6 .

The behavior of the anionic polyacrylamide was somewhat different from that of the poly(acrylic acids) (see Fig. 2, curves 3, 4, 5, and 7). Although the relative drag of the dilute solution changed approximately in proportion to the concentration of PEI added (Fig. 2, curve 5), the value had increased to unity when only 50% of the equivalent quantity of PEI had been added. Similarly, with the concentrated solution, the "endpoint" occurred when 50% of the equivalent quantity of PEI had been added (Fig. 2, curves 3 and 4). However, the "percentage equivalence" values for these curves were calculated on the total number of functional groups (acid plus amide) present in the anionic polyacrylamide. In fact, the polymer contained only 12% of anionic groups, and the amount of PEI required to destroy the drag-reducing capability of this polymer thus corresponded to about 400% of that required to neutralize the anionic groups. The maximum polarization at 20°C was 0.25, compared with 0.38 for the poly(acrylic acid) complexes;

and with increasing additions of PEI beyond the equivalence point, the polarization decreased very approximately according to values calculated for mixtures of PEI complex and free PEI.

It was found that the addition of ethylenediamine or triethylenetetramine (i.e., the equivalent of monomeric and trimeric PEI) was without effect on the relative drag of solutions of the poly(acrylic acids) or the anionic polyacrylamide. It seems, therefore, that a polymerized base is necessary to produce significant interaction at the concentrations concerned, and this implies cooperative bonding between adjacent acidic and basic groups. If the PEI aggregates were much smaller than the poly(acrylic acid) molecules, they would be expected to distribute themselves among the latter, and the addition of PEI would cause a much greater loss of drag-reducing capability than is indicated by the curves in Figure 2. For example, 75% neutralization would convert a 10-ppm solution of S25 (molecular weight 40×10^6) into the equivalent of a 2.5-ppm solution of E21 (molecular weight 9×10^6). The latter would have a negligible drag reduction, whereas the 75% neutralized S25 still showed almost its full effect. It seems likely, therefore, that the PEI is aggregated into particles having a molecular weight equal to or greater than that of the poly(acrylic acid). Cooperative binding by adjacent acid and basic groups would then result in attachment of each poly(acrylic acid) to a single PEI aggregate. The quantity of poly(acrylic acid) "neutralized" by the PEI would then be directly proportional to the quantity of PEI added, and the remaining "unneutralized" poly(acrylic acid) would still exert its full drag-reducing capability. The results in Figure 2 could then be accounted for. Thus 80% neutralization of a 10-ppm solution of S25 gave a residual drag of about 0.6 (Fig. 2, curve 1); a 2-ppm solution of S25 alone (not shown) was found to give a residual drag of about 0.7.

The fact that linear high polymers in general and poly(ethyleneoxide) in particular are susceptible to shear degradation, whereas highly branched polymers are less so, prompted the experiment to determine whether the presence of the branched-chain polyethylenimine was capable of protecting the linear poly(ethylene oxide) against shear degradation. It was found that a 5-ppm solution of poly(ethylene oxide) alone, which initially gave a relative drag value of 0.49, after 14 more passes through the tube gave a value of 0.82, indicating that a substantial degree of shear degradation had occurred. Solutions containing the same concentration of poly(ethylene oxide) together with 0.6 and 3 equivalents of polyethylenimine gave the same value of relative drag on the first pass and almost the same values (0.80 and 0.81, respectively) after a further 14 passes, indicating that the polyethylenimine provided a negligible degree of protection against shear degradation.

CONCLUSIONS

In aqueous solutions, polyethylenimine forms large aggregates by hydrogen bonding. The size of the largest unit observed to rotate inde-

pendently has a rotary relaxation time equivalent to a sphere of volume $3-6 \times 10^3 \text{ cm}^3$, but the molecular weight of the aggregates themselves is probably 10^7 or greater.

Polyethylenimine interacts to a negligible extent with nonionic linear polymers but forms large aggregates with anionic linear polymers. These aggregates contain considerably larger rotating units than those in the aggregates of PEI alone. The drag-reducing capability of these complex aggregates is considerably less than that of the linear polymers alone.

It seems unlikely that more efficient drag-reducing systems can be produced by complex formation, at least with materials at present available. The most efficient systems (assessed solely on a concentration basis) are still those consisting of high molecular weight linear polymers, although these have the disadvantages of slow rate of solution and susceptibility to shear degradation. Complex systems of lower concentration efficiency could therefore offer some advantages, but systems based on anionic-cationic combinations such as those investigated here are unlikely to be suitable.

Finally, it is worth noting that the measurement of residual drag provides a simple and sensitive method for investigating the association of linear high polymers with other species, and it can be applied at very low concentrations at which other methods are difficult to use.

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