Moreover, the systems studied show negative deviations of refractive indices and densities from the additivity rule. The largest deviation is observed in the system HMDS–acetic acid, where a minimum of $\Delta d^{20}{}_4$ amounts to 10.27% and occurs at the mole fraction acetic acid of 0.7. However, the deviations of refractive indices are generally small. Only for the mole fraction 0.7 of acetic acid, the deviation exceeds the experimental error and reaches 0.026%.

The largest differences in the composition of the liquid and the vapor phases are observed in the system HMDS–butyric acid. The components of the system may thus be most readily separated by fractional distillation.

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Drag Reduction Characteristics of Poly(acrylamides) in Aqueous Magnesium Sulfate and Acetone Solutions

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The drag reduction efficiency of four commercial poly(acrylamide) samples was determined in water and aqueous solutions of acetone and magnesium sulfate. Intrinsic viscosity measurements were made in the magnesium sulfate solutions over the shear rate range of 15–100 sec^{-1}. In general, increasing concentrations of salt or acetone produced progressive decreases in the drag reducing efficiencies of these polymers. In contrast to the data previously obtained with the poly(ethylene oxide) polymers in salt solutions, no simple relation between the drag reduction efficiency and intrinsic viscosity could be established as the salt concentration was varied. The data do show, however, that the drag reduction efficiency of poly(acrylamide) is much less affected by increases in salt concentration than is the efficiency of poly(ethylene oxide).

The drag reduction characteristics of an important nonionic polymer, poly(ethylene oxide) (PEO) in solutions of varying salt content have been successfully correlated with the intrinsic viscosity of the polymer in those solutions (*9*). It was suggested that those solvent properties which bring about decided conformational changes in these polymer molecules also affect, in an apparently analogous fashion, the turbulent friction reducing efficiencies of these same molecules. However, these conclusions were specific to nonionic polymer solutions. Changes in drag reduction and reduced viscosity do not necessarily go hand-in-hand in polyelectrolyte solutions, the effect of pH on the performance of polyacrylic acid being specifically cited as evidence for this conclusion (*5*). Clarke (*2*) has reported the behavior of two commercial samples of poly(acrylamide) (PAM) in water, 0.02 and 1.0*M* sodium chloride. He noted very high intrinsic viscosities in water (shear rate unspecified) for both the slightly hydrolyzed and 33% hydrolyzed PAM samples. He further stated that the ionic nature of the polymer did not directly affect its drag reducing properties and could be explained in terms of the usual drag reduction characterization procedures.

Frommer et al. (*3*), on the other hand, have made drag reduction and reduced viscosity measurements on a hydrolyzed commercial PAM sample in a series of low molarity barium chloride solutions. Their data suggest that a rough parallelism exists between the two sets of data in the low molarity range. However, it may be of further interest to expose PAM samples of varying molecular weight and type to environments which contain high concentrations of ions, particularly those which are divalent, observing any effect on the drag reducing efficiencies of these polymers. It may also be of further value to compare these results with those previously reported for PEO to determine the relative merits of each family in hostile ionic environments.

Experimental

Materials. The following commercial poly(acrylamides) were selected: Separan NP-20 (Dow), Cyanamer P-250 (American Cyanamide), and two samples of Magnifloc 905N (American Cyanamide). According to the manufacturers, Separan NP-20 is mildly nonionic with 3.9% of the monomer units charged; Cyanamer P-250 and Magnifloc 905N are advertised as pH-insensitive with regard to their viscosities and are therefore supposedly nonionic in nature. Freshly distilled water was used exclusively in preparing all solutions. Since irreproducible mixing techniques can cause large variations in solution properties, all solutions were prepared carefully by the following procedures.

The additives in powder form were sprinkled uniformly over a large surface of distilled water to avoid clumping of particles. Solution was allowed to take place through diffusion at 6°C for a period of several days. Occasional gentle stirring with a glass rod ensured adequate dispersion of solute. To obtain the desired concentration of polymer, a stock solution of reagent grade magnesium sulfate was slowly added with gentle stirring to the required amount of polymer solution. Stock solutions of polymer were always stored at 6°C and were discarded after a two-week period. The pH of all solu-

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tions measured was 6.5 ± 0.1. $MgSO_4$ was selected because of its high solubility and the nearly neutral pH of its solutions.

Methods. *Intrinsic viscosity determinations.* The viscosity measurements were made with a Cannon 50-S400 multiple-bulb viscometer at 25°C, and the intrinsic viscosity was calculated at a shear rate of 20 sec^{-1}. The viscosity-average molecular weight determined from the 0.5*M* $MgSO_4$ solution data was estimated from the relation $[\eta] = 3.77 \times 10^{-4} Mv^{0.66}$ (shear rate unspecified) established by Suen et al. (*10*) in 1*M* $NaNO_3$.

Drag reduction measurements. The apparatus used has been previously described in some detail (*7*). Essentially, it was an automated version of a type previously described by Hoyt (*4*). The flow pipe, however, was a pyrex capillary tube with the first tap 200 diameters from the entrance, and the second tap 100 diameters from the first and 54 diameters from the tube exit. The tube diameter was 0.1575 cm. The pressure transducer output and the dc generator output (which monitored the flow rate) were converted to logarithmic signals and fed to an x-y recorder. For a fixed flow rate the percent drag reduction was computed by the following relationship

$$DR\% = \frac{\tau(\text{water}) - \tau(\text{polymer})}{\tau(\text{water})} \times 100\% \qquad (1)$$

where $\tau(\ )$ is the wall shear stress.

Results and Discussion

Intrinsic viscosity results. Commercial polyacrylamides are somewhat anionic in nature dependent upon the extent of hydrolysis of the amide groups on the chain. It can therefore be expected that behavior typical of a polyelectrolyte will be observed. As a matter of fact, none of the four commercial PAM samples yielded suitable viscosity data in pure water because of the rapid change in viscosity caused by extension of the polyion with decreasing concentration. However, data obtained in the magnesium sulfate solutions were more suitable for analysis. Figure 1 shows a plot of the reduced specific viscosity vs. the shear rate for solutions of Separan-NP-20 in 1*M* $MgSO_4$ solutions. The rather strong effect of shear rate is evident even in such strong salt solutions. The data could, however, be conveniently extrapolated to zero concentration to determine the intrinsic viscosity for any selected shear rate. Such data are shown in Figure 2 for the same system for shear rates ranging from 15 to 50 sec^{-1}.

Table I provides a summary of the intrinsic viscosity determinations for the four polymers at a shear rate of 20 sec^{-1} and an estimate of their viscosity-average molecular weights. The viscosity-average molecular weights reported here are useful only for comparative purposes since 0.5*M* $MgSO_4$ rather than 1*M* $NaNO_3$ solutions were employed, and the shear rate conditions under which the intrinsic viscosity-molecular weight relations were established were not specified by Suen et al. (*10*). From Table I, the 0.5*M* $MgSO_4$ solution produces, in general, a minimum intrinsic viscosity condition, and no further reduction is obtained in going to the 1*M* concentration. Attempts to make intrinsic viscosity measurements in 0.33*M* salt solutions met with limited success since linear extrapolations to zero concentration could not easily be made presumably owing to a remaining polyelectrolyte effect.

Drag Reduction Tests

The efficiency of drag reducing polymers may be conveniently cataloged through the use of Virk's universal drag reduction relation (*12*). This equation may be conveniently cast into the following form (*8*) at a given Reynolds number:

$$\frac{DR}{DR_m} = \frac{c}{[c] + c} \qquad (2)$$

where *c* is concentration, *DR* is percent drag reduction, DR_m is the "maximum" drag reduction as $c \to \infty$, and $[c]$ is intrinsic concentration. Rearrangement of Equation 2 leads to

$$\frac{c}{DR} = \frac{[c]}{DR_m} + \frac{c}{DR_m} \qquad (3)$$

Equation 3 indicates that a linear relationship exists between *c/DR* and *c* when the concentration dependence of drag reduction obeys Equation 2. This was tested by applying Equation 2 to the results obtained in the present system, and this relation holds very well for most polymer solutions over a

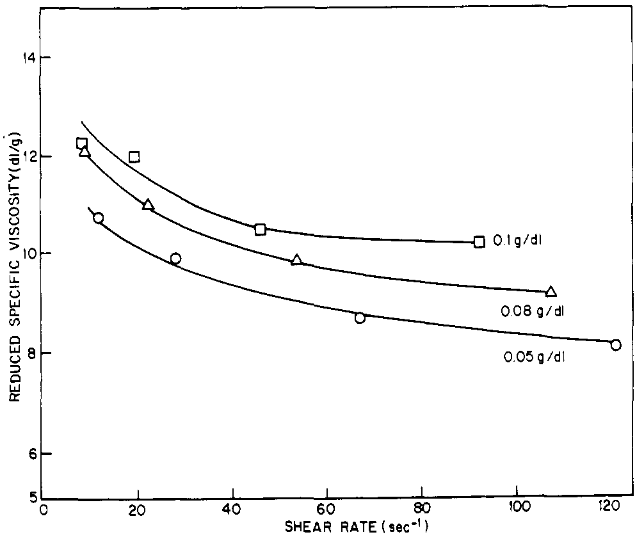

Figure 1. Reduced specific viscosity vs. shear rate for NP-20 in 1*M* magnesium sulfate solution

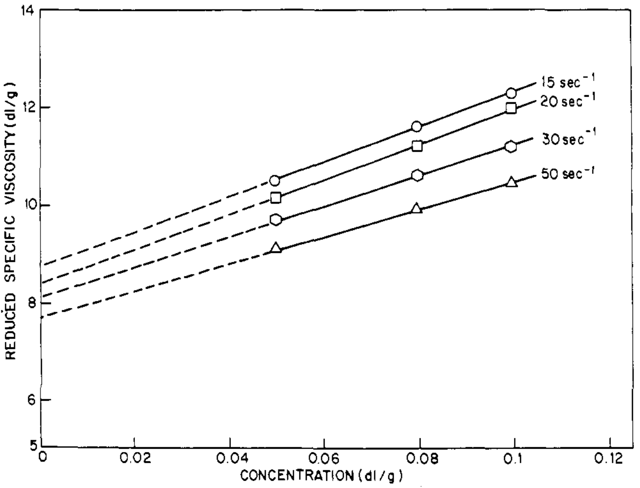

Figure 2. Reduced specific viscosity of NP-20 vs. concentration at several shear rates in 1*M* magnesium sulfate solution

Table I. Intrinsic Viscosity (at 20 Sec^{-1}) of Commercial Poly(acrylamides) Vs. Molarity of $MgSO_4$ Solution

Compound	Mol wt	0.5*M*	0.67*M*	1.0*M*
905N (L)	1.8×10^6	4.5	. . .	4.5
NP 20	4.5×10^6	10.0	10.3	8.4
P-250	6.0×10^6	10.7	9.8	10.0
905N (G)	9.4×10^6	13.6	. . .	13.4

Table II. Drag Reduction Index as Function of $MgSO_4$ Concentration for Commercial Poly(acrylamides) at Re = 9000

Compound	0	0.33*M*	0.50*M*	0.67*M*	1.0*M*
905N (L)	3.4	3.0	3.4	3.1	3.8
NP-20	18.9	13.6	10.6	10.6	9.45
P-250	17.2	14.1	12.8	11.2	8.9
905N (G)	27.3	20.6	21.3	23.0	13.0

Table III. Variation of Drag Reduction Index of Commercial Poly(acrylamides) with Acetone Concentration at Re = 9000

	% Acetone				
Compound	0	5	10	17	25
905N (L)	3.4	4.1	3.1	2.8	2.4
NP-20	18.9	14.6	14.5	11.8	8.3
P-250	17.2	17.3	11.9	9.5	10.9
905N (G)	27.3	27.7	21.5	17.0	10.4

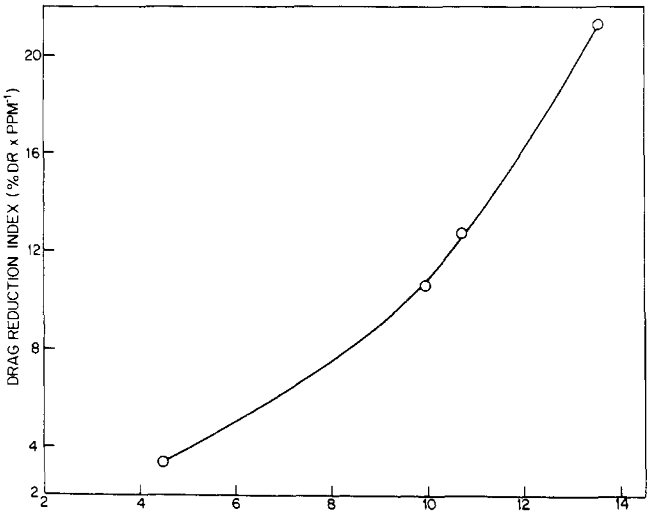

Figure 3. Drag reduction index of commercial poly(acrylamides) vs. intrinsic viscosity in 0.5*M* magnesium sulfate solution

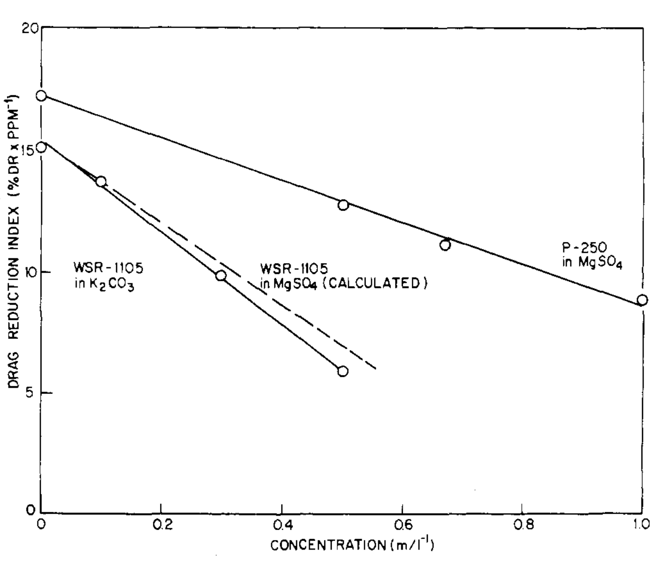

Figure 4. Drag reduction index of poly(acrylamide) and poly(ethylene oxide) polymer in salt solutions

wide range of percent drag reduction values provided the polymer concentration was not too high. In general, a plot of *c/DR* vs. *c* is linear and shows the validity of Equation 2. The intercept value at *c/DR* = 0 yields the intrinsic concentration, $[c]$, and this quantity divided by the intercept at $c = 0$ permits evaluation of DR_m. The parameters $[c]$ and DR_m, being constants characteristic of a given polymer compound, serve as a measure of the drag reduction effectiveness and thus are handy tools for laboratory characterization of drag reducing polymers. The physical significance of these parameters becomes very clear (*8, 11*) if the limit of Equation 2 at zero concentration is examined.

$$\lim_{c \to 0} \frac{DR}{c} = \lim_{c \to 0} \frac{DR_m}{c + [c]} = \frac{DR_m}{[c]} \qquad (4)$$

This parameter, $DR_m/[c]$, becomes a measure of the "efficiency" of the polymer additives on a unit concentration basis at infinite dilution and is termed the drag reduction index of the polymer. Plots of $DR_m/[c]$ vs. molecular weight have been shown to be linear for the Polyox family of polymers (*11*).

Table II lists the drag reduction index for the four commercial PAM samples in water and in four salt solutions. High values of the index indicate high efficiency, and low values the converse. Two types of behavior are noted. An increase in salt concentration to 1*M* progressively cuts the drag reduction index to one-half of that observed in water in the case of NP-20, P-250, and 905N-(G). For the Magnifloc 905N-L, however, virtually no salt effect on the observed drag reduction efficiency between water and the strongest salt solution was observed.

The drag reduction efficiency of the four polymers in acetone–water solutions was also noted as reported in Table III. In this case, the addition of acetone caused progressive decreases in the drag reduction efficiency for all four polymers. Intrinsic viscosities could not be determined in acetone–water mixtures, of course, because of polyelectrolyte charge effects. The behavior of the commercial PAM's, however, appears to be complex in the presence of salt. No generalized correspondence can be found in this group, for example, between the intrinsic viscosity in a given salt solution and its drag reduction in that solution. Specifically, while $[\eta]$ for P-250 changes relatively little from 10.7 dl/g in 0.5*M* $MgSO_4$ to 10.0 in 1.0*M* $MgSO_4$, the drag reduction index changes from 13.0 to 8.9. On the other hand, both the intrinsic viscosity and drag reduction index change relatively little in the case of the 905N (L) sample.

Interestingly enough, a plot of the drag reduction index of each compound vs. its intrinsic viscosity for measurements in 0.5*M* $MgSO_4$ solution produced a smooth curve as shown in Figure 3. Because of the varying ionic nature of these samples, however, a precise family relationship is not necessarily indicated here. As a matter of fact, the behavior of the commercial samples contrasts sharply with the laboratory-synthesized nonionic PAM's previously reported (*6*) where a minimum intrinsic viscosity of 8.5 dl/g was needed before drag reduction was observed in that family. That is, on a molecular-weight basis a minimum viscosity-average molecular weight of 3×10^6 is required to observe drag reduction for the nonionic PAM's, whereas in the present case the 905N (L) sample is strongly drag reducing at the relatively low molecular weight of 1.8×10^6. This is undoubtedly due to the more extended structure of the anionic polymer caused by repulsion of like charges on the side groups along the chain.

It is of interest, finally, to compare the drag reduction ability of polyethylene oxide with that of polyacrylamide in strongly ionic environments. Figure 4 compares two polymers having nearly the same drag reduction efficiency in pure water, WSR-1105 and P-250. Although the drag reduction data for WSR-1105 were originally taken in K_2CO_3 solutions, the effect of $MgSO_4$ solutions can be estimated with the aid of literature data which rate the relative influence of the two individual salts on polyethylene oxide solution properties in general (*1*). The drag reduction efficiency of the anionic PAM is much less affected by increases in salt concentration than is PEO. As a matter of fact, the data suggest that the PAM sample will continue to function quite efficiently long after the drag reducing activity of the PEO sample has ceased (about 0.9*M* in $MgSO_4$). However, as already pointed out, the progressive decreases in drag reduction efficiency in the case of the commercial PAM's cannot be correlated with polymer intrinsic viscosity in the same solutions as was the case with PEO. No useful explanation for the dissimilar behavior observed with polyelectrolytes as compared with nonionic polymers can be easily offered at the present time.

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Osmotic and Activity Coefficients of Solutions of $(NH_4)_2B_{10}H_{10}$, $Na_2B_{12}H_{12}$ in H_2O, and of Four Tetraalkylammonium Halides in H_2O and in D_2O at 25°C

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Osmotic and activity coefficients of aqueous $(NH_4)_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$ solutions were measured at 25°C by the isopiestic comparison method and differed considerably for the two borates. In addition, the osmotic and activity coefficients of the D_2O solutions of $(CH_3)_4NBr$, $(C_4H_9)_4NBr$, $(CH_3)_4NF$, and $(C_4H_9)_4NF$ were determined at 25°C and compared with the corresponding values of the H_2O solutions to see the solvent isotope effect.

Stability of the $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ ions toward heat, acids, and bases, as well as oxidizing agents, is well documented (*4, 6*). Alkali metal and ammonium salts of these anions are soluble in water and form stable aqueous solutions. In spite of many similarities in behaviors of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$, they are not chemically equivalent (*7*). Inasmuch as two salts, $(NH_4)_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$, were made available to us, we determined the osmotic and activity coefficients of the aqueous solutions at 25°C. Interactions between water and the cage anions (bicapped square antiprism and icosahedron) (*2, 20*) are of particular interest to us.

In a separate study, we have measured the osmotic and activity coefficients of the D_2O solutions of $(CH_3)_4NBr$, $(C_4H_9)_4NBr$, $(CH_3)_4NF$, and $(C_4H_9)_4NF$. They are compared with the corresponding values of the H_2O solutions to see the solvent isotope effect, if any.

Experimental

Materials and analyses. Ammonium decahydrodecaborate, $(NH_4)_2B_{10}H_{10}$, and the hydrate of sodium dodecahydrododecaborate, $Na_2B_{12}H_{12}$, were kindly supplied to us by H. L. Friedman of the State University of New York at Stony Brook who obtained the compounds from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co. These salts were used without further purification except drying. $(NH_4)_2B_{10}H_{10}$ was dried at 50°C in vacuo for 16 hr to a constant weight (density: 0.9862 g/cc). The anion content was determined gravimetrically using $AgNO_3$ as the precipitant, indicating 99.44 ± 0.43% purity. The hydrate of $Na_2B_{12}H_{12}$ was dried at 110°C to a constant weight; gravimetric analysis indicated the anion content to be 91.65 ± 0.63% (density: 1.1765 g/cc).

The D_2O purchased from Matheson Coleman & Bell was used without further purification. The mole percent of D_2O was checked by the density measurement by means of the following relation:

$$\text{mol \% } D_2O = \frac{924.64\ \Delta d}{1 - 0.0328\ \Delta d}$$

where Δd is the measured density minus that of H_2O. Our result indicated that the heavy water used contained 99.72% D_2O.

$(CH_3)_4NBr$ and $(C_4H_9)_4NBr$ were obtained from Eastman Kodak Co. and recrystallized before use. $(C_4H_9)_4NF$ solutions were prepared by the following methods. The H_2O and D_2O hydrates of $(C_4H_9)_4NF$ were made by the double metatheses of BaF_2, Ag_2SO_4, and $(C_4H_9)_4NI$ in H_2O or D_2O (*12*). The resultant AgI, $BaSO_4$, and excess BaF_2 were removed by filtration and clear $(C_4H_9)_4NF$ solutions of about 1*M* concentration were cooled to 5°C to produce the crystalline hydrates. These hydrates were purified by recrystallization from H_2O or D_2O. The melting point of $(C_4H_9)_4NF{\cdot}32.8H_2O$ is 25°C, whereas the melting point of $(C_4H_9)_4NF{\cdot}32.8D_2O$ is 30–30.5°C.

For the H_2O solution, $(C_4H_9)_4NF$ was also prepared by the titration of $(C_4H_9)_4NOH$ with the HF solution to a pH of 8. The hydrates prepared were dissolved in H_2O or D_2O to make stock solutions. The stock solution was analyzed for both cat-

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