

Poly(1,2-dimethyl-5-vinylpyridinium Methyl Sulfate). **Part II. Polymer Properties**

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Synopsis

Aqueous solutions of poly(1,2-dimethyl-5-vinylpyridinium methyl sulfate) have good viscosity stability at neutral or acid pH's at temperatures up to 100°C. Strongly basic solutions have poor viscosity stability even at room temperature. At the same ionic strength the relative effectiveness of three sodium salts in the reduction of polymer intrinsic viscosity was: sodium phosphate > sodium sulfate > sodium chloride. This trend toward lower intrinsic viscosities with increased ionic strength reversed itself at high ionic strengths. This polymer is very effective in the flocculation of 5% aqueous kaolin suspensions as indicated by several hundred-fold increases in the initial settling rates. A study of some of the important variables (polymer adsorption, polymer intrinsic viscosity, and agitation) related to this property is presented. The mechanism of flocculation is discussed.

I. INTRODUCTION

Almost all of the studies on the properties of water-soluble polymers with cationic functionality have been carried out with poly(1-butyl-4-vinylpyridinium bromide). This polymer is prepared by the quaternization of poly-4-vinylpyridine with *n*-butyl bromide.¹

This publication will describe the properties of a cationic polymer which was prepared by the homopolymerization of 1,2-dimethyl-5-vinylpyridinium methyl sulfate (DMVPMS).²

RESULTS AND DISCUSSION

General Properties

Water appears to be the only good solvent for poly(DMVPMS). This polymer is slightly soluble in highly polar solvents like dimethylformamide, methanol, and ethanol; the presence of water in these solvents enhances the polymer solubility. The polymer can be dispersed in a nonsolvent like acetone by the addition of a dilute aqueous solution of the polymer to acetone.

Aqueous solutions of this polymer are compatible with most simple electrolytes, but precipitation sometimes occurs (potassium iodide, potassium dichromate, and potassium ferriocyanide). Anionic surfactants and anionic polymers can also cause precipitation.

Films of this polymer are brittle and not sticky at moderate humidities. The methyl group in the monomer unit is sufficiently activated by the pyridinium group to permit reactions. For example, aldehydes react with the polymer in the presence of basic catalysts.³

Viscosity Characteristics

Aqueous solutions of poly(DMVPMS) are quite stable at room temperature as indicated by a 0.2% loss in intrinsic viscosity per day (Fig. 1).

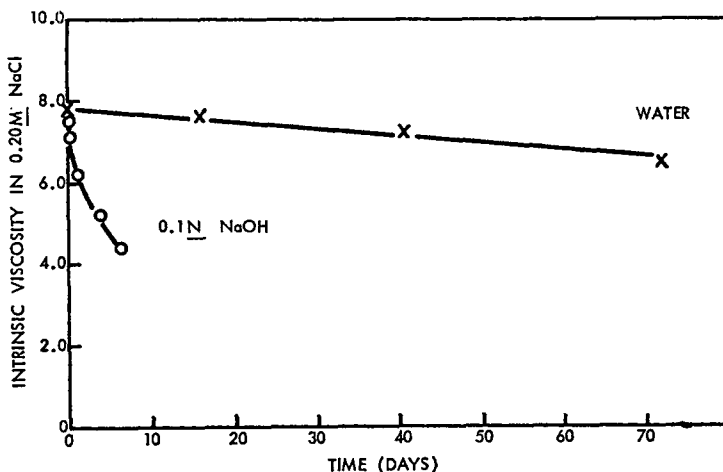


Fig. 1. Viscosity stability of 1.0% aqueous solutions of poly(1,2-dimethyl-5-vinylpyridinium methyl sulfate) at room temperature.

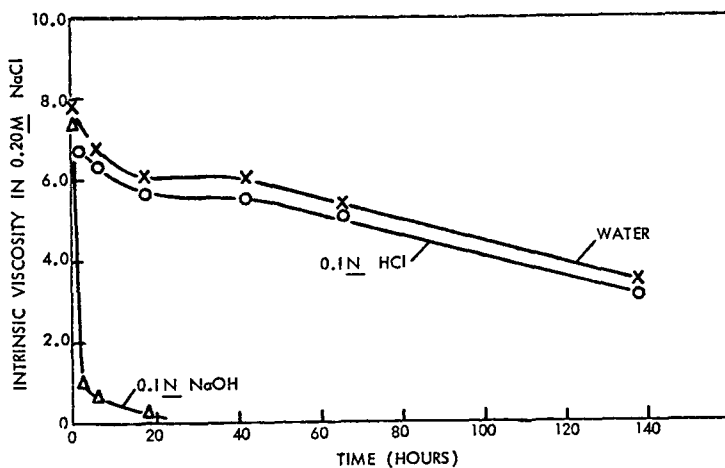


Fig. 2. Viscosity stability of 1.0% aqueous solutions of poly(1,2-dimethyl-5-vinylpyridinium methyl sulfate) at 100°C.

However, there is about a hundred-fold increase in the initial rate of loss of intrinsic viscosity when a similar solution is strongly basic.

At 100°C., an aqueous solution of this polymer initially loses its intrinsic viscosity about one hundred thirty times faster than at room temperature (Fig. 2). A decrease in the rate of intrinsic viscosity loss to about forty times that at room temperature follows. A similar viscosity stability is found in acid solutions.

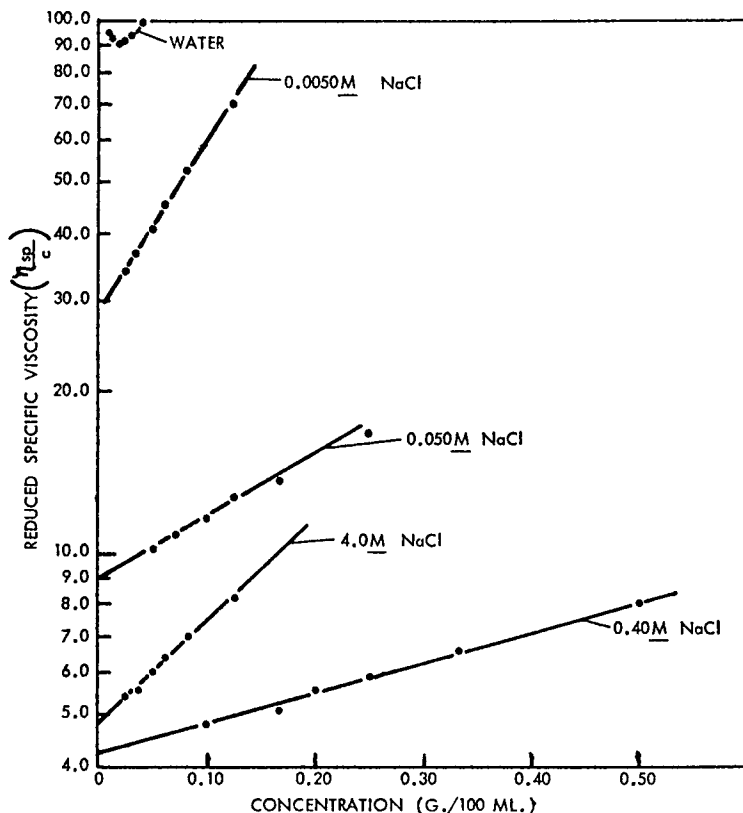


Fig. 3. Effect of sodium chloride concentration on the intrinsic viscosity of poly(1,2-dimethyl-5-vinylpyridinium methyl sulfate).

A strongly basic solution of this polymer loses about 87% of its intrinsic viscosity in 1 hr. at 100°C. (Fig. 2).

A deep red color develops when this polymer is degraded in basic solution. This color disappears to leave a light yellow solution when the solution is neutralized.

The explanation for the poor stability of this polymer at high pH's is most likely associated with reactions which are similar to those of simple pyridinium bases:⁴ tautomeric equilibria with a pseudo-base (I) or anhydrobase (II), ring opening to form a derivative of glutamic aldehyde

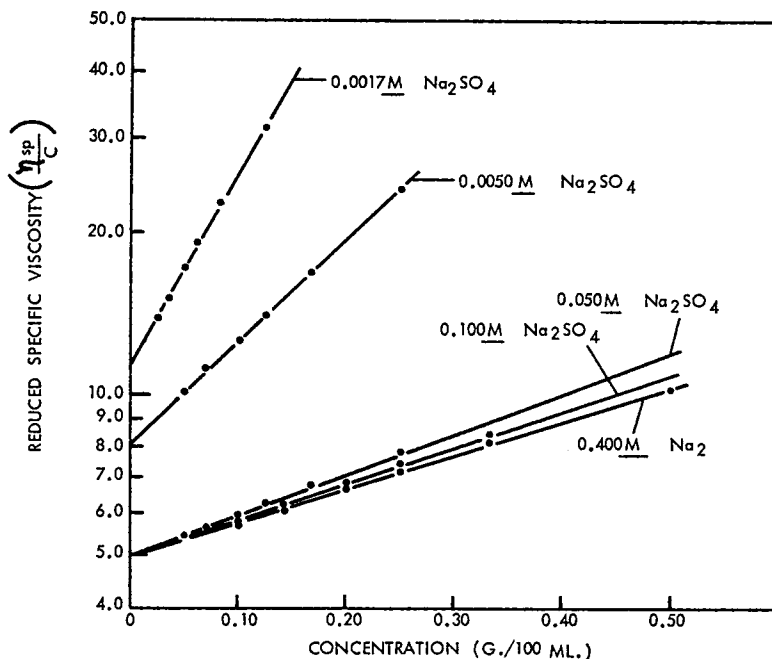
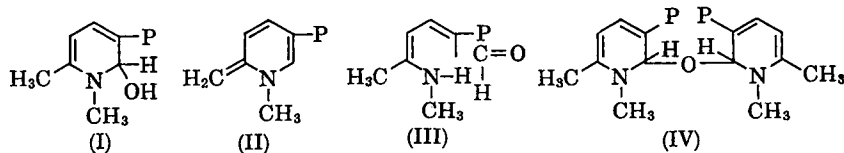


Fig. 4. Effect of sodium sulfate concentration on the intrinsic viscosity of poly(1,2-dimethyl-5-vinylpyridinium methyl sulfate).

(III), and ether formation (IV). (In structures I–IV, P denotes the polymer backbone.) Thus, loss of the ionic functionality or



internal crosslinking would give a less expandable polymer molecule and thus a lower intrinsic viscosity.

As is characteristic of polyelectrolytes, it was necessary to add simple electrolytes to aqueous solutions of this polymer in order to permit intrinsic viscosity measurements. Figures 3–5 show some intrinsic viscosity measurements on the same sample of poly(1,2-dimethyl-5-vinylpyridinium methyl sulfate) in the presence of varying amounts of three sodium salts.

These results are presented in Figure 6 as the Fuoss-Strauss⁵ relationship between intrinsic viscosity and ionic strength. At the same ionic strength the order of effectiveness of the salts in the reduction of viscosity is: sodium phosphate > sodium sulfate > sodium chloride. This result appears to be associated with the increasing charge on the anion. Thus, the sharing of a phosphate anion between several positive sites along a single

polymer molecule could decrease the extension of the molecule (i.e., internal crosslinking).

Figure 6 also shows that there is an increase in the intrinsic viscosities for the highest ionic strengths with sodium chloride and sodium phosphate. A similar failure of the Fuoss-Strauss relationship at high salt concentrations has been reported for the polyacrylate ion by Kagawa and Fuoss.⁶

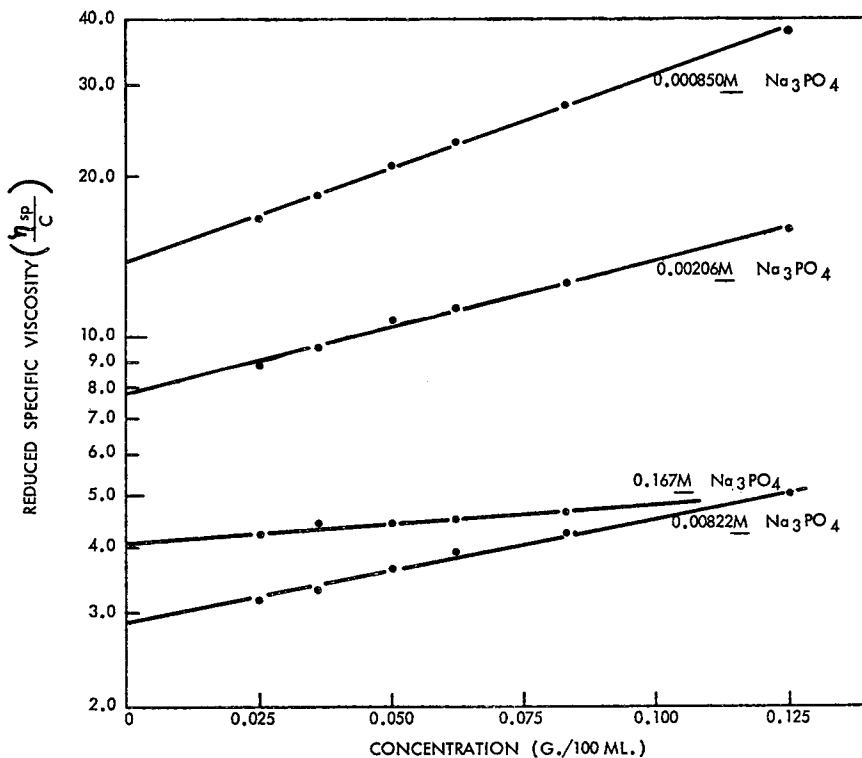


Fig. 5. Effect of sodium phosphate concentration on the intrinsic viscosity of poly(1,2-dimethyl-5-vinylpyridinium methyl sulfate).

These reversals in the intrinsic viscosities might be related to the tendency of this and other polyelectrolytes to precipitate from dilute solution in a colloidal form.^{2,7} Thus, as the ionic strength is increased, the common ion effect⁸ might promote the precipitation of one or several polymer molecules in a single colloidal particle. At still higher ionic strengths, there might be a redispersal of individual polymer molecules with a corresponding rise in the intrinsic viscosity. That such redispersals are possible is suggested by the effects of adding sodium iodide to a polyacrylate solution.⁶ At 1.5*N* sodium iodide, a translucent gel was formed. The polymer redispersed at 3.0*N* salt, and the intrinsic viscosity was higher than before precipitation. Precipitation again occurred at 6.0*N* salt.

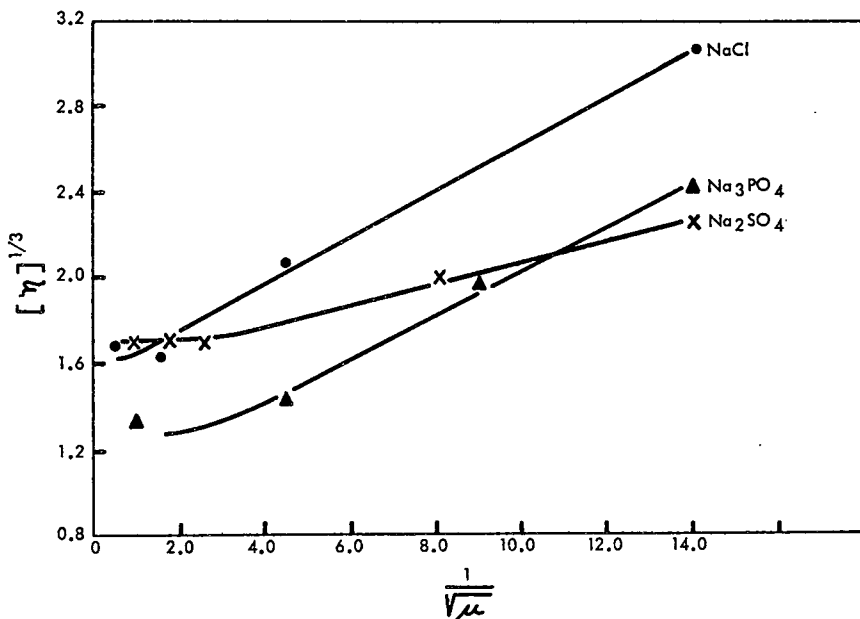


Fig. 6. Fuoss-Strauss plot of intrinsic viscosity vs. ionic strength μ for aqueous solutions of poly(1,2-dimethyl-5-vinylpyridinium methyl sulfate).

Flocculation of Kaolin Suspensions

The results of a study of the flocculation of 5% aqueous suspensions of kaolin by poly(DMVPMS) are given in Figures 7-10. Since the intrinsic viscosity is generally accepted as being the most important characteristic of a polymeric flocculant,⁹ an intrinsic viscosity range of 0.9-10.5 (0.200M NaCl) was considered. One method of agitation, a cylinder turned end over end 20 times, corresponded to that generally used in the determination of settling rates of flocculated suspensions.¹⁰ The other method of agitation, a cylinder turned end over end at 3.5 rpm for 18 hr., was a convenient interval of time until no measurable changes occurred. Sediment volumes were also recorded, since they are related to the interaction between flocs during the packing stage.¹¹

From this study, the following points can be made.

(1) At low levels of added polymer, the adsorption of polymer is rapid and complete for the polymer intrinsic viscosity range of 1.5 to 7.5.

(2) With gentle agitation, the saturation level for adsorbed polymer is dependent on the polymer intrinsic viscosity and on the agitation time. After the same interval of agitation, the saturation level is highest for the lowest intrinsic viscosity polymer. Although continued agitation can lead to the adsorption of more polymer, the saturation levels still remain dependent on the intrinsic viscosity of the polymer.

(3) Flocculation does not necessarily occur when polymer is adsorbed. A polymer intrinsic viscosity of 10.5 can lead to a several hundredfold

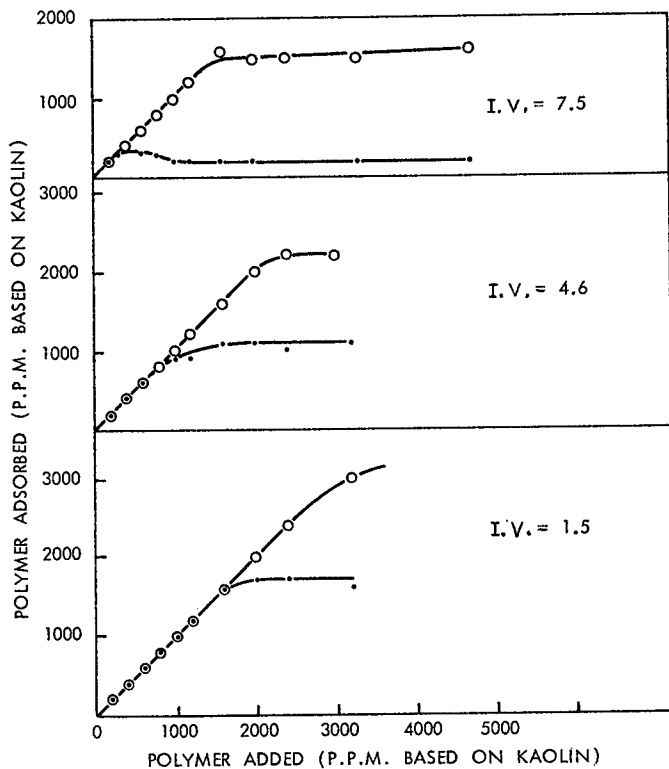


Fig. 7. Dependence of the adsorption of poly(1,2-dimethyl-5-vinylpyridinium methyl sulfate) on amount of polymer added, polymer intrinsic viscosity (I.V.), and agitation: (●) 20 inversions, (O) = 1 hr. at 3.5 rpm.

increase in the initial settling rates after the formation of large flocs. There is, however, no observable floc buildup or any significant change in the initial settling rates with a polymer intrinsic viscosity of 0.9. Intermediate polymer intrinsic viscosities give intermediate effects.

(4) Under comparable conditions, the adsorption of more polymer gives increased initial settling rates up to the adsorption saturation level where there is no further change.

(5) Continued gentle agitation can lead to several-fold increases in the initial settling rates as compared to those obtained after the initial mixing. Also, it leads to a wide range of floc sizes, especially at the higher amounts of added polymer.

(6) Vigorous agitation quickly breaks down the flocs so that the impressive improvements in the initial settling rates obtained with gentle agitation are completely lost.

(7) After the initial mixing with flocculated slurries, the sediment volumes increase and then level-off with increasing amounts of added polymer. Continued gentle agitation tends to decrease the sediment

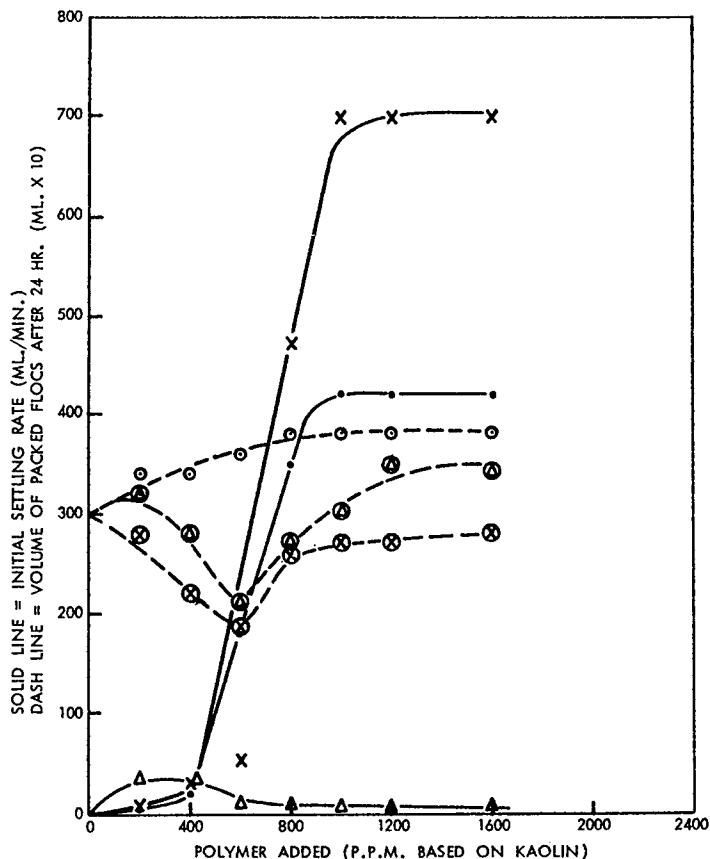


Fig. 8. Dependence of (—) initial settling rates and (--) sediment volumes on the amount of polymer added and on the agitation in the flocculation of 5% kaolin slurries with poly(1,2-dimethyl-5-vinylpyridinium methyl sulfate) of polymer with intrinsic viscosity = 10.5: (●) 20 inversions, (×) 18 hr. at 3.5 rpm; (Δ) 1 min. vigorous shaking.

volumes to below that of the control and these then level-off with increasing amounts of added polymer.

(8) After vigorous agitation of flocculated slurries, the sediment volumes tend to increase with increasing amounts of added polymer, as compared with those obtained after 18 hours of gentle agitation. These increases in sediment volumes are greatest at the higher amounts of added polymer, when there is excess polymer in solution.

(9) With polymer that does not promote the visible buildup of flocs, the sediment volumes tend to be higher than that for the control. Continued gentle agitation increases the sediment volumes up to a certain level of added polymer and then sediment volumes decrease.

The following discussion will outline some of our thoughts about a dynamic mechanism of flocculation which is needed to explain the above trends.

First, it should be pointed out that examination of an unflocculated kaolin under a microscope revealed that the primary particles ($1-5\mu$) are well dispersed although a few aggregates were present. The very slow settling rates can be attributed to the small size of these particles. The high sediment volume (30 ml. for 5 g. of kaolin) can be due to an electrostatic interaction between the positive edges and the negative faces of the primary kaolin platelets during the packing stage to give a "card house" structure to the sediment.¹²

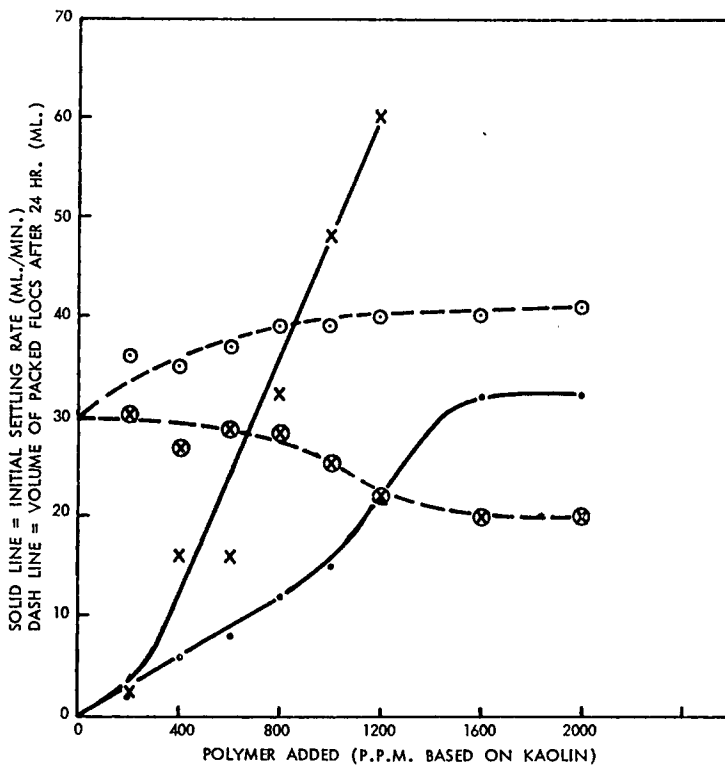


Fig. 9. Dependence of (—) initial settling rates and (--) sediment volumes on the amount of polymer added and on the agitation in the flocculation of 5% kaolin slurries with poly(1,2-dimethyl-5-vinylpyridinium methyl sulfate) of polymer with intrinsic viscosity = 6.2: (●) 20 inversions; (×) 18 hr. at 3.5 rpm.

When a kaolin suspension is mixed with a dilute solution of polymer, there is a rapid adsorption of the polymer onto the kaolin particles. Flocculation occurs when the long polymer molecules are adsorbed between two particles (or flocs) so as to cause them to stick to one another.¹³ A polymer molecule is wasted as far as bridging is concerned once it lies flat on the surface of a single particle. Such a covered surface cannot provide anchorage for a polymeric bridge from another particle. This bridging phenomenon is governed by laws of chance, so polymer molecules with the great-

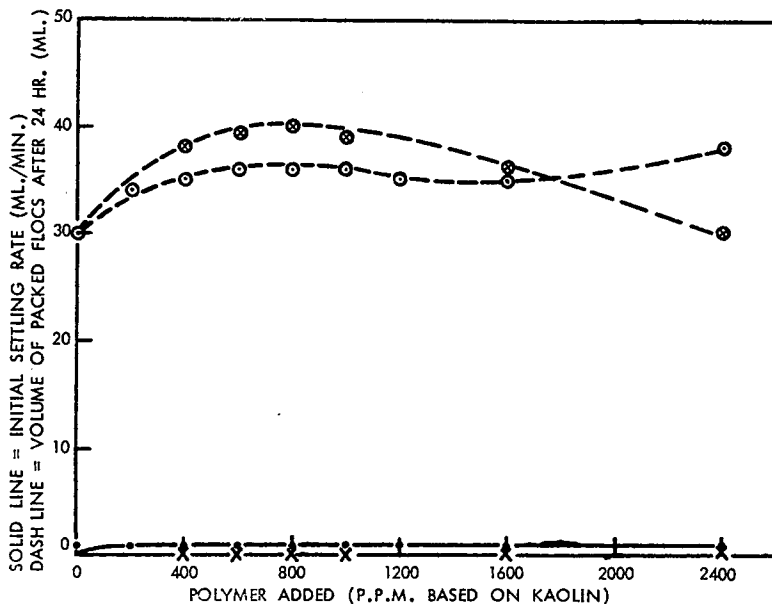


Fig. 10. Dependence of (—) initial settling rates and (---) sediment volumes on the amount of polymer added and on the agitation in the flocculation of 5% kaolin slurries with poly(1,2-dimethyl-5-vinylpyridinium methyl sulfate) of polymer with intrinsic viscosity = 0.9: (○) 20 inversions, (×) 18 hr. at 3.5 rpm.

est effective volume (high intrinsic viscosity) are best for promoting the buildup of flocs.

At low shear rates with a sufficiently high intrinsic viscosity polymer, the rate of floc buildup is initially much greater than the rate of floc breakdown. Thus, large flocs are quickly formed and these contain much hidden active surface. As agitation is continued, the rate of floc buildup decreases as the availability of suitable polymer in solution decreases or as the liberation of active surface decreases. This leads to decreased floc size and possibly some densification of the flocs.

It is necessary to postulate another way for the rate of floc buildup to decrease to explain the irreversible nature of the floc breakdown process. When one end of a polymeric bridge is slipped away from the surface of the second particle, it must be deactivated in some manner. One possibility for this would be the adsorption of another polymer molecule from solution so as to deactivate the liberated site on the second particle. Another possibility is a reorientation of the polymeric bridge so that it lies flat on one of the two particles after they are separated.

The relative rates of floc buildup and floc breakdown determine the trends in the floc sizes and densities as agitation is continued. Since the "popcorn-like" flocs are approximately spherical, their settling rates increase approximately as the square of their radii and as the first power of the difference between the density of the flocs and the density of the aqueous medium.¹¹

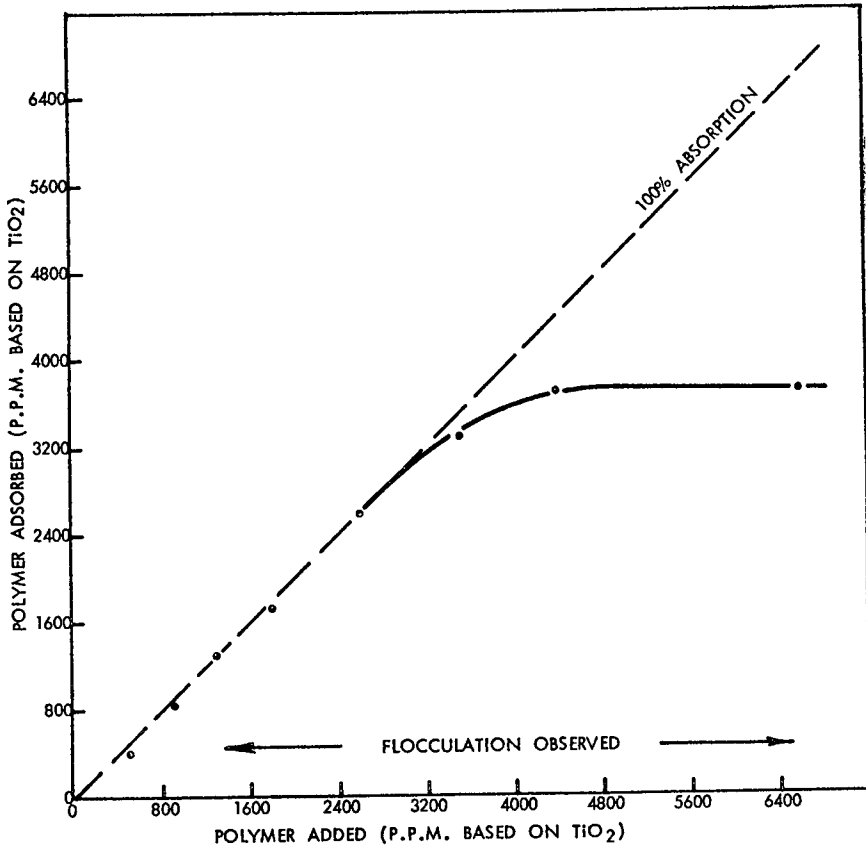


Fig. 11. Adsorption of poly(1,2-dimethyl-5-vinylpyridinium methyl sulfate), intrinsic viscosity = 9.2, on titanium dioxide in a 5% aqueous slurry.

Increased sediment volumes would result with increased floc size, increased uniformity in floc size, and increased interaction between flocs during packing. In relation to this last possibility, it appears that the presence of adsorbed polymer on kaolin particles leads to increased resistance to packing, which is indicated by the higher sediment volumes with the lowest intrinsic viscosity polymer as compared with the control.

Flocculation of Other Systems

High intrinsic viscosity poly(1,2-dimethyl-5-vinylpyridinium methyl sulfate) can also be used to flocculate suspensions of titanium dioxide, cellulose, coal, aluminum ore, phosphate ore, and sewage. The criterion for flocculation in these systems was the visual observation of floc buildup.

Over twice as much polymer is adsorbed in a 5% titanium dioxide suspension (Fig. 7) as in a 5% kaolin suspension after 18 hr. of agitation. This result is probably due to the higher surface area associated with the smaller particle sizes in the much slower settling titanium dioxide suspensions.

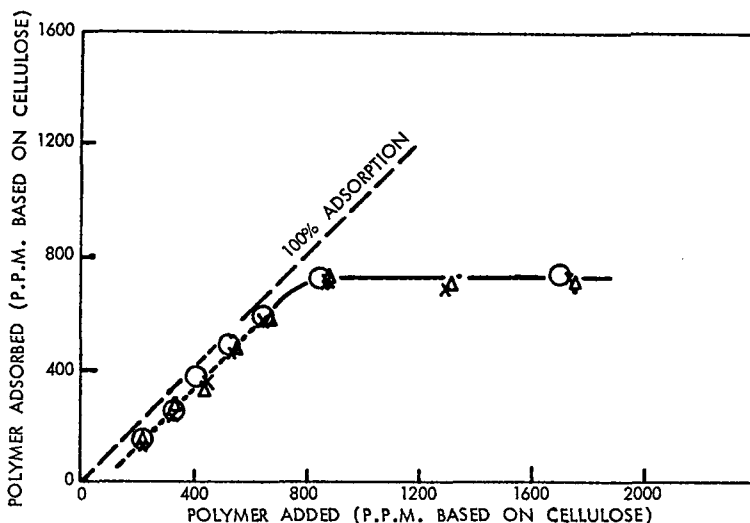


Fig. 12. Effect of polymer intrinsic viscosity (I.V.) on the adsorption of poly(1,2-dimethyl-5-vinylpyridinium methyl sulfate) on cellulose in a 5% aqueous slurry: (●) I.V. = 9.2; (×) I.V. = 6.9; (Δ) I.V. = 4.8; (○) I.V. = 0.4.

The polymer adsorption saturation level on a 5% slurry of cellulose fibers (filter paper) appears to be independent of the polymer intrinsic viscosity (Fig. 8). This result can be rationalized if all of the fiber surface is covered with polymer. If the polymer molecule tends to lay down on the surface rather than to protrude from the particle surface into the aqueous phase, the amount of polymer necessary to cover the surface will be independent of molecular weight. That rigid molecules like polyelectrolytes tend to lie flat on a particle surface was suggested in a discussion of the mechanism of the stabilization of colloidal solutions.¹⁴

EXPERIMENTAL

Polymer Synthesis

The polymer samples used in these studies were prepared by polymerizations in water containing potassium persulfate as described in the first paper of this series.² Since the polymerizations went to completion, the reaction mixtures were diluted with water and used without any purification.

Viscosity Measurements

Intrinsic viscosity measurements were estimated from measurements of reduced specific viscosities at 25°C. in dilution type No. 1 Ubbelohde viscometers and extrapolation of the data to infinite dilution by the method of Martin.¹⁵

Adsorption Studies on Kaolin

Water was added to 50 ml. in a 100 ml. graduated cylinder containing 5.0 g. of kaolin (Georgia kaolin, Hydrite R). The mixture was agitated for 18 hr. at room temperature by turning the cylinder end over end at 3.5 rpm.

To this hydrated slurry was added 50 ml. of an aqueous solution of polymer. In one type of agitation, the cylinder was turned end over end 20 times. In the other type of agitation, the cylinder was turned end over end at 3.5 rpm at room temperature for 18 hr. After the appropriate agitation, the slurry was permitted to settle so that some clear supernatant solution could be removed for ultraviolet analysis for unadsorbed polymer.² Hazy samples were centrifuged before analysis.

Settling Rates and Sediment Volumes

A polymer solution was added to a hydrated kaolin slurry in a 100 ml. graduated cylinder using the above procedure. After the cylinder was turned end over end 20 times, the initial settling rate was measured. A typical settling rate curve consisted of an initial linear relationship between the volume of clear supernatant solution and time. A sharp boundary between the supernatant and the slurry indicated uniform floc sizes. The linear relationship was followed by a decrease in the settling rate as the flocs began to interact during packing. The slurry was left undisturbed for 24 hr. at room temperature and the sediment volume was noted.

This same slurry was turned end over end at 3.5 rpm for 18 hr. at room temperature, and the initial setting rate was measured. It was found that with higher amounts of added polymer it was difficult to see the boundary between the supernatant solution and the slurry because some of the large flocs had broken down to tiny, slower-settling flocs. These caused an observable turbulence by interaction with the faster settling flocs. The recorded settling rates were for the majority of the flocs and the tiny flocs were not considered. After 24 hr., the sediment volume was recorded.

The same slurry was used to determine the effect of 1 min. of vigorous shaking by hand.

Adsorption Studies on Titanium Dioxide and Cellulose

As with kaolin, 5% suspensions of titanium dioxide (New Jersey Zinc, Anatase A410) and cellulose strips (Whatman No. 41 filter paper) were tumbled in the presence of polymer for 18 hr. The aqueous supernatant solutions were analyzed for unadsorbed polymer.

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References

1. Fuoss, R. M., and U. P. Strauss, *J. Polymer Sci.*, **3**, 246 (1948).
2. Shyluk, W. P., *J. Polymer Sci.*, to be published.
3. Leubner, G. W., J. L. R. Williams, and C. C. Unruh, U.S. Pat. 2,811,510 (October 29, 1957), to Eastman Kodak Co.
4. Sidgwick, N. V., *The Organic Chemistry of Nitrogen*, Clarendon Press, Oxford, 1942, p. 525.
5. Fuoss, R. M., and U. P. Strauss, *J. Polymer Sci.*, **3**, 602 (1948); *Ann. N. Y. Acad. Sci.*, **51**, 836 (1949).
6. Kagawa, I., and R. M. Fuoss, *J. Polymer Sci.*, **18**, 535 (1955).
7. Jones, G. D., and S. J. Goetz, *J. Polymer Sci.*, **25**, 201 (1957).
8. Marshall, C. A., and R. A. Mock, *J. Polymer Sci.*, **17**, 591 (1955).
9. Toyoshima, Y., *Bull. Chem. Soc. Japan*, **34**, 1734 (1961).
10. LaMer, V. K., R. H. Smellie, Jr., and Pui-Kum Lee, *J. Colloid Sci.*, **12**, 230 (1957).
11. Mysels, K. J., *Introduction to Colloid Chemistry*, Interscience, New York, 1959, p. 75.
12. Michaels, A. S., and J. C. Bolger, *Ind. Eng. Chem. (Fundamentals)*, **1**, 24 (1962).
13. Michaels, A. S., and O. Morelos, *Ind. Eng. Chem.*, **47**, 1801 (1955).
14. Heller, W., and T. L. Pugh, *J. Polymer Sci.*, **47**, 203 (1960).
15. Martin, A. F., *Tappi*, **34**, 363 (1951).

Résumé

Les solutions aqueuses de poly(1,2-diméthyl-5-vinylpyridinium méthyle sulfate) possèdent une bonne stabilité viscosimétrique à des pH neutre ou acide et à des températures allant jusqu'à 100°C. Les solutions fortement basiques ont une faible stabilité viscosimétrique, même à température de chambre. A la même force ionique l'efficacité relative de trois sels de sodium dans la réduction de la viscosité intrinsèque du polymère était: phosphate de sodium > sulfate de sodium > chlorure de sodium. Cette tendance vis-à-vis des viscosités intrinsèques plus faibles lorsqu'on augmente la force ionique se renverse elle-même à des forces ioniques élevées. Ce polymère est très efficace dans la floculation de suspensions aqueuses de kaolin à 5% comme cela est montré par des augmentations dans les vitesses de floculation initiales plusieurs centaines de fois supérieures. On présente une étude de certaines variables importantes reliées à cette propriété: adsorption du polymère, viscosité intrinsèque du polymère et agitation. On discute du mécanisme de la floculation.

Zusammenfassung

Wässrige Lösungen von Poly-(1,2-Dimethyl-vinylpyridiniummethylsulfat) weisen bei neutralem oder saurem pH bei Temperaturen bis über 100°C gute Viskositätsstabilität auf, während diese in stark basischen Lösungen sogar bei Raumtemperatur gering ist. Bei gleicher Ionenstärke nimmt die relative Wirksamkeit von drei Natriumsalzen bei der Erniedrigung der Viskositätszahl des Polymeren in der Reihenfolge Natriumphosphat > Natriumsulfat > Natriumchlorid ab. Die Tendenz zur Abnahme der Viskositätszahl mit steigender Ionenstärke erfährt bei hoher Ionenstärke eine Umkehrung. Das Polymere wirkt auf 5%ige wässrige Kaolinsuspensionen stark ausflockend, wie aus der Erhöhung der anfänglichen Absetzgeschwindigkeit auf das mehrere Hundertfache hervorgeht. Eine Untersuchung einiger im Zusammenhang mit dieser Eigenschaft wichtigen Variablen (Polymeradsorption, Viskositätszahl des Polymeren und Rührung) wird beschrieben und der Mechanismus der Ausflockung diskutiert.

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