

Flocculation of Microcrystalline Cellulose with Cationic Ionene Polymers

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Synopsis

Suspensions of microcrystalline cellulose particles were flocculated with two cationic ionene polymers differing only in charge density. A comparison of the flocculation (residual absorbance) and electrophoretic data showed that optimum destabilization corresponded to neutralization of the particle charge and that both polyelectrolytes had the same flocculating ability on a charge basis. These results, when combined with specific adsorption measurements, suggest that flocculation of the cellulose particles is accomplished by a recently proposed, "mosaic" charge neutralization mechanism.

INTRODUCTION

The papermaking industry utilizes a wide variety of natural and synthetic flocculants to improve water drainage and pigment retention characteristics during the formation of the fibrous mat. Currently, the use of synthetic cationic polymers for this purpose is receiving particular attention. Unlike the traditional inorganic flocculants such as alum, these are relatively insensitive to, and have little effect on, the pH of the paper furnish. Furthermore, since cellulose suspensions are negatively charged, cationic polyelectrolytes are effective at considerably lower concentrations than anionic polymer additives.¹

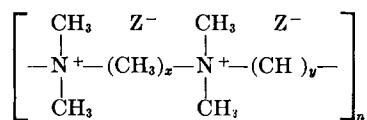
The mode of action of cationic polymers on negatively charged colloids has been extensively studied, principally for inorganic and latex suspensions. Flocculation in these systems may be accomplished by charge neutralization,²⁻⁴ bridge formation,^{5,6} or a combination of both mechanisms.^{7,8} Although these factors are undoubtedly operative in papermaking systems, few attempts have been made to determine the relative importance of each mechanism to the destabilization of cellulose suspensions.⁹ This may be due to the fact that pulp stock is a highly complex colloidal system and the polymer additives are generally poorly characterized proprietary materials.

Consequently, to effectively evaluate flocculating mechanisms in cellulose suspensions, it was felt that systematic studies should be undertaken on

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relatively simple systems consisting of colloidal microcrystalline cellulose and a well-defined class of cationic polyelectrolytes. The choice of microcrystalline cellulose as the model cellulose surface simplifies the problem of electrokinetic measurement since microelectrophoresis can be used conveniently as opposed to the more cumbersome streaming current methods required for fibers.¹⁰ Furthermore, recent evidence suggests that colloidal-size fines show the same electrokinetic properties as long fibers when specific adsorption effects are present.¹¹ Thus, the flocculation-redispersion characteristics of a model cellulose system probably reflect those of a fiber suspension to a greater degree than anticipated.

The cationic polymers used as flocculants were from a well-characterized series of polyelectrolytes, the x,y ionene halides.¹² These polymers have the following general structure:



where x and y are integers, Z^- is a halogen, and n is the degree of polymerization. Rembaum et al. have shown that the ionenes are efficient flocculants for inorganic suspensions of clay¹³ and silica as well as polystyrene latex particles.¹⁴ By controlling the conditions of synthesis, both the molecular weight and the charge density along the chain (i.e., the values of x and y) can be varied at will, thus allowing a systematic analysis of the flocculation behavior as a function of cationic polymer structure.

In this first phase of our polymer flocculation studies, the effect of variation in polymer charge density on the flocculation of microcrystalline cellulose is reported. Two ionene polymers, one of high charge density ($x = 3$ and $y = 3$) and the other with a lower charge density ($x = 6$ and $y = 10$) were used as flocculants. Both cationics had molecular weights of about 60,000.

The parameters measured were the extent of flocculation, polymer adsorption, and electrophoretic mobility. The results of this initial study make it possible to formulate a mechanism of flocculation which may also be applicable to other cationics in this molecular weight range.

EXPERIMENTAL

Materials

Cellulose Sols

Microcrystalline cellulose sols were prepared from Avicel PH105 powder supplied by the FMC Corporation, Marcus Hook, Pa. Twenty grams powder were mixed with 180 ml water in a Waring Blender for 5 min. The thick blenderized material was then gradually diluted with stirring to a final volume of 1 liter. The diluted suspension was left undisturbed in a refrigerator for three days. The resulting sediment was separated by de-

cantation, and only the supernatant layer was saved for use in the flocculation studies.

The powder used in some initial experiments had been pretreated by a three-stage continuous extraction in water, benzene/methanol (3/2), and dichloroethane (24 hr each stage) to remove residual impurities which might have interfered with the flocculation studies. This pretreatment, however, modified the microcrystalline surfaces as evidenced by the fact that the pH of the resultant sols was frequently below 4, a value low enough to induce spontaneous flocculation. Blending times in excess of 15 min with untreated powder also produced the same behavior.¹⁵ Consequently, for this work sols were prepared from unextracted Avicel. These were stable and reproducible in their flocculation behavior for periods over one month when stored in a refrigerator. The unadjusted pH varied from 5.7 to 6.0, and the solids content, from 0.10% to 0.12%.

Electron micrographs indicated that most of the sol particles consisted of individual rod-shaped microcrystals with lengths of about 0.25 μm and widths of approximately 0.015 μm . These dimensions are close to those reported by other workers for Avicel prepared from high-alpha wood cellulose.^{16,17} A fraction of the material remained in the form of unattrited fiber fragments. It is unlikely, however, that these would significantly affect the colloidal properties of the sol.

Polymers

Samples of 3,3-ionene chloride (3,3) and 6,10-ionene bromide (6,10) with weight-average molecular weights of about 60,000 were generously donated by Dr. Alan Rembaum of the Jet Propulsion Laboratory, Pasadena California. Stock solutions of the polymers were prepared in double-distilled water at concentrations of 200 ppm and 12 ppm for the 3,3 and 200 ppm and 30 ppm for the 6,10. Addition of the polymer solutions to the cellulose sols did not significantly affect the pH of the sol.

Flocculation Tests

The extent of flocculation was determined by measurement of the residual absorbance of the supernatant. The tests were carried out in 25-ml graduate cylinders. A predetermined volume of stock ionene solution was added to the cylinder and diluted to the 10-ml mark. A 1 $\frac{1}{2}$ -in. magnetic Teflon-coated stirring bar was inserted vertically in the cylinder, and the solution was stirred at a constant speed of about 375 rpm. Cellulose sol, 10 ml, was then rapidly pipetted into the cylinder, and stirring was continued for 2 more minutes. (The final sol concentration was 0.05–0.06%.) The stirring bar was removed and the cylinder was allowed to stand undisturbed for 1 hr. An aliquot of supernatant was removed from the cylinder with a long-needle syringe, and its absorbance was measured in a Beckman DU spectrophotometer at 546 nm using 1-cm cells.

Electrophoretic Mobility

Mobility measurements were conducted in a particle microelectrophoresis apparatus manufactured by Rank Brothers, Bottisham, Cambridge, England, using a thin-walled cylindrical cell thermostatted at 25°C. In order to conduct mobility measurements, it was necessary to work at a lower solids concentration than the 0.05–0.06% used in the flocculation tests. Simple dilution of the suspensions was not suitable since this would have altered the ionic strength or the extent of polymer adsorption, both of which would affect the mobility of the particles. The following procedure was therefore devised to reduce the particle concentration to workable levels without altering the ionic strength or residual polymer concentration of the suspension. The sol was mixed with the polymer solution in the cylinders exactly as described for the flocculation tests. After standing for 15 min, the cylinder was gently shaken to redistribute the settled particles. Approximately 19 ml out of the total volume of 20 ml was poured into centrifuge tubes and centrifuged for 1 hr at 12,500 rpm. The supernatant in the centrifuge tubes was then carefully removed with a long-needle syringe and recombined with the 1 ml of original suspension left in the cylinder. Mobility measurements were performed on the recombined suspensions. At least ten particles were timed in each direction at field strengths of 7.3 and 9.8 V/cm. Timings were made at the top stationary layer and checked at the bottom stationary layer.

Absorption Measurements

The amount of polymer adsorbed on the particles was determined by measuring the residual polymer concentration after adsorption using a colloid titration technique. The method is based on the observation that cationic polyelectrolytes will react stoichiometrically with anionic polyelectrolytes to produce insoluble polysalt precipitates.¹⁸ The equivalence point may be visualized by the development of turbidity¹⁸ or by the use of a cationic indicator, *o*-toluidine blue.^{19,20} This indicator gives a blue color in the free state, i.e., in the presence of excess positively charged polymer. When complexed with excess anionic polymer, the indicator color changes to purple.

The anionic polyelectrolyte used as the complexing reagent was 90% esterified poly(vinyl alcohol) potassium sulfate (PVSK) purchased from Wako Pure Chemical Industries, Osaka, Japan. The polymer reagent was dissolved in distilled water to produce a 0.001*N* standard solution. The indicator was prepared by dissolving *o*-toluidine blue powder in distilled water at a concentration of 0.004%.

A series of ionene polymer solutions of known concentration were made up in the range of 0.1 to 50 ppm. Five drops of indicator were added to these solutions producing a light-blue color. The solutions were titrated to a purple endpoint with standard PVSK which was dispensed from a Gilmont ultramicroburet fitted with a 1-ml pipet. A calibration curve

of ionene concentration versus the volume of 0.001*N* PVSK was prepared after correcting for the amount of PVSK required to titrate a blank containing 5 drops of the indicator. The linearity of the calibration curves was excellent, except in the range below 1 ppm, where the correction for the indicator was as large as 20–80% of the total titer.

Adsorption measurements were conducted in 50-ml Erlenmeyer flasks. A predetermined volume of stock ionene solution was added to the flask, diluted to 15 ml, and stirred at 375 rpm using a Teflon-coated miniature stirring bar. Cellulose sol, 15 ml, was rapidly pipetted into the flask, and stirring was continued for 2 more minutes. The flask was then allowed to stand undisturbed for 15 min. Since the presence of suspended solids interfered with detection of the endpoint, the solids were separated out by centrifugation. Duplicate 10-ml aliquots of the supernatant were titrated with PVSK exactly as described above. Ionene concentrations in the supernatant were determined from the calibration curve, and the extent of adsorption was calculated.

RESULTS

Residual absorbance, electrophoretic mobility, and specific adsorption data are plotted as functions of the ionene dosage in Figures 1 and 2. Both

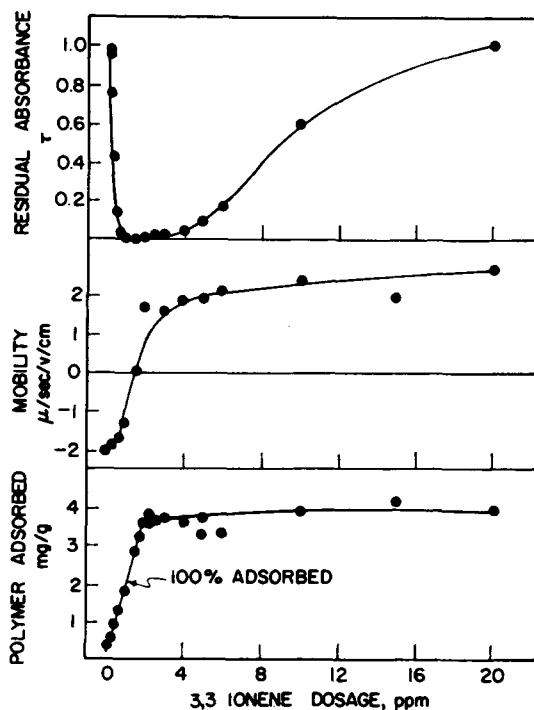


Fig. 1. Flocculation, electrophoretic mobility, and specific adsorption curves for cellulose suspensions containing 3,3-ionene.

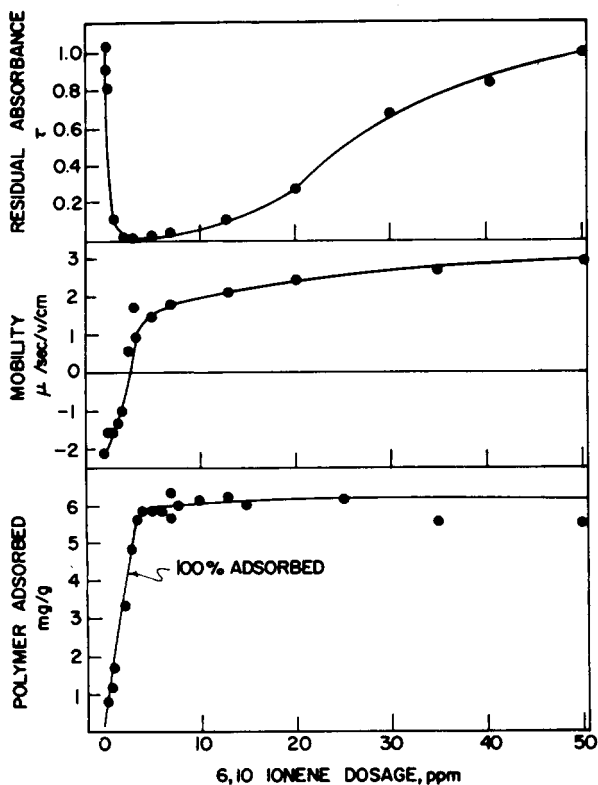


Fig. 2. Flocculation, electrophoretic mobility, and specific adsorption curves for cellulose suspensions containing 6,10-ionene.

polymer-cellulose systems showed flocculation characteristics similar to those reported for other cationics of this molecular weight range in inorganic suspensions.⁷ The important results may be summarized as follows:

1. The adsorption isotherms are of a high-affinity type in which adsorption is rapid and complete up to a constant saturation level. The saturation level decreases with increasing polymer charge density.

2. The electrokinetic charge of the cellulose is strongly affected by small dosages of polymer and is reversed at dosages below the saturation level of adsorption. The amount of polymer required to reverse the charge decreases with increasing polymer charge density.

3. Optimum flocculation, corresponding to the complete removal of turbidity in the supernatant, is achieved in the mobility range of -1.5 to $+1.5 \mu\text{m sec}^{-1} \text{V}^{-1} \text{cm}^{-1}$. The optimum polymer dosage for flocculation (OPD) decreases as the polymer charge density increases, which is consistent with the findings for these polymers in inorganic suspensions.^{13,14}

4. High polymer dosages redisperse the cellulose suspensions. The degree of redispersion is much more sensitive to the dosage of the higher charge-density ionene.

DISCUSSION

The results indicate that 3,3-ionene is a more efficient flocculant for cellulose than the lower charge-density 6,10-ionene. The flocculating abilities of the two polymers can be compared quantitatively by inspecting the OPD, redispersion, and molecular weight per unit charge (equivalent weight) ratios, as shown in Table I.

The experimentally determined efficiency ratios indicate that approximately twice as much of the 6,10 (on a weight basis) is required to achieve optimum flocculation or a given degree of redispersion. The reasonable agreement between the experimental and theoretical ratios shows, however, that both ionenes have the same flocculating capacity per unit charge, which is in accord with Rembaum's observations for clay and polystyrene latex suspensions.¹⁴

For both polymers, the OPD is also the dosage required to give zero electrophoretic mobility, implying that the surface charge on the particle must be neutralized for optimum flocculation. The polymer is completely adsorbed, at least up to the neutralization point, and it is only after neutralization is reached that redispersion begins. The negative charge on the cellulose surface can be estimated by calculating the number of positive charge equivalents required for neutralization. At zero mobility, the amount of ionene adsorbed on the particles is 2.8 mg/g for 3,3-ionene and 4.4 mg/g for 6,10-ionene, which corresponds to 2.3 and 1.9 millequivalents of positive charge per 100 g of cellulose, respectively. These values are close to the measured carboxyl content of Avicel. Consequently, it would appear that the surface charge arises primarily from ionized carboxyl groups. Another indication of this is given by the effect of pH on the flocculation behavior. Preliminary studies show that the OPD decreases with decreasing pH and spontaneous flocculation occurs at pH \sim 4. Since the pK of carboxyl groups on hydrolyzed cellulose²¹ is 4, spontaneous flocculation would be expected at this pH if carboxyl groups are responsible for the surface charge.

The equivalency of both ionenes on a charge-for-charge basis and the coincidence of the optimum flocculation point with neutralization of the particle charge indicate that flocculation in these systems is due entirely to a charge neutralization mechanism. Recent work by Gregory on the flocculation of polystyrene latex particles by cationic polyamines supports this conclusion.⁴ He found that with a polyamine of molecular weight 20,000, the OPD corresponded to neutralization of the latex charge. He concluded that this polymer was effective through charge neutralization.

TABLE I
Efficiency Ratios

Theoretical	Flocculation	Redispersion
$\frac{\text{equiv. wt. (6,10)}}{\text{equiv. wt. (3,3)}} = 1.9$	$\frac{\text{OPD (6,10)}}{\text{OPD (3,3)}} = 1.8$	$\frac{\text{dosage for } \tau = 0.1 \text{ (6,10)}}{\text{dosage for } \tau = 0.1 \text{ (3,3)}} = 2.4$

Optimum flocculation with a high molecular weight polyamine ($\sim 10^6$) was achieved only at negative mobilities of $-3 \mu\text{m sec}^{-1} \text{V}^{-1} \text{cm}^{-1}$, which was attributed to a bridging process.

Although the overall charge on the cellulose particle is reduced to zero at the OPD, a calculation of the extent of surface coverage by the polymer suggests that the detailed picture must be more complicated than a simple one-to-one correspondence of positive and negative charges. Ionene molecules may be expected to adsorb on the particle surface in a fairly extended configuration because of the extremely low ionic strength of the suspension. Most of the polymer segments should be in contact with the surface as a consequence of this extension and the high coulombic adsorption energy.¹⁴ Under these assumptions, the surface area occupied per ionene molecule can be equated with the projected area of an extended-chain molecular model, which is $1.5 \times 10^2 \text{ nm}^2$. The amount of ionene adsorbed at saturation is 3.9 mg/g and 6.2 mg/g for the 3,3 and 6,10, respectively, and the surface area of a cellulose particle of $0.015 \mu\text{m}$ cross section is $170 \text{ m}^2/\text{g}$. These figures lead to saturation coverages amounting to just 3.5% and 5.5% of the total surface, respectively. As only a small fraction of each particle is covered by polymer, it is apparent that all of the surface carboxyl groups cannot be neutralized individually. Thus, at overall neutrality, an uneven charge distribution must exist on the cellulose surface in which areas of high positive charge density are surrounded by larger regions of relatively weak negative charge. This "charge mosaic" model has been proposed very recently by Rembaum et al.¹⁴ and Gregory²² as a refinement of the polymer charge-neutralization picture. Gregory postulated that the uneven charge distribution could give rise to an additional electrostatic contribution to the attractive interaction between particles. This accounted for the observation that polycations flocculated latex particles at a higher rate than simple salts which reduce the surface charge in a uniform manner. Such residual attractive forces could similarly be present in the cellulose-ionene system. Further polymer flocculation studies conducted in the presence of salts might help clarify this point. However, evaluation of the behavior would be difficult because of complicating effects arising from the strong hydration of cellulose particles.¹⁵

Finally, some remarks should be made regarding the adsorption-redispersion results. Figures 1 and 2 show that when polymer adsorption is constant, the flocculation curves display continued redispersion. These results differ from those generally observed. For example, Black et al.⁷ found that adsorption continued until redispersion was constant. However, in their system, the ratio of sol to polymer particles was $\ll 10^{-2}$ at the OPD while in this study the ratio is nearly 1. As a result of this situation, the mixing conditions may be responsible for the observed results. Support for this suggestion is contained in the work of Kasper²³ who showed that the relative rates of particle aggregation and polymer adsorption are a function of the ratio of sol to polymer particles.

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