The effects of some electrolytes on flocculation with a cationic polyacrylamide

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Abstract: The effects of sodium chloride, sodium sulfate, and alum (aluminum sulfate) on the performance of a cationic polyacrylamide flocculant in a papermaking suspension consisting of bleached (hardwood: softwood, 50:50) kraft wood-pulp fibres and anatase (TiO$_2$) were investigated. Sodium chloride and sodium sulfate, 1×10^{-5} to 1×10^{-2} M, in the presence of polymer, caused negligible changes in the electrophoretic mobility of the TiO$_2$ and in the first-pass retention of TiO$_2$ (heteroflocculation of TiO$_2$ and fibres). Alum at concentrations from 1×10^{-5} to 1×10^{-4} M at pH 4.0 and 4.5 increased retention with polymer; higher alum concentrations resulted in lower retentions. At pH 4.0 the electrophoretic mobility of the TiO$_2$ was positive over the entire range of alum concentrations investigated ($1 \times 10^{-5} - 3.2 \times 10^{-3}$ M) whereas at pH 4.5 the mobility was negative at 1×10^{-5} M alum and charge reversal was observed at about 4×10^{-5} M alum.

The intrinsic viscosity of the cationic polyacrylamide was decreased by the addition of alum, sodium chloride or sodium sulfate. The effect of alum on the polymer conformation appeared to be that of the non-specific interaction of sulfate ions with a cationic polyelectrolyte.

Retention results are discussed in terms of the colloidal stability of TiO$_2$, the adsorption of polyacrylamide on TiO$_2$ and the conformation of adsorbed polymer.

Key words: Titanium dioxide, aluminum sulfate, polyacrylamide, flocculation, cellulose fibers

Introduction

Paper is made by rapid filtration of a suspension containing wood pulp fibres and other additives which may include colloidally dispersed kaolin and titanium dioxide. Flocculants are often added in order to retain in the paper the colloidal components of the papermaking stock. Originally papermakers' alum (Al$_2$(SO$_4$)$_3$ $\times$ 16 H$_2$O) was used as a flocculant and it is still used although primarily for sizing. Anionic copolymers of acrylamide were the first synthetic organic polymers which were widely used as flocculants for papermaking. These polymers were generally added in conjunction with alum in order to enhance adsorption of the anionic polyelectrolyte onto the dispersed phase [1, 2]. More recently cationic copolymers of acrylamide have become available and materials of this type are now the most common flocculants for papermaking in North America [3].

Lindstrom et al. [4, 5] have reported the effects of cationic substitution and molecular weight of polyacrylamide on its adsorption properties on cellulose and on the flocculation of cellulosic fines (small particles). Adsorption was found to decrease with increasing molecular weight and increasing degree of cationic substitution. Flocculation increased with increasing molecular weight and was maximal around 5 to 10 mole percent cationic monomer. In the same study it was shown that the presence of electrolytes inhibited the performance of the polymeric flocculant.

In recent publications, Jaycock and Pearson described the flocculation behaviour of various inorganic colloids in the presence of bleached wood pulp fibres [6, 7]. They concluded that, in terms of colloidal stability, the system behaved as an electrostatically stabilized dispersion and they interpreted their results in terms of DLVO theory. An important observation in this work was that after exposure to the pulp suspension the electrokinetic properties of the inorganic colloids changed to resemble those of the fibres. This behaviour was attributed to the adsorption of polymers and small fragments from the wood onto the surface of the inorganic colloids. This study also confirmed the results of earlier investigations which concluded that alum addition increased retention

coincident with decreasing the magnitude of the electrokinetic potential of the dispersed colloids.

Alum and cationic polyacrylamide are used together on a great many paper machines making fine papers. However, there is some confusion in the literature regarding the influence of alum on the performance of cationic polyacrylamide flocculants. Nicke and Hartmann [8] published evidence which showed that the addition of alum improved the performance of cationic polyacrylamide flocculants, and Moore [9] showed that alum addition improved drainage in the presence of cationic polymer. On the other hand, both the paper by Watts and Windhager [10] and that by Guender and Auhorn [11] stated that alum interferes with cationic polyacrylamide flocculants in papermaking dispersions. Contradictory conclusions are not surprising in light of the complex solution chemistry of alum which would vary with the different pulps, pH values and tests used in the various studies.

The object of the present work was to clarify the interactions between alum and a cationic polyacrylamide (PAM) in a papermaking suspension. In addition to retention measurements, interactions between alum and PAM were investigated by viscosity measurements and alum-solid interactions were followed by electrophoresis. The papermaking furnish for this study consisted of bleached kraft (hardwood : softwood, 50:50) pulp and titanium dioxide (TiO_2).

Experimental

Materials

All water was once-distilled in a glass distillation apparatus, with the exception of the water used for the viscosity measurements, which was twice-distilled.

ACS-grade electrolytes were used without further purification. A stock alum solution was prepared from Baker Chemical Co., ACS-grade $Al_2(SO_4)_3 \cdot 18 H_2O$ and the concentration was found to be 0.208 M by atomic absorption spectroscopy. Alum solutions with concentrations below 0.01 M were prepared daily, as these undergo hydrolysis with time [12].

The cationic polyacrylamide used in this investigation was Betz 1260, a copolymer of acrylamide and an unspecified cationic monomer. At was supplied by the Betz Chemical Co. The polymer was a white solid with a moisture content of about 8 percent and was found to have no significant ash content. The molecular weight was estimated to be 2×10^6 (see discussion section) and results from conductometric titration of ion-exchanged polymer indicated an equivalent weight of about 2×10^3. Polymer solutions were made daily at 0.03 percent and were allowed at least 19 hours to dissolve. When handling very dilute polymer solutions, the glassware was pretreated with dilute polymer and lightly rinsed in order to minimize the loss of polymer by adsorption onto the glass.

Anatase A-HR (A-HR is a brand designation), manufactured by Tioxide of Canada Ltd., was used without further modification. The particle size has been reported to be 0.15 μm [6]. Microelectrophoresis measurements at various pH values indicated an isoelectric point in the pH range 3.0 to 3.5 which is similar to that found by Jaycock and Pearson [7]. They state the electrophoretic behaviour of the A-HR is a consequence of the presence of adsorbed phosphate ions.

A 50:50 blend of fully bleached hardwood (from Quebec) and softwood (from Saskatchewan) kraft pulps was employed. The dry lap pulps were separately disintegrated, beaten to 350 Canadian Standard Freeness (an industry test which approximately measures specific surface areas), and stored at about 10 percent consistency at 4.4 °C. The pulps were mixed and diluted with distilled water before use.

Retention measurements

Retention measurements were made with the Dynamic Drainage Jar. This device, developed by Britt and Unbehend [13], consisted of a vertical plastic cylinder with an inner diameter of 10 cm and a capacity of 1.2 l. At the bottom of the cylinder was a screen and, rotated just above the screen, a propeller mounted on a shaft concentric with the axis of the cylinder and entering from above. Below the screen the cylinder tapered down to a clamped hose, the drainage valve, which in turn was attached to the tip of a 50 ml Pyrex brand pipette, the drainage nozzle. A detailed description of our Dynamic Drainage Jar was given previously [14].

Operation of the Dynamic Drainage Jar consists essentially of filtration with stirring. The propeller has two functions. Firstly, it is a source of hydrodynamic turbulence and crudely simulates the hydrodynamic conditions produced in a paper machine. Secondly, the propeller prevents the formation of a fibre mat on the screen which, in turn, means the suspension is filtered through a constant, well-defined mesh. Furthermore, under these conditions TiO_2 must be adsorbed onto fibres to be retained because the screen mesh size was sufficiently large to permit coagulated TiO_2 to pass through but not fibres. Without stirring a fibre mat forms on the screen and the result is complex and irreproducible filtration. A typical retention experiment was carried out in the following manner.

TiO_2 (352 mg) was added with stirring to 400 g of pulp at 0.486 percent consistency and the mixture was equilibrated to 25 °C in a water bath for 1 to 6 hours. To the pulp was added 10 ml of 0.01 M alum and the pH was adjusted to 4.0 with H_2SO_4 or NaOH. The pulp, TiO_2 and alum mixture sat at 25 °C for 3 to 5 minutes prior to polymer addition. The pH of 86 ml of water was adjusted to 4.0 and to it was added 4 ml of 0.03 percent polymer. The diluted polymer was added, with stirring, to the pulp suspension and the mixture was gently agitated for 2 minutes with a magnetic stirrer. The propeller speed of the Dynamic Drainage Jar was adjusted to 500 RPM and the pulp suspension was added. After 2 minutes stirring the clamp was removed from the tube to the drainage nozzle, which initiated flow into a tared 250 ml beaker. After about 100 ml of filtrate, or so-called white-water, had been collected, the beaker was replaced with another, and an additional 50 ml was collected for electrophoresis measurements.

The pH and conductivity of the first 100 ml was measured and about 20 ml of 0.25 percent PAM was added to cause complete flocculation of the dispersed TiO_2. The suspension was filtered through 11 cm diameter Whatman No. 40 filter paper in a Büchner funnel. The filter paper was dried in an oven at 105 °C and subsequently ashed at 900 °C for 20 minutes. The first-pass retention (FPR) was calculated from the following formula.

$$FPR = 100 \times \left(1 - \frac{\% \text{ ash in filtrate}}{\% \text{ ash in initial suspension}}\right) \quad (1)$$

In some cases complete filtration of TiO_2 in the white-water did not occur. Na_2SO_4 and more polymer were added to the white-water to aid filtration, or, the white-water was collected in a beaker lined with Saran Wrap[1]), the water was evaporated in the oven and the Saran Wrap was ashed. In experiments using high concentrations of NaCl or Na_2SO_4 the filter was washed with water to remove the electrolyte and results from this procedure agreed with those obtained after dialyzing the white-water to remove the excess salts. At pH 4.5 and concentrations of 1×10^{-3} M and greater, alum precipitated and thus contributed to the ash weight; for these conditions it was necessary to measure TiO_2 by chemical analysis (TAPPI Method T439 M-60) to measure retention.

Electrophoresis

Mobilities were measured with a Rank Brothers microelectrophoresis instrument in the flat-cell configuration. Undiluted white-water samples were measured at 25 °C; thirty measurements were done at each stationary layer and the polarity of the applied potential was reversed for alternate measurements.

Viscosity measurements

Polymer solutions were filtered through No. 36060, Pyrex brand, fine, sintered glass funnels. Viscosity measurements were made with Cannon 50 M241 Ubbelohde dilution viscometers at 25 °C. Shear dependency of the intrinsic viscosities was not considered [15]. Figure 1 shows examples of reduced viscosities as functions of polymer concentration for various alum concentrations and pH values.

Results and discussion

The first-pass retention of TiO_2 in pulp suspensions, in the absence of PAM, was measured as a function of
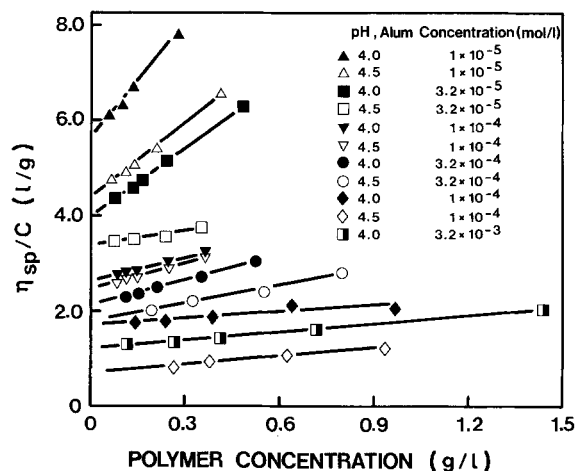

Fig. 1. Reduced viscosity as a function of PAM concentration in aqueous solutions with various concentrations of alum at pH 4.0 and 4.5

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[1]) Trademark of the Dow Chemical Company.

the concentration of added sodium sulfate and alum and the results are shown in figure 2. Over the range of sodium sulfate concentrations from 1×10^{-5} to 1×10^{-3} M the first-pass retention of TiO_2 was less than 10 percent and unaffected by sodium sulfate; above 1×10^{-3} M it rose rapidly to 40 percent at 1×10^{-2} M. TiO_2 retention was generally higher in the presence of alum than with sodium sulfate. Over the alum concentration range from 1×10^{-5} to 1×10^{-4} M, at pH 4.5, retention was nearly 60 percent. Higher alum concentrations resulted in decreased retention values. More detailed studies of the influence of alum on TiO_2 retention have been published [6, 7, 16].

Figure 3 shows retention as a function of sodium chloride and sodium sulfate concentration at pH 4.5 in the presence of 2.4 mg/l PAM. Comparison of the sodium sulfate results in figure 2 with those in figure 3 shows that the polymer increased TiO_2 retention from less than 10 percent to around 60 percent. The first-pass retention showed a rather remarkable insensitivity to the concentration of both salts; only at 0.01 M electrolyte was there a slight decrease in retention. The electrophoretic mobilities of the unretained TiO_2 are also shown in figure 3. For both electrolytes the mobilities were negative and nearly constant. Usually electrophoretic mobilities of hydrophobic colloids decrease with increasing electrolyte concentration. Perhaps the electrophoresis results were affected by the presence of traces of materials dissolved from the wood fibres.

The intrinsic viscosity of the PAM is shown as a function of the concentration of sodium chloride and sodium sulfate in figure 4. Increasing the concentration of either electrolyte resulted in a decrease in the intrinsic viscosity. This is a common feature in the behaviour of polyelectrolytes and is a result of the added salts shielding the repulsive forces between charged groups on the polymer chain, thereby effecting a decrease in the hydrodynamic volume of the polymer. Also, it is known that divalent ions, oppositely charged to the polymer chain, cause a greater contraction than do monovalent ions. Thus, results in figure 4 are typical of the response of a flexible cationic polyelectrolyte to the addition of salts [17].

TiO_2 retention was measured as a function of alum concentration at pH 4 and 4.5 in the presence of 2.4 mg/l PAM; the results are shown in figure 5. At most concentrations the retentions were higher with alum than with sodium chloride or sodium sulfate. Retention was relatively independent of the concentration of alum when it was low, but decreased at higher values. The pH appeared to be a significant
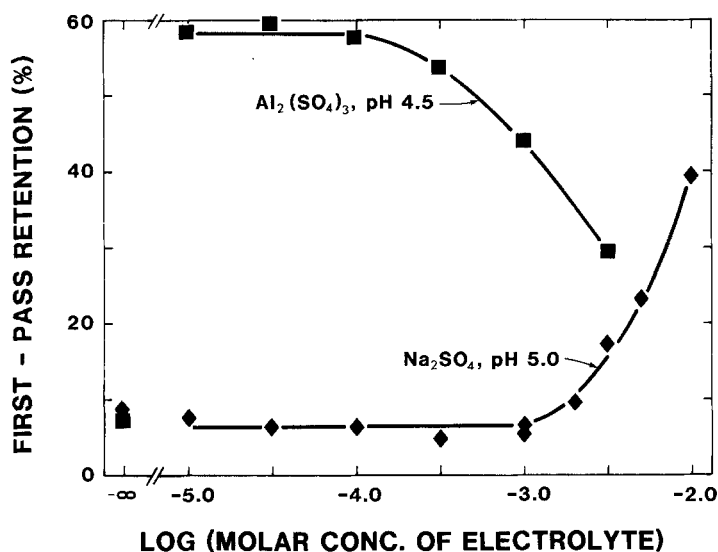
Fig. 2. First-pass retentions of TiO_2 on the Dynamic Drainage Jar as functions of the concentration of added alum and sodium sulfate in kraft pulp. No PAM was present
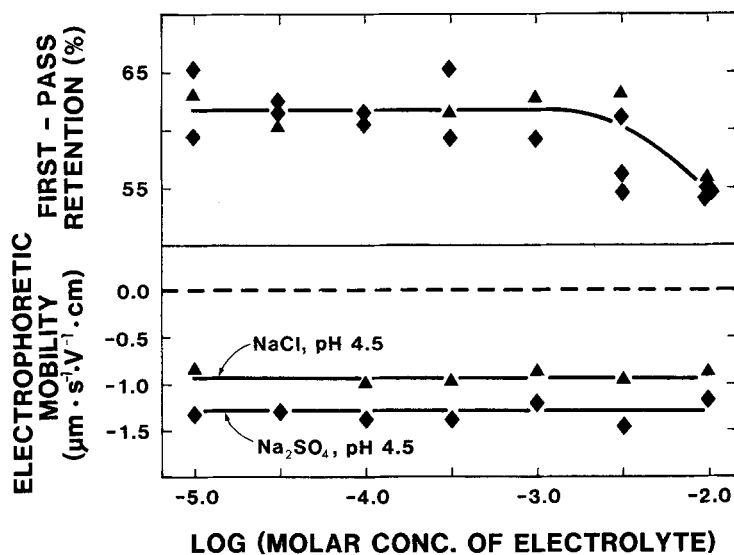

Fig. 3. First-pass retention of TiO_2 and electrophoretic mobility of unretained TiO_2 as functions of sodium sulfate and sodium chloride concentration in kraft pulp. PAM concentration 2.4 mg/l

variable since the retention was higher at pH 4 than at pH 4.5.

The electrophoretic mobilities of the TiO_2 in the white-water of the retention tester were measured and are shown in figure 5. At pH 4 the mobility was positive over the range of alum concentrations from 1×10^{-5} to 3.2×10^{-3} M, whereas at pH 4.5 the mo-

bility was negative at low concentrations of alum and charge reversal occurred between 1×10^{-4} and 3.2×10^{-5} M. Also shown (diamonds) are mobility measurements which correspond to the retention experiments in the absence of polymer (fig. 2). The presence of 2.4 mg/l PAM had no influence on the electrophoretic mobility of TiO_2.
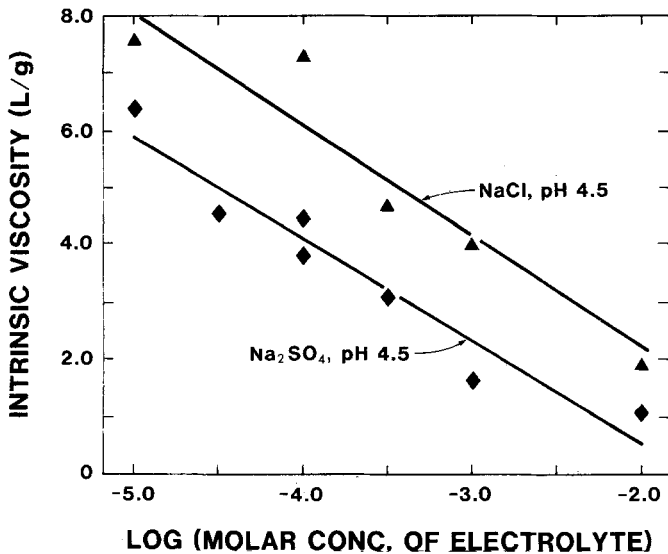
Fig. 4. The influence of sodium sulfate and sodium chloride concentration on the intrinsic viscosity of PAM in water

The electrophoresis and retention data in figure 5 indicate that the mobilities showed the greatest change over the range of alum concentrations where the retention was approximately constant and, conversely, that the mobilities were constant and positive at the higher alum concentrations where the retention was decreasing. Therefore, there is no apparent correlation between electrophoretic mobility and retention. It is, of course, assumed that the mobilities of the retained and unretained TiO_2 particles are the same. Another implication of the results in figure 5 is that the

polymer caused high retention even when the TiO_2 particles were positively charged. This suggests that positively charged polymer was able to adsorb onto TiO_2 surfaces with a net positive charge.

The intrinsic viscosity of the polyacrylamide is shown in figure 6 as a function of alum concentration at pH 4.0 and 4.5. Increasing concentrations of alum caused the intrinsic viscosity to decrease; this is a similar behaviour to that shown in figure 4 for the addition of sodium chloride and sodium sulfate. The intrinsic viscosity at every alum concentration was higher at pH 4.0 than at pH 4.5, which is the same trend observed in the retention results in figure 5.

The intrinsic viscosities of PAM, at pH 4.5 in the presence of various concentrations of alum and sodium sulfate, are shown in figure 7 as a function of the logarithm of the sulfate ion concentration. At the same sulfate ion concentration, the two electrolytes had a similar influence on the solution conformation of the polyacrylamide. Therefore, the presence of the complex hydrolysis products of aluminum sulfate had no specific influence on the PAM, but instead the alum acted simply as a source of sulfate ions.

General discussion

The retention results can be summarized in the following manner. Without polymer or electrolytes the retention was less than 10 percent. Na_2SO_4 did not influence retention at concentrations less than 0.001 M; retention rose to 40 percent in 0.01 M Na_2SO_4. Retention was higher in the presence of alum.
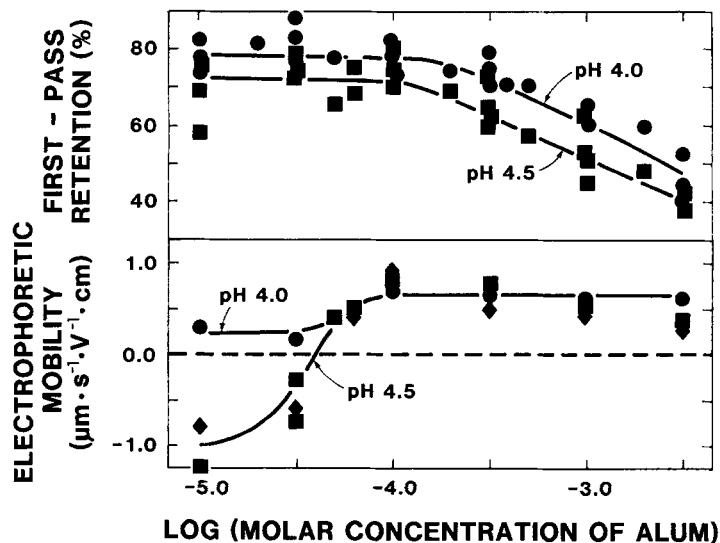

Fig. 5. First-pass retentions and electrophoretic mobilities of TiO_2 in kraft pulp as a function of alum concentration. Squares (pH 4.5) and circles (pH 4.0): 2.4 mg/l PAM. Diamonds (pH 4.5): no PAM present
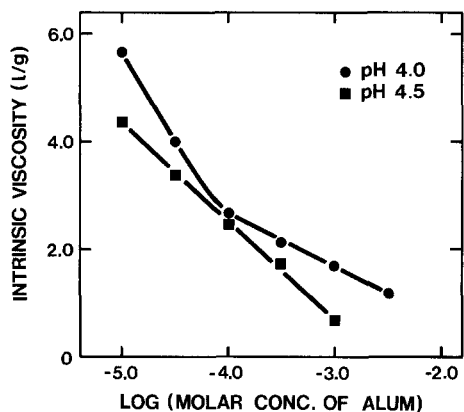
Fig. 6. Intrinsic viscosity of PAM in aqueous solutions of alum plotted as a function of alum concentration at pH 4.0 and 4.5
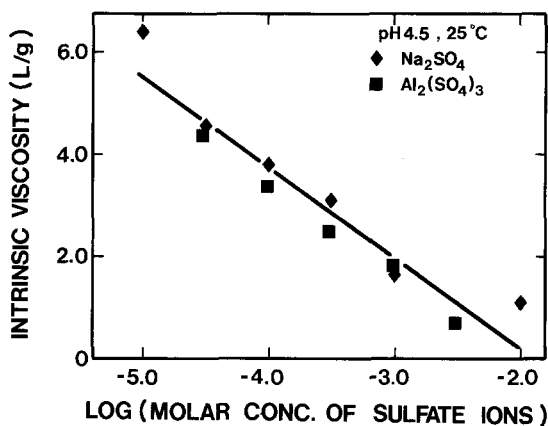

Fig. 7. Intrinsic viscosity of aqueous solutions of PAM as a function of sulfate ion concentration for alum and sodium sulfate addition

At 1×10^{-5} M the retention was about 60 percent; however, the first-pass retention did decrease at alum concentrations of 3.2×10^{-4} M and higher. The addition of 2.4 mg/l cationic polyacrylamide increased retention to about 60 percent and the performance of the polymer was remarkably insensitive to the concentration of NaCl or Na_2SO_4. The highest retentions, 80 percent at pH 4.0, were obtained with mixtures of alum and polyacrylamide. When the alum concentration was increased above 1×10^{-4} M in the presence of polymer, retention decreased. At alum concentrations greater than 1×10^{-3} M retention was much worse than the 66% which was observed with polymer in the absence of alum.

The technological significance of this last finding is clear. Paper mills using both alum and cationic polyacrylamide to increase retention can negate the positive effect of the polymer by adding too much alum.

There is general agreement that very high molecular weight flocculants work by a mechanism called bridging [17]. According to this theory the polymer adsorbs at the solid-solution interface with loops and tails extending out into the aqueous phase. The extended polymer chains subsequently adsorb onto a second particle, thus bridging together the two particles. Although the quantitative description of this theory is not complete, it does, in a qualitative way, explain many of the common features of the behaviour of high molecular weight flocculants. These include: the effectiveness of the polymer increases with molecular weight; flocculation when measured as a function of polymer dosage is usually a bell-shaped curve; flocculation is not necessarily sensitive to the zeta potential of the dispersion; and the optimum content of cationic comonomer (i. e. active adsorption sites) in the flocculant is low (i. e. 5 to 10 mole percent).

The influence of NaCl and Na_2SO_4 on flocculation with polyacrylamide can be interpreted in terms of the bridging theory. A requirement of this mechanism is that loops and tails of the adsorbed polymer must extend sufficiently far into the aqueous phase so that the polymer can touch a second particle or, in other words, the adsorbed layer thickness must be greater than the interparticle distance at closest approach. We were unable to measure directly the adsorbed layer thickness of the PAM in a papermaking suspension; however, estimates were made from the viscosity results by assuming the conformation of the adsorbed molecule to be the same as that of the molecule in solution. Therefore, the adsorbed layer thickness was assumed to be equal to the diameter of the random coil in solution. The Einstein relationship, equation (2), gives the hydrodynamic volume of the polymer as a function of the intrinsic viscosity and thus the diameter of the polymer molecule in solution was calculated from the hydrodynamic volume of the molecule on the basis that the polymer coil was spherical [17].

$$V_h = \frac{M\eta}{2.5 \, N} \tag{2}$$

where V_h is the hydrodynamic volume, M is the molecular weight, N is Avogadro's number, and η is the intrinsic viscosity.

The molecular weight, M, is not precisely known; however, it was estimated to be 2.3×10^6 by applying the viscosity-molecular weight relationship for polyacrylamide of Collinson et al. [19] to the viscosity results for cationic polyacrylamide in 0.01 M sodium sulfate. In other words, it was assumed that the cationic polyacrylamide behaved as nonionic polyacrylamide in the presence of 0.01 M sodium sulfate.

The hydrodynamic diameters of the polymer were calculated from equation (2) and are shown in figure 8 as a function of the concentration of sodium sulfate and sodium chloride. In both electrolytes the hydrodynamic diameter decreases approximately linearly with the increasing logarithm of the electrolyte concentration.

The distance of closest approach was also estimated. Colloidal stability in the system consisting of TiO_2, bleached pulp fibres, electrolytes and distilled water, has been shown to be a consequence of electrostatic stabilization [6, 7]. Therefore, the distance of closest approach between two particles or between a particle and a fibre is determined by the nature of the electrical double layers. For high potentials $1/\varkappa$, the inverse of the Debye-Hückel constant, can be used as an estimate of the double layer thickness [20]. Therefore, $2/\varkappa$ is an estimate of the distance of closest approach of two particles. The solid line in figure 8 gives $2/\varkappa$ for a 1:1 electrolyte and the dotted line is for a 2:1 electrolyte. For every electrolyte concentration the estimate of the adsorbed layer thickness is greater than the estimate of the distance of closest approach. Thus, this analysis predicts that flocculation will occur over the entire range of NaCl and Na_2SO_4 concentrations; this was observed experimentally.

Comparison between an estimate of the adsorbed layer thickness and the distance of closest approach was not done in the case of alum and polyacrylamide because there is no simple relationship between the alum concentration and double layer parameters such as $1/\varkappa$. Nevertheless, some features of the role of alum are known and these can be used to explain the alum-polyacrylamide retention data.

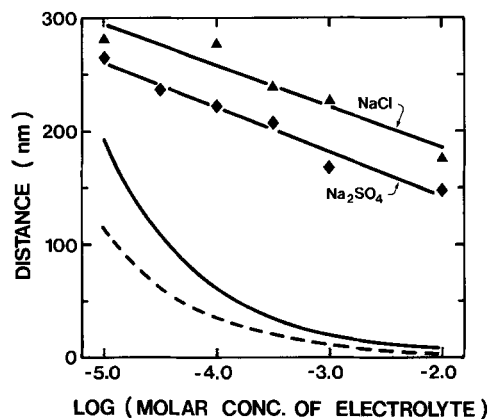Aluminum sulfate is known to hydrolyze to form polyvalent cations which can adsorb at solid-solution

interfaces. The observation that alum changed the electrophoretic mobility of TiO_2 from negative to positive is evidence for adsorption in this system. TiO_2 was colloidally unstable over a range of alum concentrations; this explained the increase in retention with alum and in the absence of polymer (fig. 2). In our experiments the alum was added to the papermaking suspension before the flocculant. Thus, the suspension would be partially coagulated when the polymer was added which would mean the polyacrylamide would be more effective than in the absence of alum because coagulation would produce a relatively low TiO_2 particle concentration and a relatively low TiO_2-liquid interfacial area. These arguments explain the high rententions obtained with polymer and alum for alum concentrations from 1×10^{-5} to 1×10^{-4} M.

High concentrations of alum would be expected to render the dispersed TiO_2 positively charged and colloidally stable, hence reduced retention at high alum concentration in the absence of polymer (fig. 2). Retention was also reduced at high alum concentrations in the presence of polymer and this could be due to the following effects. Firstly, the cationic polyacrylamide may not adsorb at the TiO_2-liquid interface if the particles are positively charged (bridging is impossible without flocculant adsorption). Secondly, we have shown that high alum concentrations caused shrinkage of the polymer in solution which implies a more compact and thus less effective adsorbed polymer layer. Neither of these two mechanisms enables a full interpretation of all the observations. For example, in the presence of high concentrations of Na_2SO_4 the polyacrylamide was contracted and, yet, retention was unaffected (fig. 3). On the other hand, decreased polymer adsorption does not explain why retention was high when the TiO_2 was positively charged at an alum concentration of 1×10^{-4} M (fig. 5). In the same experiment retention decreased at higher alum concentrations even though the electrophoretic mobility of the TiO_2 was constant.

A complete explanation of the influence of alum on flocculation with a polyacrylamide flocculant may require consideration of hydrodynamic effects [21]. The retention experiments were carried out under conditions of hydrodynamic turbulence. It has been shown that under such conditions retention decreases as a function of stirring time and stirring speed in the Dynamic Drainage Jar, which suggests that TiO_2-polymer-fibre bonds are broken by hydrodynamic forces and that some of the broken bonds cannot reform. Therefore, very high alum concentrations may not inhibit the formation of polymer bridges but instead may cause weaker bonds to form. The effects

Fig. 8. Hydrodynamic diameters of PAM (straight lines) and $2/\varkappa$ values for a 1:1 electrolyte (solid curve) and for a 2:1 electrolyte (dashed curve) as a function of electrolyte concentration

of the chemical environment on the strength of flocs formed with polymer is currently under investigation in our laboratory.

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