Flocculation Behavior of Some Cationic Polyelectrolytes

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SYNOPSIS

The settling rates and adsorption isotherms produced by a variety of suites of cationic polyelectrolytes in 3% kaolin suspensions were measured. Settling rates increased with molar mass even for low-mass, high-charge polymers. The very high settling rates produced by cationic copolymers of acrylamide decreased as the charge density of the polymer used increased. Hydrolysis of unbuffered polymers occurred over time and produced large changes in the effectiveness of the polymers. This is attributed to conformational changes. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Cationic polyelectrolytes are of great importance in many industrial applications and in water treatment in general. They adsorb onto a variety of substrates and can be used as both flocculants and stabilizers. We are particularly interested in the adsorption/flocculation process. The postulated mechanisms by which cationic polymers can bring about flocculation are bridging,[1] charge neutralization, or a charge-patch mechanism.[2] In many situations, a combination of mechanisms may be involved. Increasing the charge density of a cationic polymer will increase its electrostatic attraction to a negatively charged surface, and will also cause the chain to be more extended because of the increased repulsion between adjacent charged segments of the chain, and thus more effective in bridging. Tiravanti et al.[3] have studied the efficacy of cationic polyacrylamides (Pams) and polyamines in waste water treatment, and their results supported charge neutralization as the predominant flocculation mechanism. Mabire et al.[4] used cationic Pams to flocculate silica and concluded that the electrostatic path model was correct. Gill and Herrington[5] reported that with polyethylenimine of low molecular mass (2×10^3 g mol^{-1}) and relatively high cationic charge density (1.6 $\times$ 10^3 C g^{-1}), particle agglomeration occurred by charge neutralization. In studies in our lab involving the flocculation of thickener feed with cationic Pams of medium molecular weight,[6] the polymer of lowest charge produced the highest settling rates. Gill and Herrington,[7] using cationic Pams of high molecular weight ($2.6-2.7 \times 10^6$ g mol^{-1}), found that the polymer of least charge produced the highest settling rate but that their polymer of highest charge gave a higher rate than one of an intermediate value. Their conclusion was that charge density was not a determining factor, that bridging was the predominant mechanism, and that the differences in settling rate must be due to small differences in molecular weight. Mabire et al.[4] found that for polymers of a given degree of polymerization, poly(trimethylaminoethylacrylate chloride) produced higher silica settling rates than did acrylamide copolymers of lower charge density.

Another factor that has been much debated in the flocculation literature is the apparent aging of Pam solutions, manifested by a decrease in their viscosity and in their effectiveness in producing flocculation. The reasons for this have been variously attributed to polymer disentanglement,[8,9] scission of weak chain links,[9] the presence of microorganisms,[10,11] or the presence of free radicals.[10,12] Mächtle[13] reported that no effects of aging were able to be detected in dilute solutions of very pure Pam, while Kulicke[14,15] concluded that aging was caused by conformational changes of the polymers. He reported that changes in η_{sp}/c with time did not depend on concentration, suggesting that viscosity changes were not due to disentanglement of polymer

chains. He reported that there were no changes found in the molecular weights, although the hydrodynamic volumes decreased with time, suggesting conformational changes.

Little has been reported in the literature on the aging of cationic polyelectrolytes. Kulicke[16] reported that poly(acrylamide-co-methacryloyloxyethyl-N,N,N,-trimethylammonium chloride) exhibited aging effects, and Gill and Herrington[7] reported using fresh solutions of cationic Pams for their experiments, but justified the necessity of such a step only by reference to the aging of nonionic Pams reported by Shyluk and Stow.[9]

If an aging mechanism occurs in Pam due to conformational changes, then one might expect a similar kind of process to occur in copolymers of acrylamide, especially those of lowest charge density.

In this study, we investigate the relationship between the charge density of a cationic polymer and its flocculating ability. We also report on the phenomenon of hydrolysis and aging in the polymer solutions.

EXPERIMENTAL

Polymers were obtained from Cyanamid (USA) and Stockhausen (Germany) and were stored away from light. Stock solutions of 1000 ppm polymer were prepared using gentle stirring. For each set of flocculations, 30 g of kaolin (Fisher) was stirred for 1 h with 900 mL water containing 10 mL of a stock salt solution ($3.3 \times 10^{-1} M$ sodium chloride (BDH), $1.5 \times 10^{-2} M$ calcium chloride (Anachemia), and $5.0 \times 10^{-3} M$ magnesium chloride (Baker Analysed)). The slurry was then dispensed in 30-mL aliquots into 100-mL measuring cylinders (90 mL per cylinder), a specified amount of polymer (1000 ppm) was added, and the volume was made up to 100 mL. The cylinders were inverted slowly five times before measuring the settling rate. Where specified, acid-washed kaolin (Fisher) was substituted. Buffers used were $0.05 M$ potassium biphthalate (pH 4.1) and $0.085 M$ tris(hydroxymethyl) amino methane (pH 10.4) (Tris) (Gram-Pacs, Fisher). The charge density of a polymer was determined by titrating a dilute solution of it with a solution of the potassium salt of polyvinylsulfate using toluidine blue O as the indicator.[7,17] Such titrations were also used to determine the residual polymer concentration after flocculation, and thus by difference the bound polymer. All water used was 10 MΩ cm resistivity water.

RESULTS AND DISCUSSION

The graphs of settling rate of kaolin versus added polymer concentration for a series of cationic polyelectrolytes (Magnifloc 567C, 572C, 573C, 577C, and 581C) based on the reaction of dimethylamine and epichlorohydrin, giving $[CH_2-CH(OH)CH_2-N(CH_3)_2Cl]$, are shown in Figure 1. The molar masses ranged from 5000 for Magnifloc 567C to 250,000 for Magnifloc 581C. Their charge density was 7×10^2 C g^{-1}. With this combination of relatively high charge density and low molecular weight, very slow settling rates were produced. Small flocs are produced by electrostatic attraction, thus giving rise to lower settling rates. Within the set, a dependence of settling rate on molecular weight was found. A similar result was found with another set of polymers, the polydiallyldimethyl ammonium chlorides Magnifloc 585C, 587C, and 591C with charge density 6×10^2 C g^{-1}. These likewise produced faster settling rates as their molecular weight increased from $\sim$ 100,000 to 500,000, and the rates were within the range of rates produced by the previous set. These suites of polymers have quite different functional groups but similar charge densities. Their similar behavior suggests that their flocculation mechanism is predominantly charge neutralization.

The kaolin settling rates obtained using freshly prepared solutions of high molar mass Pams were very fast and thus difficult to determine accurately, especially since sharp boundaries were only formed when the lowest concentrations of Pam were used. Times measured were as low as 2 s. An error of 0.5 s is therefore a 25% error. Because of this, the settling rates determined for the higher polymer concentrations (3.6 cm/s corresponds to a 2-s measurement) have much larger uncertainties.

Magnifloc 491C, 492C, 494C, and 496C (molecular mass 5–7 million and cationicity 6, 10, 20, and 40%, respectively) are copolymers of Pam with the methyl chloride quaternary of dimethyl aminoethyl acrylate, $[CH_2 = CHCO_2CH_2CH_2N(CH_3)_3Cl]$ and are thus similar to the polymers used by Gill and Herrington[5] in their study examining the effects of charge density of polymers on the flocculation of kaolin, albeit a little larger. When these Magnifloc polymers (491–496C) were used to flocculate kaolin, the settling rates were all significantly higher than those reported by Gill and Herrington,[5] and the maximum (or plateau) settling rate was found to increase as the charge density of the Pam copolymer used decreased (Fig. 2). When the experiments were repeated using suspensions of kaolin in water with
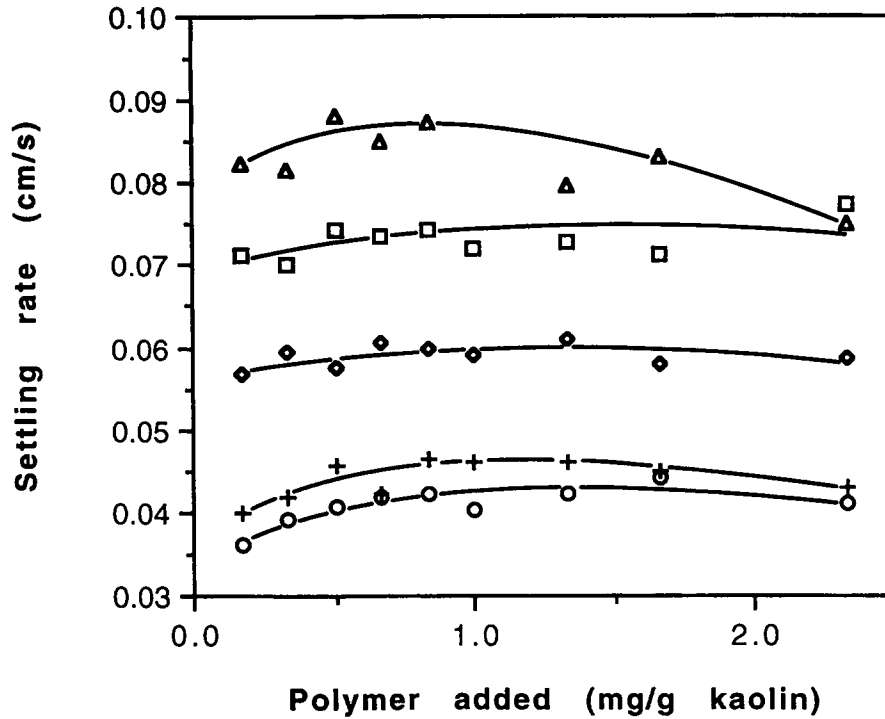
Figure 1 Plots of settling rate of 3% kaolin in salt solution vs. the amount of added polymer for Magnifloc 567C (O), 572C (+), 573C (◊), 577C (□), and 581C (△).
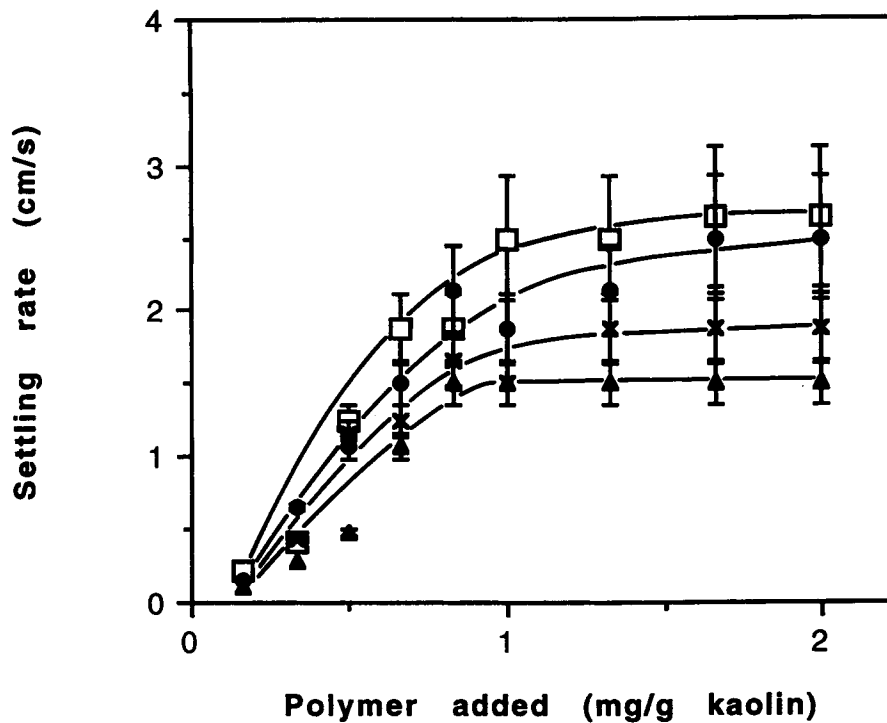

Figure 2 Plot of settling rate of 3% kaolin in salt solution vs. the amount of added polymer (prepared in pH 4 buffer) for Magnifloc 491C (□), 492C (●), 494C (×), and 496C (▲).

no added salt, the flocculation rates produced were only slightly reduced. However, with no added salt anionic polymers produced very much lower rates. If acid-washed kaolin was used, the flocculation rates generally increased, although settling rates were never higher than 3.6 cm s^{-1}. We suggest that these high molecular weight cationic polymers produce such high settling rates that small changes due to variations in conditions are hard to detect, especially when the changes might be expected to increase rates.

Thus although bridging may indeed play the predominant role in the flocculation process, the charge on the polymer is also important. One would expect to find a greater affinity for a positively charged polymer binding to a negatively charged surface than for nonionic polymers binding to the same surface. Settling rates produced in the standard kaolin by Pams (< 1% charge) with molar mass ranges of 2–4 million and 12–15 million were of the same order of magnitude (Fig. 3) as the rates produced by the cationic polymers, but even with the Pam of molar mass 12–15 million, the rate was not actually as fast as those produced by the cationics of lowest charge density, but smaller molar mass.

The settling rates of kaolin were also measured

upon addition of each of a second suite of cationic acrylamide copolymers, Praestol (611, 644, 650, 655, and 666) of nominal molar mass 6–8 million, and charge densities 25, 45, 60, 80, and 90%, respectively, with the cationic monomer being dimethylamino-propylacrylamide quaternized with methyl chloride (Fig. 4). The settling rates produced by the four polymers of lowest charge were very close, and the plateaus were in the same range as those produced by the Magnifloc series of polymers. The two most highly charged polymers produced much lower settling rates. Because of problems experienced with such highly charged cationic copolymers, these higher ones are at the lower end of the mass range given, and this could contribute to their lower settling rates. However, it seems unlikely that this completely accounts for the large difference.

Hydrolysis and Aging

Cationic polymers containing esters are known to undergo hydrolysis on standing.[18] Hydrolysis of these polymers will generate carboxylic acid functional groups, as does hydrolysis of Pam itself under strongly basic conditions. The hydrolysis can be followed using charge density titrations. Figure 5 shows
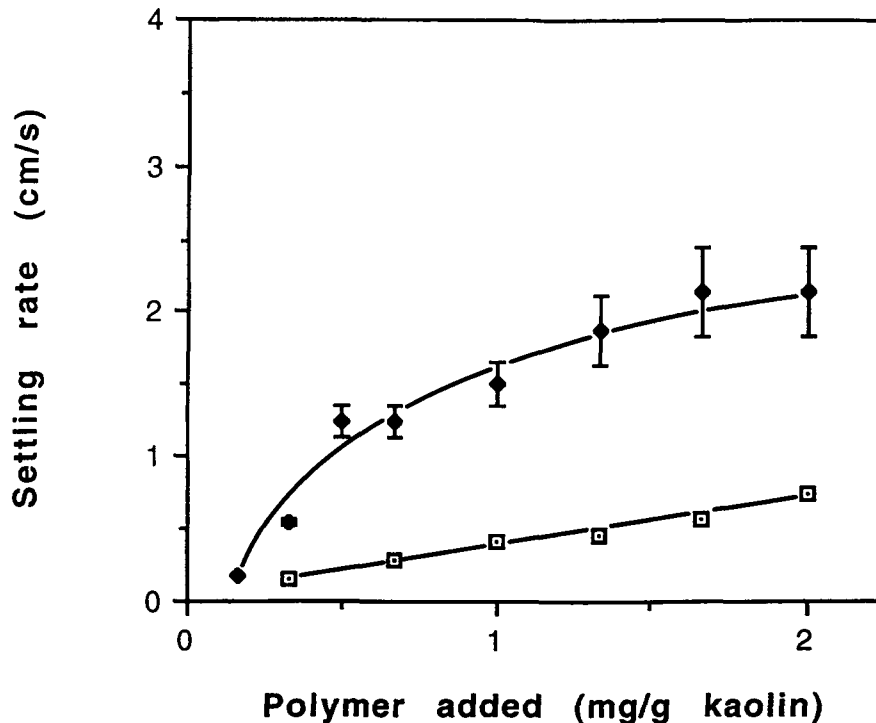
Figure 3   Plots of settling rate of 3% kaolin in salt solution vs. the amount of added polymer (prepared in pH 4 buffer) for Magnifloc 905n (♦) and 900n (▣).
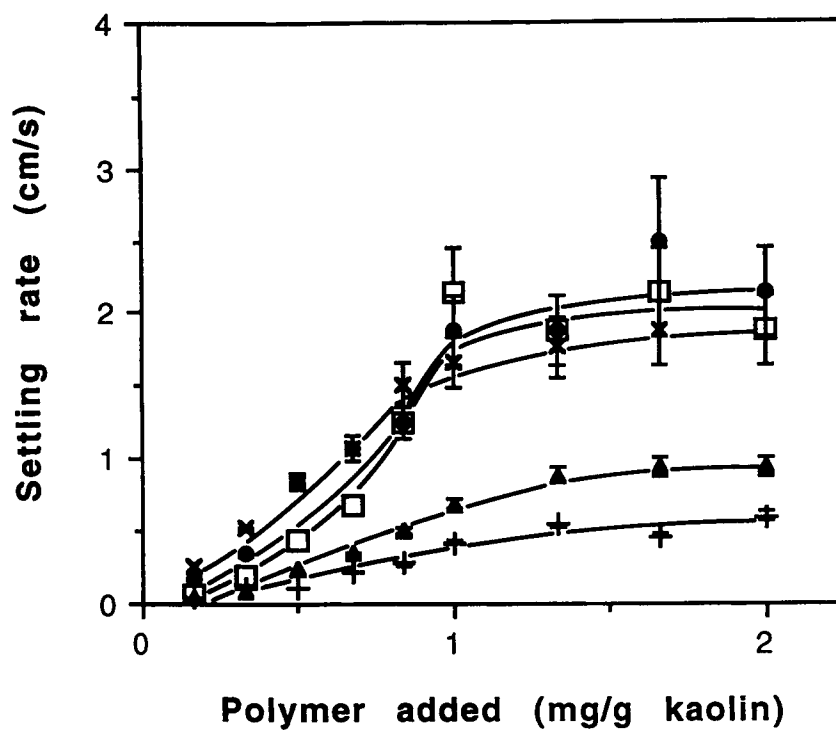
Figure 4 Plot of settling rate of 3% kaolin in salt solution vs. the amount of added polymer for Praestol 611 (X), 644 (□), 650 (●), 655 (▲), and 666 (+).
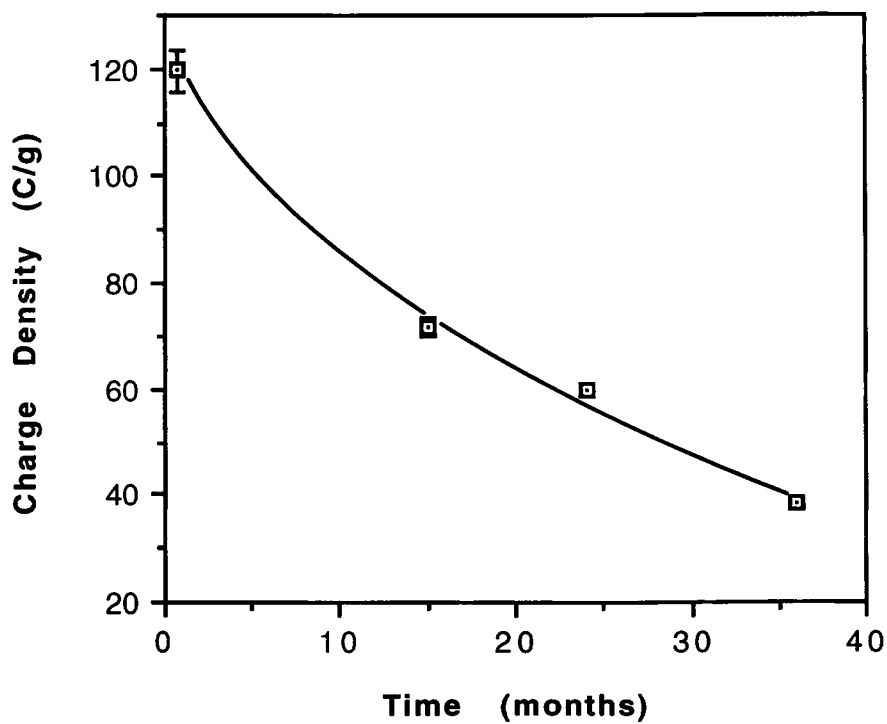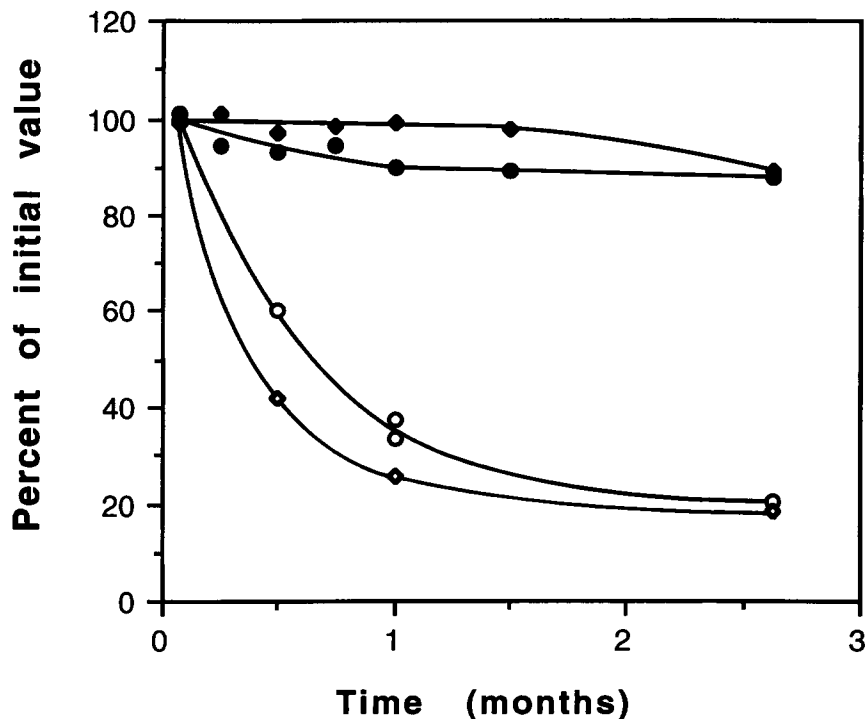

**Figure 5** Plot of charge density vs. time for Magnifloc 492C.

the change in the charge density of Magnifloc 492C with time. Initially the hydrolysis was quite slow and a significant change was not seen until 4 or 5 months had elapsed. The presence of mixed anionic and cationic charge would cause attraction between adjacent segments and a much less extended polymer configuration. Thus although only a marginal amount of hydrolysis occurred in the first few weeks, the settling rates produced by Magnifloc 491C and 492C were severely reduced (Fig. 6). The settling rates produced by Magnifloc 494C and 496C were constant for a longer time period, and a change was not apparent until a decrease in charge density could be detected. We attribute this difference to their larger charge density and the need for a greater amount of hydrolysis before significant contraction of the polymer.

Once all the charges had become anionic in nature, the extended configuration would again be expected. However, as the particle surfaces are negatively charged, anionic polymers will not bind as readily as those of cationic or neutral charge, and reduced rates such as those generally reported by users of anionics would be expected. More rapid hy-

drolysis of the functional groups can be achieved by using more alkaline conditions. For example, when Magnifloc 492C was dissolved in a pH 10.4 buffer, it immediately lost all cationic character, i.e., toluidine Blue O indicator turned pink immediately on addition. Settling rates produced by anionics Magnifloc 836A and 837A, which are copolymers of acrylamide and acrylic acid with charge densities of 18–19 and 7–8%, respectively, prepared in pH 10.4 buffer, showed the same shaped curves with just slightly lower rates (Fig. 7). Under these conditions, little hydrolysis of the amide groups should occur (borne out by the fact that both the anionics and the hydrolyzed cationics still showed flocculation behavior proportional to their nominal charge density). At pH 10.4, any carboxyl groups present will be ionized, and these polymers will have a more negative character than those in unbuffered solution or those held at an acidic pH and thus produce lower settling rates. Hydrolysis was also facilitated, but not as effectively, when the cationic copolymers were prepared in buffers of pH 6.5 or 8.0. Note that for polymers prepared in aqueous solution, the hydrolysis is not complete even after 3 years. Preparation

Figure 6   Plots of the change in charge density with time for Magnifloc 491 (●) and 492 (◆), and of the change in maximum settling rate of 3% kaolin in salt solution that could be brought about by Magnifloc 491 (○) and 492 (◇).
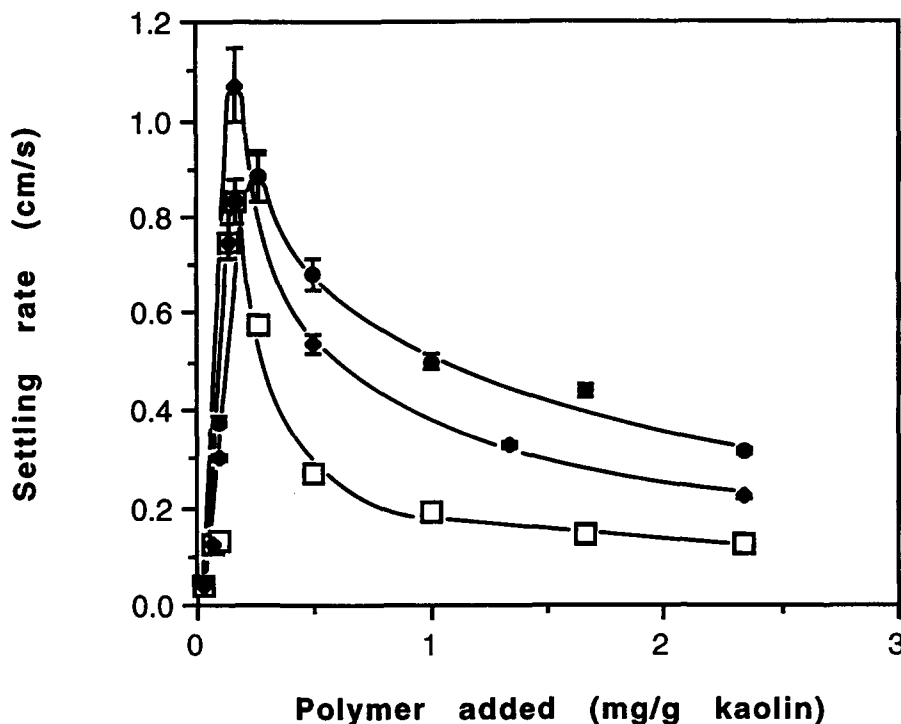
Figure 7 Plots of settling rate of 3% kaolin in salt solution vs. the amount of added polymer (prepared in pH 10.4 buffer) for Magnifloc 492C (●), 836A (□) and 837A (◆).

of the polymers in a pH 4.1 buffer (0.05M potassium biphthalate) lead to stable solutions with respect to both charge density and flocculation ability.

The Praestol series polymers (611–666) all produced dramatically reduced settling rates with barely significant reductions in charge density, and this aging could be prevented by buffering the polymers at pH 4. In fact, we generally found the same or better performance for all our polymers prepared in this buffer, including Pam itself.

The Magnifloc 567C–591C polymers prepared in water did not show aging effects even when sonicated or stirred. Not only are these polymers of much smaller molecular mass than the acrylamide copolymers and therefore not expected to undergo as large conformational changes, but, just as importantly, their functional groups do not contain ester linkages and therefore aging due to hydrolysis does not occur.

Polymer Adsorption

At high settling rates, the amount of each polymer adsorbed was very small, and this can be attributed to the speed of the flocculation process. As the poly-

mers hydrolyzed and the settling rates became slower, large amounts of polymer were adsorbed. A typical set of adsorption isotherms are shown in Figure 8. It has been frequently reported that during the flocculation of coals, silica, and clays, the relationship between polymer adsorption and settling rate is an inverse one.[7] In adsorption studies onto polystyrene latices and cellulose fibers, adsorption has been found to increase with polymer size.[19-21] However, the processes of adsorption and flocculation are often difficult to separate[22] and the formation of flocs must influence the extent of adsorption. This was demonstrated in experiments by Tanaka et al.[21] using cationic Pams and cellulose fiber suspensions. They reported that under conditions where flocculation occurred, the polymer of highest molecular weight was adsorbed least. However, under conditions where no flocculation occurred (in a more dilute suspension of the same composition), the reverse was true. If a flocculation is occurring very fast, the surfaces available for adsorption to occur on are depleted rapidly, thus restricting the adsorption. As settling rates decreased as polymers aged, the adsorption of polymer increased.
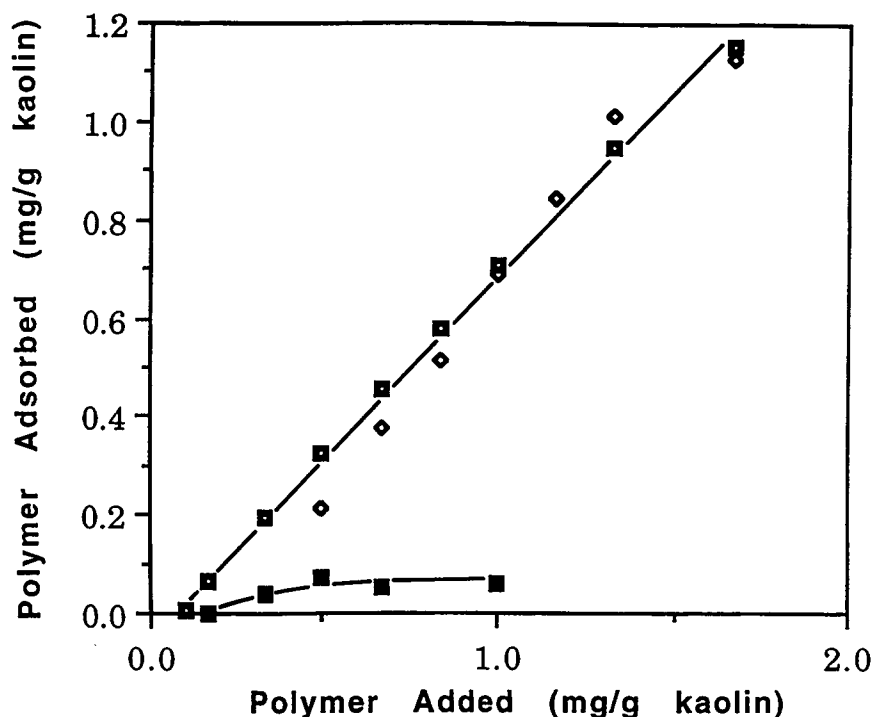
Figure 8 Adsorption isotherms in 3% kaolin in salt solution for Magnifloc 492C prepared in pH 4.1 buffer (■), for 12-month-old unbuffered Magnifloc 492C (◊) and for 24-month-old unbuffered Magnifloc 492C (■).

CONCLUSIONS

Cationic copolymers of Pam of high molar mass produce high flocculation rates of kaolin. Settling rates are inversely related to the charge density of the polymer being used. The high flocculation rates suggest that bridging plays an important role in the flocculation mechanism. However, flocculation rates are higher than for nonionic polymers of even higher molar mass. This can be attributed to the effect of the charges, which repel each other and thus leave the polymer in an extended form for better bridging. If this was the only effect of the charge on the mechanism, the settling rates would increase with charge density up to a charge density of ~ 30% (which one might expect to lead to a completely extended form). An opposing effect is the tendency of positively charged polymers to have large trains sitting flat on the negatively charged silica surface rather than larger tails into solution, effectively a contribution of the "neutralization mechanism." This would lead to less bridging and lower flocculation rates with polymers of higher charge density, as found experimentally. The fact that very small amounts of hy-

drolysis seem to cause major reductions in settling rate suggests that the main effects of the charge are conformational. This would explain why the polymers of lowest charge are most affected: the same absolute amount of hydrolysis is large when considered relative to the overall charge.

And finally, use of the pH 4.1 buffer prevents problems of aging and hydrolysis and allows polymers to produce fast settling rates.

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