

The Flocculation of Kaolin by Cationic Polyacrylamides and the Effect of Cationic Surfactant on This Process

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ABSTRACT: The flocculation of kaolin suspended in a dilute salt solution was studied as a function of the addition of cationic surfactant and cationic polyacrylamide (CPAM) added separately, consecutively, or simultaneously. Cationic polyacrylamide caused flocculation by bridging when added in low concentrations, but at higher concentrations, charge neutralization became the dominant mechanism and the flocculation rate was highly dependent on the charge density of the polymer. Adsorption of sufficient polymer or surfactant (cetyl pyridinium chloride) prevented immediate adsorption of the other, although surfactant could replace polymer after extended agitation. The adsorption of polymer was greatest when small flocs were formed by charge neutralization or by prolonged shaking. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2382–2389, 2002

Key words: flocculation; kaolin; cationic surfactant; CPC; cationic polyacrylamide; adsorption; settling rate

INTRODUCTION

Cationic polymers are commonly used as retention aids in paper making, as flocculants for clarification of drinking water and waste water, and in many industrial and commercial dispersions. These real systems tend to be complex, multicomponent systems that may contain surfactants. The interplay of the surfactants and polymers depend on the charge-type of each (positive, negative, nonionic), the size and chemical characteristics, and the nature and charge of the suspended material and the matrix itself. Much research has been done on interactions between polymers and surfactants of opposite charge,¹ but fewer investigations have been carried out on the competition between polymers and surfactants of the same

charge. Kurenkov et al.² found that adding anionic surfactant to kaolin suspensions caused an increase in the flocculating ability of the anionic copolyacrylamide, which was attributed to the formation of surfactant–polymer complexes, by hydrophobic interactions, on the surfaces of the kaolin. Esumi et al.³ examined the competitive adsorption of negatively charged surfactant (SDS) and negatively charged polymer (poly(styrene sulfonate)) (PSS), onto a positively charged surface (alumina) after agitation for 24 h. Both species could adsorb from a mixture but were affected to some extent by the presence of the other. Somasundaran and Cleverdon⁴ found that the adsorption of acrylamidemethacrylamidopropyltrimethyl ammonium chloride polymer onto quartz masked the effect of adsorbed dodecyl ammonium chloride. Cetyl trimethyl ammonium bromide (CTAB) adsorption onto flat silica surfaces was hindered by coadsorption with polylysine.^{5,6} Preadsorption of sufficient CTAB onto silica prevented the adsorption of quaternary derivatives of hydroxy-

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ethyl cellulose to various extents that depended on the molar mass of the polymer.⁷

We are interested in the competitive adsorption of cationic copolyacrylamide and cationic surfactants onto kaolin, particularly the effect on flocculation. The rapid formation of flocs immediately changes the nature of the system. We are interested in the immediate results of the competition as well as the outcome after equilibration. In this article, we studied the effect of adding cetyl pyridinium chloride (CPC) and various cationic polyacrylamides (CPAMs) to kaolin suspensions, especially the effect of higher than normal concentrations. The CPC was added before, with, or after, the flocculant, and the results were compared to those obtained when a nonderivatized polyacrylamide was substituted as flocculant.

EXPERIMENTAL

All water used was purified in the Millipore Purification System. The polymers used were from Cytec (West Paterson, NJ) and were sold under the trade name Superfloc. The cationic polymers, denoted CPAM35, CPAM20, CPAM10, and CPAM5 in this text, have 35, 20, 10, and 5% charged monomer (triethyl ammonioethylacrylate chloride) respectively, incorporated with polyacrylamide. The non-ionic polyacrylamide is denoted PAM.

Polymer solutions (1000 $\mu\text{g}/\text{mL}$) were prepared with gentle mixing in 0.05M sodium acetate buffer, pH 4.1, and were refrigerated to prevent the growth of mold. CPC, from Sigma (Oakville, ON), was made up to either 1000 or 2000 $\mu\text{g}/\text{mL}$ with water. The titration indicator, Toluidine Blue O, also from Sigma, had an original dye content of $\sim 89\%$. It was diluted to $\sim 0.1\%$ with water. The poly(vinyl sulfuric acid) potassium salt (PVSK) was from the Eastman Kodak Co. (Rochester, NY). A stock solution was made by shaking 1.64 g PVSK in ~ 30 mL water for at least 3 h. The solution was gravity filtered and diluted to 1000 mL. The kaolin (k2-500) was from Fisher Chemicals/Fisher Scientific (Fair Lawn, NJ) and had a surface area of 18 m^2/g as determined by BET (nitrogen). A stock salt solution containing sodium chloride ($3.3 \times 10^{-1}\text{M}$), magnesium chloride ($5.0 \times 10^{-3}\text{M}$), and calcium chloride ($1.5 \times 10^{-2}\text{M}$) in water was added to the kaolin mixture in amounts sufficient to give final concentrations 100-fold less than in the stock. The Sudan III dye was from Matheson, Coleman, and Bell (Norwood, OH) and had a total dye content of 91%.

CPC Analysis

CPC has absorption maxima at 213 and 258 nm. The absorbance at 258 nm, as measured by using 10-mm path length quartz samples and reference cells in a Cary 100 Scan UV-Visible Spectrophotometer (Fisher Scientific), was used to determine the amount of CPC present in the supernatant. At this wavelength, less dilution was necessary than if 213 nm was used. The supernatant was generally centrifuged [UV International Centrifuge from the International Equipment Company (Needham, MA)] for 30 min before the absorbance reading was taken. Supernatant containing high concentrations of CPC, which prevented flocculation, was centrifuged for 1 h.

Charge Density Titration

Water (50 mL), 6% acetic acid (50 mL), and ~ 3 mL Toluidine Blue O solution were added to aliquots of polymer solution (typically 20 mL) before titration with the potassium salt of PVSK.^{8,9} Blanks were titrated and the value subtracted from each titration result. For analysis of mixtures of CPAM and CPC, the CPC concentration was calculated by absorption and the titration results were appropriately corrected before calculating the CPAM35 concentration. Supernatant was centrifuged before analysis as described above.

Determination of CMC for CPC

A dye solubility test, as described by Burke and Palepu,¹⁰ was performed to determine the critical micelle concentration of CPC in standard salt solution. Varied concentrations of surfactant were added to 1 mg Sudan III dye in a 250-mL volumetric flask. For CMC determination in the presence of polymer, specific polymer concentrations were added. The volumetric flask was then filled to the mark, shaken, and left standing for 2 days. The inflection point of the plot of absorbance versus concentration of surfactant occurred at the CMC.

Flocculation Procedure

Stock kaolin suspensions consisting of 30 g kaolin in 900 mL water and 10 mL stock salt solution were stirred for 1 h. Each suspension was divided among ten 100-mL graduated cylinders, placing 30 mL kaolin into each cylinder at a time. The polymer or surfactant, or mixture thereof, was

added to each cylinder along with a predetermined amount of sodium hydroxide, and the cylinder was filled to the 100-mL mark with water. The appropriate amount of sodium hydroxide was determined in a duplicate experiment in which the flocculation was carried out without pH adjustment, and the amount of base necessary to readjust the pH to 5¹¹ was determined by titration with sodium hydroxide from a 10-mL burette. When the larger amounts of polymer and/or surfactant were to be added to the cylinders, the initial kaolin mixture consisted of 30 g kaolin in 600 mL water and 10 mL salt solution. For the experiments where CPC and polymer were added consecutively, one was added and the cylinder was inverted five times at constant speed. The other was then added and water was used to fill the cylinder to the 100 mL mark. The tops of the cylinders were covered with plastic wrap and the cylinders were inverted five times at a slow, constant speed. The flocculation rate was calculated from the time required for the kaolin mixture to settle 40 mL (7.3 cm). One hour later, the turbidity readings were taken (2100A Turbidimeter from the HACH Chemical Co.). The supernatant was removed from the cylinders and centrifuged before titration or the taking of UV absorbance readings. In some cases, the suspensions were shaken for 24 h or longer as specified on a wrist action shaker.

RESULTS

All experiments were carried out in a standard salt solution whose composition, given in the experimental section, is that of typical coal washery water. Its overall ionic strength was 0.5 mM. We initially considered carrying out competitive adsorption experiments by using CTAB and CPAM35. As both respond to charge-density titrations, we attempted to find a dye that would interact selectively with the surfactant. The adsorption of methyl orange decreased only slightly in the presence of cationic polymer, while the addition of surfactant caused both a large decrease in adsorption and a wavelength shift. However, the addition of buffer caused similar shifts, so although the method seemed promising, it was decided that a better option would be to change to a surfactant with a chromophore. CPC was chosen because its strong UV absorptivity enabled us to determine its residual concentration after adsorption without interference from the polymer solutions, providing they were prepared in a pH 4.1 acetate buffer rather than the

bipthalate used previously.¹² The polyelectrolytes were prepared in buffer to prevent hydrolysis of the ester linkages.^{12,13}

Addition of CPC

The adsorption isotherms for CPC onto kaolin at pH 3 and 5 are shown in Figure 1 and are effectively the same within experimental error. The isotherms reached a plateau after the adsorption of 2 mg CPC/m² kaolin at a CPC equilibrium concentration of 0.17 mg/m² kaolin (0.32 mM), in agreement with the CMC determined for CPC in the standard salt solution. The addition of CPC to kaolin caused some flocculation, but, at most, increased the settling rate from 0.008 to 0.011 cm/s. When amounts of CPC greater than 1.5 mg/m² were added to kaolin at pH 3, or amounts of CPC greater than 1.7 mg/m² were added at pH 5, the suspensions were completely stabilized and no flocculation occurred. Under the former conditions, 1.4 mg CPC/m² kaolin was adsorbed, whereas with the greater surface ionization under the latter conditions, 1.6 mg CPC/m² kaolin was adsorbed. As the maximum adsorption of CPC when added alone was 2 mg CPC/m² kaolin, we will assume that monolayer coverage would require 1 mg CPC/m² kaolin, half the maximally adsorbed amount. Thus, as might be expected, stabilization occurred after significant double-layer formation.

Addition of CPAM

When CPAM35 was added to kaolin, it was not immediately adsorbed as completely as was CPC,

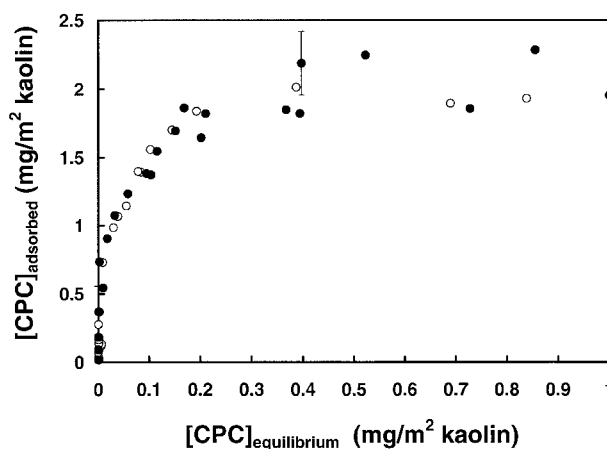


Figure 1 Adsorption isotherm for CPC onto kaolin in a 3% suspension in a standard salt solution at pH 3 (○) and pH 5 (●) as determined by UV absorption.

although 0.07 mg CPAM35/m² kaolin was adsorbed completely after shaking overnight. In the absence of prolonged shaking, the extent of adsorption depended on the nature of the flocculation. Significant flocculation occurred on addition of CPAM35. The lowest turbidity was produced after the first addition of polymer, at 0.01 mg CPAM35/m² kaolin, whereas the maximum settling rate was produced after the addition of 0.1 mg CPAM35/m² kaolin (Fig. 2), which corresponds to what might be considered the plateau region of the adsorption isotherm, shown in Figure 3. The error bars are much larger near the maximum settling rate as the floc structure seemed to undergo a change near this point and the settling boundary was not well-defined. The adsorption data were fitted to a Langmuir isotherm and the maximum amount adsorbed was calculated to be 0.01 mg/m² kaolin. When the polymer dose was increased well above 0.1 mg CPAM35/m² kaolin, the settling rates were greatly diminished (Fig. 2) but, at least in the concentration range examined, the suspension was not stabilized. Flocs at the maximum settling rate were roughly spherical, but those formed at higher dosages were smaller and similar to small hairs or clumps thereof, leading to the reduced settling rates. The change in the nature of the flocs points to a change of mechanism at this point. The extended adsorption isotherm is shown in Figure 4. The second adsorption plateau of 0.25 mg CPAM35/m² kaolin occurred with an equilibrium concentration of 1.75 mg CPAM35/m² kaolin. Resuspension of the treated kaolin in salt solution did not cause any desorption of adsorbed polymer, indicating that the adsorption was irre-

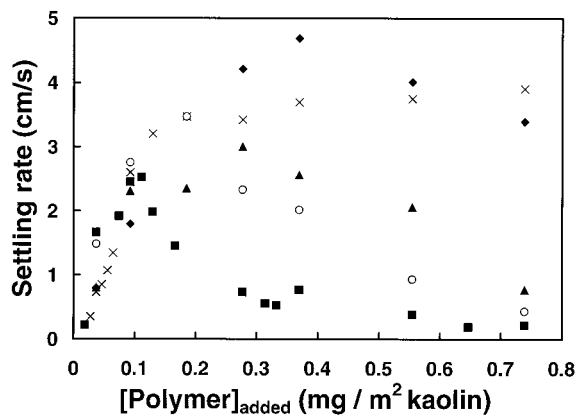


Figure 2 The settling rates of a 3% kaolin suspension in standard salt solution at pH 5 as a function of the amount of added CPAM35 (■), CPAM20 (○), CPAM10 (▲), CPAM5 (◆), and PAM (×).

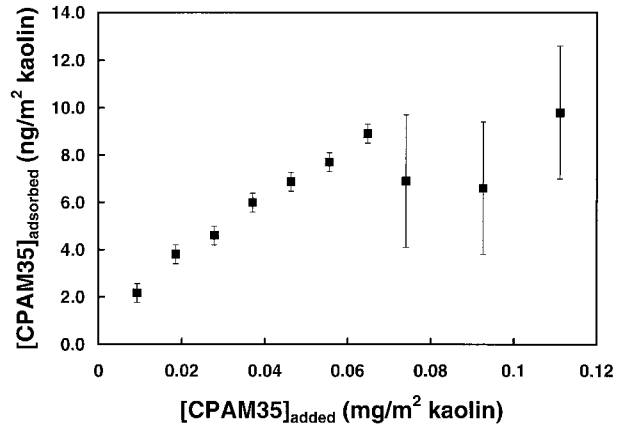


Figure 3 Adsorption of CPAM35 onto kaolin in a 3% suspension in a standard salt solution as a function of the amount added, up to the amount necessary to produce the highest settling rates.

versible under these conditions. Note that the adsorption data for CPAM35 are plotted versus the amount added so it is easy to compare Figure 2 with Figures 3 and 4. A small shift in the position of the maximum settling rate was seen when pH 3 was used instead of pH 5, but the settling rates were very similar. The remainder of the investigation was carried out at pH 5.

Significant flocculation also occurred on addition of CPAMs of lower charge density, or on addition of polyacrylamide itself, and these flocs also readily settled (Fig. 2). Maxima in the plots of the settling rate versus the concentration of added polymer occurred after the addition of 0.2 mg CPAM20/m² kaolin, 0.3 mg CPAM10/m² kaolin, or 0.4 mg CPAM5/m² kaolin. The settling

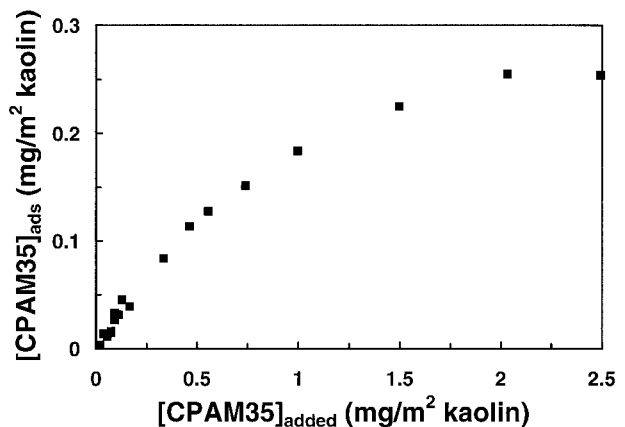


Figure 4 Adsorption of CPAM35 onto kaolin in a 3% suspension in a standard salt solution as a function of the amount added, over the entire concentration range examined.

rates produced by PAM were slightly lower than those produced by CPAM35 at the lower concentrations, even though the M_w of PAM was 14–17 million as compared to 5–7 million for CPAM35. At higher concentrations, PAM was more effective than all except CPAM5. As the charge density of the flocculant was increased, there was a more pronounced maximum in the settling rate curve with the settling rate subsequently being reduced to a greater extent.

Addition of CPC and CPAM Sequentially or Together

In the next set of experiments, CPC was mixed into the suspension just before addition of CPAM35, to determine how much blocking of surface sites could occur before the ability of CPAM35 to produce flocculation was affected. The experiments were carried out in the lower dosage range for CPAM35, because this is more typical of real situations. It was found that initial adsorption of CPC in amounts up to 0.5 mg/m^2 kaolin, equivalent to half monolayer coverage, had no significant effect on the settling rates of the flocs produced (Fig. 5) and thus must not have impeded adsorption of flocculant. All the added CPC was adsorbed, and the amount adsorbed was not changed by the subsequent addition of varying amounts of CPAM35.

The presence of 0.9 mg CPC/m^2 kaolin reduced the adsorption of CPAM35 when amounts over $0.04 \text{ mg CPAM35/m}^2$ kaolin were added, as indicated by the lowered settling rates. If 1.5 mg CPC/m^2 kaolin was added initially, the settling rates produced by the addition of CPAM35 were greatly reduced, and if enough CPC was added to allow complete double-layer formation by adsorbed CPC, the suspension was stabilized and the addition of CPAM35 produced no destabilization of the suspension, even after a week of shaking.

Experiments were then carried out to determine how much CPAM35 could be adsorbed without affecting the subsequent adsorption of CPC. When CPAM35 was added to a kaolin suspension and mixed in by inverting the cylinder, flocculation occurred. The subsequent addition of CPC required further mixing that caused some breakup of the flocs. This occurred even if the flocs were subjected to mixing without added surfactant, as can be seen by comparing the settling rates shown in Figure 2 for the addition of CPAM35 alone, and the settling rates in Figure 6, which resulted after water was mixed into an

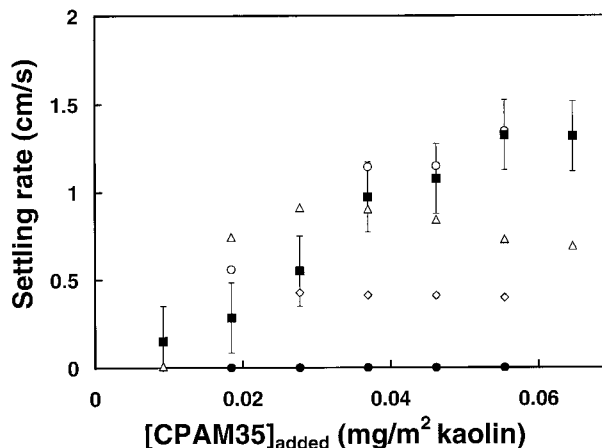


Figure 5 The settling rates of a 3% kaolin suspension in a standard salt solution as a function of the amount of added CPAM35, after prior addition of no CPC (■), 0.50 mg CPC/m^2 kaolin (○), 0.92 mg CPC/m^2 kaolin (△), 1.5 mg CPC/m^2 kaolin (◇), and 3.0 mg CPC/m^2 kaolin (●).

already flocculated suspension. It was also noted that the reproducibility in measuring settling rates was reduced. The amount of CPC that was adsorbed depended on how much CPAM35 had initially been added (Fig. 7). The CPC presumably adsorbed in between the loops, trains, and tails of CPAM35 and could penetrate to sites within flocs that were inaccessible to CPAM35. Complete adsorption of 0.09 mg CPC/m^2 kaolin occurred, but adsorption of larger amounts was less complete than in the absence of CPAM35. When the amount of adsorbed CPAM35 was increased by adding larger aliquots initially, the amount of CPC able to be adsorbed was reduced. Identical results were obtained when PAM was substituted for CPAM35, before or after CPC addition. This indicates that the exclusion was steric rather than electrostatic in origin.

Although addition of surfactant after premixing CPAM35 with the suspension had little effect on the immediate flocculation process, after a week of shaking CPAM35-coated kaolin in the presence of 3 mg CPC/m^2 kaolin, CPC had replaced the CPAM35 to an extent that flocculation no longer occurred. Absorbance measurements indicated that 1.3 mg CPC/m^2 kaolin had been adsorbed. When flocculated samples such as this were allowed to shake for these extended periods of time, the flocs were broken and the resulting settling rates were very much smaller than noted previously, but actual stabilization of the suspension only occurred in the presence of sufficient CPC.

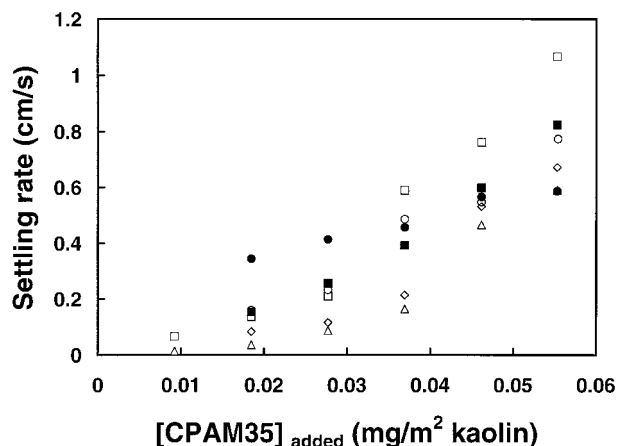


Figure 6 The settling rates of a 3% kaolin suspension in a standard salt solution as a function of the amount of added CPAM35, after subsequent addition of no CPC (■), 0.09 mg CPC/m² kaolin (□), 0.50 mg CPC/m² kaolin (○), 0.92 mg CPC/m² kaolin (△), 1.5 mg CPC/m² kaolin (◇), and 3.0 mg CPC/m² kaolin (●).

If the surfactant and CPAM35 were mixed before being added to suspended kaolin, the settling rates were not affected by the presence of up to 1.5 mg CPC/m² kaolin, but the presence of 3 mg CPC/m² kaolin stabilized the suspension. The adsorption of the CPC was still affected by the presence of the CPAM35, but somewhat less than when the CPAM35 was preadsorbed. Only one mixing step was needed under these conditions, and thus the flocs were not broken up by a second mixing step as happened when CPC was added after CPAM35. Less CPAM35 was able to be adsorbed by the large flocs and thus the adsorption of CPC suffered less interference.

DISCUSSION

The adsorption isotherm for CPC was similar to that reported by Sjöblom and Söderlund¹⁴ and did not display the two steps¹⁵ that are found for CTAB adsorption on silica, but rather increased progressively to a plateau. Although this could be attributed to a lack of data at low concentrations (we were primarily interested in adsorption of sufficient CPC to interfere with polymer adsorption), it can more likely be attributed to the different nature of the kaolin surface as compared to that of silica.¹⁶ The absence of flocculation after the addition of 1.7 mg CPC/m² kaolin was attributed to stabilization of the kaolin by formation of significant amounts of a double layer of surfactant creating positively charged particles.

The fact that CPAM35 was adsorbed to a much smaller extent than CPC was attributed to the mixing being of short duration before flocculation occurred, after which the suspension was left to stand and settle. The large CPAM35 molecules did not have access to the interior of the flocs and thus were excluded from adsorption sites. This observation is supported by the fact that 0.07 mg CPAM35/m² kaolin was totally adsorbed if it was left to shake with the flocs for 24 h, during which time the flocs were broken apart and their interiors exposed. In contrast, only 0.009 mg CPAM35/m² kaolin was adsorbed if the flocs were allowed to settle immediately after five inversions of the suspension. Diminished adsorption of larger polymers because of exclusion from porous flocs was reported previously for CPAMs.¹⁷

The initial high settling rates produced by adding up to ~ 0.1 mg/m² kaolin of any of the CPAMs were all similar and attributed to large floc formation by means of polymer bridging. The increased efficiency of the CPAM35 as compared to PAM was attributed to the greater extension of its chains because of repulsion between the charged groups.¹² The nonionic polymer had a molecular weight twice that of the cationic polymer and on this basis might have been expected to produce the higher settling rate. Previous studies on such systems have also attributed a limited dependence of the settling rate on the charge density to the predominance of a bridging mode of action.^{12,18} In contrast, the settling rates at higher

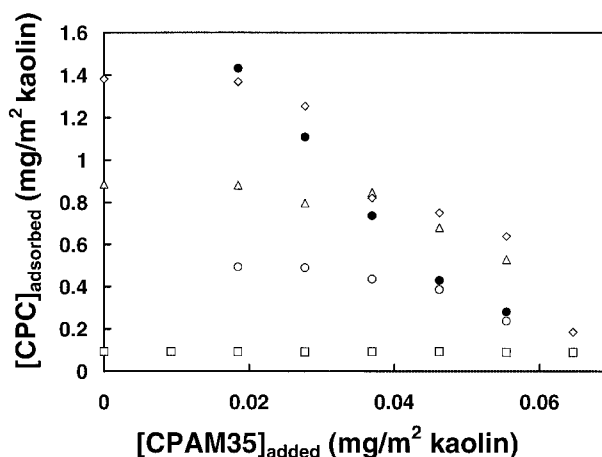


Figure 7 Adsorption of CPC onto kaolin in a 3% suspension in a standard salt solution as a function of the amount of CPAM35, which was added with mixing just prior to the addition of CPC. The amounts of CPC added were 0.09 mg/m² kaolin (□), 0.50 mg CPC/m² kaolin (○), 0.92 mg CPC/m² kaolin (△), 1.5 mg CPC/m² kaolin (◇), and 3.0 mg CPC/m² kaolin (●).

polymer concentrations were vastly different from each other. The settling rates resulting from CPAM35 addition dramatically decreased after the addition of 0.1 mg CPAM35/m² kaolin, whereas increasing the amount of PAM past this point resulted in even higher settling rates, with a plateau (with a slight rise) after the addition of 0.15 mg PAM35/m² kaolin. Such high concentrations of polymer were not used in previous studies and thus this marked difference was not previously reported. We attribute the change in floc structure at this point to the CPAM35 having produced significant charge neutralization at the surface. Polymers of lower charge density did not so dramatically change the nature of the flocs (Fig. 2). Even though adsorption sites were still available, and more polymer was able to be adsorbed, the charge on the extended loops and chains must neutralize the surface charge sufficiently to allow close approach of the kaolin particles. Although one molecule may be able to approach the surface to further adsorb, the approach of a polymer near other polymers must be less favorable. As the charge density of polymer was decreased, the settling rate maxima shifted higher. Although CPAM5 was able to induce the same maximum settling rate as PAM, increased CPAM5 dosage (but not that of PAM) led to a reduction in settling rate. This supports our suggestion that the charged nature of the adsorbed CPAM resulted in neutralization of the surface charge, with consequent reduction in floc size and settling rate. This explains why the maxima in the settling rate curves of flocculants of lower charge density occurred at higher polymer concentrations (Fig. 2). The first part of the adsorption isotherm is comparable to those reported previously for kaolin.⁸ However, as more polymer was added, the floc size decreased. This resulted in there being a bigger total surface area exposed to the surrounding polymer solution and this bigger surface area would facilitate the adsorption of larger amounts of polymer. The final adsorption maximum was about 25 times larger than the adsorption at maximum floc size. We can thus infer that a charge-neutralization mechanism became of greater importance as the concentration of polymer was increased and that as the surface charge was neutralized, the closer approach of particles led to smaller flocs.

The minimum turbidity was achieved with a very low polymer concentration, whereas at high polymer concentrations the supernatant was very cloudy. The flocculated suspension was left to stand for an hour before the turbidity was mea-

sured. Thus, the turbidity measurement was not so much an indication of the completeness of flocculation as an indication of the extent of stabilization of the fines. With the large amount of polymer that was left in solution, one can assume that any fines that were not immediately incorporated into flocs would be stabilized by adsorbed polymer. This occurred to a greater extent as the supernatant polymer concentration increased, as indicated by the increase in turbidity as more polymer was added.

CPAM35 and CPC were able to coadsorb as long as the overall surface coverage was incomplete. If we assume that the number of surfactant molecules necessary to give monolayer coverage is half the total amount adsorbed, then monolayer coverage by surfactant would require 1 mg CPC/m² kaolin or 2.8 μ mol CPC/m² kaolin. This would also be the maximum concentration of charged groups with alkyl chains that could bind to the kaolin. In contrast, the maximum concentration of CPAM35-charged functional groups that were adsorbed at the first adsorption plateau was 0.03 μ mol/m² kaolin. This suggests that a maximum of about 1% of the total sites was accessible to the polymer. The real number is probably a lot less, as not all of the functional groups on the polymer chains are necessarily in contact with a surface site.

Thus, if 0.9 mg CPC/m² kaolin had already been adsorbed, and full surface coverage is 1 mg/m² kaolin, only about 0.001 mg CPAM/m² kaolin could be expected to subsequently be adsorbed, if all the CPC had gone on as a monolayer. However, a reduction in the effectiveness of CPAM as a flocculant under these conditions only occurred with CPAM additions above 0.04 mg/m² kaolin. In the absence of CPC, this latter addition would have resulted in the adsorption of 0.006 mg CPAM35/m² kaolin. This comparison suggests that the surfactant does not adsorb completely as a monolayer but rather that a certain amount of micellar adsorption, or local double-layer formation, occurs. This would predict that there should be some surface available for coadsorption after adsorption of 1.0 mg CPC/m² kaolin. Indeed, even after the addition of 1.5 mg CPC/m² kaolin, some flocs were still formed, which suggests that the CPAM still did have some access to the surface, or was able to bind to the hydrophobic chains of the surfactant. Some CPAM may bind to the hydrophobic tails by means of dispersion forces, as polyacrylamide is known to adsorb to a small extent because of hydrophobic interactions, and similar interactions could occur with CPAM35. When

enough CPC was added to give maximal adsorption of CPC (double layer), flocculation was prevented. Neither polyacrylamide nor CPAM35 bind to a strongly positively charged surface.

The same trend in settling rates was observed with additions of CPC and nonionic polymer, PAM, as were observed for comparable additions of CPC and CPAM35. Preadsorption of surfactant did not change the settling rate unless high concentrations of both surfactant and polymer were used. The settling rate for kaolin with small concentrations of preadsorbed CPC, after the addition of nonionic polymer, was the same as the settling rate for kaolin after the addition of nonionic polymer alone, and as found with CPAM as flocculant, preadsorption of 1.4 mM CPC caused a reduction in settling rate for flocculant concentrations above 0.04 mg/m² kaolin. This confirms the notion that the CPC is actually blocking surface access and that the charged nature of the CPAM is not a factor at this point. Likewise, adsorption of sufficient PAM blocked access of CPC to the surface.

Simultaneous addition of CPC and CPAM was a more effective method of producing a flocculated suspension in the presence of surfactant. CPAM could obviously compete effectively for adsorption on a kinetic basis such that settling rates were not affected unless very high surfactant concentrations were used. Large flocs were able to be formed because there was only one mixing step. The CPAM excluded less surfactant. However, this was not a stable situation over extended times, especially if further shaking occurred.

CONCLUSION

Polymer cannot penetrate flocs to the same extent as can much smaller surfactants. Thus, when the maximum settling rate is produced and large flocs are present, CPAM is adsorbed much less (by about a factor of 200) than is CPC at its maximum adsorption. Thus, the relative amounts of polymer and surfactant adsorbed are controlled by the floc size and porosity as well as the order of addition and the extent of prior surface coverage.

At low concentrations, the efficacy of CPAM35 as a flocculant is similar to that of CPAM5, suggesting that bridging is the dominant mechanism. This is supported by the rapid production of large flocs. However, the charge density of the polymer became an increasingly important factor as the dosage was increased. The floc size was reduced,

and it was concluded that charge neutralization became the dominant mechanism.

CPAM35 was able to coadsorb with small amounts of CPC, but once enough CPC was added to prevent flocculation, addition of CPAM35 or PAM could not produce destabilization. Even after prolonged shaking, polymer was not able to displace surfactant.

Initial adsorption of CPAM35 or PAM decreased the amount of CPC able to be subsequently adsorbed, but the adsorption of the CPC did not impact on floc formation. Replacement of polymer by surfactant occurred but was slow on an industrially useful time scale. Thus, addition of CPC after flocculant had no immediate practical consequences.

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