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Flocculation of kaolin by waxy maize starch phosphates

Randal L. Shogren *

Plant Polymer Research Unit, National Center for Agricultural Utilization Research, USDA/ARS/NCAUR, 1815 N. University St., Peoria, IL 61604, USA

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Waxy maize starch phosphates were tested as flocculants in order to determine if they have the potential to replace petroleum-based polymer flocculants currently used commercially. Phosphorylation was carried out by dry heating of starches and sodium orthophosphates at 140 °C for 4 h. Native and phosphorylated waxy maize starches were ineffective as flocculants for kaolin in deionized water. However, in the presence of small amounts of Ca^{2+} (1–4 mM), starch phosphates were effective flocculants of kaolin at concentrations as low at 3–4 ppm. The optimal degree of substitution (DS) for flocculation was 0.024 but the effect of DS was rather small over the range DS 0.007–0.08. Although a common synthetic polymer flocculant (polyacrylamide-*co*-acrylic acid) was effective at 1 ppm, the lower cost of starches should make them economically competitive.

Product names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

1. Introduction

Polymeric flocculants are used in a number of industrial processes to precipitate suspended solids from wastewater before disposal or recycling (Bratby, 2006). Reducing soil erosion in irrigated agriculture by binding together soil particles is another important application (Orts, Sojka, & Glenn, 2000; Weaver & Fanta, 1987). Polymers usually are high molecular weight and have positive and/or negatively charged groups in order to bind to the polar surfaces of suspended particles (Bratby, 2006; Sharma, Dhuldhoya, & Merchant, 2006). Polymers used frequently include polyacrylamide, polyacrylic acid and various cationics. Drawbacks of these polymers include increasing costs of petroleum feedstocks, very slow biodegradation in soil and water and toxicity of residual monomer which is usually present in small amounts.

As a result, there has been increasing interest recently in developing new biobased, biodegradable flocculants such as modified starches (Khalil & Aly, 2002), celluloses (Sharma et al., 2006) and bacterial polysaccharides (Prasertsan, Dermlim, Doelle, & Kennedy, 2006). Chemically modified starches such as starch graft copolymers (Burr, Fanta, Doane, Russell, & Jones, 1975; Rath & Singh, 1997), cationic starches (Caldwell, Wurzburg, & Sun, 1961; Järnström, Lason, & Rigdahl, 1995; Khalil & Aly, 2001a; Krentz et al., 2006; Pal, Mal, & Singh, 2005), starch xanthates (Maher, 1983; Orts et al., 2000), carboxymethyl starches (Khalil & Aly, 2002; Zhao & Wen, 2006), starch sulfates (Khalil & Aly, 2002), starch phosphates (Meiczinger, Dencs, Marton, & Dencs, 2005; Solarek, 1986) and starch carbamates (Khalil & Aly, 2001b) have been studied as flocculants. Starch phosphates, in particular, are attractive candidates since they are fairly easy to prepare and the cost of the reactant (sodium phosphate) is low.

Starch phosphates were shown to be helpful in the sedimentation of red mud in the Bayer process (Hollo et al., 1964) and in the precipitation of iron oxide (Chang, 1954). Bode (1966) described the combination of starch phosphate pastes and multivalent metal salts to precipitate wastes from fish, meat, egg, vegetable, fruit, paper pulp, oil and ore processing. Concentrations of starch phosphate utilized were quite high (0.6%) as were phosphorus levels (0.5–5.0%). Wheat starch phosphate (0.6% P) was found to be an effective flocculant for coal tailings at 4–10 ppm (Jonason, 1973). Meiczinger et al. (2005) showed that waxy corn starch phosphates were effective flocculants for kaolin in water but DS values were not characterized and concentrations of starch phosphates required were not given. None of the above studies compared the effectiveness of starch phosphates to a good industrial flocculant such as PAM. In summary, little is known about the detailed effects of DS, molecular weight, concentration and divalent cations on the effectiveness of starch phosphates as flocculants.

The goal of this study was to prepare starch phosphates with a range of DS and to assess the importance of this factor, along with concentration and the presence of divalent cations on the flocculation of kaolin. These results were also compared to those for a poly(acrylamide-*co*-acrylic acid) to assess their commercial potential.

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* Tel.: +1 309 681 6354; fax: +1 309 681 6691.
E-mail address: Randy.Shogren@ars.usda.gov

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2. Materials and methods

2.1. Materials

Waxy maize starch was purchased from A. E. Staley, Inc. (now Tate and Lyle) and had a moisture content of 10.4%. Sodium dihydrogen phosphate, sodium hydroxide, calcium chloride and calcium acetate were ACS reagents from Sigma–Aldrich. α-Amylase (from *Bacillus* sp., type IIa) and β-NAD sodium salt were from Sigma. Kaolin and poly(acrylamide-*co*-acrylic acid) (acrylic acid 1 wt%, M_w 5,000,000) were from Aldrich.

2.2. Preparation of starch phosphates

The experimental design is shown in Table 1. Sodium phosphate was dissolved in deionized water, pH was adjusted to 6 or 8.5 with 10 M NaOH and then water was added to bring the total volume to 100 ml. Waxy maize starch (90.4 g, 81 g dry basis) was added and the mixture was stirred by hand to give a very thick consistency, then allowed to equilibrate for 4 h. The mixture was dried in pans in a forced air oven at 50 °C overnight then reacted at 140 °C for 4 h. Unreacted sodium phosphate was extracted by washing with water or hot (60 °C) ethanol/water 50/50 on a Buchner funnel (Table 1). Ethanol was required for extraction for samples 3–6 since these swelled or dissolved in water. Samples were dried in the hood for 1 day followed by vacuum drying at 60 °C for 1 day.

2.3. Characterization of phosphate content

Phosphorus content was measured using a ^{31}P NMR method similar to that of Kasemsuwan and Jane (1996). Briefly, samples (0.5 g) were mixed with 1.9 ml D_2O, amylase (0.5 mg) was added followed by heating at 90 °C for 15 min. After cooling, an additional 0.5 mg amylase was added followed by heating at 50 °C for 2 h. Samples were then heated at 100 °C for 10 min, a small amount of internal standard was added (NAD) and pH was adjusted to 8.0 with 0.5 M NaOD. All spectra were obtained on a Bruker Avance 500 spectrometer (500.11 MHz 1H) using a 5-mm BBO probe. All spectra were acquired at 27 °C using inverse gated decoupling and a 10 s recycle delay to insure accurate quantization. Chemical shifts are reported as ppm from 85% H_3PO_4 calculated from the lock signal. Relative concentrations of starch phosphate ester, inorganic phosphate and NAD were estimated from peak areas at 3–5 ppm, 2.5 ppm and -11.5 ppm, respectively.

Table 1
Experimental design[a].

Sample	Sodium phosphate/starch (mol/mol)	pH	Extractant
1	0.025	6.0	H_2O
2	0.05	6.0	H_2O
3a	0.10	6.0	EtOH/H_2O 1/1
3b	0.10	6.0	EtOH/H_2O 1/1
3c	0.10	6.0	EtOH/H_2O 1/1
4	0.20	6.0	EtOH/H_2O 1/1
5	0.40	6.0	EtOH/H_2O 1/1
6	0.80	6.0	EtOH/H_2O 1/1
11	0.025	8.5	H_2O
12	0.05	8.5	H_2O
13a	0.10	8.5	H_2O
13b	0.10	8.5	H_2O
13c	0.10	8.5	H_2O
14	0.20	8.5	H_2O

[a] 81 g (0.5 mol) starch used for each sample.

2.4. Molecular weight measurement

Weight average molecular weights (M_w) and *z*-average radii of gyration (R_g) were determined using a Dawn EOS light scattering instrument in the batch mode (Wyatt Technology, Santa Barbara, CA). Samples (0.1%) were dissolved by boiling in nanopure water for 5 min, filtered through 5 µm nylon filters, and diluted with filtered water into scintillation vials (0.001–0.002%). Intensity readings were taken at scattering angles of 28–90°, values for solvent were subtracted and Rayleigh ratios were calculated using toluene as a standard. Values of M_w and R_g were calculated using a Berry plot and a refractive index increment (d*n*/d*c*) value of 0.146 cm^3/g following previous light scattering studies of starch in water (Yoo & Jane, 2002). Water solubilities of samples were determined by drying and weighing 10 ml aliquots of starch phosphate solutions before and after filtration.

2.5. Flocculation of kaolin

Starch phosphate samples, 1% in nanopure water, were gelatinized by boiling while magnetically stirring for 5 min. This solution was diluted with water to 0.1% for most tests (<10 ppm). Flocculation performance was assessed using essentially the method of Xie, Feng, Cao, Xia, and Lu (2007). Kaolin (1 g) and nanopure water (100 g) were mixed at high speed in a 150 ml beaker using a 2.5 cm long magnetic stir bar for 5 min. Stirring speed was reduced to 300 rpm, flocculant was added and mixing was continued for 2 min. Stirring speed was then reduced to 180 rpm (just enough to keep kaolin in suspension) for 5 min. The flocs were then allowed to settle for 2 min without stirring. After the settling period, aliquots were taken at half height of the liquid column for measurement of percent transmittance at 670 nm and weight of suspended solids. The latter was determined by drying a 10 ml aliquot at 60 °C for 1 day followed by weighing.

3. Results and discussion

3.1. Preparation and molecular characterization of starch phosphates

Values of DS and reaction efficiency (RE) for the phosphorylation of waxy maize starch at pH 6.0 are shown in Table 2. DS values range from 0.0077 for sample 1 (P/starch = 0.025) to 0.10 for sample 6 (P/starch = 0.8). Reaction efficiency is highest for sample 1 (31%) and decreases with increasing ratio of sodium phosphate/starch. Reaction efficiencies are rather low probably for two reasons: (1) the amount of sodium phosphate or other reagent which can diffuse into the starch granule is limited by the semi-crystalline structure and rigidity of starch granules (Kavitha & BeMiller, 1998) and (2) the solid state reaction condition limits the mobility of the phosphate reactant so that only starch and phosphate molecules close to each other will react. Thus, a smaller proportion of the sodium phosphate will react as more is added. Free orthophosphates (^{31}P = 2.5 ppm) were found to be present at levels of 3–10% of the phosphate ester on a molar basis. At large ratios of sodium phosphate/starch (#5, 6), an additional ^{31}P peak at -7 ppm was noted. This resonance likely corresponds to sodium pyrophosphate since a peak was found at a similar value (-5.3 ppm) for pure pyrophosphate in previous work (Sojka & Wolfe, 1978). Values of DS and reaction efficiency (RE) for the phosphorylation of waxy maize starch at pH 8.5 are also shown in Table 2. DS values and reaction efficiencies are much lower than those obtained at pH 6, in agreement with previous findings (Solarek, 1986).

Molecular weights (M_w) and radii of gyration (R_g) for starch phosphates in water are given in Table 2. Values of M_w and R_g for unmodified waxy starch (1×10^9, 394 nm) are similar to those determined previously (8.3×10^8, 372 nm) (Yoo & Jane, 2002).

Table 2
Composition and properties of starch phosphates.

Sample	DS	Reaction efficiency (%)	M_w	R_g (nm)	Water solubility (%)
Waxy maize	0	–	1.03×10^9	394	100
1	0.0077	31	100×10^6	303	100
2	0.012	25	64×10^6	288	100
3	0.025 ± 0.002	24 ± 2	$55 \pm 2 \times 10^6$	281 ± 9	100 ± 1
4	0.042	21	47×10^6	287	99
5	0.076	19	44×10^6	312	100
6	0.10	13	47×10^6	351	100
11	0.0017	5.8	168×10^6	354	96
12	0.0026	5.3	149×10^6	366	99
13	0.0033 ± 0.0001	3.3 ± 0.1	$126 \pm 8 \times 10^6$	340 ± 10	99 ± 1
14	0.0053	2.7	98×10^6	319	97

Molecular weights decreased to 44–168 × 10^6 after phosphorylation. M_w generally declined with increasing P/starch ratio and with lower pH. Both high temperatures and low pH are known to cause starch chain cleavage resulting in lower molecular weights (Dintzis & Fanta, 1996). Values of R_g for starch phosphates (281–354 nm) were still quite large even though starch phosphate molecular weights were much lower than the native starch. This is due to the compact, spherical shape of amylopectin in water which results in $R_g \sim M^{0.3}$ and also to repulsion of negatively charged phosphate groups resulting in chain expansion. The latter effect can be observed in samples 4–6 where M_w is constant and R_g increases significantly with DS.

There have been many previous studies of the preparation of starch phosphates particularly at pH 6 and the DS values obtained above are generally in line with this previous work (Kerr & Cleveland, 1960; Nakano et al., 2003; Sitohy, Labib, El-Saadany, & Ramadan, 2000; Solarek, 1986). There have been, however, few previous reports of reaction efficiency since excess sodium phosphate is usually filtered off prior to reaction making the initial composition uncertain. Also, amounts of residual inorganic phosphate after reaction are usually not measured since most DS measurements were based on total P rather than starch ester P from the ^{31}P technique. Meiczinger et al. (2005) determined molecular weights of <1–18 × 10^6 for waxy maize starch phosphates. These values are much lower than ours and this could be due to the long heating time (24 h at 95 °C) used to dissolve the samples as well as their observation that some of the starch phosphate was absorbed onto the SEC column.

3.2. Flocculation of kaolin

The extent of flocculation of kaolin in water by starch phosphates prepared at pH 6.0 are shown in Figs. 1 and 2. The two methods used to characterize the amount of kaolin left in suspension after settling, optical transmission (Fig. 1) and weight of suspended solids (Fig. 2) gave similar results. As shown in Fig. 1, some kaolin remains in aqueous suspension (%T < 50%) with added starch phosphates up to 100 ppm. As DS increases, %T actually decreases with increasing starch phosphate concentration, indicating that these high DS starch phosphates act as suspending agents rather than flocculants. As indicated in Fig. 2, all kaolin is removed from suspension by 100 ppm unmodified waxy maize starch. Likewise, the data in Table 3 indicate that starch phosphates prepared at pH 8.5 are also ineffective at flocculating kaolin. These results show that starch phosphates are ineffective as flocculating agents in water while unmodified waxy maize starch is effective only at high concentrations (100 ppm).

The behavior noted above can be rationalized based on the solubility and charge densities of starches and kaolin. Native starches tend to be poorly soluble in water, are neutral or slightly anionic (starch OH group p$K_a \sim 10.7$) and thus have a tendency to absorb

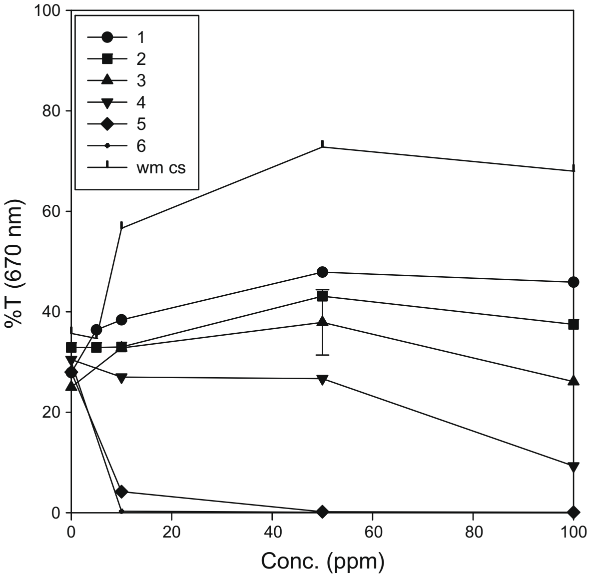

Fig. 1. Flocculation of kaolin in water as measured by light transmission for different starch phosphate concentrations and DS.

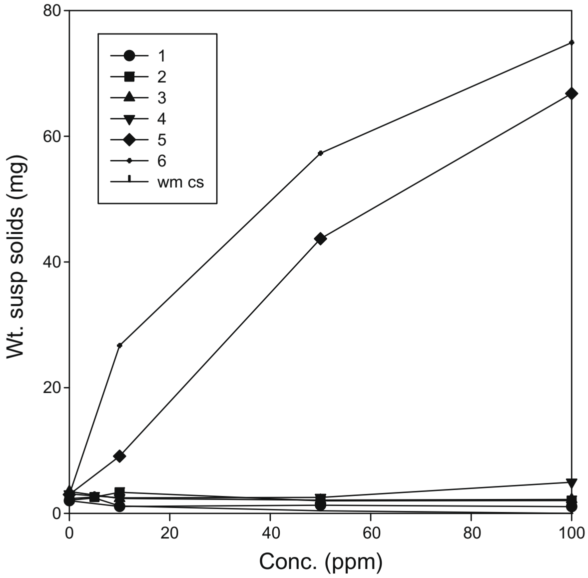

Fig. 2. Flocculation of kaolin in water as measured by weight of suspended solids for different starch phosphate concentrations and DS.

Table 3
Flocculation results for starch phosphates prepared at pH 8.5.

Sample	Concentration (ppm)	%*T* (670 nm)	
		Water	2 mM $CaCl_2$
11	10	33.1	42.9
12	10	27.4	60.2
13	10	32.2 ± 3.1	61.1 ± 5.1
14	10	39.9	67.7

onto insoluble surfaces. Starch phosphates, in contrast, are more highly anionic and water soluble and thus the free energy of absorption to a solid substrate would be less favorable. Since kaolin ($Al_2O_32SiO_22H_2O$) has a net negative charge at neutral pH, negatively charged starch phosphates would not tend to interact strongly with kaolin. Instead, starch phosphate molecules would tend to surround the kaolin particles and prevent them from agglomerating into larger particles and flocculating.

The effects of a low concentration of divalent cation (2 mM $CaCl_2$) on the flocculation of kaolin by starch phosphates made at pH 6 are shown in Figs. 3 and 4. For samples 1–4, flocculation is virtually complete at 5 ppm, based on both light transmission and weights of suspended solids. Thus, flocculation of kaolin by starch phosphates is much more rapid in dilute $CaCl_2$ than water. The calcium ions likely serve to bind the anionic starch and kaolin together and thus facilitate precipitation of kaolin from suspension. Based on the data in Figs. 3 and 4, sample #3 was effective at the lowest concentration (4 ppm), suggesting that a DS of 0.024 is optimal for flocculation. Fig. 5 indicates that there is no significant change in flocculation behavior over the $CaCl_2$ concentration range of 1–4 mM. Starch phosphate (#3) was also an effective flocculant as low as 3 ppm in the presence of 2 mM calcium acetate (Fig. 5).

In contrast, starch phosphates prepared at pH 8.5 were ineffective as flocculants in the presence of $CaCl_2$ even at 10 ppm concentration (Table 3). This may be due to the lower DS of the starch phosphates prepared at pH 8.5 than at pH 6.0. This finding contradicts the results of Meiczinger et al. (2005) who found shorter settling times for kaolin by waxy starch phosphates made at pH 8.7 and 9.7 than at pH 7. It is not clear why different results were obtained although the flocculation test used by Meiczinger et al. (2005) was somewhat different and their starch phosphate concentration range was much higher (10–50 ppm). It was not mentioned in their paper whether distilled or tap water was used which could also impact the results as clarified in this report.

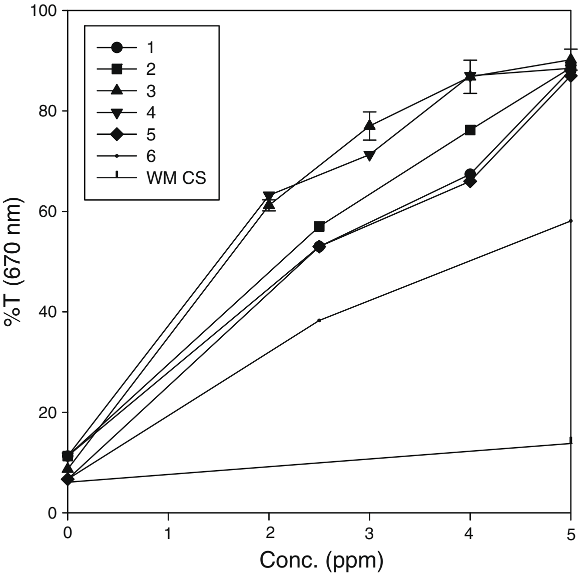

Fig. 3. Flocculation of kaolin in 2 mM $CaCl_2$ as measured by light transmission for different starch phosphate concentrations and DS.

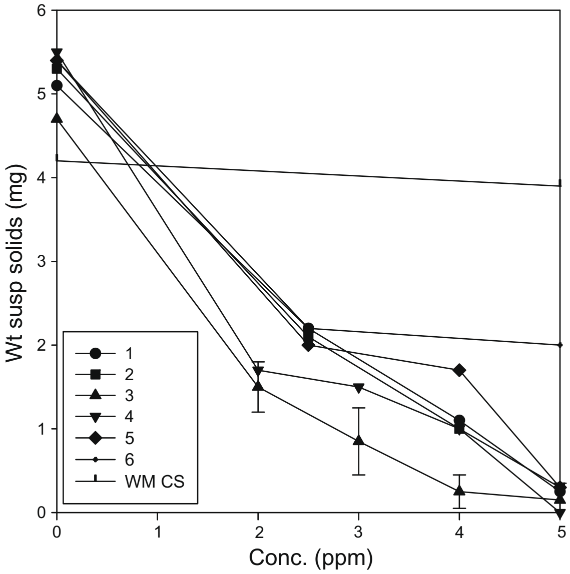

Fig. 4. Flocculation of kaolin in 2 mM $CaCl_2$ as measured by weight of suspended solids for different starch phosphate concentrations and DS.

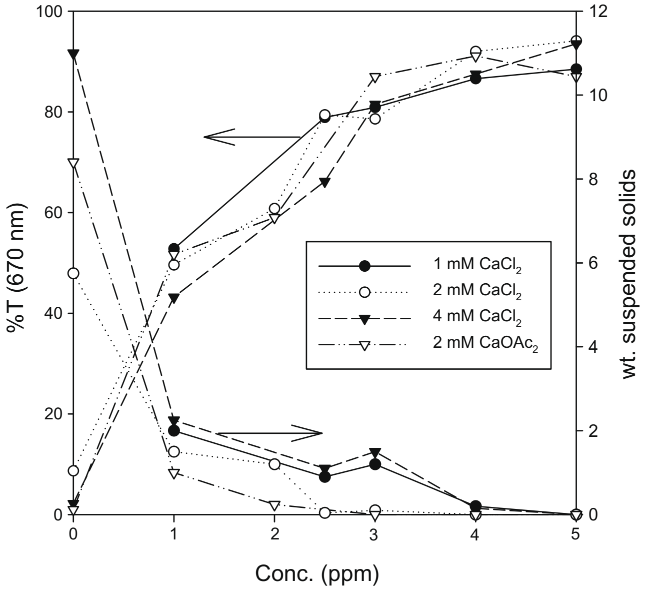

Fig. 5. Flocculation of kaolin in 1–4 mM $CaCl_2$ and 2 mM $CaOAc_2$ at different starch phosphate concentrations (#3, DS 0.024).

For comparison, the effect of poly(acrylamide-*co*-acrylic acid) (PAM) on the flocculation of kaolin is shown in Fig. 6. Light transmission approaches 90% at 1 ppm PAM both in water and in 2 mM $CaCl_2$. Thus, PAM is an effective flocculant at 1/4–1/3 the concentration required for waxy starch phosphates.

The reason PAM is a more effective flocculant than waxy maize starch phosphate is likely due to the linear backbone of PAM and random coil conformation which leads to a larger R_g for PAM than starch at similar molecular weights. For example, light scattering data from Yoo and Jane (2002) for amylopectins

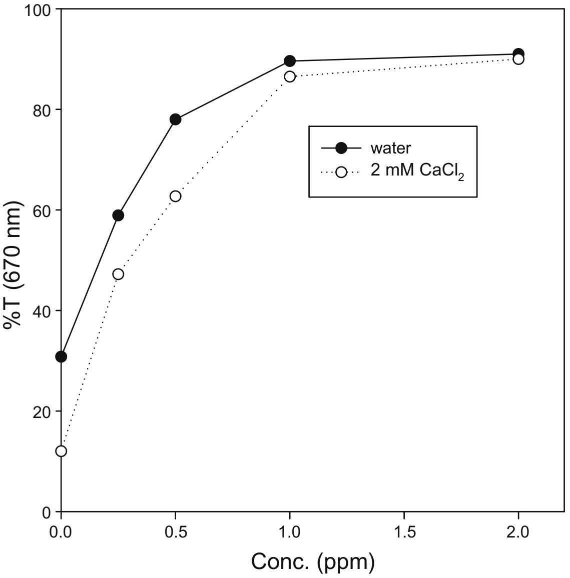

Fig. 6. Flocculation of kaolin in water and 2 mM CaCl$_2$ with poly(acrylamide-*co*-acrylic acid).

in water gave $R_g = 0.425\ M_w^{0.334}$ compared to $R_g = 0.0147\ M_w^{0.59}$ for PAM in water (Patterson & Jamieson, 1985). A scaling exponent of 0.60 usually reflects a linear polymer in a good solvent while an exponent of 0.33 reflects a compact, spherical conformation. The more compact structure of highly branched amylopectin molecules decreases the extent of bridging contacts with kaolin particles and thus a higher concentration of starch phosphate is needed for flocculation. The insensitivity of kaolin flocculation with PAM to the presence of divalent cations is probably due to the much weaker interaction of Ca^{2+} with carboxylate anions than with phosphate anions.

The optimal condition of DS 0.024 for the flocculation of kaolin in CaCl$_2$ may be due to a number of factors such as surface concentration of adsorbed calcium ions on the kaolin particles, concentration of starch phosphate groups, changes in starch phosphate conformation or self-association and free energy of adsorption versus hydration. Presumably, when there are more starch phosphate groups than necessary to interact with the calcium ions bound to kaolin, preference for solubility in water increases over adsorption so flocculation would be less effective.

Although the effect of molecular weight on the ability of starch phosphates to flocculate kaolin was not explicitly studied, one may speculate that it may not be an important parameter over the range of molecular weights studied. This follows from the fact that R_g is rather insensitive to M_w and chain dimensions as reflected by R_g are presumably important in bridging kaolin particles within the floc. Also, it was observed that starch phosphates prepared at pH 8.5 were much less effective as flocculants than those made at pH 6 even though molecular weights were larger at pH 8.5.

Even though starch phosphates are less effective flocculants than PAM, the cost of starch phosphates is much lower than PAM thus making starch phosphate flocculants potentially economically competitive. For example, the cost of PAM is around $8/kg (Orts et al., 2000) versus approximately $1/kg for typical chemically modified starches of low DS. Therefore, even if a 3- to 4-fold higher concentration of starch phosphate is required, the cost may be comparable to or even less than PAM. The requirement for a low concentration of calcium ions (or presumably other multivalent cations) would probably not be an impediment as most tap water contains some calcium and magnesium ions. There are also several possibilities for improving the flocculation efficiency of starch phosphates such as increasing starch molecular weight, increasing branch length and increasing chain linearity (high amylose starches). The possibility of selective breeding of tuberous plants to produce native starches having high phosphate content may also be attractive.

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