Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Chen, Wen-Jang(1998) 'Effects of Surface Charge and Shear During Orthokinetic Flocculation on the Adsorption and Sedimentation of Kaolin Suspensions in Polyelectrolyte Solutions', Separation Science and Technology, 33: 4, 569 — 590

To link to this Article: DOI: 10.1080/01496399808544997

URL: http://dx.doi.org/10.1080/01496399808544997

SEPARATION SCIENCE AND TECHNOLOGY, 33(4), pp. 569–590, 1998

Effects of Surface Charge and Shear During Orthokinetic Flocculation on the Adsorption and Sedimentation of Kaolin Suspensions in Polyelectrolyte Solutions*

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ABSTRACT

Suspensions of negatively charged kaolin clay as a model system have been flocculated by adsorbing nonionic, cationic, and anionic polyelectrolytes under shear. Test results show that the maximum rate of settling increases with charge density of the cationic polymer being used. Both cylinder test and jar test using low shear conditions tend to underestimate the polymer dose requirements for the orthokinetic flocculation process. Under prolonged shear conditions, the optimum polymer doses required for maximum turbidity removal or minimum residual turbidity coincide with those required for zero zeta-potential or plateau adsorption of polymer. An explanation of the experimental observations based on the charge density of polymers and the shear conditions is given. It is suggested that both polymer bridging and charge neutralization mechanisms may operate in the adsorption/flocculation process. The relative importance between them in determining the optimum polymer doses was analyzed with supplementing rheological measurements of such flocculated systems. It was pointed out why a higher charge density polymer produces a floc structure with higher sensitivity for a shear field.

Key Words. Orthokinetic flocculation; Polymer adsorption; Polyelectrolytes; Charge density; Zeta potential

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*Part of this paper was presented at the 7th Congress of Asian Pacific Confederation of Chemical Engineers, Taipei, March 3–6, 1996.

INTRODUCTION

The flocculation of colloidal particles by the introduction of a polymer into the liquid suspension is an important solid–liquid separation process in various industrial mineral processing and municipal water and wastewater treatments (1). In fact, adsorption of polyelectrolytes at the particle/liquid interface has a profound effect on the flocculation and stabilization behavior of colloidal suspensions. Typically, flocculation of particles in the suspension can occur at low polymer doses, while the suspension can be restabilized at high polymer doses. It has been well documented in the literature that the adsorbing polymers can affect the particle flocculation through two postulated mechanisms—polymer bridging and electrostatic patch attraction. Ruehrwein and Ward (2) were the first to point out the concept of polymer bridging between particles. Very long and extended polymer chains may become adsorbed on more than one particle in a suspension, and thereby the bridging mechanism between particles produces flocculation. This is well understood in nonionic polymer systems, and it has also been successfully extended into systems containing both a polymer and particle carry the same type of charge (both anionic or both cationic). However, the majority of particles found in nature mainly bear negative charges (e.g., clay particles), so generally their suspensions are flocculated by using cationic polyelectrolytes, It is believed that the low molecular weight (MW $\approx 10^4$) polycations cause flocculation because they neutralize the particle charge, and the high molecular weight polycations work via a combined electrostatic and bridging mechanism. Lindquist and Stratton (3) studied the flocculation power of cationic polyethylenimines on negatively charged silica sol particles as a model system. They proposed both polymer bridging and charge neutralization may function simultaneously, and the relative importance between them is pH-dependent. At high pH (>9), polymer bridging should dominate flocculation due to the low cationic charge of basic polymers; and at low pH (<9), strong electrostatic attraction between polycations and negative particles is the dominant mechanism. Kasper (4) and Gregory (5) independently proposed the electrostatic patch model in which patches of uneven charge distribution on the particles are attributed to partially adsorbed polycations of moderately high molecular weight, and the strong attractive electrostatic interactions between oppositely charged patches contribute to the higher flocculation rate. Elaborating on the electrostatic patch model, Mabire et al. (6) and Tiravanti et al. (7) were able to explain that increasing the charge density of polymers will increase their electrostatic patch attraction to particles of the opposite charge, and that more extended adsorbed polymer configurations will favor flocculation. On the contrary, Gill and Herrington (8) and Smith-Palmer et al. (9) studied the flocculation of kaolin suspensions using cationic polyacrylamides of similar high molar mass (MW $\approx 10^6$) but of different charge densities, and they found the settling rates decreased as the charge density increased. They reported that charge neutralization is less likely to affect flocculation behavior and that polymer bridging is the only predominant mechanism of suspension destabilization. Over a long time many researchers have reported the best flocculation conditions in polymer dosage, the so-called optimum flocculation concentration (OFC), as used to assess polymer performance in terms of maximum rates of subsidence, minimum residual turbidity, the isoelectric point of zero charge, complete adsorption of polymer, or maximum rates of dewatering in the settled beds of flocs, etc. (10, 11). Despite these, investigations did not show the differences between their OFC definitions, the discrepancies in the flocculation literature regarding the OFC values might partly be the result of the use of different experimental methods to monitor flocculation. Most important, the basic disagreements between them could arise from the effect of conformational changes of adsorbed polymer chains under the various shear conditions during mixing time (12), so they may lead to confusing interpretations. The flocculation mechanism, either dominated by polymer bridging or dominated by electrostatic patch attraction, turned out to be an extremely complicated issue, very often depending upon the solution properties and hydrodynamic conditions.

In the water industry it is generally accepted that the mechanism of orthokinetic flocculation for a given system is mainly due to the optimized shear conditions such as mixing intensity (or velocity gradient, G value) and retention time (t value) during flocculation so that large separable flocs of suitable density are rapidly formed and leave no residual primary particles or small aggregates. Furthermore, the shear resistance and rheological behavior of polymer-flocculated sludge may play an important role in determining the optimum polymer dosage (OFC value), which now can be defined as the minimum amount of polymer dosed under the best mixing conditions to achieve the maximum flocculation (13). The objective of this study is therefore to investigate orthokinetic flocculation behavior in a suspension containing negatively charged kaolin clay as a model system in the presence of a series of polyelectrolytes of various charge densities. Toward this aim, the sedimentation rate, supernatant turbidity, polyelectrolyte adsorption, zeta potential, and shear resistance of flocculated kaolin suspensions have been determined under various shear conditions. With the help of these measurements, interesting information about the influence of the surface properties of kaolin particles, the charge density of polyelectrolytes, and the hydrodynamic conditions upon the mechanism of orthokinetic flocculation process can be provided.

EXPERIMENTAL MATERIALS AND METHODS

Materials

The kaolin clay used in this study was obtained from Sigma Chemical Co. This aluminum silicate hydroxide powder, in which the particle size has a broad distribution ranging from 0.1 to 4 μm, was used as received except for the microelectrophoretic measurements. For these measurements the sonicated and well-dispersed kaolin was fractionated through sedimentation and filtration to ensure that all the particles were submicron in size.

The seven different polyelectrolytes used as flocculants in this study were received from Taiwan Hopax Chemicals Co. The nonionic polyacrylamides that carry a charge density of less than 1% were denoted as Polymer (a). Four cationic polyelectrolytes denoted as Polymers (b)–(e) are the copolymers of acrylamide with a comonomer of dimethylaminoethyl acrylate, quaternized with methyl chloride, in which their charge densities are reported to be 10, 20, 30, and 50%, respectively, as the molar percentage of cationic functional groups in the polymers that carry a charge. Two anionic polyelectrolytes denoted as Polymers (f) and (g) are the copolymers of acrylamide with 10 and 30% anionic comonomers of acrylic acid based on the overall moles of acrylate repeating units. The molecular weights of the polymers were determined by measuring the intrinsic viscosities in 1.0 M NaCl solution at 25°C, using an Ubbelhode viscometer. The viscosity-average molecular weights were calculated from the Mark–Houwink equation (14):

$$[\eta] = KM^a \tag{1}$$

where $[\eta]$ is the intrinsic viscosity (in dL/g) of the polymers, M is the viscosity-average molecular weights of the polymers, $K = 3.73 \times 10^{-4}$ dL/g, and $a = 0.66$ at 25°C. Polymers (a)–(g) all have a high molecular weight (ca. $1.5–2.0 \times 10^6$ g/mol approximately) except for Polymer (e) which has a smaller molar mass (ca. $1.0–1.5 \times 10^6$ g/mol). All salts and reagents used were of AR grade. Double-distilled water was used in the preparation of all solutions. The characteristics of the polyelectrolytes are summarized in Table 1.

TABLE 1
Polyelectrolyte Characteristics

Polymer	Molecular weight × 10^{-6} (g/mol)	Charge type	Charge density (%)
(a)	1.5–2	Nonionic	<1
(b)	1.5–2	Cationic	10
(c)	1.5–2	Cationic	20
(d)	1.5–2	Cationic	30
(e)	1–1.5	Cationic	50
(f)	1.5–2	Anionic	10
(g)	1.5–2	Anionic	30

Determination of Polyelectrolyte Adsorption

Adsorption of polyelectrolytes was determined by measuring the changes in the concentration of polymers in water after equilibration with colloidal particles by tumbling the polymer-dosed suspensions in a rolling mill at 120 rpm for 24 hours. The suspended colloidal particles were centrifuged at high speed until all the residual colloidal particles had subsided, leaving a crystal clear supernatant which was then transferred to a standard test vial for titration with a solution of the potassium polyvinylsulfate (KPVS) using toluidine blue dye as the indicator. Such types of titrant were used to estimate the changes in cationic polyelectrolyte concentration, because only a cationic polymer forms a polyelectrolyte complex with negatively charged KPVS. When the dye is present in solution, the excess KPVS complexes with the oppositely charged cationic dye to produce a color change from blue to purple at the end point, which is monitored by a UV-VIS spectrophotometer. As for determination of the changes in anionic polyelectrolyte concentration, the techniques of colorimetric titration were used in a modified form. The negatively charged polymer solution must be first treated with an excess solution of polydimethyldiallylammonium chloride (PDMDAAC), which is then backtitrated with KPVS using toluidine as the indicator.

Microelectrophoretic Measurements

Microelectrophoretic measurements in very dilute suspension of colloidal particles were made with the Zeta-Meter 3.0, using the capillary electrophoresis cell. We also made electrophoretic light-scattering (ELS) measurements with the Brookhaven Zetaplus, using the rectangular electrophoresis cell. The zeta potentials were computed from the Smoluchowski equation (15):

$$\zeta = u_e \eta / \epsilon_0 \epsilon_r \tag{2}$$

where ζ is the zeta potential (in volts) of colloidal particles, u_e is the electrophoretic mobility in m/V·s, η is the viscosity in N·s/m, ϵ_0 is the permittivity of free space in SI units, and ϵ_r is the dielectric constant of the dispersing medium.

Assessments of Bench-Scale Orthokinetic Flocculation and Sedimentation

The kaolin particles were dispersed in a stock solution of constant salt electrolyte and constant pH via high-speed stirring for 1 hour, and the resulting suspensions were allowed to stand overnight. Assessments of orthokinetic flocculation and sedimentation were conducted at room temperature using the standard cylinder-test and jar-test techniques. For cylinder tests the stock colloidal suspension was dispensed into several glass cylinders which had a flat bottom and cap, and were graduated up to 100 mL. Then a specific amount of stock polymer solution was added to the individual cylinders, which were immediately inverted five times end-over-end manually. The settling rates were determined by measuring the height of the interfacial plane between the slurry and the supernatant as a function of time and by estimating the initial slope of subsiding height versus time curves. Then the same samples used for measurements of settling rate were allowed to subside continuously for 24 hours and the sediment volumes were read on the graduated cylinders. For jar tests the stock colloidal suspension was transferred into six 1000-mL glass beakers positioned in series within a jar-test apparatus and simultaneously stirred with the addition of varying polymer doses under the following conditions: typically pH 5.5, temperature = 22 ± 3°C, kaolin = 300 mg/L, NaCl = 0.001 M, mixing intensity = 100–300 rpm for 20 minutes. After standing for 20 minutes for visual inspection of floc settling, geometric shape, and size distribution, the supernatant turbidity of the individual samples was measured by using a HACH turbidimeter 2100A. The percentages of residual turbidity were computed by dividing the supernatant turbidity of the kaolin suspension with treatment of polymer by the value without treatment of polymer. Then normalized values of residual turbidity were plotted as a function of polymer dose and of shear conditions. The jar-test apparatus is a mixing device consisting of a set of six beakers which are simultaneously stirred by a single flat-bladed paddle. The beakers are normally graduated up to 1000-mL capacity and contain 800 mL of kaolin suspension, and the mixing intensity can be easily varied by controlling the rotational speed of the paddle stirrer. For the given stirrer dimension and geometry of the paddle-type jar-test apparatus, the mean velocity gradient G can be estimated from the equation developed by Camp and Stein (16):

$$G = [C_D A_P (u_p - u)^3 / 2\nu V]^{0.5} \tag{3}$$

where C_D is the drag coefficient, A_p is the projected area of the blade normal to the direction of rotation, u_p is the velocity of the paddle, u is the velocity of water, ν is the kinematic viscosity, and V is the volume of water in the beaker. The jar-test stirrer used in this study is the standard type as described by Bhole (17), so that stirrer speeds ranging from 100 to 300 rpm can be correlated to G values ranging from 100 to 300 1/s according to the calibration curve.

Rheological Measurements

The rheological behaviors of stable versus flocculated kaolin suspensions were measured with a Brookfield cone-and-plate rheometer LVDV-III. Since shear history and temperature can affect the shape of flow curves, all samples of kaolin particles, after tumbling equilibration with polyelectrolytes for 24 hours and followed by half-minute dispersing with a sonication probe, were added to the rheometer, and the measurements were started immediately using the same shear rate program at constant temperature. The shear rate was increased from 0 to 100 rpm in 5 minutes (up curve), and was decreased from 100 to 0 rpm in another 5 minutes (back curve). The relationship between the rotation speed ω of the cone and the shear rate G at the surface of cone can be computed according to the following equation (18):

$$G = \omega / \sin \theta \tag{4}$$

where θ is the angle between the cone and the flat plate. The cone spindle used in this study was type CP-42 with a very obtuse geometry, 1.565° in angle and 2.4 cm in radius. The cone speed of 100 rpm typically corresponds to a shear rate of 384 1/s.

RESULTS AND DISCUSSION

Polymer Dose for Flocculation and Adsorption Isotherms

Typical results of cylinder tests and adsorption tests measured for 30 g/L kaolin suspensions in polyelectrolyte solutions are shown in Figs. 1, 2, and 3. The flocculation power of cationic polymers for the negatively charged kaolin particles is greater than that of the nonionic or anionic ones. Figure 1 presents the graph of kaolin settling rates obtained from a series of cationic polymers of high molecular weight (ca. 1.5–2.0 million), which are similar to the polymers used by Smith-Palmer et al. (9), except for small differences in molecular weight. The maximum rate of settling increases incrementally with charge density of cationic polyelectrolytes from a charge density of less than 1% up to a charge density of 30%. Furthermore, it is seen from Fig. 2 that the sediment volumes produced by cationic Polymers (b)–(e) with 10, 20, 30, and 50% in charge density sharply increased and then gradually decreased with incremental polymer dosing. It is also noted that both settling rates and sediment volumes produced by Polymers (b)–(d) go through a maximum within the 0.6–0.7 mg/g range, indicating the formation of very loose voluminous flocs. When the experiments were repeated by using nonionic or anionic polymers, the settling rates were not as fast as those produced by the cationics of lowest charge density, and the sediment volumes did not vary to a significant extent. Therefore, it may be expected that the high-affinity adsorption isotherm for a positively charged polymer binding to a negatively charged

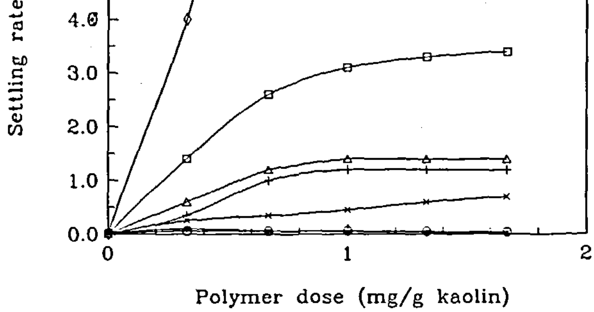

FIG. 1 Settling rate of 30 g/L kaolin in 10^{-3} M NaCl solution vs polymer dose. +, Polymer (a); △, Polymer (b); □, Polymer (c); ◇, Polymer (d); ○, Polymer (e); ×, Polymer (f); *, Polymer (g).

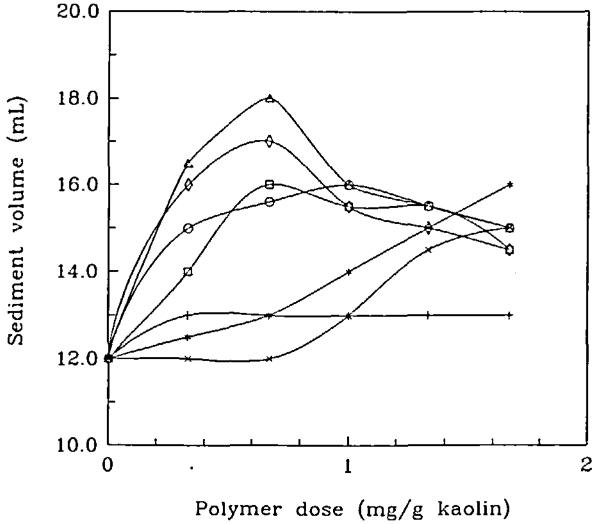

FIG. 2 Sediment volume of 30 g/L kaolin in 10^{-3} M NaCl solution vs polymer dose. +, Polymer (a); △, Polymer (b); □, Polymer (c); ◇, Polymer (d); ○, Polymer (e); ×, Polymer (f); *, Polymer (g).

particle will be greater than those for a nonionic or anionic polymer binding to the same particles. As indicated in Fig. 3, the adsorption behavior of a polymer onto kaolin particles is very dependent on the charge density of each polymer. The isotherms for the adsorption of polymers (c)–(g) are of the common type, approaching a plateau at 1.7, 1.5, 0.5, 0.6, and 0.5 mg/g of polymer dosing concentration, respectively. The isotherm for Polymer (b) tends to climb continually rather than reaching a plateau, suggesting that the polymer concentrations which were dosed up to 1.7 mg/g in the adsorption tests may not be sufficiently high for a plateau, values. Accordingly, it can be seen from Fig. 3 that the plateau adsorbance of cationic Polymers (c)–(e) is ca. 1.4, 0.9, and 0.5 mg/g, which increases inversely proportionally to the charge density of 20, 30, and 50%, respectively. Besides, Polymers (c), (d), and (e) exhibited similar strong adsorption isotherms, in which about 95–99% of the added polymer was adsorbed at all concentrations until a plateau was reached. The enhanced initial slope of isotherm curves near the region of the lower doses indicated that the higher the charge density, the stronger was the initial adsorption. These results confirm the predominance of charge neutralization over polymer bridging mechanism. Increasing the cationicity of polyelectro-

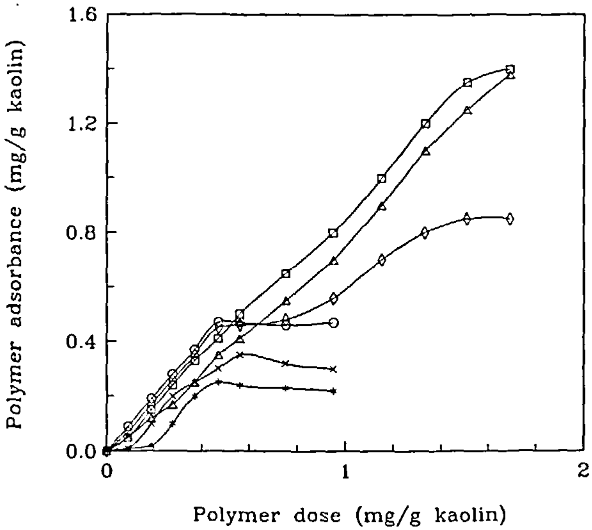

FIG. 3 Adsorption isotherms in 30 g/L kaolin in 10^{-3} M NaCl solution vs polymer dose. △, Polymer (b); □, Polymer (c); ◇, Polymer (d); ○, Polymer (e); ×, Polymer (f); *, Polymer (g).

lytes will increase their electrostatic attraction to the negatively charged surface sites of kaolin particles, and will facilitate the adsorption/flocculation process at the initial stage of mixing. On the contrary, settling rates and adsorption isotherms of the standard kaolins produced by cationic Polymer (e), which carry a moderately high charge density (50%) and a smaller molar mass (ca. 1.0–1.5 million), were found to decline dramatically as compared with those produced by the initial set of cationic Polymers (b)–(d). We suggest that although their flocculation mechanism is predominantly charge neutralization, polymer bridging conformation is also important. In fact, the conformational changes of cationic polymer chains adsorbed onto kaolin particles are found to be quite dependent upon the charge density. Besides, it is observed from our viscosity measurements that the highly charged polymer chains will be more extended in length due to intramolecular charge repulsion between the adjacent cationic groups. As the polymer uncoils, the solution viscosity increases, so the flocculation power of cationic polymers increases with charge density up to 30%, as found experimentally. However, it should be noted that such uncoiling of polymer chains may cause an opposing effect on the adsorption/flocculation process of Polymer (e) in the region of the saturation doses (ca. 0.4 mg/g kaolin) or over. The overshooting of charge density in a polymer (>30%) results in a loss of flocculation power because the previously adsorbed cationic polymer chains could rapidly saturate the negative surface sites of particles and create particles coated with a layer of cationic polymers, thereby blocking the newly-approaching cationic polymer chains via electrostatic repulsion between the same type of cationic groups. As a result, there are less bridging conformations and lower flocculation rates, indicative of restabilization in kaolin suspensions. Smith-Palmer et al. (9) also observed that the most highly charge density (80 and 90% in cationicity) produced much lower settling rates because of the adsorbed polymer chains sit flat on negative silica particles. As reported by Eriksson et al. (10), the lower flocculation rates produced by cationic polyelectrolytes with high charge density were attributed to their flat conformations in the adsorption layers on polystyrene latex particles. Therefore, the best charge density of polymers for a given application balances considerations for many factors. For instance, two of them discussed below are the surface charges of particles and the shear conditions in flow.

Surface Charges and Zeta Potentials of Polymer-Treated Kaolin Particles

The Kaolin suspensions without polymer treatments were found to have isoelectric points at pH 2, independent of the added NaCl. At a pH greater than 5 the zeta potentials were more negative than -30 mV, and the suspensions were easily restabilized. After the polyelectrolytes were added to adsorb on kaolin particles in a suspension at constant pH and salt electrolyte, the zeta potentials of polymer-treated and redispersed kaolin particles were found to vary as a function of polymer dose. In Fig. 4 we can roughly divide the zeta potential versus polymer dose curves into three categories: (A) the curve remaining independent of the anionic polymer dose, possibly due to the repulsive electrostatic interactions between negatively-charged polymers and negative surface sites of particles; (B) the curve representing the slightly reduced zeta potential of particles with incremental nonionic polymer dose, indicating a certain extent of preferential polymer adsorption on particles; (C) the curve exhibiting the appreciably reduced zeta potential of particles with incremental cationic polymer dose, indicating that the particles underwent charge neutralization and subsequent charge reversal via an electrostatic attraction between the positively charged polymers and negative surface sites of particles. According to the adsorption isotherms in Fig. 3, the plateau adsorption of cationic polymers is observed near the zero point of charge. The amount

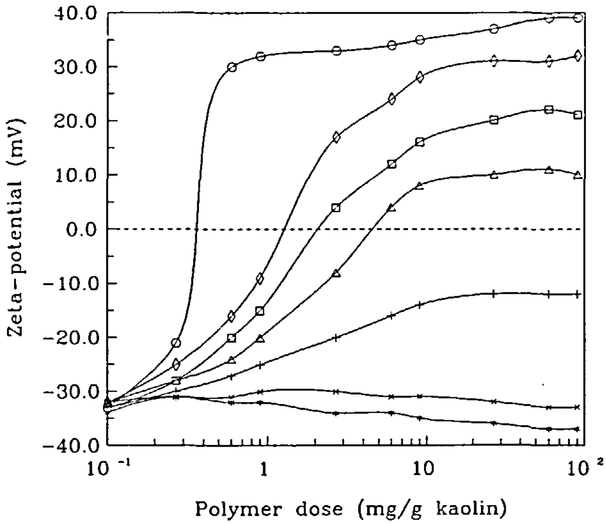

FIG. 4 Zeta potential of 30 g/L kaolin in 10^{-3} M NaCl solution vs polymer dose. +, Polymer (a); △, Polymer (b); □, Polymer (c); ◇, Polymer (d); ○, Polymer (e); ×, Polymer (f); *, Polymer (g).

of polymer required to neutralize the particle charge is found at 4.0, 2.0, 1.5, and 0.4 mg/g for Polymers (b)–(e), respectively. These coincide with that required for plateau adsorption of each polymer. The polymer dosage at zero charge increases inversely proportionally to the charge density of the cationic polymer being used. This again confirms the predominance of the charge neutralization mechanism. In contrast, treatments with nonionics or anionics were unable to produce zero zeta-potentials within the measurable dosing range, and that is attributed to the predominance of the polymer bridging mechanism. As indicated in Fig. 1, the maximum rate of settling occurs well before the zero point of charge is reached. It is suggested that the maximum attraction of electrostatic charge-patch interactions may occur along with a partial coverage of cationic polymer chains on negative surface sites of a particle, as evidenced in Fig. 3. As reported by Higashitani and Kubota (19), a transition of flocculation state from initial bulky flocs to discrete or pelleted flocs could increase the amount of polymers adsorbed on particles, especially under a certain intensity of mixing. In fact, during the initial nonequilibrium flocculation and followed by excess shearing treatments, the breakage of voluminous flocs results in new particle/floc surfaces that are not yet covered with polymer chains. Further, those new surfaces act as a sink for excess polymers in the liquid phase which are not consumed by adsorption until a quiescent state of equilibrium flocculation/adsorption is reached. This explains why the optimum polymer dose required for a maximum rate of settling under low shear conditions tends to underestimate the polymer dose requirement for complete charge neutralization or plateau adsorption of polymers. As represented in Fig. 2, the experimental observations of a sharp increase and then a gradual decrease in sediment volumes with incremental polymer dosing may be partly due to the densification and contraction of the voluminous flocs under gravity sedimentation.

Effect of Shear on Turbidity Removal

As already discussed, variables such as charge density of polyelectrolytes and surface charges of specific particles affect the choice of polymer for best flocculation performance. After the initial sets of constant-shear measurements including cylinder test, adsorption test, and electrophoretic mobility test on 30 g/L kaolin suspensions, a series of cationic polymers carrying incremental levels of charge density, denoted as Polymers (a)–(d), were chosen for further bench-scale flocculation tests under varying shear conditions. In this investigation the experimental results produced from a series of jar tests on 300 mg/L kaolin suspensions are reported by plotting the percentage of residual turbidity, measured after a certain time period of flocculation/sedimentation, as a function of polymer dose and mixing intensity (or velocity gradient, *G* value). As indicated in Figs. 5–8, the effectiveness of cationic polymers in terms of maximum turbidity removal or minimum residual turbidity appears to be more pronounced with increasing charge density and mixing intensity. Figure 5 shows that the effectiveness of nonionic Polymer (a) is improved significantly by increasing the *G* value from 100 to 200 1/s. Since the diffusion rate of high molecular weight polymer to the solid/liquid interface for adsorption is very low in a suspension, increasing the mixing intensity could increase the frequency of particle collisions required for polymer adsorption and floc formation, as evidenced by the shear-enhanced flocculation of nonionic Polymer (a) under a mixing intensity of 100–200 1/s. As the *G* value increases from 200 to 300 1/s, the effectiveness of nonionic Polymer (a) and the polymer dose requirement for maximum turbidity removal remain unchanged at 2.5 mg/g. This may reflect that the nonionic polymers adsorb and flocculate via an irreversible bridging mechanism and produce flocs that have good shear resistance within a wide range of mixing intensity 100–300 1/s.

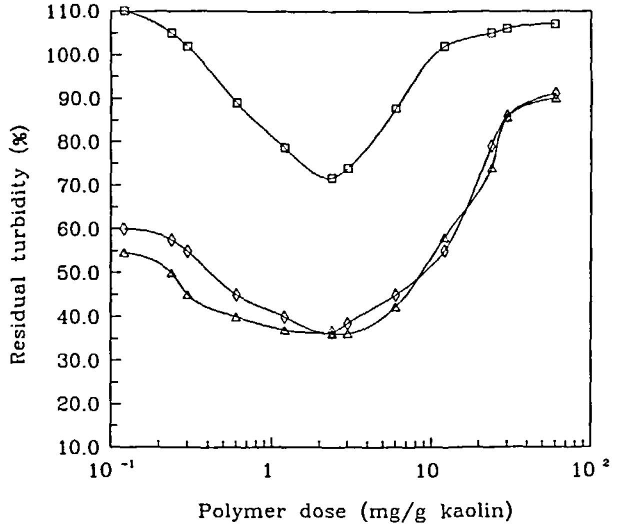

FIG. 5 Residual turbidity of 300 mg/L kaolin treated with Polymer (a) in 10^{-3} M NaCl solution vs polymer dose and mixing intensity. □, *G* value 100 1/s; △, *G* value 200 1/s; ◇, *G* value 300 1/s.

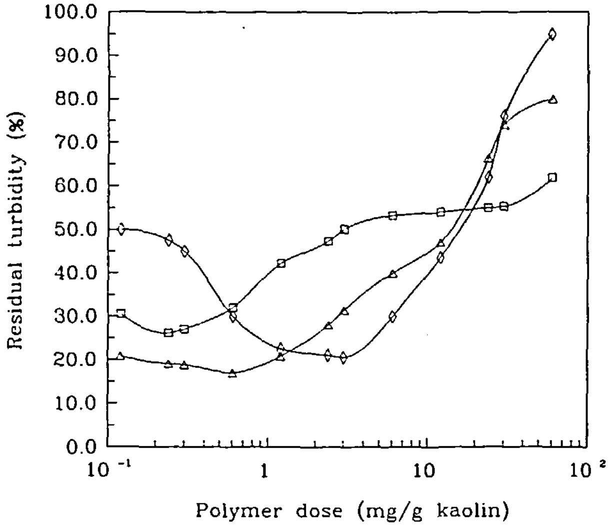

FIG. 6 Residual turbidity of 300 mg/L kaolin treated with Polymer (b) in 10^{-3} M NaCl solution vs polymer dose and mixing intensity. □, *G* value 100 1/s; △, *G* value 200 1/s; ◇, *G* value 300 1/s.

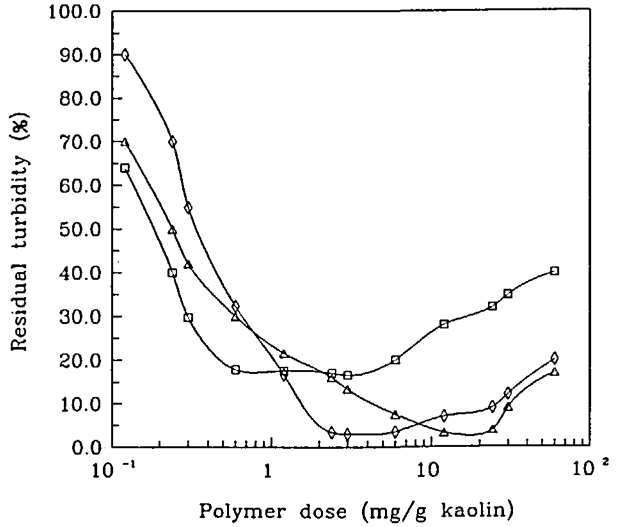

FIG. 7 Residual turbidity of 300 mg/L kaolin treated with Polymer (c) in 10^{-3} M NaCl solution vs polymer dose and mixing intensity. □, *G* value 100 1/s; △, *G* value 200 1/s; ◇, *G* value 300 1/s.

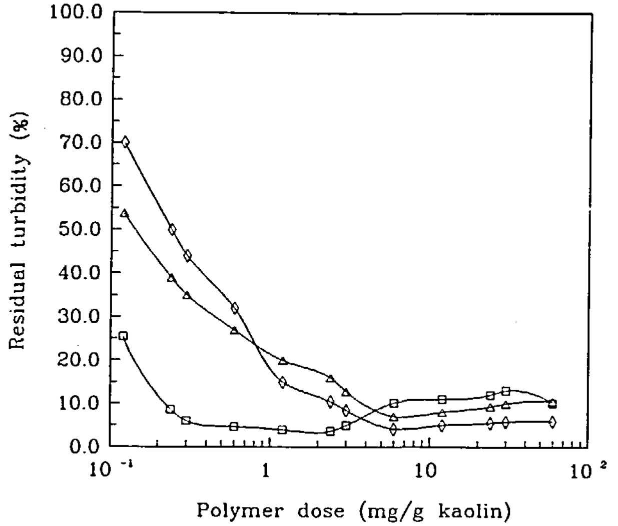

FIG. 8 Residual turbidity of 300 mg/L kaolin treated with Polymer (d) in 10^{-3} M NaCl solution vs polymer dose and mixing intensity. □, *G* value 100 1/s; △, *G* value 200 1/s; ◇, *G* value 300 1/s.

As reported by Otsubo (20), the shear-induced flocculation of silica suspensions is due to the irreversible adsorption of nonionic polyacrylamides under shear conditions because the polymer chain may attach to the surface at many points and not be able to desorb simultaneously from all sites. The presence of looser interparticle bridges gives a larger freedom of particle movement, and then more mechanical energy can dissipate within it. This therefore increases the shear resistance of flocs produced by such nonionic polymer bridging. On the other hand, it was also experimentally found that the region of optimum polymer doses for kaolin suspensions flocculated by cationic polymers are generally broader than those produced by nonionic polymers. Meanwhile, increasing the charge density of cationic polymers produces lower settled-residual turbidity but higher sensitivity for the shear field. This may be attributed to that polymer flocculation via a combined mechanism of polymer bridging and electrostatic patch attraction will result in rapid-forming nonequilibrium flocs consisting of very large interacting particulate units. In addition, charge repulsion between adjacent cationic groups of individual polymers will uncoil the bridging chain conformations between particles, as discussed earlier. This decreases their shear resistance compared with those produced by nonionic polymers. A high mixing intensity in the region of polymer underdosing will therefore accelerate floc destruction and conformational changes of adsorbed polymer chains from a train type to a loop type, eventually leading to the erosion of primary particles or small fragments not covered with polymers. Thus the capability of turbidity removal for cationic polymers with higher charge densities become poorer or require much higher polymer doses to overcome the effects of shear. As the region of optimum polymer doses is approached, it will take an optimized shear to achieve a complete charge neutralization and the desirable change in polymer conformations. As found experimentally, the polymer dose requirement for maximum turbidity removal at a constant *G* value of 300 1/s is within the 2.0–4.0 mg/g range for Polymers (b) and (c). This coincides with that required for zero zeta-potential or plateau adsorption, respectively. The experimental results in Fig. 8 show that the capability of turbidity removal for cationic Polymer (d) at polymer doses greater than 4.0 mg/g seems resistant to deterioration under a mixing intensity of 100–300 1/s. This may be due to shear-enhanced pelleting flocculation resulting from strong electrostatic patch attraction. According to the floc formation mechanism recently proposed by Langer et al. (13), the higher the charge density of a cationic polymer, the more stable are the flocs and the more energy required to destroy the floc structure. Especially when more polymer is dosed, the energy needed to deform and stretch the bridging bonds is higher. In spite of that, the flocculated systems produced by Polymer (d) at polymer doses less than 4.0 mg/g are still very sensitive to a mixing intensity of 100–300 1/s.

Rheological Considerations

As reported previously by Michaels and Bolger (21), flocculation of kaolin suspensions results in a significant changes in the bulk viscosity and rheological properties of the suspension. As described by Campbell and Crescuolo (22), sludge flocculated with a series of polyelectrolyte dosages exhibited many rheological characteristics including the plastic (or pseudoplastic) viscosity, the Bingham yield value, and the thixotropy, depending on the shape of the flow curve and the use of shear-rate versus shear-stress modeling equations. It is generally accepted that the flocs possess an elastic bridging structure which will deform and stretch at lower shear fields and gradually break down at higher shear fields. Also, displacement of the two shear curves produces a hysteresis loop during the ascending and descending shear cycle under a certain programmed time. The magnitude of the hysteresis area is referred to as the index of thixotropy, meaning that the degree of floc structure loss is a function of shear strength and time. As discussed earlier, the optimum polymer dose (OFC value) required for maximum turbidity removal or minimum residual turbidity of flocculated systems produced by cationic Polymers (b), (c), and (d) is found to increase appreciably with mixing intensity. This was thought to be closely related to the shear resistance of their floc structure. Based upon the experimental results confirmed by a variety of test methods, the investigation then narrowed to focus on Polymers (b) and (c). We hope that comparing the rheological behavior of two such flocculated systems might be helpful for verifying the bonding nature of floc structure as resulting either from electrostatic patch attraction or from polymer bridging mechanism. According to the floc rupture model of Hunter et al. (23), the Bingham yield value obtained from the extrapolated intercept at $G = 0$ is a measure of the excess dissipation energy needed to provide energy from the shear field to separate contacting flocs, and the plastic viscosity is obtained from the slope of the linear portion in flow curves. Then the model can be used here to explain the effects of polymer dose and temperature on the plastic viscosity, the Bingham yield value, and the thixotropy index. As shown in Figs. 9, 10, and 11, increases in viscosity, yield value, and thixotropy with initial increases in the adsorbed amount of polymer are due to bridging flocculation of particles. This agrees with the results by Otsubo and Umeya (24) who showed that bridging flocculation of silica particles in polyacrylamide solutions resulted in a sharp increase in viscosity. With further increases in the surface cover-

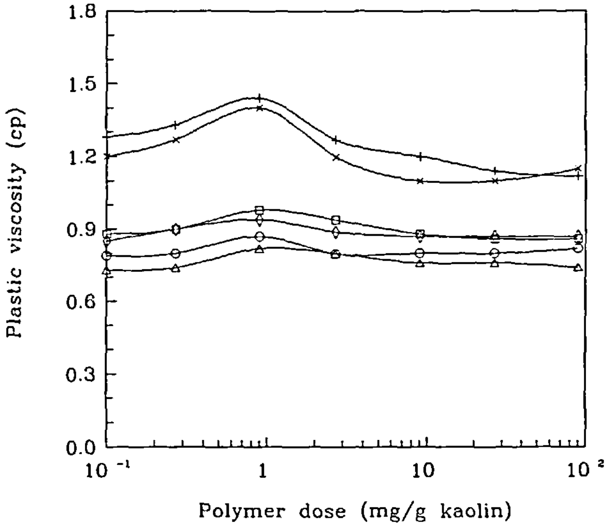

FIG. 9 Plastic viscosity of 300 mg/L kaolin treated with polymers in 10^{-3} M NaCl solution vs polymer dose and temperature. +, Polymer (b) at 15°C; ×, Polymer (c) at 15°C; □, Polymer (b) at 25°C; ◇, Polymer (c) at 25°C; ○, Polymer (b) at 30°C; △, Polymer (c) at 30°C.

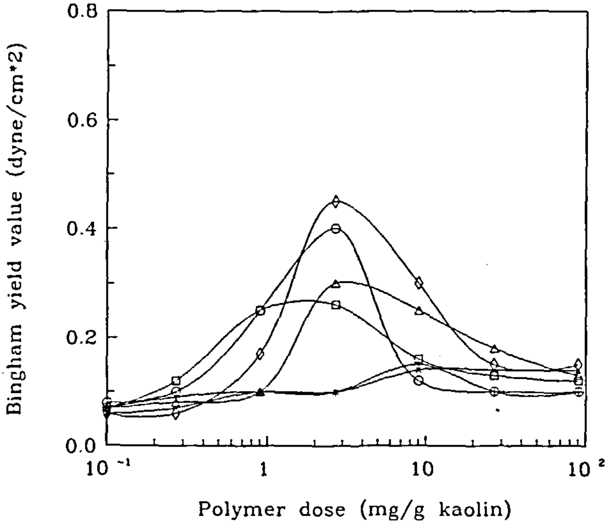

FIG. 10 Bingham yield value of 300 mg/L kaolin treated with polymers in 10^{-3} M NaCl solution vs polymer dose and temperature. +, Polymer (b) at 15°C; ×, Polymer (c) at 15°C; □, Polymer (b) at 25°C; ◇, Polymer (c) at 25°C; ○, Polymer (b) at 30°C; △, Polymer (c) at 30°C.

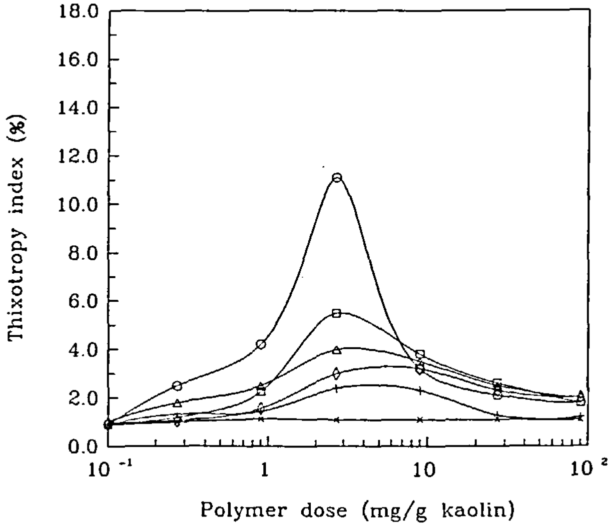

FIG. 11 Thixotropy index of 300 mg/L kaolin treated with polymers in 10^{-3} M NaCl solution vs polymer dose and temperature. +, Polymer (b) at 15°C; ×, Polymer (c) at 15°C; □, Polymer (b) at 25°C; ◇, Polymer (c) at 25°C; ○, Polymer (b) at 30°C; △, Polymer (c) at 30°C.

age, a sharp decrease in viscosity, yield value, and thixotropy indicates the improved deflocculation of suspensions. Also, its temperature dependence is of the normal type as indicated by the decrease in viscosity with increasing temperature in Fig. 9. The value of plastic viscosity of flocculated systems produced by Polymer (c) is lower than that produced by Polymer (b) at each temperature. This is attributed to the enhanced shear sensitivity of flocculated systems produced by polymers of higher charge density. We also observed that the maximum of yield value and thixotropy occur near zero zeta-potential, where the floc bonding rupture may contribute to a significant part of the energy dissipated. Hence, the temperature dependence of the thixotropic behavior of the two flocculated systems could provide a means of comparing the floc structures which had first been subjected to continuous shearing destruction with sonication for 0.5 minutes. Figures 10 and 11 show that both cationic Polymers (b) and (c) exhibit consistent peaks values at 2.0–4.0 mg/g, and the heights of the peaks are found to increase with temperature. We thought that increasing temperature might decrease the rate at which floc structure is rebuilt after being disrupted. It is noteworthy that the thixotropy index of the flocculated system produced by Polymer (c) is much lower than that produced by Polymer (b), as found experimentally. This may be due to the enhanced reflocculation capacity of the reversible broken floc structure produced by polymers of higher charge density. It also agrees with the results of Ditter et al. (25), who attributed the enhanced sensitivity for shear field and reflocculation capacity of reversible breakdown flocs produced by highly charged polyethylenimines to the predominance of electrostatic patch attraction over polymer bridging mechanism.

CONCLUSIONS

The importance of polymer charge density and shear conditions in the flocculation-sedimentation process of negatively charged kaolin suspensions was investigated to understand how it plays a role in determining the optimal flocculation conditions. The maximum rate of settling increases with charge density of cationic polyelectrolytes from a charge density of less than 1% up to a charge density of 30%. The very low settling rates produced by moderately high charged polymer (50% in cationicity) is attributed to conformational changes during the adsorption/flocculation process under shear. The polymer dosage required for plateau adsorption of polycations or complete neutralization of negative particle charge increases inversely proportionally to the charge density of the cationic polymer being used. The mixing intensity is found to affect the polymer dose requirements for best flocculation-sedimentation. Both cylinder tests and jar tests using low shear conditions tend to underestimate the polymer dose requirements for the orthokinetic flocculation process. The optimum polymer doses required for maximum turbidity removal or minimum residual turbidity under prolonged shear conditions coincide with those required for zero zeta-potential or plateau adsorption of polymer. An explanation proposed is that the transition from the nonequilibrium state to the equilibrium state of flocculation may increase the amount of polymers adsorbed on particles. It is suggested that both polymer bridging and charge neutralization mechanisms may operate in the adsorption/flocculation process. A supplementary investigation on the rheological characteristics of such flocculated systems was also conducted and revealed a qualitative relation between the shear resistance of floc structure and the polymer dose requirements. The higher shear sensitivity observed with a higher charge density polymer may be due to the predominance of electrostatic patch attraction over polymer bridging mechanism, thereby conferring a more or less constantly forming, breaking-down, reforming floc structure under conditions of shear stress and temperature. In order to better understand the interrelations between the dynamics of conformational change and the optimum surface coverage of polymers on particles quantitatively, much more investigation needs to be done.

ACKNOWLEDGMENT

The author is grateful to the National Science Council of the Republic of China for financial support.

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Received by editor March 28, 1997