Effect of the Structure of Cationic Polysulfone on the Flocculation of Kaolinite*

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Synopsis

The behavior of polycations as flocculants for kaolinite was examined by means of turbidity measurement, with the use of the following four kinds of cationic polysulfones, with molecular weights ranging from 14,000 to 330,000; diallyldimethylammonium chloride SO_2 copolymer [P(DADMAmCl–SO_2)], diallyldiethylammonium chloride–SO_2 copolymer [P(DADEAmCl–SO_2)], diallylmethylamine hydrochloride–SO_2 copolymer [P(DAMA–HCl–SO_2)], diallylamine hydrochloride–SO_2 copolymer [P(DAA–HCl–SO_2)]. The effect of the degree of polymerization on the flocculation was remarkable at low molecular weight range. The flocculation value, which is defined as the quantity of the polycation required to obtain 50% transparency at 660 mμ of the supernatant fluid of 2% kaolinite suspension, was inversely proportional to the degree of polymerization to the 0.734 power in the case of P(DADMAmCl–SO_2). This can be understood as the extension of Schulze-Hardy's law. The four different kinds of polysulfones having a similar molecular weight show almost the same capacity for flocculation in acidic or neutral solution. In alkaline solution, however, P(DAMA–HCl–SO_2) and P(DAA–HCl–SO_2) are less effective and have higher flocculation values than P(DADMAmCl–SO_2) and P(DADEAmCl–SO_2), which are classified as polyquaternary ammonium chlorides. Moreover the difference increases with increasing pH. This may be attributable to the difference of the dissociability of the polycation. The degree of dissociation of P(DAMA–HCl–SO_2) or P(DAA–HCl–SO_2) decreases with increasing pH and more additive is required to neutralize negative charges on kaolinite. On the other hand, P(DADMAmCl–SO_2) and P(DADEAmCl–SO_2) are almost completely dissociated and are good flocculants over a wide range of pH.

INTRODUCTION

Recently interest in the use of cationic polymers for flocculation of negatively charged solids dispersing in water has been increasing. The use of several cationic polymers for flocculation of a number of solids has been studied.[1,2] Dixon et al.[3] reported recently on the effect of the molecular weight of polyethyleneimine on the flocculation of crystalline silica. Polyethyleneimine prepared by usual polymerization methods is considered as a polymer of a secondary amine containing primary and tertiary amine units.

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In the present study, the effect of the chemical structure of cationic polymers and their molecular weight on the flocculation of kaolinite was investigated by means of turbidity measurements, using four kinds of cationic polysulfones, the syntheses of which were reported in previous papers[4-6] and which are classified as poly(secondary amine hydrochloride) [diallylamine hydrochloride–SO₂ copolymer], poly(tertiary amine hydrochloride) [diallylmethylamine hydrochloride–SO₂ copolymer], or poly(quaternary ammonium chloride) [diallyldimethylammonium chloride–SO₂ copolymer and diallyldiethylammonium chloride–SO₂ copolymer].

EXPERIMENTAL

Materials

Kaolinite (a commercial grade from Dantani Chemical and Mining Materials Company, Japan) was purified and converted to the hydrogen form by electrodialysis. The cation-exchange capacity calculated from the nitrogen content of the sample which had been treated with ammonium chloride was 2 meq/100 g.

Four kinds of polyaminesulfone prepared by the method described in the previous papers[4-6] were used.

P(DADMAmCl-SO₂)   P(DADEAmCl-SO₂)

P(DAMA-HCl-SO₂)   P(DAA-HCl-SO₂)
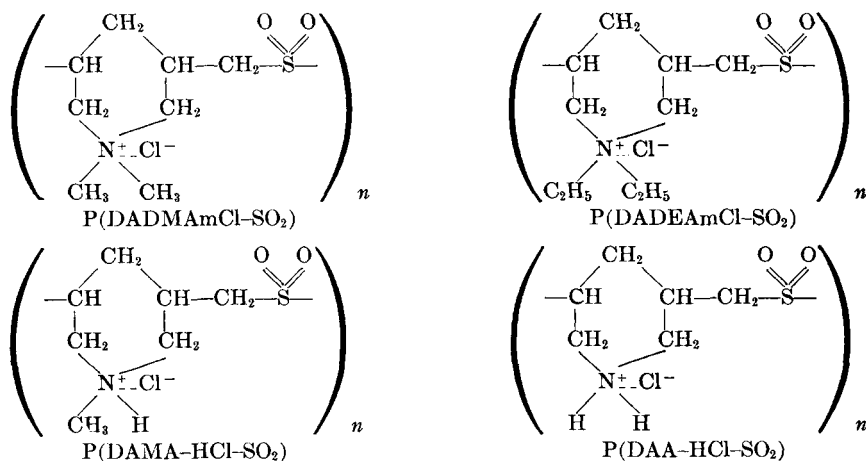
In Table I are summarized the polymerization conditions and the inherent viscosity of the polymers (ln η_{rel}/c) for 0.5 g of polymer/100 ml of 0.1N NaCl at 30°C.

P(DADMAmCl-SO₂) samples 1-1 to 1-6 were obtained by the fractionation of P(DADMAmCl-SO₂)-1 in the following manner. Three parts of P(DADMAmCl-SO₂)-1 was dissolved in 100 parts of a 2:3 mixture of water and methanol (v/v). To this solution, 6 parts of 35% hydrochloric acid was added as precipitant. Then by lowering the temperature over the range of 55–33°C, ten fractions were obtained.

The molecular weight of the fractionated samples was determined with the aid of a high-speed membrane osmometer in aqueous NaCl solution.[7]
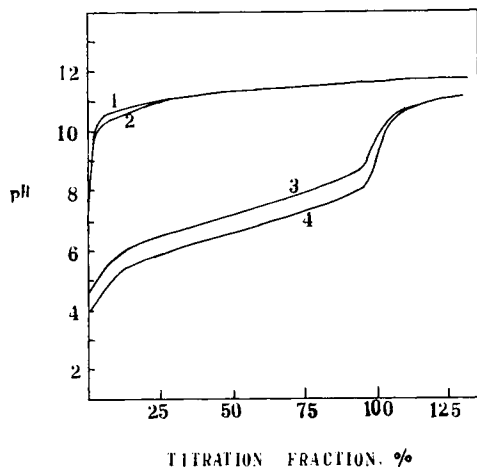
Fig. 1. Titration curve of polyaminesulfone by $0.1N$ NaOH at 30°C: (*1*) P(DADMAmCl–SO$_2$)-2, $4.76 \times 10^{-3}N$; (*2*) P(DADEAmCl–SO$_2$)-3, $4.91 \times 10^{-3}N$; (*3*) P(DAA-HCl-SO$_2$)-3, $4.68 \times 10^{-3}N$; (*4*) P(DAMA-HCl-SO$_2$)-2, $4.70 \times 10^{-3}N$.

The relation between the molecular weight of P(DADMAmCl–SO$_2$) and the limiting viscosity number or the inherent viscosity can, in the entire measured range, i.e., from $\bar{M}_n = 9.16 \times 10^4$ to $\bar{M}_n = 2.79 \times 10^5$, be represented by eq. (1):

$$[\eta] = 1.20 \times 10^{-5}\bar{M}_n^{0.99}$$

where $[\eta]$ is the limiting viscosity number in $0.1N$ NaCl at 30°C,

$$\eta_{\text{inh}} = 6.56 \times 10^{-5}\bar{M}_n^{0.827} \qquad (2)$$

where η_{inh} is the inherent viscosity for 0.5 g of polymer/100 ml of $0.1N$ NaCl at 30°C.

The polycations were titrated with $0.1N$ NaOH with Horiba-Hitachi, Model P pH meter under nitrogen at 30°C. The concentration was kept constant during the titration. The titration curve is shown in Figure 1.

Coagulation Test

The following example will illustrate the general procedure of the coagulation test. A 4-g portion of kaolinite was dispersed in 180 ml of distilled water and the pH was adjusted to the desired value. Polymer stock solution, either as 0.1% or 0.5% by weight, was diluted to 20 ml in water and added to the suspension of kaolinite during stirring. The pH was again adjusted to the same value as that of kaolinite suspension. After stirring for 5 min in the still and standing for 20 min, the supernatant fluid was pipetted out and transferred to a glass cell of 10 mm thickness, and the transmittance at 660 mμ was measured by a spectrophotometer (Shimazu QR 50).

Electrophoresis measurements were carried out at 30°C in a cylindrical electrophoresis cell with two platinum electrodes.[13]

TABLE I
Conditions of Polymerization and Inherent Viscosity of Polysulfones

| Polymer | Sample | Molar ratio of monomer SO_2:amine | Catalyst | | Solvent | Monomer concn, wt-% | Temp, °C | Time, hr | η_{inh}[b] | $\overline{DP}$[c] |
			Type[a]	Amt., mole-%						
P(DADMAmCl-SO$_2$)	1	4:5	APS	2	Methanol	50	20-30	93	1.98	1160
	2	1.4:1.5	tBHP	5	Methanol	20	5-14	2	0.51	224
	3	1:1	tBHP	1	Acetone–methanol (5/95 wt-%)	20	31-40	2	0.32	128
	4	1:1	APS	2	acetone	40	31-40	24	0.18	64
	1-1								2.36	1430
	1-2								1.88	1090
	1-3	obtained by fractionation of P(DADMAmCl-SO$_2$)-1							1.60	894
	1-4								1.31	702
	1-5								1.18	619
	1-6								0.76	363

Copolymer of diallyldiethylammonium chloride and SO_2

P(DADEAmCl–SO_2)	1	1:1	APS	2	Methanol	50	30	68	1.60
	2	1:1	APS	2	Acetone	50	30	90	0.76
	3	1:3	APS	2	DMSO	16	30	72	0.49

Copolymer of diallylmethylamine hydrochloride and SO_2

P(DAMA–HCl–SO_2)	1	1:1	APS	2	Methanol	50	30	50	0.90
	2	1:2	APS	2	DMSO	20	30	45	0.39
	3	1:1	APS	2	DMSO	21	30	45	0.16

Copolymer of diallylamine hydrochloride and SO_2

P(DAA–HCl–SO_2)	1	3:10	APS	1	DMSO	50	30	20	1.22
	2	1:2	APS	2	DMSO	50	30	20	0.63
	3	1:1	tBHP	2	Methanol	50	20–35	2	0.19

[a] APS = ammonium persulfate, tBHP = *tert*-butylhydroperoxide (purity abt. 60%).

[b] η_{inh} = inherent viscosity (ln η_{rel}/c) for 0.5 g of polymer/100 ml of 0.1N NaCl at 30°C.

[c] $\overline{DP}$ = degree of polymerization (number-average).

RESULTS AND DISCUSSION

Effect of Molecular Weight of Polycation

When P(DADMAmCl-SO₂) was added to kaolinite suspension, it flocculated and sedimented rapidly. In Figure 2 the amount of P(DADMAmCl-SO₂) added to the suspension is plotted against the transparency of the supernatant fluid. With increasing amounts of added polycation, the quantity of sediment increases and the transparency of the supernatant fluid become high. However it becomes turbid again by the further addition of the polymer. The amount of P(DADMAmCl-SO₂) for best flocculation of kaolinite is about $1/_{10}^4$ part relative to the clay.

It was observed by means of electrophoresis that the charge on kaolinite changed from negative to positive on addition of excess P(DADMAmCl-SO₂). This observation is in accord with the result for coagulation of other negatively charged colloids by polycations.[3,8,9]

By electrostatic interaction, P(DADMAmCl-SO₂) may be absorbed on the negatively charged kaolinite, neutralizing the charge of particles and consequently electrostatic repulsion. La Mer[10-12] emphasized the role of short-range hydrogen-bonding force in the case of nonionic or anionic polymer to cause polymer bridges to form between particles. In the case of the cationic polymer, in addition to hydrogen-bonding, ionic bonding might be responsible for polymer bridges between particles, on the assumption that polycation is adsorbed on negatively charged particles by ion exchange. The nature of adsorption of P(DADMAmCl-SO₂) on bentonite will be discussed in the next paper.

In Figure 3 the relations between the added amount of P(DADMAmCl-SO₂) of various molecular weights and the transparency of the supernatant fluid are shown. It is obvious that a polymer of high molecular weight is more effective than one of low molecular weight.

The same experiments were carried out with other polymers, i.e., P(DADEAmCl-SO₂), P(DAMA-HCl-SO₂), and P(DAA-HCl-SO₂), and
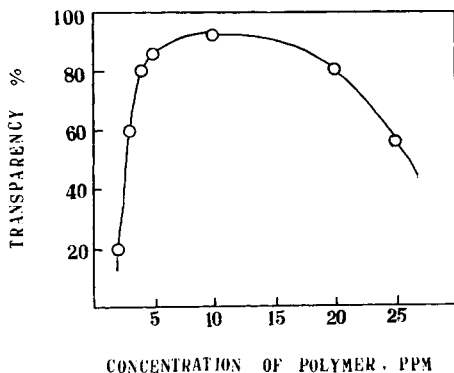

Fig. 2. Flocculation of kaolinite by P(DADMAmCl-SO₂)-1-4 ($\overline{DP}$ = 702) kaolinite concentration, 2%; pH 7.1.
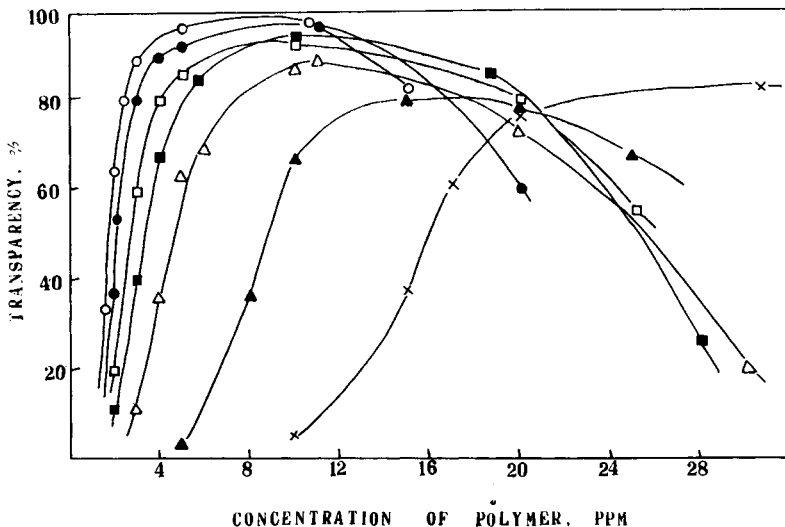
Fig. 3. Effect of molecular weight of P(DADMAmCl-SO₂) on flocculation of kaolinite: (O) P(DADMAmCl-SO₂)-1-1 ($\overline{DP}$ = 1430); (●) P(DADMAmCl-SO₂)-1-2 ($\overline{DP}$ = 1090); (□) P(DADMAmCl-SO₂)-1-4 ($\overline{DP}$ = 702); (■) (PDADMAmCl-SO₂)-1-5 ($\overline{DP}$ = 619); (△) P(DADMAmCl-SO₂)-1-6 ($\overline{DP}$ = 363); (▲) P(DADMAmCl-SO₂)-3 ($\overline{DP}$ = 128); (×) P(DADMAmCl-SO₂)-4 ($\overline{DP}$ = 64). Kaolinite concentration 2%; pH 7.1.
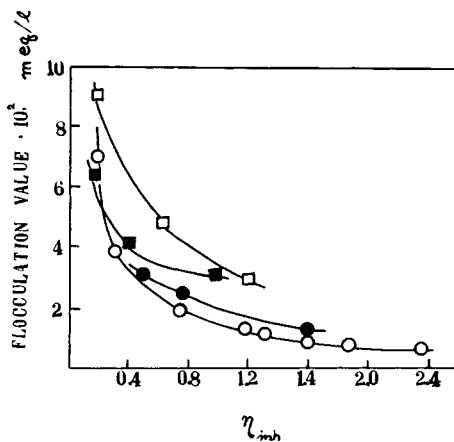

Fig. 4. Effect of molecular weight of polyaminesulfone on flocculation value: (O) P(DADMAmCl–SO₂); (●) P(DADEAmCl–SO₂); (□) P(DAA–HCl–SO₂); (■) P(DAMA–HCl–SO₂). Kaolinite concentration 2%; pH 7.1.

similar results were obtained. In Figure 4 the amount of polycation required to obtain 50% transparency of the supernatant fluid (this quantity is hereafter referred to as "flocculation value") is plotted against the inherent viscosity of the polymer in 0.1N NaCl. In any polymer the effect of molecular weight was marked. The flocculation value C (meq/l) of
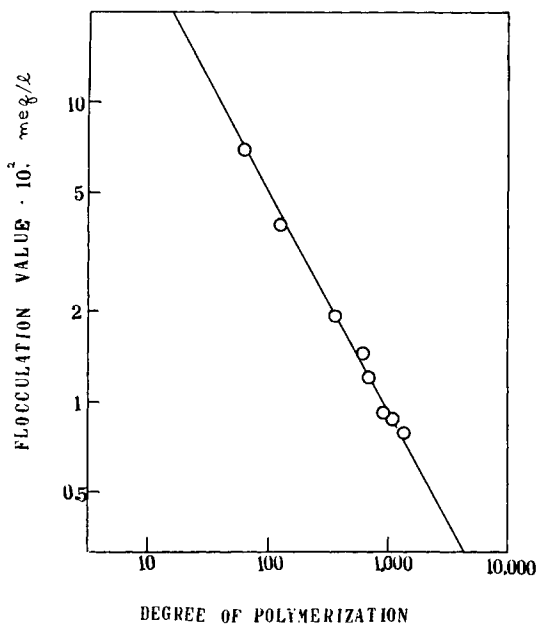
DEGREE OF POLYMERIZATION

Fig. 5. Relation between the degree of polymerization of P(DADMAmCl–SO₂) and flocculation value. Kaolinite concentration 2%; pH 7.1.

P(DADMAmCl–SO₂) was plotted against the degree of polymerization N, which is considered as the ionic value of the polymer, on a logarithmic scale. This plot in Figure 5 gives a straight line over a range of degree of polymerization of 64–1430 and from it the relation

$$C = k/N^{0.734} \qquad (3)$$

was obtained, where k is constant. The flocculation value decreases exponentially for the ionic value of the polymer. If the degree of polymerization of one polymer is 10 times that of another, the flocculation value of the latter is about 8.5 times that of the former. This might be understood as the extension of the Schultze-Hardy rule[13–16] for polymeric ions.

Effect of Basicity of Polycation

Kaolinite consists of alumina and silica and has a low but measurable cation-exchange capacity. It has been postulated that the ion exchange-ability of kaolinite is due to ionization of OH groups attached to the surface of alumina or silica.[17] The cation-exchange capacity of kaolinite depends on the pH of the environment in which kaolinite is suspended. It increases with the pH of the medium, since both alumina and silica behave as weak acids, the ionization of which is favored by the reduction of hydrogen ion concentration.

The relation between the pH of suspension and the flocculation value, defined above, was investigated (Fig. 6). Four kinds of polymer were used,
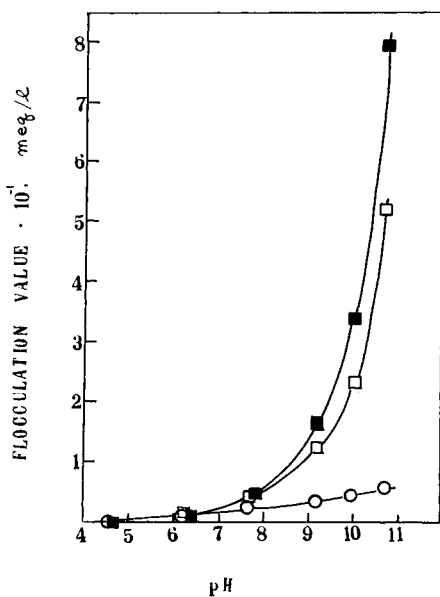
Fig. 6. Dependence of flocculation value of polyaminesulfone on pH of suspension: (O) P(DADMAmCl-SO₂), P(DADEAmCl-SO₂); (□) P(DAA-HCl-SO₂); (■) P(DAMA-HCl-SO₂).

i.e., P(DADMAmCl-SO₂)-2 (η_{inh} = 0.51), P(DADEAmCl-SO₂)-3 (η_{inh} = 0.49), P(DAMA-HCl-SO₂)-2 (η_{inh} = 0.39), and P(DAA-HCl-SO₂)-3 (η_{inh} = 0.63); all of these have similar degrees of polymerization. It is obvious that the amount of the polymer required to flocculate kaolinite increases with pH of the suspension. This is attributed to an increase in the degree of ionization of kaolinite, resulting in stabilization of the suspension. It should be noticed that in the acidic and neutral range each polymer has almost the same capacity for flocculation; however, in the alkaline range a larger amount of polymer is necessary to flocculate kaolinite in the case of P(DAMA–HCl-SO₂)-2 or P(DAA–HCl-SO₂)-3 than in the case of P(DAD-MAmCl-SO₂)-2 or P(DADEAmCl-SO₂)-3. Moreover the difference between the two groups increases with decreasing hydrogen ion concentration. Such difference is considered to come from properties such as the basicity of these polymers.

From the titration curve of Figure 1, the apparent degree of dissociation of the polymer α_p was calculated by eq. (4):

$$\alpha_p = [(a_{OH} - a_H)/c_p + [(c_A - c_K)/c_p] \tag{4}$$

where a_H, a_{OH} are activity of hydrogen ion and hydroxide ion, respectively; c_P, c_K, and c_A denote concentration of polymer, cations except H⁺, and anions except OH⁻, respectively.

In Figure 7 the degree of dissociation of polymer is plotted as function of Hp of the solution. It is obvious that P(DADMAmCl-SO₂) or P(DADEA-
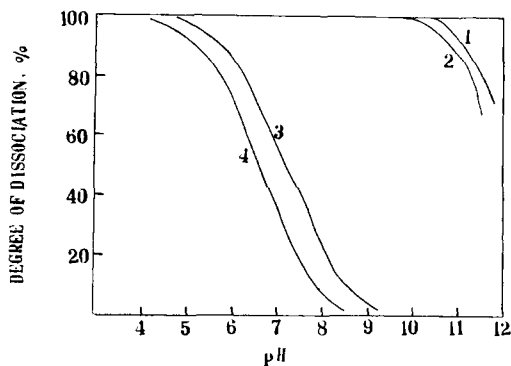
Fig. 7. Dependence of the degree of dissociation of polyaminesulfone on pH of solution at 30°C: (*1*) P(DADMAmCl–SO$_2$)-2, 4.76 × 10^{-3}N; (*2*) P(DADEAmCl–SO$_2$)-3, 4.91 × 10^{-3}N; (*3*) P(DAA–HCl–SO$_2$)-3, 4.68 × 10^{-3}N; (*4*) P(DAMA–HCl–SO$_2$)-2, 4.70 × 10^{-3}N.

mCl–SO$_2$), which is poly(quaternary ammonium salt), is almost completely dissociated over a wide range of pH. On the other hand, the degree of dissociation of P(DAMA–HCl–SO$_2$) and P(DAA–HCl–SO$_2$), which are the polymers of the salt of tertiary and secondary amine, respectively, decrease with the reduction of the hydrogen-ion concentration in solution. The order of basicity is considered P(DADMAmCl–SO$_2$) = P(DADEAmCl–SO$_2$) ≫ P(DAA–HCl–SO$_2$) > P(DAMA–HCl–SO$_2$).

It should be noticed that Figure 6 appears to correspond with Figure 7, i.e., at the same pH, the higher the degree of dissociation of polycation in solution, the smaller the flocculation value. P(DAA–HCl–SO$_2$) and P(DA-MA–HCl–SO$_2$) are not good flocculants in the alkaline range because of their low degree of dissociation; on the other hand P(DADMAmCl–SO$_2$) and P(DADEAmCl–SO$_2$) are excellent flocculants for kaolinite over a wide range of pH.

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