Adsorption of Cationic Polysulfone on Bentonite

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Synopsis

The adsorption of a polycation (diallyldimethylammonium chloride–SO₂ copolymer) on bentonite, a hydrophilic and negatively charged clay, was investigated. The cation-exchange capacity of bentonite decreased with the adsorption of polycation. From this fact it may be concluded that the adsorption of the polycation on bentonite proceeds in a cation-exchange manner. Bentonite came to have some anion-exchange capacity as a result of adsorption of the polycation. This may be attributed to the existence of the parts in the polymer chain which do not take part in the combination with bentonite. The anion-exchange capacity increased and the complex became somewhat hydrophilic if a simple salt such as sodium chloride was added to bentonite with the polycation. The polymer was not desorbed from the complex by treatment with NaCl or CaCl₂. The adsorption reaction of the polymer on bentonite may be considered to be irreversible.

INTRODUCTION

Interaction between hydrophilic colloids with opposite signs of charge has been studied extensively in recent years. Mutual coagulation of cationic and anionic polyelectrolyte was investigated by Deuel,[1] Fuoss,[2] and Michaels.[3,4] Interactions between protein and polyelectrolyte,[5] protein and nucleic acid,[6,7] and protein and detergent[8] were also studied.

In the preceding paper[9] the flocculation of kaolinite, which is rather hydrophobic and negatively charged, by the cationic polyelectrolyte was reported. In this paper, the mechanism of adsorption of a polycation (copolymer of diallyldimethylammonium chloride and SO₂) on bentonite, which is a fairly hydrophilic clay with a negative charge, is discussed quantitatively, and the properties of the adsorption product are investigated.

EXPERIMENTAL

Materials

The bentonite was a commercial grade from Teikoku Bentonite Company (Tokyo) and had a SiO_2/Al_2O_3 ratio of 5.57.[10] It was dispersed in distilled water, and after a week sedimented material was removed. It was then converted to the sodium form by passing a 1% suspension at 70°C through

an ion-exchange column containing Amberlite IR 120 in the sodium form. The cation exchange capacity of the bentonite was 62.4 meq/100 g.

The polycation used in this experiment was the copolymer of diallyldimethylammonium chloride and sulfur dioxide, P(DADMAmCl-SO₂) which was described in detail in a previous paper.[11] Polymers of molecular weight 167,000 (copolymer I) and 14,000 (copolymer II) were employed. The conditions of polymerization are shown in Table I.

TABLE I
Conditions of Polymerization

	Solvent	Molar ratio amine:SO_2	Monomer concn., wt-%	Catalyst (ammonium persulfate) concn., mole-%	Temperature, °C
Copolymer I	Dimethyl sulfoxide	1.08:1	30	0.89	30
Copolymer II	Acetone	1:1	40	2.0	30

Adsorption Experiment

The adsorption experiment was carried out at 30°C as follows. A 6-g portion of bentonite was dispersed in 300 ml of distilled water. Polymer stock solution, either 2 or 4% by weight, was diluted to 100 ml and added to suspension with stirring. After the addition, stirring was continued for 30 min. Then the sediment was filtered, washed sufficiently with water, and dried at 70°C. The amount of the polymer adsorbed on bentonite was calculated from the nitrogen content of the sample, as measured by the Kjeldahl method. The values of three measurements were averaged.

Ion-Exchange Capacity

The cation- and anion-exchange capacity of bentonite which adsorbed the polycation was measured twice as follows and the average was taken.

Cation-Exchange Capacity. Exchangeable cation in a sample was converted to nickel form by passing 1N NiCl₂ solution through the column containing sample. After it was washed sufficiently with water, the nickel ion was eluted from the column by passing through 1N KNO₃ solution. The amount of the nickel ion in solution was determined quantitatively by the dimethylglyoxime method,[12] and from it the cation-exchange capacity of the sample was calculated.

Anion-Exchange Capacity. Exchangeable anion in a sample was converted to chloride form by passing 1N NaCl solution through the column containing the sample. After it was washed sufficiently with water, chloride ion was eluted from the column by passing through 1N KNO₃ solution. The amount of chloride ion in the solution was determined

quantitatively by the Mohr method,[13] and from it the anion-exchange capacity of the sample was calculated.

RESULTS AND DISCUSSION

As is well known, a bentonite is a hydrophilic, negatively charged clay, and its suspension in water is very stable.   When a few per cent of P(DA-DMAmCl–SO$_2$) was added to this suspension, the bentonite coagulated rapidly and sedimented.   The quantity of copolymer I adsorbed on the bentonite was constant and independent of the mixing time, which indicates that the adsorption of copolymer I on the bentonite has occurred rapidly.

In Table II the relation between the amount of the added and adsorbed copolymer I is given.   As the amount added is increased, the copolymer adsorbed is increased.

TABLE II

Adsorption of Copolymer I on Bentonite at 30°C and Ion-Exchange Capacity of Bentonite–Copolymer I Complex[a]

Amount of added copolymer I, g/100 g	Amount of copolymer I adsorbed on bentonite A		Cation-exchange capacity B, meq/100 g	Anion-exchange capacity C, meq/100 g	Amount of copolymer I actually adsorbed D, meq/100 g[b]	B + D meq/100 g
	g/100 g	meq/100 g				
0	0	0	62.4	0	0	62.4
2.67	1.93	8.56	49.5	0	8.56	58.1
5.33	4.18	18.5	44.6	0	18.5	63.1
10.0	7.57	33.6	30.7	0.97	32.6	63.3
13.3	9.18	40.7	24.5	3.85	36.8	61.3
20.0	9.82	43.5	23.9	5.34	38.2	62.1
26.7	10.8	47.9	21.4	6.68	41.2	62.6
33.3	10.5	46.6	23.7	6.37	40.2	63.9
43.3	13.0	57.7	15.8	13.2	44.5	60.3
56.7	13.2	58.5	14.4	15.1	43.4	57.8
73.3	14.2	63.0	12.8	15.5	47.5	60.3
93.3	14.5	64.3	11.1	18.2	46.1	57.2

[a] Concentration of bentonite in suspension: 1.5%.
[b] $D = A - C$.

In the third column of Table II, values of the cation-exchange capacity of the formed bentonite–copolymer I complex are given.   The capacity decreased as the quantity of adsorbed copolymer I increased.   This fact suggests that the adsorption of copolymer I on bentonite take place by an ion-exchange mechanism as follows:

$$R^-Na^+ + P^+Cl^- \rightleftharpoons R^-P^+ + Na^+Cl^- \tag{1}$$

where R^-Na^+ and P^+Cl^- denote bentonite and copolymer I, respectively.

Copolymer I may combine with anionic sites of the bentonite to form bridges over some bentonite particles, and the latter may lose electric charge and be coagulated.

The untreated bentonite has no detectable anion-exchange capacity. It is interesting to verify whether the bentonite–copolymer I complex shows anion-exchange properties. In the fourth column of Table II, results of measurements of the anion-exchange capacity of the complex are given. When the amount of copolymer I adsorbed on the bentonite is small, the complex has no anion exchangeability. With increasing amount of adsorbed copolymer I, however, the capacity of the complex increases to some extent. The capacity of the complex for anion-exchange may be attributed to the existence of portions of the polymer chain which do not take part in combination with bentonite, i.e., crosslinks and isolating parts.

Therefore the quantity which is obtained by subtracting such anion-exchange capacity (C) of the complex from the amount of copolymer I adsorbed on bentonite (A) is regarded as the actual quantity D of copolymer I adsorbed (fifth column of Table II).

As mentioned above, if the adsorption reaction proceeds according to an ion-exchange mechanism, the sum of the quantity of truly adsorbed copolymer I D and the cation-exchange capacity of the complex B must be constant and equivalent to the cation-exchange capacity of the bentonite, say, 62.4 meq/100 g. The values of ($B + D$) in Table II are all practically the same. Thus it may be concluded that the adsorption of copolymer I to bentonite proceeds by an ion-exchange mechanism. It should, moreover, be noted that the bentonite–copolymer I complex has a dual ion exchangeability.

A similar adsorption experiment was carried out with copolymer II, which had a degree of polymerization of 64 (Table III). For the same

TABLE III
Adsorption of Copolymer II on Bentonite at 30°C and Ion-Exchange
Capacity of Bentonite–Copolymer II Complex[a]

Amount of added copolymer II, g/100 g	Amount of copolymer II adsorbed on bentonite A		Anion-exchange capacity B, meq/100 g	Amount of adsorbed copolymer II actually C, meq/100 g[b]	Cation-exchange capacity (calcd). D meq/100 g[c]
	g/100 g	meq/100 g			
0	0	0	0	0	62.4
2.67	2.71	12.0	0	12.0	50.4
5.33	5.44	24.1	0	24.1	38.3
10.0	9.18	40.7	0	40.7	21.7
13.3	11.8	52.3	2.34	50.0	12.4
20.0	14.5	64.2	6.15	58.0	4.4
25.0	14.7	65.1	6.15	58.9	3.5

[a] Concentration of bentonite in suspension: 1.5%.
[b] $C = A - B$.
[c] $D = 62.4 - C$.

quantity of added polymer, the amount of copolymer II adsorbed was more than that of copolymer I which had higher degree of polymerization (DP = 790). The anion-exchange capacity of the bentonite–copolymer II complex was nearly the same as that of the bentonite–copolymer I complex; consequently the cation-exchange capacity of the former was less than that of the latter.

In eq. (1), the adsorption reaction is that proceeding from left to right, and the reverse reaction is desorption. An experiment was carried out to determine whether copolymer I is indeed desorbed from the bentonite–copolymer I complex on adding a simple salt such as sodium chloride or calcium chloride. The complex was immersed in an aqueous solution of sodium chloride (or calcium chloride) and left for one day with stirring. Then the content of copolymer I in the complex after the treatment was compared with that in the original sample. From the measurement it was found that no desorption of copolymer I occurred on treatment with a solution of sodium chloride or calcium chloride, even with $3N$ $CaCl_2$ solution, as well as with dilute solution.

In addition, the effect of sodium chloride on the adsorption of copolymer I to bentonite was examined. The amount of copolymer I adsorbed on bentonite in the presence of NaCl was determined (Table IV). As is shown in Table IV, on addition of NaCl, the amount of copolymer I adsorbed on bentonite is increased rather than decreased, and this is accompanied by an increase in the anion-exchange capacity of the complex. The bentonite–copolymer I complex is more hydrophobic than the bentonite itself, but the complex prepared in the presence of NaCl is fairly hydrophilic and difficult to handle because of its pasty nature. This tendency increases with increasing anion-exchange capacity, which results from the adsorption

TABLE IV
Effect of Sodium Chloride on Adsorption of Copolymer I to
Bentonite at 30°C[a]

NaCl concn, N	Amount of adsorbed copolymer I, A		Anion-exchange capacity B, meq/100 g	Amount of copolymer I actually adsorbed C, meq/100 g[b]	Cation-exchange capacity (calcd) D, meq/100 g[c]
	g/100 g	meq/100 g			
0	9.66	42.8	5.03	37.8	24.6
0.02	11.4	50.4	13.3	37.1	25.3
0.05	12.2	54.1	17.7	36.4	26.0
0.15	13.5	59.8	21.8	38.0	24.4
0.5	13.5	59.8	23.0	36.8	25.6
1.25	13.4	59.5	21.4	34.4	28.0

[a] Concentration of bentonite in suspension: 1.5%; amount of added copolymer I: 20.8 g/100 g bentonite.
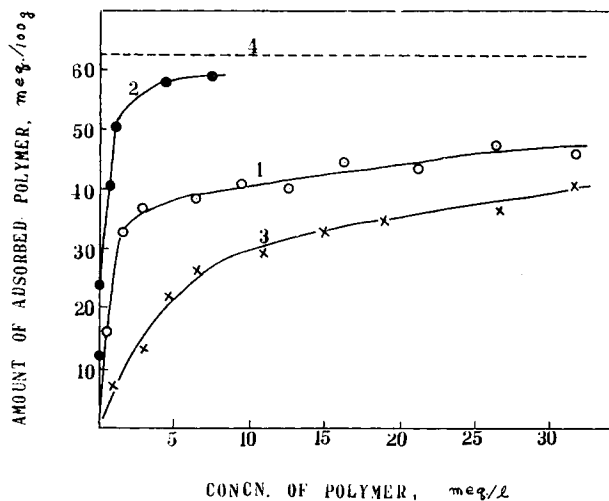[b] $C = A - B$.
[c] $D = 62.4 - C$.

Fig. 1. Adsorption isotherms for P(DADMAmCl-SO₂) and ammonium acetate on bentonite at 30°C: (O) copolymer I, $\overline{DP}$ = 791; (●) copolymer II, $\overline{DP}$ = 67; (×) ammonium acetate.

of copolymer I.   The increase of the amount of copolymer I adsorbed on bentonite by the addition of NaCl may be explained as follows reason. The polymer chain of copolymer I in a sodium chloride solution exists in a coiled configuration and is adsorbed on the bentonite surface with retention of this configuration.   Therefore cationic sites inside the polymer coil can not combine effectively with anionic sites of bentonite, with the result that the amount of apparent adsorption of copolymer I increases.

The amount of copolymer I actually adsorbed on bentonite and the cation-exchange capacity of the complex are given in the last two columns of Table IV.   It should be noticed that they are constant and independent of the concentration of NaCl in solution.   It will be concluded that in eq. (1) the reaction proceeds from left to right exclusively.

Figure 1 shows the adsorption isotherm of P(DADMAmCl-SO₂) on bentonite at 30°C.   The amount of the copolymer adsorbed on bentonite was plotted against the concentration of the copolymer in solution.   Curves 1 and 2 are the adsorption isotherms for copolymers I and II, respectively. Curve 3, for reference, is the isotherm for ammonium acetate, in which ammonium ion is considered to be adsorbed to bentonite reversibly.   Curve 4 shows the ideal case in which the added material is completely adsorbed on bentonite.

Curve 2 for copolymer II, which has a comparatively low molecular weight, is close to curve 4 for the complete adsorption.   On the other hand, curve 1 for copolymer I, which has a high molecular weight, lies between the curves for complete adsorption and reversible adsorption (ammonium acetate).   This might mean that there exist in bentonite anionic sites into which polymer molecule of a high molecular weight can not enter because of

steric hindrance.   Results of x-ray examination of this problem will be presented in a future paper.

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