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INTERACTIONS OF POLYCATIONS OF ALUMINUM AND IRON WITH CLAYS

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Abstract—Polycations of limited molecular size were prepared from 0.1 M solutions of $Fe(III)(NO_3)_3$ and $Al(NO_3)_3$ by ultrafiltration. Various amounts of the polycations were added to Na-kaolinite, Na-montmorillonite, and a Na-soil clay and the effect on the flocculation of the clay and electrophoretic mobility compared. Flocculation occurred just before zero net charge was obtained. Addition of further polycation resulted in the dispersion of clay with a net positive charge. The Al polycations possessed a high positive charge (0.49 per gram atom of Al), and their interaction with the clays indicated a planar shape. Adsorption of Al polycations decreased markedly the cation-exchange capacities of the kaolinite and the soil clay but had little effect on surface areas determined by low-temperature N_2 adsorption. The Fe polycations were spheres 10–100 Å in diameter with a positive charge of 0.2 per gram atom. The surface areas of the kaolinite and the soil clay were substantially increased by the addition of the Fe polycations but their cation-exchange capacities were reduced by one fifth. Al polycations increased the surface areas of the montmorillonite (to 300 m^2) presumably by propping open the interlamellar spaces and rendering the a-b planes accessible for nitrogen adsorption. The Al polycations in interlamellar spaces prevented collapse to 14 Å on heating to 150°C. There was no evidence of regular interlayer Fe as might be anticipated from the size of the spheres.

Key Words—Aluminum, Electrophoresis, Intercalation, Iron, Kaolinite, Montmorillonite, Polycations, Surface charge.

INTRODUCTION

Studies of the interaction of aluminum and iron hydroxides and oxyhydroxides with clays have shown that when several percent of oxide is added to the clay, the surface properties of the clay are dominated by the oxides. The interactions, however, are always complex because of the tendency of Al and Fe species to hydrolyze, polymerize, and eventually precipitate in the presence of the clays unless low pH is maintained. The amount of polycation required to produce charge reversal is small. The purpose of the present paper is to describe the manipulation of positive charges on clays by polycations of limited molecular size in order to study the influence of net charge on the physical properties of the colloids.

POLYCATIONS OF Fe(III) AND Al

The hydrolysis of Fe(III) is a complex process, and the sequence of events which leads to the precipitation of a recognizable mineral is sensitive to minor changes in Fe(III) and ionic concentration, temperature, the nature of anions present, time, pH, and how the pH is changed (Sylva, 1972; Baes and Mesmer, 1976). In the absence of anions which complex Fe(III), polynuclear complexes are produced which possess positive charges countered by the anion present, e.g., nitrate (Dousma and de Bruyn, 1976; Murphy *et al.*, 1976a; Rengasamy and Oades, 1977a).

Earlier workers proposed formulae for the polycations that suggested discrete molecular species. Dousma and de Bruyn (1976) classified the polymers as large or small and proposed that the larger polymers contained Fe–O–Fe linkages which rendered them more acid-stable than smaller polymers which were produced at lower pH at the same Fe(III) concentration. Gel filtration and ultrafiltration have shown that the products of hydrolysis of ferric nitrate solutions may be polydispersed (Murphy *et al.*, 1975; Rengasamy and Oades, 1977a). Electron microscopy has also indicated that the polycations are spherical and range from 10 to 100 Å in diameter. Depending on conditions, the hydrolysis products may age to ferrihydrite, goethite, hematite, and even lepidocrocite or to mixtures of these minerals (Schwertmann and Taylor, 1977).

There is convincing evidence that mononuclear Al species exist in dilute solution (Baes and Mesmer, 1976; Bottero *et al.*, 1980). A range of polymeric Al species has been proposed, but rather than a complete polydispersed system it appears that smaller polymers with less than about 15 Al atoms may exist up to an OH/Al ratio of about 2, depending on electrolyte concentration. At higher OH/Al ratios the polymers rapidly condense to produce a precipitate which ages quickly to gibbsite (Rengasamy and Oades, 1978; Stol *et al.*, 1976).

For the present study of the sorption of polycations on clay surfaces polycations with molecular weights, based on filtration techniques, from about 10,000 to 100,000 were used (Rengasamy and Oades, 1977b, 1978; Kavanagh and Quirk, 1978).

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METHODS

Preparation of Fe(III) polycations

It was difficult to obtain polycations with the same molecular weight distributions from different volumes of $Fe(NO_3)_3$ because the volume used influenced the time taken for various procedures. Because the system does not reach equilibrium, it was necessary to sample at definite times after the addition of NaOH in a standard manner. The relaxation of pH as described by Dousma and de Bruyn (1976) was observed, but the pH became almost constant 2 days after addition of NaOH.

The procedure adopted for the production of polycations involved storage for 2 to 4 days at 20°C after the base had been added and before ultrafiltration. To 100 cm^3 of 0.1 M $Fe(NO_3)_3$ (BDH Analar), 1.0 M NaOH was added using an automatic burette and stirrer assembly associated with a Titrigraph pH meter. The time taken to achieve the final pH desired ranged from 15 min (pH 1.7) to 2 hr (pH 2.2). Any precipitate formed was allowed to dissolve before further NaOH was added. Solutions were stirred for 1 hr and remained at 20°C for 2 to 4 days before ultrafiltration.

Larger volumes (500 cm^3) of 0.1 M $Fe(NO_3)_3$ were treated similarly, using a 100-cm^3 beaker and vigorous mechanical stirring. Four days after the addition of the NaOH the sample (500 cm^3) was placed on an Amicon filter XM50 and washed through until the eluant was free from iron. The filtrate and washings were filtered on a PM10 filter to obtain the fraction 10,000 to 50,000 nominal molecular weight.

Preparation of Al polycations

One molar NaOH was added to 0.1 M $Al(NO_3)_3$ as described for the Fe system. The pH values obtained ranged from 3.4 to 5.8. The procedure adopted for the preparation of Al polycations with nominal molecular weights 10,000 to 100,000 was to add 134 cm^3 of 1 M NaOH to 500 cm^3 of 0.1 M $Al(NO_3)_3$ over a 4-hr period. The pH of the solutions after NaOH addition ranged from 5.15 to 5.31 and fell to 4.8 during 14 days at room temperature (~20°C). Four days after the addition of the NaOH, the sample (400 cm^3) was placed on an Amicon filter XM100 and washed through until the eluent was free from Al. The filtrate and washings were refractionated on a PM10 filter to obtain the fraction 10,000 to 100,000 nominal molecular weight.

Charge on polycations

The residual nitrate associated with filtered preparations of polycations was assumed to counter positive charges on the polycations. The nitrate was reduced and determined as ammonium after steam distillation. Samples of the polycation preparations were dialyzed against distilled water and the nitrate determined again to check that the nitrate was associated with the polymers and not present as acid or salt.

Clays

Three clays were used; (1) montmorillonite, Wyoming bentonite from John Lane Tract, Upton, Wyoming; (2) kaolinite, Blackpool kaolinite from English Clays, Lovering, U.K.; and (3) a soil clay obtained from the 0–10 cm layer of a red-brown earth at the Waite Institute, Adelaide, South Australia. The clay fraction of the soil contained kaolinite, illite, and some randomly interstratified material. All samples were Na-saturated and the <2-μm fractions separated. The Na-saturated clays were washed with distilled water until they began to disperse and were stored in suspension in the presence of NaCl. No attempt was made to 'clean' the surface of the clays. Samples of the suspension were dialyzed against distilled water until the conductivity of the suspension was similar to distilled water. The 'salt free' clays were used for sorption of polycations.

Cation-exchange capacity of clays

A weighed amount of clay was spread evenly on a ceramic disc under suction. The clay was washed 3 times with 1 M $BaCl_2$ and then washed with distilled water until free from chloride. The Ba remaining in the clay was determined by X-ray fluorescence spectrometry.

Flocculation of the clays

Polycation solution was added to 10 cm^3 of dialyzed clay suspension (1 g/100 cm^3) in a graduated cylinder and the volume made up to 20 cm^3 using distilled water before shaking for 30 sec. According to Stokes' law all particles >2 μm equivalent spherical diameter would settle out of the top 12 cm^3 of liquid in the cylinders in 24 hr. Optical densities at 615 nm were plotted against a range of concentrations of each of the three clays suspended in water and shaken. Using these standard graphs the dispersed clay which remained in the top 12 cm^3 of liquid after 24 hr was estimated by spectrophotometry. The critical coagulation concentration (CCC) expressed as the amount of Fe(III) or Al required to flocculate the suspension so that no clay remained in the top 12 cm^3 of suspension after 24 hr was determined (Rengasamy and Oades, 1977b). Various quantities of polycation less than and more than the CCC were added to the clay suspensions and dispersed clay plotted against amount of polycation added.

Electrophoretic mobilities

Electrophoretic mobilities of the clays, with and without adsorbed polycations, in 0.01 M $NaNO_3$ were determined using a Rank Brothers Particle Microelectrophoresis Apparatus Mark II.

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Table 1. Fe(III) in molecular weight fractions of Fe(III) polycations in 0.1 M $Fe(NO_3)_3$ as a function of pH.

	Fe(III) content[1] Nominal molecular weight range			
pH	<10,000 (%)	10,000–100,000 (%)	100,000–300,000 (%)	>300,000 (%)
1.7	92.2 (3.0)	4.7 (2.6)	0.9 (2.7)	2.3 (1.9)
1.8	86.1 (3.0)	2.0 (2.4)	1.1 (1.7)	10.8 (1.6)
1.9	82.4 (3.3)	12.8 (0.5)	2.8 (0.7)	2.0 (0.1)
2.0	70.7 (3.5)	20.4 (0.3)	1.7 (0.2)	7.3 (0.2)
2.1	43.7 (6.4)	26.0 (0.4)	4.9 (0.2)	25.4 (0.1)
2.2	29.3 (9.1)	20.2 (0.3)	22.2 (0.1)	28.2 (0.1)

[1] Values in brackets represent nitrate expressed per gram atom of Fe(III).

Surface area

Specific surface areas of the Na-clays before and after sorption of polycations were determined using low-temperature adsorption of nitrogen and applying the equation of Brunauer *et al.* (1938). Samples were evacuated at 70°C before the adsorption of nitrogen. The montmorillonite + Al polycations had to be outgassed for one week at 70°C before all the water vapor was removed.

Water uptake

About 200 mg of clay was pressed into a pellet 10 mm in diameter using a pressure of about 500 MPa. The pellets used for the determination of surface area were those used to determine water uptake and swelling characteristics as influenced by the sorption of the polycations. The water contents and the diameters of the pellets were determined after equilibration at 96% and 98% RH, i.e., −80 and −50 MPa, and at −0.1 kPa on a sintered glass funnel. The diameter of the pellets was measured to enable calculation of swelling; unfortunately the swelling of montmorillonite was not isotropic so the data are not presented.

X-ray powder diffraction (XRD)

Suspensions of clay were dried on ceramic tiles and diffractograms obtained using CoKα radiation analyzed with a goniometer fitted with a graphite post-diffraction monochromator. Samples were also examined at about 150°C on a small electrically heated stage.

RESULTS AND DISCUSSION

Preparation of Fe(III) polycations

The choice of a molecular weight range of 10,000–50,000 was based on electron microscopy, XRD, and infrared (IR) studies of polycations fractionated by ultrafiltration. Polycation fractions of molecular weight <10,000 gave no XRD pattern of ferrihydrite or goethite when they were examined immediately after separation. During electron microscopy of such fractions, focusing was difficult. In most samples, very small particles (10 Å) were evident but the electron micrographs usually exhibited electron-dense 'clumps' and 'holes' associated with shrinkage of gel-like materials in the vacuum under the electron beam. The higher polymers were more obviously spherical as seen in the electron microscope, but above a nominal molecular weight of 50,000 the rods and rafts described in detail by Murphy *et al.* (1976b) were evident. When rods were distinguishable in electron micrographs, an XRD pattern of goethite was obtained with spacings at 4.98, 4.18, 2.69,

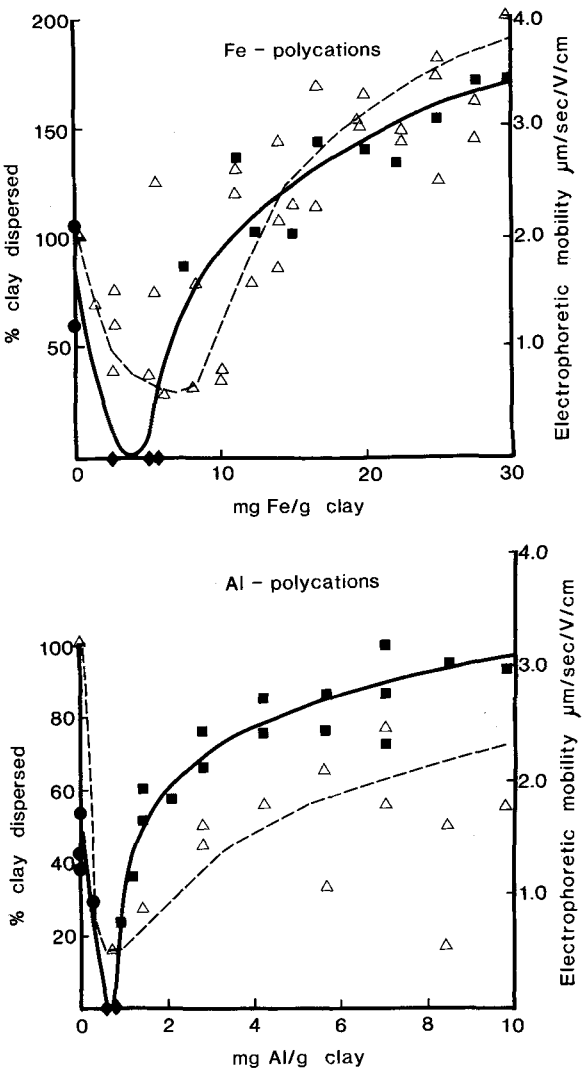


Figure 1. Influence of Fe and Al polycations on the dispersion and electrophoretic mobility (μ) of kaolinite. ● = negative and ■ = positive electrophoretic mobilities. △ = percent age of clay dispersed.

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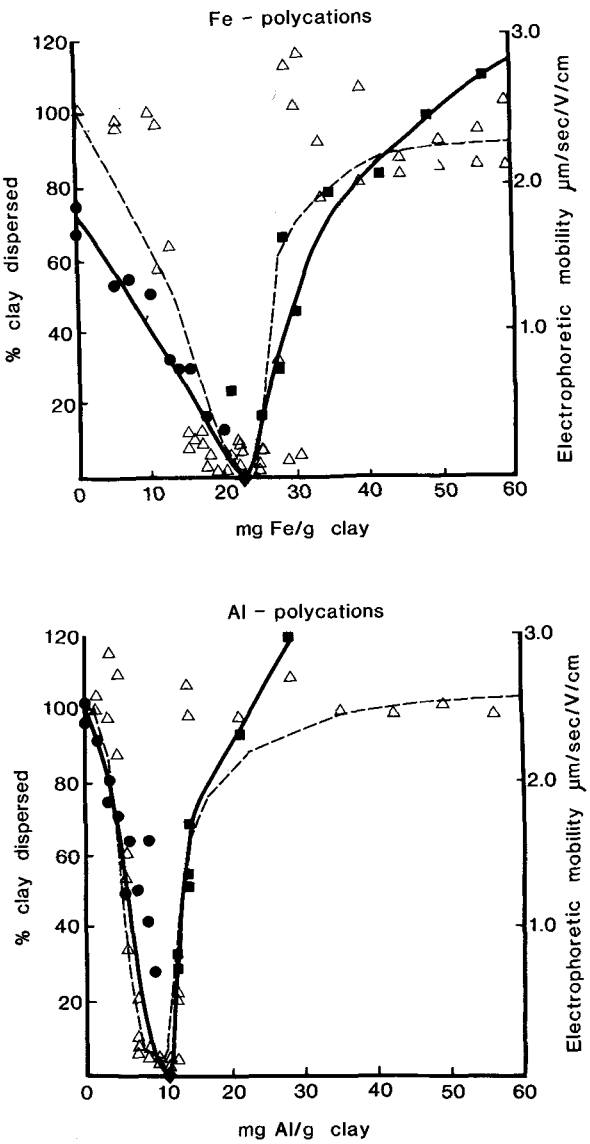


Figure 2. Influence of Fe and Al polycations on the dispersion and electrophoretic mobility (μ) of a soil clay. ● = negative and ■ = positive electrophoretic mobilities. △ = percentage of clay dispersed.

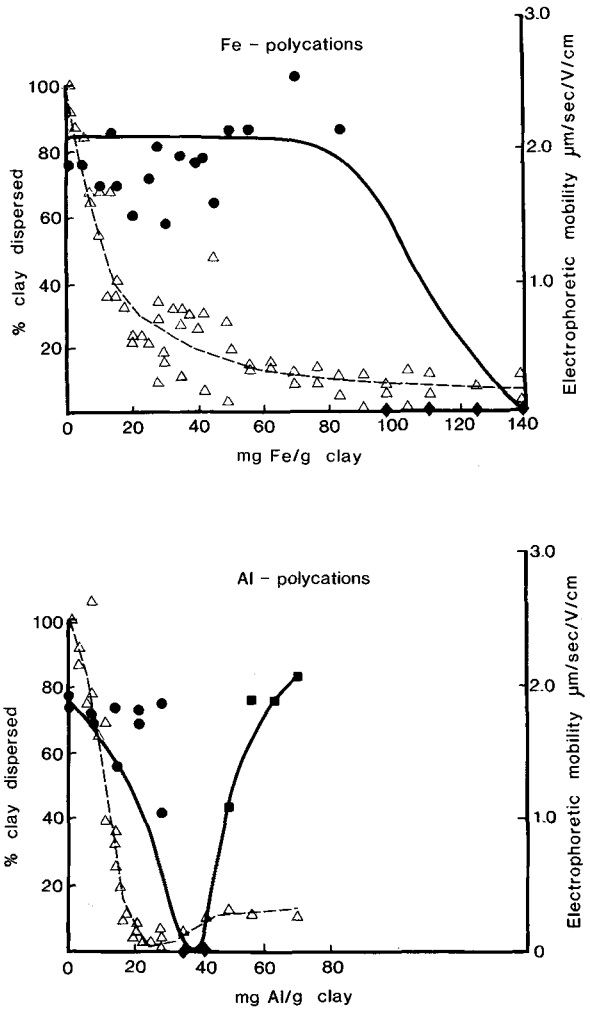


Figure 3. Influence of Fe and Al polycations on the dispersion and electrophoretic mobility (μ) of montmorillonite. ● = negative and ■ = positive electrophoretic mobilities. △ = percentage of clay dispersed.

and 2.2 Å. The presence of goethite was confirmed by IR absorption due to (OH) and OH at 980 and 797 cm^{-1}, respectively (Ryskin, 1974). In addition to goethite, ferrihydrite was present as evidenced by a broad XRD peak at 40° to 42°2θ and IR bands at 460–474, 580–600, and 680–700 cm^{-1} which resolved into a hematite spectrum when the sample was heated at 150°C in KBr discs.

Detailed studies of polycations by Mössbauer spectroscopy have indicated that the structure of goethite was present even though laths were not evident under the electron microscope (D. G. Lewis, Waite Institute, Glen Osmond, South Australia, unpublished). It also became clear that during the time taken for ultrafiltration the polycations continued to grow or aggregate. Thus, a large proportion of the fraction supposedly 10,000–50,000 molecular weight had a molecular weight >300,000 (equivalent to a cube with edge of 76 Å) when rerun on filters XM50 and XM100. The size of the spherical particles seen in electron micrographs confirmed that larger particles up to about 100 Å in diameter were present. The polycations seem to be the precursors of ferrihydrite and when dried their properties were indistinguishable from ferrihydrite. The polycation preparation used to study interactions with

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Table 2. Critical coagulation concentrations of polycations for clays.

Clay	Al (mg/g)	Fe (mg/g)
Kaolinite	2.8	5.5
Soil clay	7	10
Montmorillonite	20	~60

clays remained in solution for more than one year at room temperature and underwent no detectable change. In the presence of monomers, i.e., unfractionated preparations or preparations <10,000 molecular weight, turbidity occurred, and a yellow precipitate containing goethite was obvious within a few days at pH 2.2 in 0.01 M $Fe(NO_3)_3$.

Size distribution of Fe(III) polycations

The molecular weight distribution of polycations prepared by the addition of 1 M NaOH to 100 cm^3 0.1 $FeNO_3$ are shown in Table 1. Whilst care was taken to add the NaOH slowly to avoid precipitation of ferric hydroxide, varous amounts of polymers >300,000 molecular size were produced by this method of addition of NaOH. As expected, the positive charge on the polymers decreased as the pH was increased and was lowest on the large polymers.

Bulk preparations of polycations 10,000–50,000 molecular size were prepared from batches of 500 cm^3 0.1 M $Fe(NO_3)_3$. The percentage of Fe obtained in polymers 10,000–50,000 according to ultrafiltration, was 5.53 ± 0.83. The charge on the polymers was about 0.2 per gram atom suggesting a mean molecular size about 100,000 based on the charges in Table 1. The Fe polycations were assumed to be spheres with a mean diameter of 50 Å (range 30–100 Å) and a positive charge of 0.2 per gram atom of Fe.

Preparation of Al polycations

Seven batches of 0.1 M $AlNO_3$ were fractionated 4 days after addition of 134 cm^3 of 1.0 M NaOH. The 10,000 to 100,000 molecular weight fraction represented only 7.0% of the original Al present as the nitrate salt. The charge on this range of polymers was 0.49 per gram atom. According to Stol *et al.* (1976), this charge corresponds to a polymer containing about 24 Al atoms arranged as a planar sheet of hexagonal rings. The behavior of the polycations in the presence of clays supports this suggestion although it is not possible to differentiate between planar rings and planar chains.

Flocculation of clays by polycations

The influence of the addition of polycations on the flocculation and electrophoretic mobilities of the three clays is shown in Figures 1–3. The kaolinite and the soil clay containing a mixture of kaolinite and illite behaved similarly, and maximum flocculation was obtained when the colloids exhibited a net charge of zero. The amounts of polycations required to just flocculate the kaolinite and soil clay were less than 50 mg/g (Table 2). The bentonite did not exhibit any definite maximum for flocculation although most of the clay was flocculated by the addition of 20 mg Al or 60 mg Fe(III) per gram of clay. For the kaolinite and the soil clay a better dispersion was obtained as positively charged colloids than as Na-saturated clays. The presence of an aluminum species on the surfaces of natural clays is known to be responsible for some positive sites and to prevent complete dispersion of clays as negatively charged colloids (Schofield and Samson, 1954).

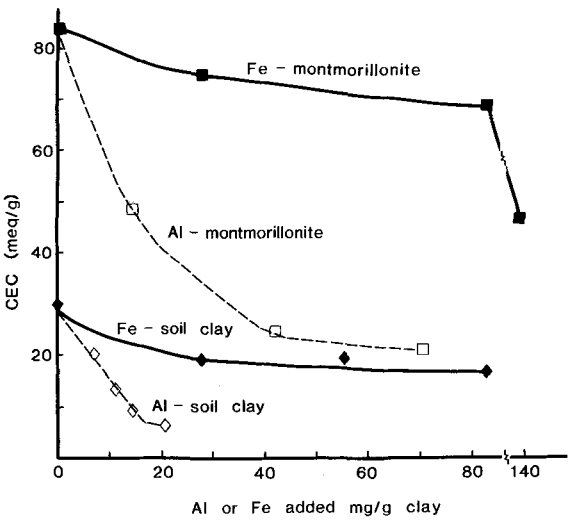
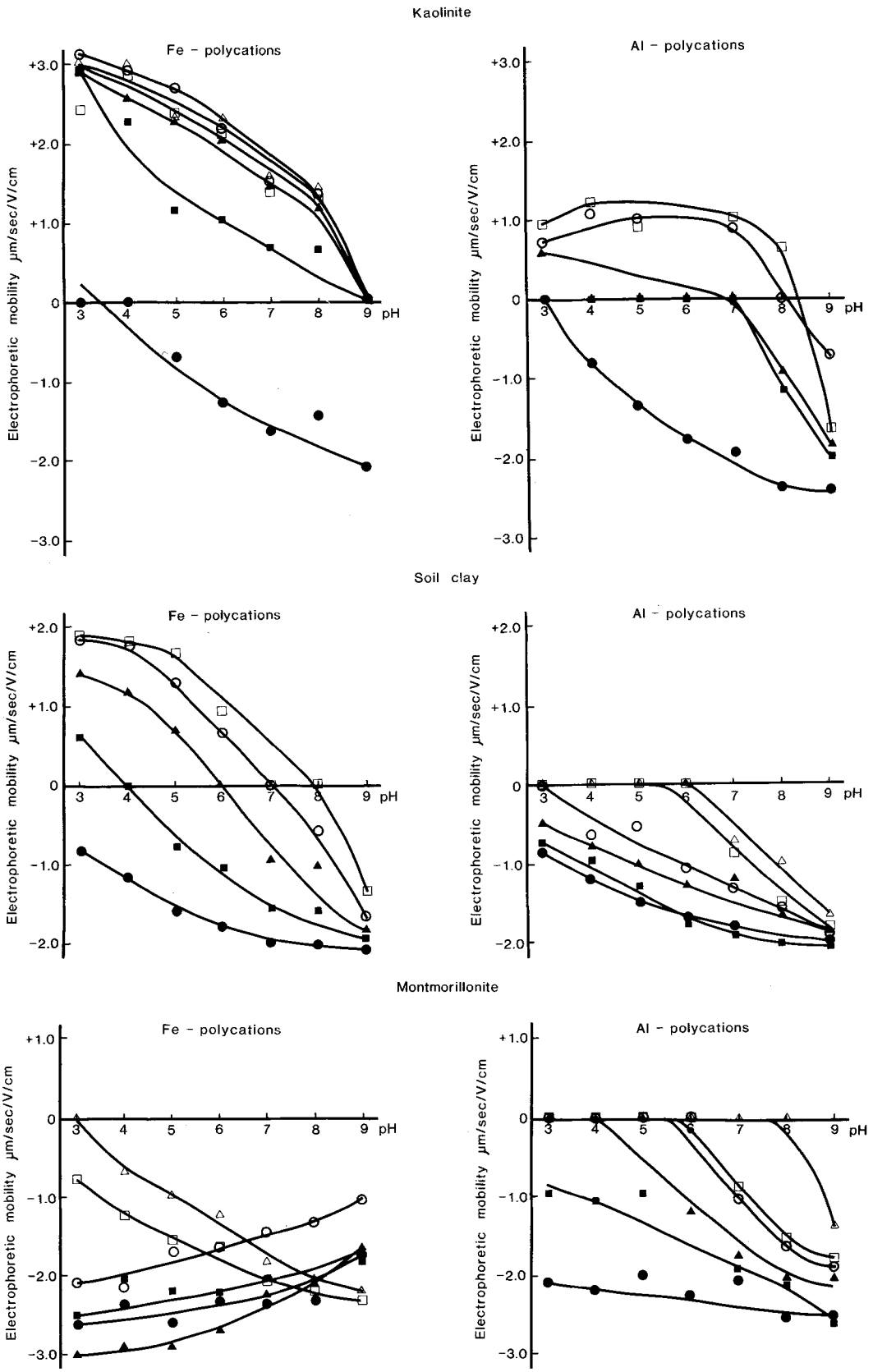


Figure 4. Cation exchange capacities (CEC) of clays after addition of Al and Fe polycations.

The results in Figure 4 show clearly that the Al polycations were much more efficient in blocking negative charges than were Fe polycations. It is proposed that this blockage is due not only to the higher charge of the Al polycations but also to their shape. Whereas spherical Fe polycations may add considerable positive charge to the clay-polycation system, the blocking of negative sites is limited and the cation-exchange capacity remained high. Planar polycations, however, not only cover a larger area and thus neutralize and block more negative sites, but for Al they can also occupy interlamellar spaces as shown by XRD.

With increasing amounts of polycation present the properties of the clays became more like those of synthetic hydrous oxides of iron which have a point of zero charge (PZC) at pH 7 to 8 (Figure 5a, 5b, 5c). The PZC of the clays was raised by addition of Fe(III) polycations, and for the kaolinite and the soil clay, the

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Table 3. Surface areas of clays treated with polycations of Al and Fe as determined by low temperature adsorption of nitrogen.

Al added (mg/g clay)	Surface area (m^2/g)	Fe added (mg/g clay)	Surface area (m^2/g)
	Kaolinite		
0	7.7	0	7.9
0.7	10.8	5.6	12.9
1.4	7.9	27.8	26.0
2.8	8.5	55.6	25.0
7.0	5.9	83.4	36.0
	Soil clay		
0	46.5	0	45.5
37.5	39.1	19.5	31.2
52.3	41.0	27.8	64.9
75.0	50.1	55.6	63.3
112.5	49.2	83.4	82.9
	Montmorillonite		
0	37.0	0	35.8
75	15.9	27.8	73.3
225	242.7	83.4	99.6
375	308.1	139.0	124.1

amounts of Fe required to raise the PZC above pH 6 were less than 2% by weight and were similar to the amounts required for maximum flocculation.

Surface area and water uptake at different potentials

The sorption of polycations of both Al and Fe clearly influenced the forces and interactions between particles. The creation of positive charges on the clay surface should decrease the potential between the surface and solution and diminish or prevent the formation of a double layer. The polycations of both Al and Fe behaved similarly with respect to flocculation of the three clays, but differences in the arrangements of particles is expected if the Fe polycations were spheres of approximately 50 Å diameter and the Al polycations were chains or planar sheets.

The differences in surface areas for the kaolinite treated with polycations of Al and Fe support the proposed shapes of the polycations (Table 3). Sorption of the Al polycations did not change the surface area of the kaolinite. Presumably chains or sheets were adsorbed onto the surfaces of the kaolinite and although this adsorption flocculated the kaolinite it did not influence the surface available for low-temperature nitrogen adsorption. On the other hand, the surface area of the kaolinite increased significantly by the addition of Fe polycations. The increase in surface area must be due entirely to the addition of spherical polycations. The increase in surface area due to addition of Fe polycation to kaolinite indicates that the Fe polycations had a surface area from 300 to 900 m^2/g Fe (this valve neglects the area of contact between the polycation and the kaolinite). The surface area in m^2/g Fe for polycation spheres about 100 Å in diameter would fall within this range. Similar results were obtained with the soil clay which is a mixture of kaolinite and illite.

Table 4. c-axis spacing of montmorillonite.

Treatment	Spacing (Å) 20°C	150°C
Na saturated	12.8	9.2
27.5 mg Fe/g clay	12.8	10.0
82.5 mg Fe/g clay	12.8	10.2
187.5 mg Fe/g clay	15.3	10.3
14 mg Al/g clay	13.7	11.2
42 mg Al/g clay	16.0	14.5
90 mg Al/g clay	17.1	14.7

The effect of adding Al polycations to the montmorillonite was different from that of the other clays. A small amount of Al polycation decreased the surface area from 37 to 16 m^2/g, but larger quantities resulted in surface areas in excess of 300 m^2/g. Presumably the Al polycations prevented collapse of lamellar space and rendered internal surfaces accessible to N_2. The interlayer positioning of Al polycations was confirmed by XRD of the clays before and after addition of polycations (Table 4). When >40 mg Al/g clay was present, the Al polycations must have occupied the interlamellar space of the montmorillonite to give a regular c-axis spacing which did not collapse below 14 Å on heating to 150°C. This c-axis spacing is similar to that of an Al-interlayered smectite (Barnhisel, 1977). Lahav and Shani (1978) and Lahav *et al.* (1978) described the process of partly filling montmorillonite with Al species as a cross linking process and considered that the products with zeolitic properties might be useful catalysts or molecular sieves.

Water uptake and swelling of the montmorillonite were decreased markedly by addition of Al polycations especially at 100-cm suction (Figure 6). Al was also significantly more efficient than Fe at RHs of 96 and

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Figure 5. (a) Points of zero charge determined from electrophoretic mobilities of kaolinite after addition of Al and Fe polycations. Fe: ● = 0; ■ = 6.95; ▲ = 13.9; ○ = 27.8; □ = 55.6; △ = 83.4 mg Fe/g clay. Al: ● = 0; ■ = 0.7; ▲ = 1.4; ○ = 2.8; □ = 7.0 mg Al/g clay. (b) Points of zero charge determined from electrophoretic mobilities of soil clay after addition of Al and Fe polycations. Fe: ● = 27.8; ■ = 41.7; ▲ = 55.6; ○ = 69.5; □ = 83.4 mg Fe/g clay. Al: ● = 0; ■ = 3.5; ▲ = 7.0; ○ = 10.5; □ = 14.0; △ = 21.0 mg Al/g clay. (c) Points of zero charge determined from electrophoretic mobilities of montmorillonite after addition of Al and Fe polycations. Fe: ● = 0; ■ = 27.8; ▲ = 55.6; ○ = 83.4; □ = 111.2; △ = 139.0 mg Fe/g clay. Al: ● = 0; ■ = 14.0; ▲ = 28.0; ○ = 42.0; □ = 56.0; △ = 70.0 mg Al/g clay.

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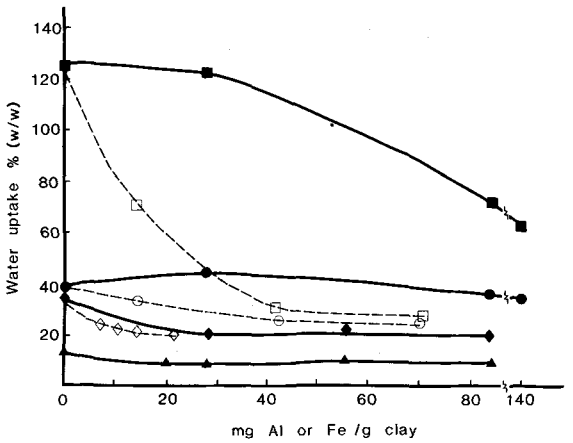


Figure 6. Water uptake by clays after addition of Al and Fe polycations. Fe-montmorillonite: ■ = −10 kPa, ● = −10 MPa; Al-montmorillonite: □ = −10 kPa, ○ = −10 MPa; Fe-soil clay: ◆ = −10 kPa, △ = −10 MPa; Al-soil clay: ◇ = −10 kPa, ▲ = −10 MPa.

98%. Thus, whereas polycations of iron were efficient with respect to flocculation of the clays, they did not restrict water uptake and swelling as effectively as Al.

CONCLUSIONS

The reactions of the Al and Fe polycations with three clays support the current consensus regarding the size and shape of the polycations. Polycations of Fe are spheres 30–100 Å diameter with a positive charge inversely related to the size of the polycations. Addition of such Fe polycations to kaolinite and a kaolinite-illite soil clay increased surface area and decreased the cation-exchange capacity by a small amount. Interaction of the polycations and clay caused flocculation at the zero point of charge. Little evidence of an Fe interlayer was noted which is consistent with the polycations being spheres 30–100 Å in diameter.

Al polycations appeared to be planar molecules containing 15–30 Al atoms and carrying a charge of 0.49 per gram atom. The thickness of the sheets was about 5 Å, similar to the thickness of a single gibbsite sheet. The polycations blocked efficiently the cation-exchange sites on clays, even those in the interlamellar spaces in montmorillonite. Adsorption of Al polycations produced large increases in surface area of montmorillonite as measured by N_2 adsorption by propping the individual montmorillonite sheets apart even under vacuum. The Al polycations were also much more efficient than Fe in reducing the water uptake and therefore the swelling of clays, particularly the montmorillonite.

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Резюме—Поликатионы ограниченного молекулярного размера были приготовлены путем ультрафильтрации из растворов 0,1 M $Fe(III)(NO_3)_3$. Разные количества поликатионов добавлялись к Na-каолиниту, Na-монтмориллониту, и Na-почвенной глине. Сравнивалось влияние этих добавок на флоккуляцию глины и электрофоретическую подвижноть. Флоккуляция проявлялась как раз перед получением нулевого заряда нетто. Поликатионы Al имели высокий положительный заряд (0,49 на грамм-атом Al) и их взаимодействие с глинами указывало на плоскую форму. Адсорбция поликатионов Al уменьшала значительно катионо-обменные способности каолинита и почвенной глины, но имела небольшой эффект на площади поверхности, определенные путем низкотемпературной адсорбции N_2. Поликатионы Fe являлись сферами диаметром 10–100 Å с положительным зарядом 0,2 на грамм-атом. Площади поверхности каолинита и почвенной глины были существенно увеличены при добавлении поликатионов Fe, но их катионо-обменные способности уменьшились на одну пятую. Поликатионы Al увеличивали площади поверхности монтмориллонита (до 300 м²) возможно в результате поддерживаемого открытия межслойных пространств и делали плоскости a–b доступнымп для адсорбции азота. Поликатионы Al в межслойных пространствах предохраняли разрушение слоев до 14 Å при нагреве до 150°C. Регулярная прослойка Fe не наблюдалась, как это могло предполагаться на основе размера сфер. [E.G.]

Resümee—Polykationen mit begrenzter Molekülgröße wurden aus 0,1 M $Fe(III)(NO_3)_3$- und $Al(NO_3)_3$-Lösungen durch Ultrafiltration hergestellt. Es wurden unterschiedliche Mengen der Polykationen zu Na-Kaolinit, Na-Montmorillonit und einem Na-reichen Bodenton hinzugegeben, und die Auswirkung auf die Ausflockung des Tons mit der elektrophoretischen Mobilität vergleichen. Flockung tritt ein, kurz bevor die Gesamtladung null wird. Die Zugabe weiterer Polykationen führt zu einer Dispergierung des Tons mit einer positiven Nettoladung. Die Al-Polykationen besaßen eine hohe positive Ladung (0,49 pro Grammatom Al), und die Art ihrer Wechselwirkung mit den Tonen deutet auf eine planare Form hin. Die Adsorption von Al-Polykationen verringerte die Kationenaustauschkapazität von Kaolinit und vom Bodenton beträchtlich aber hatte kaum Auswirkung auf die Oberflächen, die mit Niedrigtemperatur-N_2-Adsorption bestimmt wurden. Die Fe-Polykationen hatten kugelige Gestalt mit einem Durchmesser von 10–100 Å und eine positive Ladung von 0,2 pro Grammatom. Die Oberflächen von Kaolinit und dem Bodenton wurden durch die Zugabe von Fe-Polykationen beträchtlich vergrößert, ihre Kationenaustauschkapazitäten wurden jedoch um $^1/_5$ verkleinert. Al-Polykationen vergrößerten die Oberfläche von Montmorillonit (auf 300 m²), wahrscheinlich, indem sie die interlamellaren Zwischenräume aufsprengten und die a-b Ebenen für die Stickstoffadsorption zugänglich machten. Die Al-Polykationen in den interlamellaren Zwischenräumen verhinderten ein Zusammenbrachen auf 14 Å bei Erwärmen auf 150°C. Es gab keinen Hinweis für ein reguläres Zwischenschicht-Eisen, wie man aufgrund der Kugelgröße hätte annehmen können. [U.W.]

Résumé—Des polycations de taille moléculaire limitée ont été préparés à partir de solutions 0,1 M de $Fe(III)(NO_3)_3$ et d'$Al(NO_3)_3$ par ultrafiltration. Des quantités de polycations variées ont été ajoutées à la kaolinite-Na, à la montmorillonite-Na et à un argile de sol Na, et on a comparé l'effet de la flocculation de l'argile et la mobilité électrophorétique. La flocculation s'est produite juste avant qu'on ait obtenu la charge net zéro. L'addition d'avantage de polycations a resulté en la dispersion de l'argile avec une charge net positive. Les polycations Al possédaient une charge positive élevée (0,49 par atome gramme d'Al), et leur interaction avec les argiles indiquaient une forme plâne. L'adsorption de polycations Al a diminué de manière significative les capacités d'échange de cations de la kaolinite et de l'argile du sol, mais elle a eu peu d'effet sur les aires de surface déterminées par adsorption de N_2 à basse température. Les polycations Fe étaient des sphères de 10–100 Å de diamètre avec une charge positive de 0,2 par atome gramme. Les aires de surface de la kaolinite et de l'argile du sol ont été augmentées substantivement par l'addition de polycations Fe, mais leurs capacités d'échange de cations ont été réduites d'un cinquième. Les polycations Al ont augmenté les aires de surface de la montmorillonite (à 300 m²), sans doute en ouvrant les espaces interlamellaires et en rendant les plans a-b accessibles à l'adsorption de nitrogène. Les polycations Al dans les espaces interlamellaires ont empeché l'effrondrement à 14 Å lors de l'échauffement à 150°C. Il n'y avait aucune évidence de Fe intercouche régulier, comme pourrait l'être anticipé par la taille des sphères. [D.J.].

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