CATION EXCHANGE CAPACITY AND CONDITION OF ZERO CHARGE OF HYDROXY-Al MONTMORILLONITE

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Abstract—The effect of interlayering montmorillonite with different amounts of hydroxy aluminum cation on the cation exchange capacity (CEC) and the point of zero charge (PZC) of the clay was studied. The CEC decreased as the Al content of the clay increased. Both the CEC and the loss in the CEC were linearly dependent on the Al content, thus indicating the predominance of a single polynuclear interlayered species. Its composition is $[Al_6(OH)_{16.5}]^{1.5+}$. Acid base titration of the interlayered montmorillonites produced values for the PZC in the range 4.5–5.9, increasing with the Al content of the materials. The values, however, did not represent real conditions of zero charge and some samples were still negatively charged at the determined PZC. The PZC values obtained by acid-base titration are thought to be adversely affected by secondary reactions involving the interlayered material with a concomitant release of soluble Al in amounts dependent on the pH and ionic strength.

Key Words—Cation exchange capacity, Pillared clay, Point of zero charge.

INTRODUCTION

Important electrochemical properties of montmorillonitic clay such as its cation exchange capacity, mobility, flocculation, and sorption of organic and inorganic substances are affected by interlaying hydroxy aluminum species between the layers of the clay. Few data have been published about the properties of the interlayered clays.

Some authors reported a change from negative to positive zeta potentials (Bottero *et al.,* 1980), some claimed the occurrence of isoelectric points (Avena *et al.,* 1990), and Oades (1984) showed that such change in polarity does not occur.

The changes in the electrochemical properties of the clay are intimately related to the amount of hydroxy aluminum complexes incorporated in the clay as well as their chemical composition and charge properties. Many hydroxy-Al species are known to exist in partially neutralized Al solutions used for interlaying clays and their charge may vary from neutral to positive seven. So far it has not been possible to identify the interlayered species.

In this report some aspects of the electrochemistry of hydroxy-Al interlayered montmorillonite will be addressed, namely the effect of the interlayered amount on the cation exchange capacity of the clay and the related property, the point of zero charge; i.e., the pH at which the cation exchange capacity is supposed to vanish. Also an attempt is made to characterize the interlayered species and its electric charge.

MATERIALS AND METHODS

For the preparation of pillared montmorillonite, a montmorillonite from Cerro Bandera, Argentina (Bus-

setti *et al.,* 1980) was used. Particles with diameter <2 μm were separated by sedimentation and were saturated with Na by successive treatment with 1 M NaCl followed by centrifugal washings with water until almost free from Cl$^-$ (traces). Particles <0.2 μm were obtained by a centrifugation sedimentation procedure.

A solution containing 40 mmol/liter of Al was prepared by adding slowly 0.1 M NaOH to 0.2 M AlCl$_3$·6H$_2$O. The solution was left for three days and had a pH of 4.2. To one liter of the Al solution, 700 ml of a clay suspension (5 g/liter) was slowly added (5 ml/min) with continuous stirring. The suspension was left overnight and had a pH of 4.2. The supernatant liquid was discarded and the clay was washed with water until free from Cl$^-$. The residue was dried at 60°C, pulverized and passed through a 200 μm sieve. The clay had 15% (wt/wt) H$_2$O and 34.2 mg Al/g (sample 2 in Table 1). Upon repeating the procedure a product with 38.3 mg Al/g was obtained (sample 3).

Sample 4 was prepared as sample 2 except that following the decantation of the supernatant liquid, 1 liter of fresh Al solution was added, the pH adjusted to 6 and the suspension was left overnight.

An additional 5 g of sample 2 was treated twice with a fresh Al solution. Each time, 1 liter of solution was used followed by 10 h of shaking, and decantation of the supernatant liquid after 24 h of setting. the pH was adjusted to 5.5 during the second shaking period. The clay was recovered, washed several times with water until Cl$^-$ free. This clay contained 89.6 mg Al/g (sample 5).

Sample 6 was prepared as described above for sample 2 and sample 7 as for sample 5, except that the clays used had particle sizes <0.2 μm. Samples 6 and 7 contained 60.1 and 93.3 mg Al/g, respectively.

The Al content of the clays was determined by treatment of 0.1 g samples with 25 ml 0.1 M HCl (four times) and determination of Al in the extracts by the eriochrome colorimetric method (Sandell, 1959).

The cation exchange capacity for each sample was determined by a Na chloride method (Perrot, 1977) and also by saturation with Ba using 1 M $BaCl_2$ at pH 5. Washing steps were done with 10^{-4} M Ba solution at the same pH. The Ba was displaced using 2 M KCl and was determined gravimetrically as a sulfate.

X-ray diffraction analyses were performed on the samples using Ni filtered CuK-α radiation (Rigaku-Danki giegerflex model D max 3C diffractometer).

Acid/base titrations of the clays were carried out using 0.1 g samples in 0.1 and 0.001 N $NaNO_3$ as supporting electrolytes and 0.1 N HNO_3 or NaOH as titrants in stepwise fashion with concurrent measurement of pH. Blank titrations were also performed and the net amounts of proton uptake were calculated (Helmy *et al.*, 1980). In parallel titration experiments, soluble Al was determined at selected pH values.

Acid/base titrations were also carried out on a mixture of montmorillonite (0.1 g) and on amorphous hydrous Al-oxide (0.5 g) from Carlo Erba (Bussetti *et al.*, 1980).

The adsorption interaction of montmorillonite and Al-interlayered montmorillonites with a positive colloid of iron oxyhydroxide was carried out as a test for the presence of negative charges on the clays. The iron sol was prepared by hydrolysis at 100°C for three days of a mixture of 0.02 M $FeCl_3$ and 0.0004 M NaH_2PO_4 (Ohmari and Matijevic, 1992). To 10 ml of the iron sol (1.1 g/liter for the montmorillonite and 0.65 g/liter for the other clays) was added 100 mg of clay followed by shaking for a few minutes and then centrifugation at 4000 rpm for 10 minutes. The iron colloid remaining in suspension was determined by measuring absorbance at 540 nm and the use of a standard curve determined with dilutions of the original sol. The amount of positive colloid adsorbed was calculated from the initial and final iron colloid concentrations.

RESULTS AND DISCUSSION

The cation exchange capacity

The Na and Ba cation exchange capacities of montmorillonite samples are given in Table 1. The values were found to decrease as the content of Al in the samples increased.

The reduction in the negative charge of the clay (its cation exchange capacity) is due to the positive charge of the incorporated hydroxy-Al species. This can be expressed as:

$$C_i - C_f = \Delta C = B \qquad (1)$$

where C_i and C_f are the initial and final exchange ca-

Table 1. Some characteristics of hydroxy-Al montmorillonites.

Sample	Diameter (µm)	d(001) (nm)	Al₂O₃ weight (%)	Al (mg/g)	CEC* (meq/g) Na	CEC* (meq/g) Ba	pH prep.	PZC	pH$_{Al}$**
1	2.0	1.54	0.00	0.0	0.84	0.98	—	—	—
2	2.0	1.83	6.46	34.2	0.48	0.56	4.2	4.50	4.85
3	2.0	1.84	7.23	38.3	0.45	0.59	4.2	4.60	5.00
4	2.0	1.53	11.34	60.0	0.20	0.44	4.2	4.70	—
5	2.0	1.84	16.92	89.6	0.07	0.25	5.5	5.50	5.80
6	0.2	1.82	11.35	60.1	0.25	0.50	4.2	4.65	5.50
7	0.2	1.92	17.63	93.3	0.10	0.18	6.0	5.90	5.65

* The cation exchange capacity for Na is at pH 7; for Ba is at pH 5.
** pH at the cross over points of soluble Al curves in Fig. 5.

pacities and B is the incorporated positive charge; all values are in units of milliequivalent (meq) of charge per g of clay (1 meq of charge is equal to 96.5 coulombs).

For each chemical composition of an Al species, the positive charge should be proportional to the amount of Al present in the species chemical formula, hence we may write

$$B = kA \qquad (2)$$

where A is the amount of Al in mg/g and k is a constant in units of meq/mg. The reciprocal of this constant gives the amount of milligrams of Al needed to balance 1.0 meq of the clay negative charge. From Eqs. (1) and (2) we have

$$\Delta C = kA \qquad (3)$$

and

$$C_f = C_i - kA \qquad (4)$$

Both Eqs. (3) and (4) give straight lines on the appropriate coordinates. In Figure 1 the experimental results are plotted according to Eq. (3). The slope of line gives a value k = 0.0087 meq/mg Al. Furthermore the intercept on the X-axis of the line in Figure 2 gives 115 mg Al/g clay. Hence to neutralize the negative charge of the clay (0.94 meq/g), 110 mg Al per g of clay are needed. All Al contents given in Table 1 are less than 110 mg/g, hence all samples should still retain a part of their cation exchange capacities.

As may be seen in Figure 1, some points fall somewhat outside the drawn line. In terms of Eq. (3) this can be taken to indicate that the incorporated Al is probably dominated by one chemical species, but others are probably present. To identify the dominant form, we calculated the ratio of charge to Al present in some hydroxy-Al species which different authors have suggested were present in partially neutralized $AlCl_3$ solutions. These are: $[Al_8(OH)_{20}]^{4+}$ (Matijevic *et*
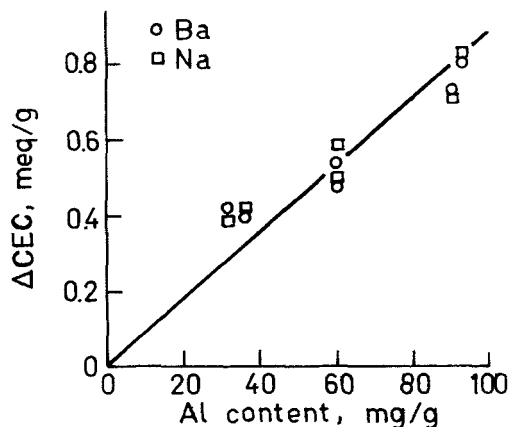
Figure 1.   The reduction in the cation exchange capacity of hydroxy-Al interlayered montmorillonite vs. interlayered Al content of the clay.
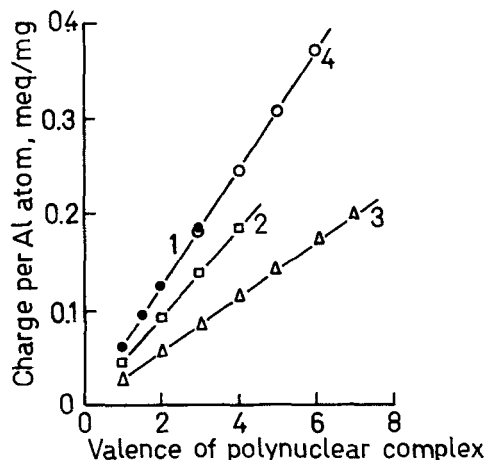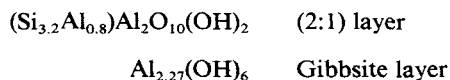

Figure 3.   The charge per Al atom in the polynuclear complex versus its valence for different complexes: 1) $[Al_6(OH)_{15}]^{3+}$, 2) $[Al_8(OH)_{20}]^{4+}$, 3) $[Al_{13}O_4(OH)_{24}]^{7+}$ and 4) $[Al_6O_{12}]^{6+}$.

al., 1961); $[Al_{13}O_4(OH)_{24}]^{7+}$ (Johansson, 1960); $[Al_6(OH)_{12}]^{6+}$ (Hsu and Bates, 1964); and $[Al_6(OH)_{15}]^{3+}$ (The last formula has an OH/Al ratio of 2.5, the same as in the solution used for the clays. Structurally, the unit would be, as in gibbsite, hexagonal shaped and formed of 6 units of Al-OH octahedra with edge sharing. It is similar to the unit suggested by Hsu and Bates but with lower charge).

The calculated ratios are plotted against hypothetical valences for each polynuclear complex in Figure 3. According to Figure 3 the species in the present work with 0.0087 meq/mg Al should have a valency of 1.5 if it is an Al_6 complex, is divalent if it is an Al_8 complex, or has a valency of 3.4 if it is an Al_{13} complex.

Assuming an Al_6 complex, the interlayered material may be represented by the formula, $[Al_6(OH)_{16.5}]^{1.5+}$, with an OH/Al ratio of 2.75, somewhat higher than the 2.5 ratio of the $AlCl_3$ solutions used in the preparation of the clays. At this point, a comparison could fruitfully be made with the mineral chlorite with the typical composition (Brindley and Brown, 1984):

$$(Si_{3.2}Al_{0.8})Al_2O_{10}(OH)_2 \qquad (2{:}1) \text{ layer}$$

$$Al_{2.27}(OH)_6 \qquad \text{Gibbsite layer}$$

This composition appears to be similar to Al-pillared montmorillonite and is characterized by a zero cation exchange capacity due to the fact that the gibbsite layer contains excess Al over the hydroxyls and thus carries a positive charge equal to the negative charge of the 2:1 layer, i.e., (0.8). For sake of comparison we may express the gibbsite layer in chlorite in the same units used for the interlayered complexes. This leads to the formula: $[Al_6(OH)_{15.88}]^{2.12+}$ with 0.0131 meq/mg Al(viz. $2.12/(27 \times 6)$) and an OH/Al ratio of 2.65. Returning now to data of other workers, recently Hsu (1992) reported a value of 0.019 meq/Al as an average for six pillared montmorillonites. This ratio would correspond to a trivalent Al_6 complex. Earlier Hsu and Bates (1964) suggested single and double rings of gibbsite for the structure of the interlayered Al-hydroxy species. Furthermore, from data given by Oades (1984) we calculate a ratio of 0.0081 meq/mg Al for his interlayered montmorillonite sample, a value similar to ours. Based on our data and those of other workers we may conclude that the hydroxy-Al complexes interlayerd in pillared montmorillonites are not highly charged and the complexes possess valences that do not exceed the value of 3.

We end this section by mentioning that though the interlayered material is probably dominated by one species, others are also present. Such condition obviously leads to some scattering in the chemical data to a degree dependent on the proportion in the material of the dominant species. If it was the only species present, all points in Figures 1 and 2 should lie on the drawn lines.
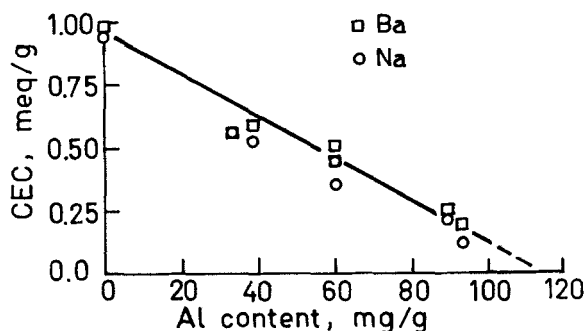

Figure 2.   The cation exchange capacity of hydroxy-Al montmorillonite vs. interlayered Al content of the clay.
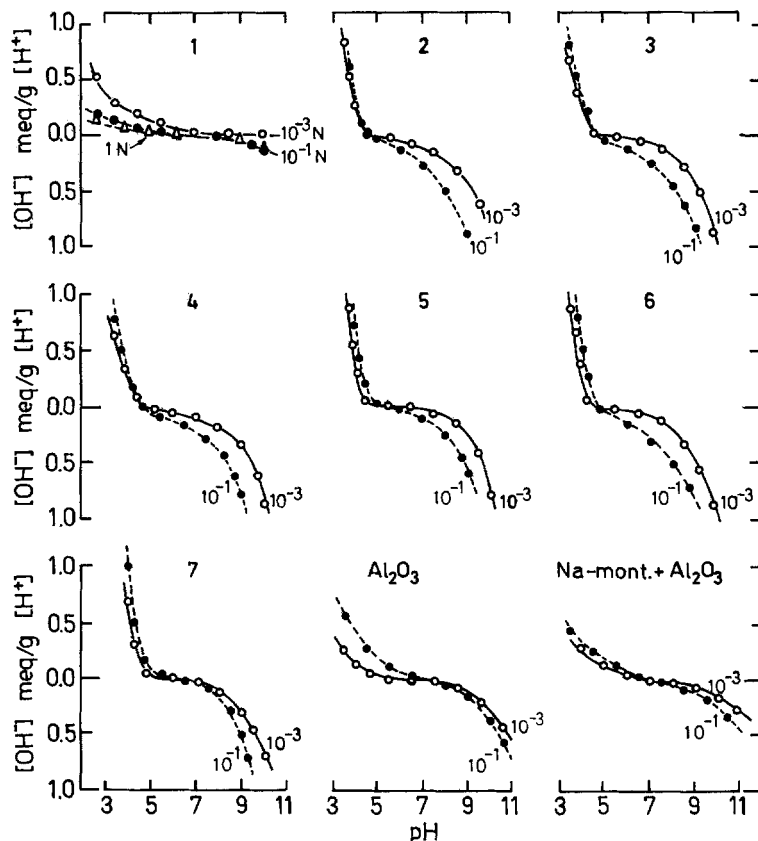
Figure 4. Acid-base titration of montmorillonite (Sample 1) and hydroxy-Al interlayered montmorillonite (Samples 2 through 7 in Table 1). Also are shown the titration curves for amorphous Al_2O_3 and its 5 to 1 mixture with montmorillonite.

The PZC of hydroxy-Al interlayered montmorillonite

The acid-base titration curves for montmorillonite, hydroxy-Al interlayered montmorillonite, Al-oxide, and a mixture of montmorillonite and Al-oxide are given in Figure 4. In Figure 5 are shown on an enlarged scale the titration curves near the cross over points as well as the curves obtained by plotting the amounts of Al released by the clay samples during the acid-base titration. The pH values at the cross over points of the Al release curves (pH_{Al}) and those of the acid titration curves (pH_O) are given in Table 1. In general the pH_O and the pH_{Al} values are higher the higher the Al contents of the $<2 \mu m$ and $<0.2 \mu m$ clays.

The point of zero charge of a material is the pH at which the material carries equal amounts of positive and negative charges. In the case of hydroxy-Al interlayered montmorillonite the negative charge is provided by the isomorphous substitutions that occur mainly in the octahedral layer of the silicate structure. The positive charge is provided by the interlayered material. Part of this positive charge, as we have seen in the first part of this report, is due to an excess of Al over OH and the other part could be provided by proton association at low pH values:

$$[-Al-OH] + H^+ \rightarrow [-Al-OH_2]^+$$
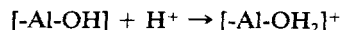
The association mechanism is expected to contribute much less positive charge than the excess Al mechanism. Published data show only about 0.2 meq/g Al oxide as a maximum value (Helmy et al., 1980) for hydrous Al-oxides.

As we have seen in the mineral chlorite all the positive charge is provided by excess Al over OH in the gibbsite layer and amounts to 4.9 meq/g gibbsite (0.8 charge per chemical formula weight of the layer), considerably higher than the association charge. For pillared clays the PZC should depend on how much positive charge is provided by each mechanism. It is therefore expected that the amount of the interlayered material per unit amount of clay and its chemical composition would be the main factors on which the PZC will depend. Since the samples in this work seem to contain the same hydroxy complex the amount of material is therefore the factor on which the location of the PZC would ultimately depend.

The method of PZC determination adopted in this work gives the PZC as the cross over point in acid-base titration curves obtained at different electrolyte concentrations (Helmy and Ferreiro, 1976). This pro-
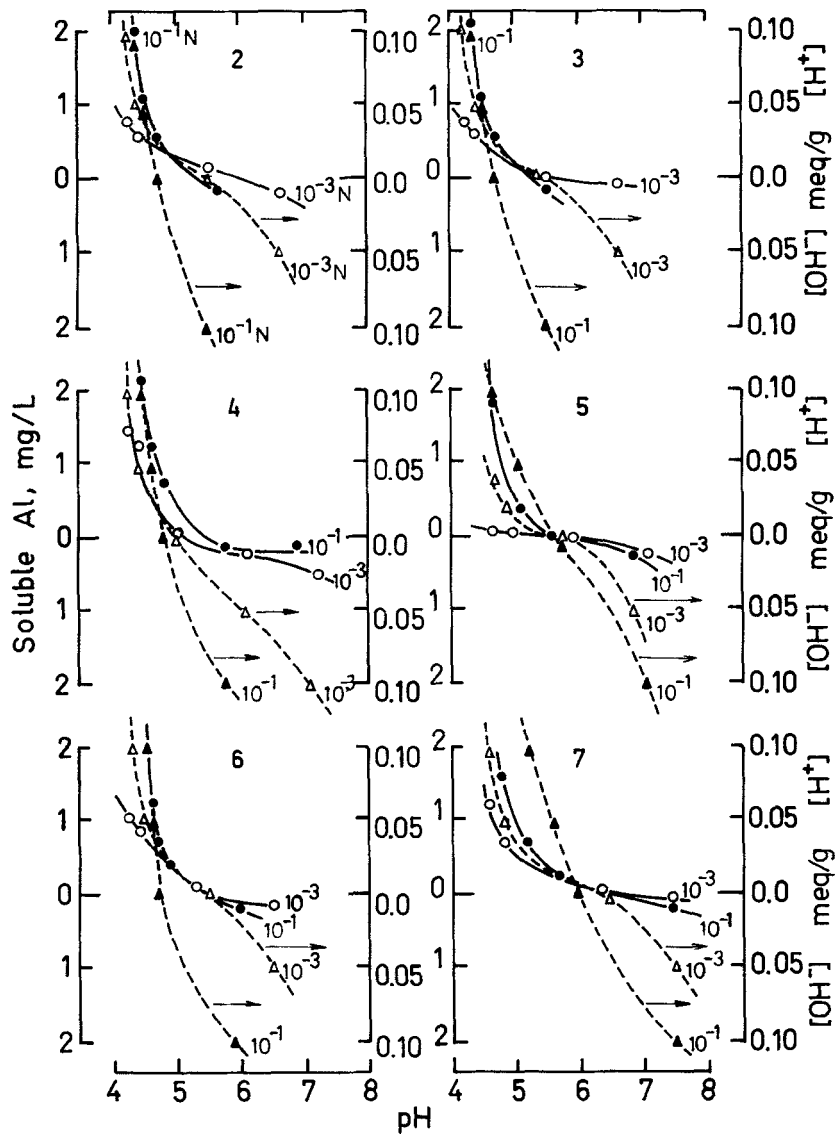
Figure 5. Enlarged scale (dashed curves) of the titration curves (given in Figure 4) near the cross over points for samples 2 through 7. Also are shown a plot of the soluble Al released during the titrations.

cedure is based on the assumption that protonation and deprotonation of surface OH groups of the incorporated hydroxy aluminum are the only reactions that take place during the titration. However, many other reactions involving protons take place simultaneously and lead to the presence in solution of many Al-hydrolysis species, including polynuclear ones. According to Baes and Mesmer (1976) suspensions of gibbsite contain 2.7 mg of soluble Al species at pH 4.5. The quantities of soluble Al species would also depend on the concentration and type of supporting electrolyte, particle concentration, as well as the presence of a clay (Ferreiro *et al.*, 1992). The soluble Al concentration is higher the higher the electrolyte concentration as shown

in Figure 5 and gives rise to cross over points in the curves of soluble Al vs. pH obtained at 10^{-1} and 10^{-3} M $NaNO_3$. The above mentioned secondary reactions are not taken into account in the acid-base method for obtaining the PZC and possibly modify the value of pH at which the curves cross and thus casts doubt on the values obtained as representing real PZC.

Further evidence for doubting the PZC values emerges from Figure 6 where the data of adsorption of positive iron oxyhydroxide colloid by montmorillonite and the pillared samples are given. As may be seen the amount adsorbed by montmorillonite is much higher than the amount adsorbed by the pillared clays reflecting a much higher negative charge for the surface

of the clay. Furthermore the adsorbed amount of positive iron oxyhydroxide particles was dependent on the Al content of the clay; being lower the higher the Al content of the clay. These results indicate that the pillared clays still carry negative charges at pH values near those supposed to represent conditions of zero charge; as is apparent from comparing the pH values given in Figure 6 and the pH_o values for the same samples in Table 1.

The titration curves of Al oxide and its mixture with montmorillonite also suggest problems with the acid-base titration method. The cross over points for both systems occur at pH 7.5. Since the clay possesses a considerable negative charge at this pH, the real PZC should have occurred at a much lower pH value, where the oxide would develop an amount of positive charge equivalent to that of the clay i.e., 0.094 meq.

Similar arguments can be used to show that sample 7 cannot have a PZC at pH 5.9. This sample contains 176 mg oxide and is expected to develop a maximum of 0.0352 meq of positive charge (according to literature data, hydrous oxides of Al develop about 0.2 meq of charge/g [Helmy et al., 1980]). The value, 0.0352 meq, is not enough to balance the 0.1 meq of negative charge this clay sample possesses (Table 1). Hence this interlayered sample should still be negatively charged at pH 5.9, the value supposed to represent the PZC of the sample.

Further support for our contention that the PZC values are unrealistic is shown by the Ba cation exchange capacity data determined at pH 5. At this pH, samples 5 and 7 still have a cation exchange capacity, though according to the values of their PZC they should carry a net positive charge at pH 5. The other clay samples have their PZC at pH values a little less than 5, nevertheless they show considerable capacities for cation exchange as judged by the values in Table 1.

Finally we conclude this section by stating that the experimentally determined PZC for hydroxy-Al montmorillonite should be treated with care due primarily to the instability of the material at low pH values where the PZC is to be found.

CONCLUSIONS

1) The cation exchange capacity and the loss in the cation exchange capacity of montmorillonite were both linearly dependent on the Al content of hydroxy-Al interlayered montmorillonite. Such behavior indicates the predominance of a single interlayered species which was identified as $[Al_6(OH)_{16.5}]^{1.5+}$.

2) The PZC of the interlayered montmorillonites determined by the acid-base titration method lied in the range 4.5–5.9 increasing with the content of Al in the clay. The values appeared to be unreal because of secondary reactions that produce the liberation of soluble Al from the interlayered clay in
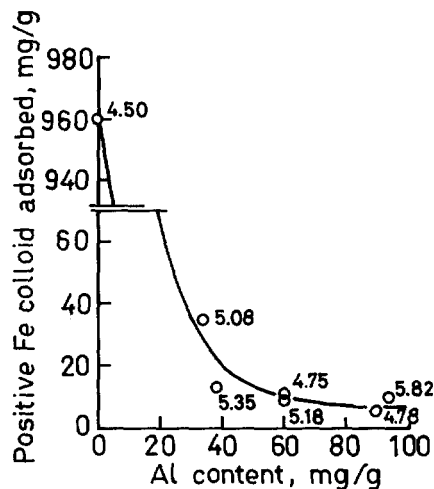

Figure 6. The amount of positive iron colloid adsorbed by montmorillonite and hydroxy-Al interlayered montmorillonite plotted against the interlayered Al content of the clay. Numbers on the curve represent the adsorption equilibrium pH values.

amounts dependent on the pH and the ionic strength of the titration system.

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