STUDY OF SOME PHYSICOCHEMICAL PROPERTIES OF PILLARED MONTMORILLONITES: ACID-BASE POTENTIOMETRIC TITRATIONS AND ELECTROPHORETIC MEASUREMENTS

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Abstract—The surface charges and the zeta potential of a Na-montmorillonite (Na-mont) and two pillared montmorillonite (MP1 and MP2) samples with different aluminum contents were determined by potentiometric titrations and electrophoretic measurements. At pH >9 the two pillared montmorillonite samples showed zeta potentials similar to those of Na-mont, but at pH <8, the negative zeta potential shifted to lower negative values as the aluminum content increased. Sample MP1, which had a greater Al content, showed an isoelectric point (IEP) of 5.0–5.5. Titration curves obtained by acid-base potentiometric titration for sample MP1 showed a well-defined cross-over point at pH = 5.0, whereas this point was not observed for sample MP2 in the pH range studied. The results indicate, in principle, that both techniques can be used to characterize surface charges in this type of material. An attempt was also made to relate the data obtained from electrophoretic mobility and potentiometric titrations.

Key Words—Electrophoretic mobility, Montmorillonite, Pillared clays, Potentiometric titration, Surface charge.

INTRODUCTION

Pillared montmorillonites have been receiving considerable attention by petroleum engineers because of their low cost and high cracking activity (Occelli *et al.*, 1985; Occelli and Finseth, 1986; Occelli, 1986; Pinnavaia, 1983; Pinnavaia *et al.*, 1985; Tasaki, 1987; Tichit *et al.*, 1988; Tokarz and Shabtai, 1985; Urabe *et al.*, 1986). More recently, their potential use in the construction of clay-modified electrodes (Rudzinski and Bard, 1986; Inoue *et al.*, 1988) has created a field of interest for electrochemists.

The fact that aluminum hydroxide can enter the interlayer of a montmorillonitic clay to form Al-interlayered montmorillonite and that the cation-exchange capacity of the clay is affected by this reaction is well known (Barnhisel, 1977; Keren *et al.*, 1977). A great deal of work has been carried out about the characteristics and behavior of montmorillonite modified with aluminum oligomers (Harsh and Doner, 1985; Carrado *et al.*, 1986; Rudzinski and Bard, 1986; Keren *et al.*, 1977), but almost no data exist that relate to surface charge determination using electrophoretic and acid-base potentiometric titration techniques (Hendershot and Laukulich, 1983; Cuisset, 1980; Delgado *et al.*, 1988). Although data about certain aspects of the surface charge of clay particles can be obtained from electrokinetic measurements, some difficulties arise in the theoretical interpretation of this behavior. This paper, therefore, compares the surface parameters of a natural and two hydroxy-aluminum intercalated montmorillonite samples studied by means of these techniques.

These surface parameters are then correlated with the aluminum content of the intercalated samples.

MATERIALS AND METHODS

The montmorillonite used in this study was obtained from Cerro Bandera, (province of Neuquén, Argentina) and was kindly supplied by A. K. Helmy. Its chemical analysis and cation-exchange capacity were reported by Peinemann *et al.* (1972); the composition reported by them is: SiO_2, 64.75%; Al_2O_3, 19.45%; Fe_2O_3, 4.25%; MgO, 3.46%; CaO, 1.16%; Na_2O, 2.94%; K_2O, 0.84%; P_2O_5, 0.53%; others, 2.62%, by weight. The <2-μm fraction was obtained by standard sedimentation methods (Black, 1965) and was then exchanged with Na^+. This sample will be referred to as Na-mont.

The Na-mont sample was pillared with aluminum polyhydroxide in our laboratory as follows: a 0.3 M $AlCl_3$ aqueous solution was titrated with 1.0 M NaOH solution to a OH/Al ratio of 2.37 and aged overnight. The resultant solution was added dropwise to a refluxing water suspension of Na-mont (3%) to about five times as much as the total cation-exchange capacity (CEC) (91.7 meq/100 g) of the clay. The boiling slurry was aged for 2 hr in accord with the method of Matsumoto *et al.* (1984). A polynuclear cation $(Al_{13}O_4(OH)_{24}(H_2O)_{12})^{7+}$ has been reported to be the predominantly formed cation at this OH/Al ratio (Occelli *et al.*, 1985). The product thus obtained was centrifuged until the supernatant was free of chlorides (negative reaction with silver nitrate) and then dried at 100°C in air. This sample hereafter will be referred

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to as sample MP1. A second pillared montmorillonite, supplied by the Grupo de Combustibles, Universidad Tecnológica Nacional, Facultad Regional de Córdoba, Córdoba, Argentina, was prepared from this same starting clay according to Corma *et al.* (1988). The oligomer solution was prepared by adding a 0.15 M NaOH solution to a 0.15 M $AlCl_3$ solution to a OH/Al ratio of 2, and aged for 6 hr. It was then added to the clay suspension to a final ratio of $(Al^{3+} meq)/(clay g) = 2$ (about twice the CEC of the clay). The intercalated clay thus obtained was filtered, thoroughly washed, and dried at 100°C in air. This sample will be referred to as sample MP2.

An aluminum hydroxide sample was obtained following the same technique as used to prepare the oligomeric solution of the sample MP1, but with a ratio OH/Al = 3. The precipitate was aged for three weeks at room temperature and used as reference.

All the solutions were prepared from analytical reagent grade chemicals and purified water (Milli-Q system). Electrophoretic measurements and acid-base potentiometric titrations were made in a purified nitrogen-saturated atmosphere at 30°C.

Specific surface area measurements and chemical analysis

The specific surface area of the different samples (Namont, MP1, and MP2) was determined by the ethylene glycol monoethyl ether (EGME) method (Carter *et al.,* 1965). Measured specific surface areas vary markedly depending on the nature of the adsorbate; for swelling clays the polar liquids, such as glycerol or EGME, give a specific surface area equal to the total of the external and interlamellar areas.

Chemical analysis for Al and Si was performed to determine the amount of oligomeric polyhydroxide species added to the clay. The samples were melted with lithium metaborate and then dissolved in a 5% HNO_3 solution (Suhr and Ingannells, 1966). The Al and Si content was measured by plasma-emission spectrometry with an Allied Analytical Systems Model IL Plasma 200 spectrometer.

X-ray powder diffraction

X-ray powder diffraction (XRD) patterns were obtained with a Philips PW 1140 diffractometer using Ni-filtered CuKα radiation (1.54 Å). Oriented powder samples mounted on glass slides were used for the determination of basal spacings [d(001)].

Thermal analyses

For thermal gravimetric analysis (TGA), differential thermal analysis (DTA), and differential thermal gravimetric analysis (DTG), 50 mg of the samples was heated under static air in a Netzsch 5TA 328 instrument from 25°C to 1100°C at a rate of 10°C/min using alumina as the reference material.

Electrophoretic measurements

Electrophoresis is often preferred over other electrokinetic techniques for the study of the electric double layer of dispersed montmorillonite particles. The determination of the zeta potential is connected with the hydrodynamic characteristics of a system, i.e., with the position of the slipping plane at the particle-solution interface. Zeta potentials are normally used as a criterion of stability in colloidal systems. In the present study the zeta potential variation was compared with the pH and the Al content of oligomeric species in the pillared samples.

The following procedure was used: an adequate amount of the sample was suspended in 0.01 M NaCl solution and ultrasonically dispersed. The resultant suspensions were allowed to equilibrate at the desired pH by adding different amounts of NaOH or HCl solutions. The measured electrophoretic mobilities were taken as the average of 20 pairs of readings carried out by alternating the polarity of the electrodes. The measured mobilities were converted to zeta potentials with the aid of a FORTRAN subroutine MOBLTY program designed by O'Brien and White (1978). The electrophoretic mobilities were determined using a micro-electrophoresis cell equipped with a Karl Zeiss citopherometre apparatus model 477500, belonging to the Comisión Nacional de Energia Atómica de Argentina.

Acid-base potentiometric titration

Acid-base potentiometric titration is one method for measuring surface charges and has been commonly used in the study of clays, metal oxides, and other compounds (Hesleitner *et al.,* 1987). The following procedure was used in the present study: measured amount of sample (0.10–0.12 g) was added to 200 ml of a decarbonated NaCl solution and ultrasonically dispersed. The resultant suspension was allowed to equilibrate overnight with continuous stirring and N_2 bubbling, prior to the addition of 1 ml of 0.08 M NaOH. When equilibration was achieved, the suspension was titrated with 0.07 M HCl. The pHs were recorded when the variation was <0.1 mV/min, that is, about 20–30 min after each addition of titrant. The pHs were measured using an Orion BN 9109 glass electrode. An Orion 900200 double-junction Ag/AgCl/Cl⁻ electrode was used as reference electrode; its outer compartment was filled with the same working solution to diminish the suspension effect (Breeuwsma, 1973). The titrations were performed using an Orion 960 automatic titrimeter. Equilibrium pHs were plotted against $(\Gamma_{H^+} - \Gamma_{OH^-})$ calculated as the difference between total H^+ or OH^- added at the suspension and those required to bring a blank solution of the same salt concentration to the same pH. The pH at which the curves intersected for the two salt concentrations was defined as PZSE (point of zero salt effect), according to Parker *et al.* (1979).

Table 1. Aluminum content and basal spacing of montmorillonite samples studied.

Sample[1]	Al content (% Al$_2$O$_3$)	d(001) (Å)
Na-mont	19.4	14.0
MP1	28.7	17.6
MP2	23.1	17.6

[1] See text for sample descriptions.

RESULTS AND DISCUSSION

Specific surface area measurements, chemical analysis, and X-ray powder diffraction

No significant difference was noticed among the measured specific surface areas of the samples, all the values being about 7 00 m^2/g. The Al content, calculated as Al$_2$O$_3$, is listed in Table 1. XRD patterns of the samples exhibited a first-order peak in the region < 10°2θ, corresponding to the basal spacing of the clay (Table 1). Na-mont had a basal spacing of 14.0 Å, which corresponds to that of a clay having 2–3 layers of intercalated water. The basal spacings of samples MP1 and MP2 were 17.6 Å, showing that their different aluminum hydroxide contents did not produce different basal spacing.

Thermal analyses

Figure 1 shows the loss of weight (TGA) as a function of temperature for the Na-mont and MP1 samples. Although not shown, the three samples were also examined by DTG and DTA. The Na-mont samples lost 10% of their initial weight due to the expulsion of surface water and an additional 4% due to the dehydroxylation of the clay. The DTG curves indicted that the latter percentage (4%) was lost in two steps of 2% each at 537° and 680°C. No relevant peaks were present in the DTA curves except for a slight exothermic peak at 920°C, which can be assigned to a phase transformation. These data are in accord with the literature (Occelli, 1986; Barnhisel, 1977).

Intercalated sample MP1 showed a less pronounced slope in the dehydration segment of the TGA curve. The temperature of the inflection point was similar to that found for the Na-mont sample, (135°C); however, the curve fell monotonically at a higher temperature (320°C), with a 13% weight loss. These data can be interpreted as an overlapping of the weight loss produced by water removal from the surface, the micropores, and the dehydroxylation of hydroxy-Al oligomers of the pillars. This overlapping did not allow the endothermic peak that results from the dehydroxylation of Al(OH)$_3$ (gibsite or bayerite) at 300°–330°C to be distinguished at temperatures > 320°C, however, the weight loss continued and the TGA curve showed a new inflection at a lower temperature (400°C) in addition to inflections at 520° and 697°C, already noted for the dehydroxylation of sample Na-mont. This new
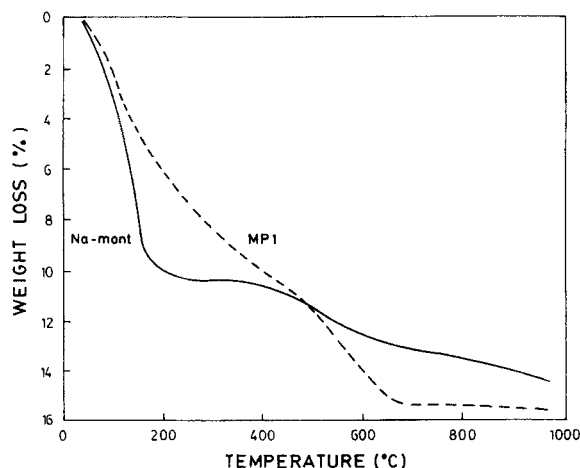

Figure 1. Thermogravimetric curves of samples MP1 and of Na-mont. (See text for description of samples.)

inflection at 400°C may have been due to the transformation of aluminum oxyhydroxide to aluminum oxide in the pillars. The overall weight loss of this sample was 18%. The DTA curves (not shown) also indicated an exothermic peak at 900°C, similar to that observed for the Na-mont sample, which can be attributed to the same phase transformation.

Although not shown, the TGA of the MP2 sample was very similar to that of the MP1 sample. Different methods of synthesis were employed for both samples, but no remarkable differences in the pillared samples were observed through the characterization techniques used in this study, except for their content of intercalated aluminum.

Electrophoretic measurements

The experimental data on the electrophoretic mobility was used to estimate the zeta potential of the particles. As specified above, the results were obtained using the treatment proposed by O'Brien and White (1978); no significant difference was observed between these results and those obtained using the Smoluchowski formula. Figure 2 shows the relation between the zeta potential and the pH for the three samples.

The Na-mont sample showed a negative zeta potential in the whole pH range (3.0–10.0), in agreement with Delgado *et al.* (1986, 1988). The decrease in the absolute value of the zeta potential as the pH diminished was probably due to the displacement of the equilibrium between the hydrogen of the solution and the hydroxyl groups of the particle edges, according to

$$SO^- + H^+ \rightleftharpoons SOH \qquad (1)$$
$$\text{and}$$
$$SOH + H^+ \rightleftharpoons SOH_2^+, \qquad (2)$$
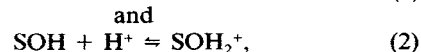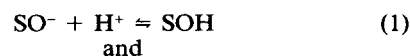
where S stands for any surface site.
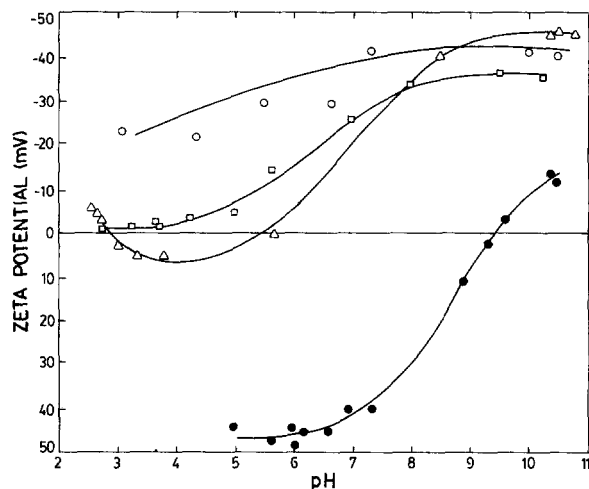
This displacement increased the variable positive

Figure 2.   Zeta potential (mV) at 30°C as a function of pH, $\bigcirc$ = Na-mont; $\triangle$ = MP1; $\square$ = MP2 and $\bullet$ = aluminum hydroxide. NaCl × 10^{-2} N. (See text for sample descriptions.)

Figure 3.   Potentiometric titration curves for $\square$ = Na-mont; $\bigcirc$ = MP1; $\triangle$ = MP2; open symbols = NaCl 10^{-2} M; filled symbols = NaCl 10^{-1} M. T = 30.0°C.

charge of the particle edges as the proton concentration in the bulk solution increased. Delgado *et al.* (1986, 1988) also pointed out that the positive charge developed on the edges is less in absolute value than the permanent negative charge on the faces. Thus, the net charge of the particle remains negative.

At pH >9 the pillared montmorillonite samples showed zeta potentials similar to those of the Na-mont sample, but at pH <8 the negative zeta potentials shifted to lower negative values. This behavior can be explained in terms of the surface positive charge developed at pH <8 by the hydroxy-Al oligomers. As reinforcement of the explanation of this behavior, the same illustration also shows the variation of zeta potential with pH for the hydroxy-Al sample. These values are in agreement with those reported by Matijević *et al.* (1973). On the other hand, the generation of positive charges on the surface of the pillars largely compensated the permanent negative charges of the particle faces in sample MP1, so that the zeta potential became positive at pH 5.0–5.5, which corresponds to the IEP value. In the same illustration, the zeta potential of sample MP1 becomes negative again at pH <4. The latter effect might have been due to the dissolution of the oligomers; thus, the negative charges of the clay became predominant again.

In sample MP2, the absolute negative zeta potential also decreased significantly, but not enough to reach positive values; hence, the IEP was not observed in the pH range studied. This result is consistent with the fact that sample MP2 contained fewer hydroxy-Al oligomers.

Acid-base potentiometric titration

Figure 3 shows the curves ($\Gamma_{H^+} - \Gamma_{OH^-}$) vs. pH for the Na-mont, MP1, and MP2 samples at two different
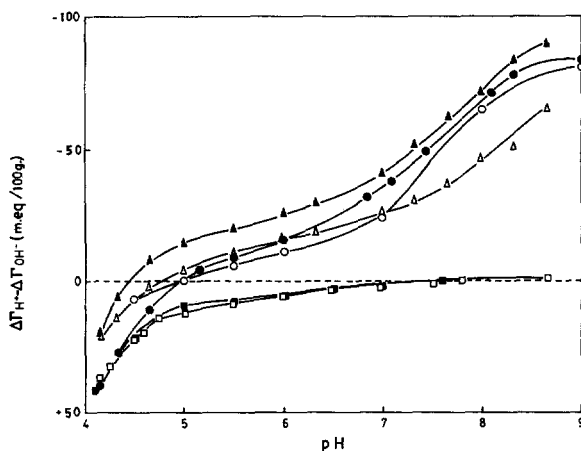
ionic strengths. The intercalation of Al species produced changes in the slope and shape of the curves as well as in the pHs where these curves intersect. The curves of sample MP1 show a well-defined PZSE at pH = 5.0. The curves of sample MP2 show no PZSE in the range of pH studied, but from their shape the cross-over point can be predicted to exist at a pH of about 4.2. The curves of the Na-mont sample are the same for both ionic strengths in the entire pH range studied, which can be explained in terms of the negligible contribution of the variable charge to the total charge of the clay. Thus, the Na-mont sample behaved as a particle having constant charge and a variable potential.

The increase in the slopes of the titration curves at pHs <5 is also of interest. This increase in the adsorption of H+ ions for the Na-mont sample can be explained by the Na+-H+ exchange according to the following equation, reported by Delgado *et al.* (1986):

$$\text{Na-mont} + \text{H}^+ \rightleftharpoons \text{H-mont} + \text{Na}^+. \qquad (3)$$
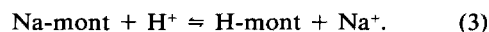
The same effect found for the pillared montmorillonite samples can be explained by the above-mentioned exchange equation, together with the dissolution of the intercalated aluminum species that produced the H+ depletion in the bulk solution. This latter effect was mentioned above as an explanation of the charge inversion observed in the mobility of sample MP1 at pH <4.0.

As seen in Figure 3, the PZSE of the samples correlates well with their intercalated aluminum content, because the PZSE values shift toward the PZSE value of Al_2O_3 (at about 9) (Sadek *et al.,* 1970) as the aluminum content increases.

Considering the PZSE to be the pH at which the net charge of the samples became zero, the amount of potential-determining ions adsorbed at pHs greater and
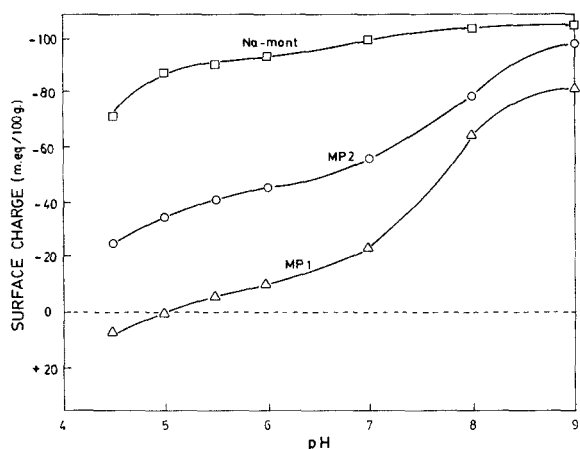
Figure 4. Charge density (μC/cm^2) variation as a function of pH of the suspension media. $\square$ = Na-mont; $\triangle$ = MP1; $\bigcirc$ = MP2 in NaCl 10^{-2} M. T = 30.0°C.

Table 2. Measured and calculated double layers parameters of different montmorillonite samples studied.[1]

pH	Ψ_Z	σ_Z	σ_0	Ψ_0	$C \times 10$
Na-mont					
8	−41.0	−1.05	−14.3	−164	7.7
7	−37.0	−0.93	−13.8	−162	7.7
6	−34.0	−0.84	−12.9	−159	7.0
5.5	−30.0	−0.73	−12.5	−157	6.7
5	−26.0	−0.62	−12.1	−155	6.4
4.5	−22.5	−0.53	−9.9	−145	5.6
MP1					
9	−42.5	−1.09	−11.3	−152	6.8
8	−39.0	−0.98	−8.97	−140	5.7
7	−32.0	−0.78	−3.28	−90	3.1
6	−15.5	−0.36	−1.51	−55	2.2
5.5	0.0	0.0	−0.83	−33	1.8
5	5.5	0.13	0.0	0.0	1.7
4.5	6.6	0.15	0.96	38	1.9
MP2					
9	−38.5	−0.97	−10.9	−150	6.4
8	−35.5	−0.88	−7.7	−132	5.1
7	−28.0	−0.68	−4.9	−110	3.8
6	−20.0	−0.47	−3.6	−94	3.0
5.5	−13.0	−0.30	−2.9	−84	2.7
5	−8.0	−0.185	−1.93	−65	2.2
4.5	−4.0	−0.092	−0.41	−18	1.7

[1] Values are given in the following units: zeta potential (Ψ_Z) and surface potential (Ψ_0) in mV; charge density in the slipping plane (σ_Z) and surface charge density (σ_0) in μC/cm^2; capacity (C) in meq/mV 100 g.

less than the PZSE is an estimation of the negative and positive charges developed on the particle, respectively. In this way, the net charge of samples MP1 and MP2 was calculated from the data in Figure 3 and are shown in Figure 4 for titrations performed in 10^{-2} N NaCl solution. As the Na-mont sample had no PZSE, the charge on this sample, (also shown in Figure 4) was calculated assuming that the edge of the particle was neutral at pH 6 (Delgado *et al.*, 1986); hence, at this pH the particle charge was its permanent structural charge (−91.7 meq/100 g). The net charge variation for other pHs was due to the adsorption of potential-determining ions on the particle edges [according to Eqs. (1) and (2)].

Experimental calculation of the double-layer parameters

Although the main goal of this investigation was to characterize the pillared material by physicochemical methods that are not frequently used for these types of materials, an attempt was also made to relate the data obtained from electrophoretic mobility and potentiometric titrations employing the semiempirical expression suggested by Loeb, Overbeek and Wiersema:

$$\sigma_Z = \epsilon_r \epsilon_0 \frac{kT}{ze} K[2 \sinh(zZ^*/2) + \frac{4}{Ka} \tanh(zZ^*/4)], \quad (4)$$

where σ_Z is the charge density at the slipping plane, a is the mean particle radius (about 10^{-4} cm for these samples), $Z^* = e\Psi_Z/kT$ is the dimensionless zeta potential, with Ψ_Z being the zeta potential calculated after O'Brien and White (1978), ϵ_r is the relative dielectric constant (80, dimensionless), ϵ_0 is the dielectric constant of vacuum = 8.854 coul^2/ N.m., k = Boltzman constant (1.38 $\times$ 10^{-16} erg K), T = 303 K, z is the

counterion's valency, and e = electron charge (−4.8 $\times$ 10^{-10} esu = 1.6 $\times$ 10^{-19} coul). For an estimation of the K value we made use of the formula $K^{-1} = 3.06$ molar concentration $^{-1/2}$ 10^{-8} cm.

From the zeta potential (Ψ_Z) obtained from electrokinetic measurements, the charge density (σ_Z) from the slipping plane was calculated at different pHs. The surface potential (Ψ_0) was also calculated from the charge values obtained from the titration curves assuming that all the charge was located on the particle surface. The surface charge density (σ_0) thus calculated was expressed in μC/cm^2. These results are summarized in Table 2 for the different samples in 10^{-2} N NaCl. Note that the charge density values calculated for the slipping plane were only about 10% of the surface charge density values. These values were in good agreement with those obtained by other authors (Delgado *et al.*, 1986), although they yielded very high capacitance values, possibly due to the fact that in the above expression the factors that arose from the presence of an electric field and the dynamic conditions of the kinetic measurements were not taken into account. Neither the porosity nor the roughness and shape of the particles were considered.

The Na-mont sample contained 19.45% Al$_2$O$_3$; samples MP1 and MP2 contained 28.70% and 23.10% Al$_2$O$_3$, respectively. These latter values comprise both

Al in its 2:1 layers and intercalated Al. Assuming that the intercalated Al was present as a polyhydroxy species having a 7+ charge, the net charge remaining on the clay, which was partially neutralized by the oligomer, was calculated. According to Peinemann *et al.* (1972), the Cerro Bandera montmorillonite has a cation-exchange capacity resulting from its structural charge of 91.7 meq/100 g. Taking into account the amount of Al in the 2:1 layers, the positive charge 7+ of the polyhydroxy species is sufficient to neutralize the entire 2:1 layer charge for sample MP1, but only about 50% of the 2:1 layer charge of the MP2 sample.

According to the literature (Hendershot and Laukulich, 1983; Sadek *et al.,* 1970), the surface charge of oxides and oxyhydroxides of Al is very small at pH ~9. Assuming that the charge of the pillars at this pH was negligible, the surface charge of samples MP1 and MP2 resulted from the charge of the clay. On the other hand, because the charge developed at the edge of the montmorillonite was small compared with the permanent structural charge, the charge of samples MP1 and MP2 was mainly structural charge. The data indicate at pH 9 a charge of -103.0 meq/100 g for the Na-mont sample, -93.0 meq/100 g for sample MP1, and -80.4 meq/100 g for sample MP2. Because 100 g of samples MP1 and MP2 contain, respectively, 90 and 95 g of montmorillonite, the clay appears to have retained most of its original charge. This effect was also observed by Sterte (1986).

The data obtained from the electrophoretic mobility agree well with those data obtained from the acid-base potentiometric titrations (Figures 2 and 4) in that: (1) the charge of the Na-mont sample was negative throughout the whole pH range studied; (2) the charge values were similar for the three samples at pH ~9; (3) the negative charge decreased markedly at pHs <8 for samples MP1 and MP2; and (4) the dissolution effect at pH <4 for samples MP1 and MP2 was as an increase in the slope of the titration curves and a shift of the zeta potential toward more negative values.

SUMMARY AND CONCLUSIONS

Some of the most important observations stemming from the present work are:

1. The potentiometric titration and electrophoretic data suggest that the intercalated material produced a shift of the PZSE and IEP (the pH at which the electrophoretic mobility = 0) of the sample as a whole toward the PZSE and IEP of the aluminum hydroxide.
2. The amount of this shift depended on the content of the hydroxy-Al oligomers.
3. The pillaring with aluminum polyhydroxy species changed the surface charge properties of the sample as a whole, although the clay retained most of its original structural charge.

4. The results obtained by both techniques, acid-base titrations and electrophoretic mobility, agreed.

The strong correlation between the surface parameters and the Al content of the intercalated samples suggests that these techniques could be useful to the characterization of such materials. Further studies are thus in progress in our laboratory.

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