

## ACIDIC PROPERTIES OF MONTMORILLONITE IN SELECTED SOLVENTS<sup>1</sup>

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**Abstract**—Montmorillonites saturated with  $\text{Al}^{3+}$ ,  $\text{H}^+\text{-Al}^{3+}$ , and  $\text{K}^+$  were titrated in  $\text{H}_2\text{O}$ , acetonitrile (AN), and dimethylformamide (DMF) to investigate the acidic properties of the clay in these solvents and to evaluate the application of nonaqueous titration procedures for studies of the acidic properties of 2:1 swelling clays. Samples were titrated with tetramethylammonium hydroxide using a combination glass electrode for potentiometric determination. Titrers of base required to reach the final potentiometric endpoints were greater in AN than in DMF and  $\text{H}_2\text{O}$ . The larger titers in AN compared to  $\text{H}_2\text{O}$  were attributed to pH-dependent sites for which an inflection was not observed in the latter solvent. Titration curves of Al-saturated montmorillonite in AN showed evidence of a salt-induced hydrolysis which was confirmed by titration curves of salt extracts. The hydrolysis reaction was more evident in AN than in  $\text{H}_2\text{O}$  and was probably due to a disruption of the  $\text{H}_2\text{O}$  structure by AN and a polarization of the  $\text{H}_2\text{O}$  of solvation. The hydrolysis reaction was enhanced in the presence of excess salt due to the ion exchange of  $\text{H}^+$  from the exchange surface. These studies indicate that acidic properties of clays may be drastically altered in organic solvents. The acidic properties may be used to advantage, for example, in the determination of edge-site acidity. In addition, they have implications concerning possible chemical reactions and/or alterations of clay in organic solvents.

**Key Words**—Acetonitrile, Acidic properties, Dimethylformamide, Hydrolysis, Montmorillonite, Water.

### INTRODUCTION

Numerous attempts have been made to quantify sources of acidity in pure clays, organic matter, or soils by means of titration curves (Jackson, 1963; Volk and Jackson, 1964; Coleman and Thomas, 1967; Loeppert *et al.*, 1977, 1979). Potentiometric and conductometric titrations with a variety of bases have been used to differentiate  $\text{H}^+$  from  $\text{Al}^{3+}$  at the clay surface (Low, 1955; Barshad, 1960; Coleman and Craig, 1961; Davis *et al.*, 1962; Shainberg and Dawson, 1967; Rich, 1970). Several researchers have used organic solvents for titrations of clay minerals. For example, Fripiat *et al.* (1960) used high-frequency conductometric titrations in ethylenediamine/benzene and acetone/benzene solvent mixtures to investigate the surface acidity of montmorillonite, kaolinite, cracking catalyst, and silica gel. Mitra and Kapoor (1969) titrated ( $\text{H}^+\text{-Al}^{3+}$ )-saturated montmorillonite in acetonitrile (AN), dimethylformamide (DMF), and  $\text{H}_2\text{O}$  and observed three endpoints in each solvent which were attributed to  $\text{H}^+$ ,  $\text{Al}^{3+}$ , and weakly acidic pH-dependent sites at the clay surface (Kapoor, 1972).

In a more recent study, Loeppert *et al.* (1977) titrated

$\text{H}^+$ -, ( $\text{H}^+\text{-Al}^{3+}$ )-, and  $\text{K}^+$ -saturated kaolinite in AN and  $\text{H}_2\text{O}$ . The significantly greater titer of base required to reach the final potentiometric endpoint with AN was attributed to (1) pH-dependent sites for which a quantitative endpoint was not obtained in  $\text{H}_2\text{O}$  due to the acidic properties of this solvent and (2) an increased surface acidity in AN. The titer of base required to reach the final endpoint of  $\text{K}^+$ -saturated kaolinite was dependent on solvent medium and increased according to the following solvent order: methanol  $\leq$   $\text{H}_2\text{O}$  < 1-propanol < 1-butanol < 2-propanol < DMF < t-butanol < dimethylsulfoxide < pyridine < AN  $\leq$  methylethyl ketone < acetone (Loeppert *et al.*, 1979).

The objectives of the present study were to determine the acidic behavior of  $\text{Al}^{3+}$ -, ( $\text{H}^+\text{-Al}^{3+}$ )-, and  $\text{K}^+$ -saturated montmorillonite in  $\text{H}_2\text{O}$ , DMF, and AN and to evaluate the application of nonaqueous titration procedures to ascertain the acidic properties of 2:1 swelling clays.

### EXPERIMENTAL

#### *Solvents*

The solvents used in this study were deionized  $\text{H}_2\text{O}$ , spectroquality acetonitrile (AN), and dimethylform-

amide (DMF). Solvents were checked for the presence of acidic impurities by titrating 20 ml of solvent with 0.033 M tetramethylammonium hydroxide (TMAOH). The solvent was considered acceptable if <0.01 ml of standard base was required to reach the final potentiometric inflection.

#### Preparation of basic titrants

The TMAOH titrant was prepared by adding 8 ml of reagent grade 24% TMAOH in methanol to 42 ml of methanol and diluting to exactly 500 ml with benzene. Titrant for aqueous media was prepared by diluting 8 ml of 24% TMAOH in methanol to 500 ml with H<sub>2</sub>O. Basic titrants, standardized with benzoic acid in methanol, were determined to have concentrations of 0.033 M.

#### Preparation of clays

The montmorillonitic sample (SWy-1) used in this study was obtained from the Source Clays Repository of The Clay Minerals Society. The <2.0- $\mu$ m fraction was obtained by sedimentation and decantation procedures (Jackson, 1967). Samples were pretreated with two 5-min mechanical shakings of the clay with an amount of 0.1 M HCl equal to 20 times the cation-exchange capacity of the clay (i.e., 20 CEC equivalents) and washed with H<sub>2</sub>O until free of Cl<sup>-</sup>. The pretreated clays were Al<sup>3+</sup>-, K<sup>+</sup>-, and Na<sup>+</sup>-saturated by four successive 10-min mechanical shakings of the clay with the appropriate 1.0 M chloride solution. The suspension was centrifuged and the supernatant discarded after each washing. The clay samples were desalted by five successive 10-min washings with the appropriate 0.0001 M chloride solution. The H<sup>+</sup>-saturated clay was prepared by passing a 0.2% suspension of the Na<sup>+</sup>-saturated clay through a H<sup>+</sup>-saturated, strong-acid ion-exchange resin. This clay immediately began autoconversion to a (H<sup>+</sup>-Al<sup>3+</sup>-Mg<sup>2+</sup>) saturation, and in the subsequent discussion is referred to as a (H<sup>+</sup>-Al<sup>3+</sup>)-saturated clay. All clays were suspended in deionized H<sub>2</sub>O, freeze-dried, and equilibrated over P<sub>2</sub>O<sub>5</sub> in a desiccator for 24 hr at 2°C prior to titration.

#### Titration procedures

Experimental procedures for nonaqueous titrations have been extensively reviewed (Kucharsky and Safarik, 1965; Huber, 1967; Fritz, 1973). Titration equipment and procedures for titration of clays were discussed by Loeppert *et al.* (1977). In the present study a Radiometer combination electrode with a porous-plug liquid junction was used for all potentiometric determinations. For titrations in DMF and AN the calomel cell was filled with a saturated solution of KCl in methanol.

Solvent (40 ml) was added to 0.1 g of Al<sup>3+</sup>- or (H<sup>+</sup>-Al<sup>3+</sup>)-saturated montmorillonite, 0.6 g of K-saturated montmorillonite, or sample plus salt, and allowed to

equilibrate for about 20 min prior to titration. The excess salt used in this study was tetramethylammonium chloride (TMACl) at an amount to give a 0.1 M solution, although the salt was not soluble at this level in all experiments.

During titration dry N<sub>2</sub> was bubbled at a rate of about 200 ml/min into the suspension which was agitated with a paddle stirrer. A stepped-titration mode was employed with a titrant-flow rate of 0.05 ml/min and vertical-sweep rate of 50 mV/min. Titration curves were plotted as potential in millivolts vs. volume of added base. Millivolt potential was recorded inasmuch as pH has little significance in the organic solvent systems. For titrations of extracts, a titrant-flow rate of 0.200 ml/min and a vertical-sweep rate of 200 mV/min were used.

#### Extraction studies

Separate 100 mg samples of (H<sup>+</sup>-Al<sup>3+</sup>)- or Al<sup>3+</sup>-saturated montmorillonite were extracted with 20-ml aliquots of AN or DMF in the presence of 0.002 moles of TMACl or KCl. Samples were centrifuged, and 10-ml aliquots were taken and diluted with exactly 10 ml of deionized H<sub>2</sub>O for titration. Following extraction, the Al<sup>3+</sup>-saturated residues were also titrated in a 1:1 solvent:H<sub>2</sub>O mixture. Titration curves of extracts were compared with titration curves of H<sup>+</sup> and Al<sup>3+</sup> in the same solvent mixtures. Solutions of H<sup>+</sup> and Al<sup>3+</sup> were prepared by adding the 1.0 M chloride salt in H<sub>2</sub>O, at an amount equivalent to that extracted from the clay extracts, to a solvent mixture containing 10 ml of AN or DMF, and 10 ml of deionized H<sub>2</sub>O. Separate samples of clay extracts were evaporated to dryness. The solute was redissolved in 0.1 M HCl, and the Al<sup>3+</sup> content was determined colorimetrically by the aluminum procedure (Barnhisel and Bertsch, 1982).

## RESULTS AND DISCUSSION

The amount of base required to reach the final potentiometric inflection in the titration of Al<sup>3+</sup>-saturated montmorillonite (Figure 1) decreased according to the following solvent order: AN  $\geq$  H<sub>2</sub>O > DMF. The slightly larger titers observed when AN was used as the titration medium may have been due to the weaker acidic character of this solvent which would aid in the titration of weakly acidic pH-dependent sites (Kapoor, 1972; Loeppert *et al.*, 1977). Also, the larger titers in AN may have been partially due to an increased acidic character of the pH-dependent sites in this solvent, as was suggested for kaolinite by Loeppert *et al.* (1977, 1979).

The presence of excess neutral salt did not noticeably affect the quantity of base required to reach the final endpoint in H<sub>2</sub>O and resulted in only a slight increase in AN. The most noticeable difference was the strong extra inflection observed with AN in the presence of excess neutral salt (Figure 1). In DMF, titers of base

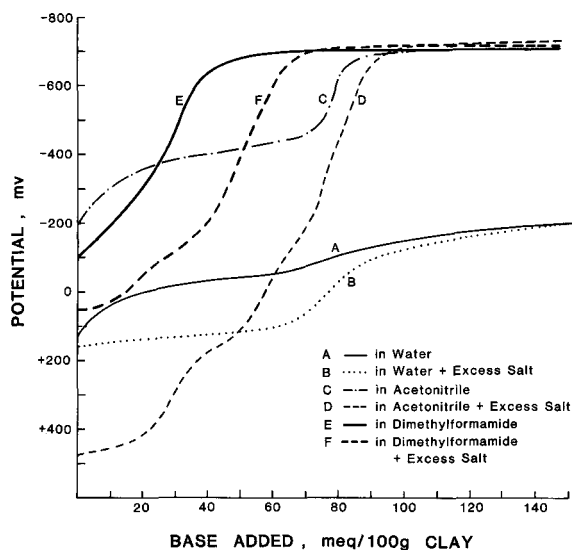


Figure 1. Titration of 0.1 g of  $\text{Al}^{3+}$ -saturated montmorillonite in 40 ml of selected solvents with tetramethylammonium hydroxide.

to the final inflection were significantly greater in the presence than in the absence of excess neutral salt.

Nuclear magnetic resonance (NMR) studies have shown that  $\text{Al}^{3+}$  ions assume octahedrally coordinated structures with six  $\text{H}_2\text{O}$  molecules in the primary hydration spheres (Connick and Fiat, 1963). Amides can successfully compete with  $\text{H}_2\text{O}$  for solvation of  $\text{Al}^{3+}$  ions (Fratello *et al.*, 1967). Because DMF can displace  $\text{H}_2\text{O}$  from the primary solvation sphere of  $\text{Al}^{3+}$ , the acidic properties of adsorbed  $\text{Al}^{3+}$  undoubtedly were altered when DMF was the solvent. This phenomenon was probably responsible for the lower titers and slower rates of reaction in DMF compared with  $\text{H}_2\text{O}$  (Figure 1).

Results of the titrations of salt extracts and residual samples are summarized in Table 1. Single TMACl extracts of  $\text{Al}^{3+}$ -saturated montmorillonite in  $\text{H}_2\text{O}$ , AN, and DMF had total extractable acidities of 40, 27, and 6 meq/100 g clay, respectively. The titration curve of the AN-TMACl extract of  $\text{Al}^{3+}$ -saturated montmorillonite in the AN- $\text{H}_2\text{O}$  mixture had two potentiometric

Table 1. Titratable acidities of  $\text{Al}^{3+}$ -saturated montmorillonite, tetramethylammonium chloride extracts and residues.

Extracting solvent	$\text{Al}^{3+}$ -saturated montmorillonite <sup>1</sup> (meq/100 g)	TMACl extract <sup>1,2</sup> (meq/100 g)	Residue following extraction <sup>1</sup> (meq/100 g)
Water	75.0	40.3	37.6
Acetonitrile	79.0	26.9	50.7
Dimethylformamide	75.1	6.4	66.3

<sup>1</sup> Titratable acidity determined in 50:50 (v:v) extracting solvent:  $\text{H}_2\text{O}$  solvent mixture.

<sup>2</sup> TMACl = tetramethylammonium chloride.

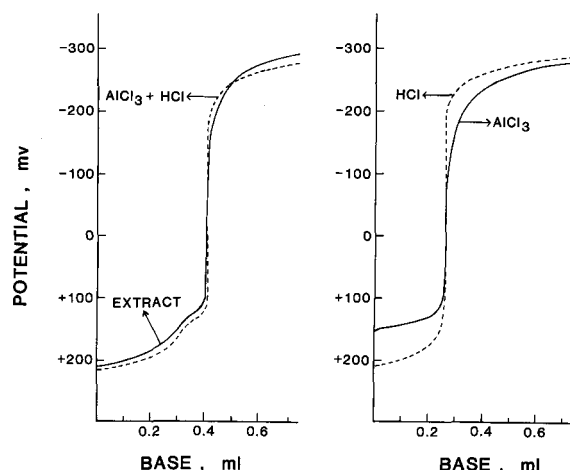


Figure 2. Titration of the acetonitrile/tetramethylammonium chloride extract of  $\text{Al}^{3+}$ -saturated montmorillonite in 50:50 (v:v) acetonitrile:  $\text{H}_2\text{O}$ . Titrations of  $\text{HCl}$ ,  $\text{AlCl}_3$ , and  $\text{HCl} + \text{AlCl}_3$  in the same solvent mixture are shown for comparison.

endpoints (Figure 2). The shape of the curve corresponded closely to that of a mixture of  $\text{HCl}$  and  $\text{AlCl}_3$  in a similar solvent mixture, thus providing evidence that both  $\text{H}^+$  and  $\text{Al}^{3+}$  were present in the AN-TMACl extract of  $\text{Al}^{3+}$ -saturated montmorillonite. Colorimetric analyses provided further evidence for the presence of  $\text{Al}^{3+}$  in the extract. Results similar to those described above were obtained when  $\text{KCl}$  was used as the extracting salt.

Titration curves of the residue in  $\text{H}_2\text{O}$ -AN following extraction with AN-TMACl showed a reduction in titratable acidity of 28 meq/100 g from the original titer observed in  $\text{H}_2\text{O}$ -AN (Table 1). This loss corresponded closely to the AN-TMACl extractable acidity.

The titration curves of DMF-TMACl and  $\text{H}_2\text{O}$ -TMACl extracts of  $\text{Al}^{3+}$ -saturated montmorillonite obtained in DMF- $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}$ , respectively, each showed a potentiometric inflection which corresponded closely to that of  $\text{Al}^{3+}$  in the same solvent mixture. Therefore, titration curves provided strong evidence that  $\text{Al}^{3+}$  was the predominant acidic species released during exchange reactions in these solvents. Colorimetric analyses confirmed that  $\text{Al}^{3+}$  was a primary source of acidity in the  $\text{H}_2\text{O}$  and DMF extracts. Therefore, the  $\text{H}_2\text{O}$ -TMACl or DMF-TMACl extracts provided no evidence of the spontaneous hydrolysis of exchangeable  $\text{Al}^{3+}$ , as was observed in the AN-TMACl system.

Of the three solvents used in this study AN is the weakest base (Kolthoff, 1974). Water has a relatively strong basic character, as indicated by its tendency to form hydrogen bonds and its relatively high autoprotolysis constant. Likewise, DMF has significant basic character due to the presence of two basic centers (Tahoun and Mortland, 1966).

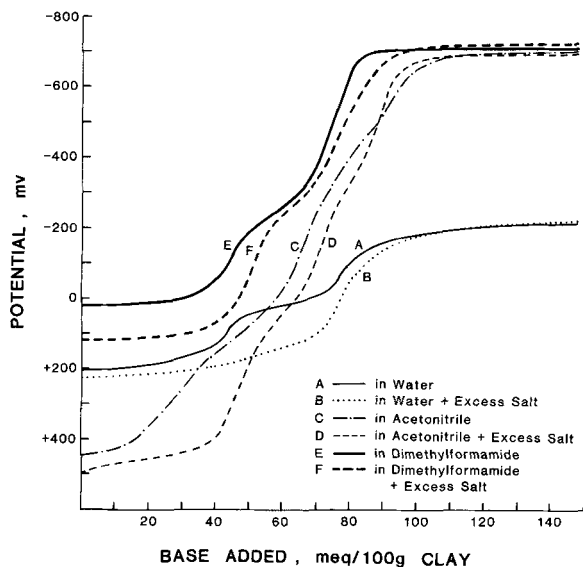


Figure 3. Titration of 0.1 g of  $H^+$ ,  $Al^{3+}$ -saturated montmorillonite in 40 ml of selected solvents with tetramethylammonium hydroxide.

Harter and Ahlrichs (1969), Mortland (1968), Mortland and Raman (1968), Solomon and Murray (1972), and Frenkel (1974) showed that surface acidity increases as the degree of surface hydration decreases. Mortland and Raman (1968) proposed a mechanism by which the degree of polarization of remaining  $H_2O$  of hydration and the resultant surface acidity increase with decreasing  $H_2O$  content. In the presence of a solvent with basic properties, the degree of polarization in the model suggested by Mortland (1968) and Mortland and Raman (1968) should be reduced because the charge associated with  $Al^{3+}$  is partially distributed by interaction of  $Al^{3+}$  and remaining  $H_2O$  of hydration with the solvent molecules. For example, for  $Al^{3+}$ -saturated montmorillonite suspended in  $H_2O$ , the charge associated with  $Al^{3+}$  and  $H_2O$  molecules in the primary hydration shell is reduced due to H-bonding with additional  $H_2O$  molecules, i.e., the effective charge density of the  $Al^{3+}$ -solvent complex is reduced. Therefore, effective charge on the primary charge centers (Al and H atoms in the primary hydration shell) is reduced, and polarization of  $H_2O$  in the primary hydration shell is reduced at the clay surface.

The reactions in organic solvents are less understood because solvation behavior of  $Al^{3+}$  in organic and mixed solvent systems at low  $H_2O$  contents is more complex. Water is a much more powerful complexant of  $Al^{3+}$  than is AN, and water displaces AN almost quantitatively from the solvation sphere (Supran and Sheppard, 1967; Fratiello *et al.*, 1967; Wehrli and Wehrli, 1981). Therefore, under the conditions of the present experiment, it is likely that in AN the  $Al^{3+}$  remained solvated with  $H_2O$ ; however, the secondary structure of  $H_2O$ ,

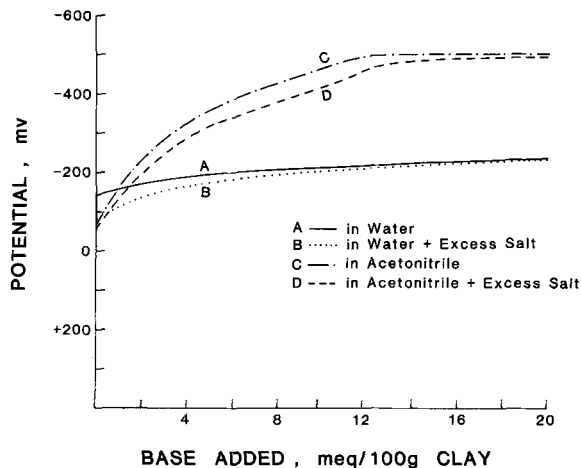
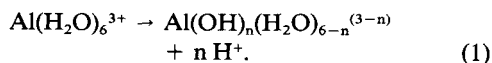


Figure 4. Titration of 0.6 g of  $K^+$ -saturated montmorillonite in 40 ml of selected solvents with tetramethylammonium hydroxide.

i.e., the outer hydration sphere, was probably totally disrupted. In AN, the charge is distributed by solvation of the  $Al^{3+}$  and/or by dipole-dipole interactions between AN and  $H_2O$  of hydration. The properties of the solvents suggest that the ionic charge should be less distributed in AN than in  $H_2O$ . Therefore, the charge should be concentrated to a greater extent at the positive charge centers, and polarization according to the model proposed by Mortland and Raman (1968) should proceed to a greater extent.

A polarization reaction similar to that described by Mortland (1968) is summarized as follows:



As the polarization reaction proceeds and the acidity at the clay surface increases, the hydrolysis reaction should continue until an equilibrium of  $Al^{3+}$  with  $H^+$  is reached. At this point, the net reaction should cease unless  $H^+$  is removed from the surface. The addition of excess neutral salt favors the continuation of the  $Al^{3+}$  hydrolysis reaction by replacing  $H^+$  from the clay surface.

Ragland and Coleman (1960) found that the hydrolysis of  $AlCl_3$  proceeded further in the presence of clay minerals and soils than in aqueous solution. In their experiments,  $Al^{3+}$ -saturated clay was leached with dilute  $AlCl_3$ , and  $Al^{3+}$  served as the replacing cation for H produced during the hydrolysis reaction. Kaddah and Coleman (1967), Rich (1970), and Kissel *et al.* (1971) demonstrated that the presence of excess neutral salt induced  $Al^{3+}$  hydrolysis at the clay surface. Similar results were observed in the present study, although the presence of the weakly basic solvent greatly accelerated the hydrolysis reaction.

Shirvington (1967) observed that hydrolysis of hydrated  $AlCl_3$  was promoted in AN to produce ion-

paired halogen acids and Al-hydroxy complexes. In the present study, the titration curves of  $\text{AlCl}_3$  in AN, in either the presence or the absence of  $\text{TMACl}$  or  $\text{KCl}$ , showed evidence for the production of a proton; however, in the presence of the clay the apparent hydrolysis of  $\text{Al}(\text{OH})_2^{3+}$  was greatly accelerated, especially in the presence of excess salt.

Titration curves for  $(\text{H}^+ - \text{Al}^{3+})$ -saturated montmorillonite in the absence and presence of excess neutral salt are shown in Figure 3. The quantity of base required to reach the potentiometric endpoints decreased in the following order:  $\text{AN} > \text{H}_2\text{O} \geq \text{DMF}$ . Titration curves in  $\text{H}_2\text{O}$  contained two inflection points, which are characteristic of  $(\text{H}^+ - \text{Al}^{3+})$ -saturated montmorillonite (Low, 1955; Barshad, 1960; Coleman and Craig, 1961; and Davis *et al.*, 1962). The curves obtained by titration in DMF yielded two endpoints, which are also attributed to  $\text{H}^+$  and  $\text{Al}^{3+}$ . Titrations in AN resulted in complex but reproducible curves containing several noticeable inflections.

The quantity of base required to reach the final potentiometric endpoint of  $(\text{H}^+ - \text{Al}^{3+})$ -saturated montmorillonite was about 7 meq/100 g more in AN than in  $\text{H}_2\text{O}$ . This increased total titer may be attributed to pH-dependent sources of acidity as suggested by Kapoor (1972) and Loeppert *et al.* (1977, 1979) and possibly to Al-hydroxy contaminants.

Titration of  $\text{K}^+$ -saturated montmorillonite in  $\text{H}_2\text{O}$  (Figure 4) in the presence of excess salt resulted in a trailing curve with no noticeable inflection, compared to titration in AN which resulted in sloping curves with a final weak inflection at approximately 11 meq/100 g of clay. The final endpoint of  $\text{K}^+$ -saturated montmorillonite in AN was slightly greater than the difference in total titer observed between curves obtained with AN and  $\text{H}_2\text{O}$  as the solvent media for either  $\text{Al}^{3+}$ - or  $(\text{H}^+ - \text{Al}^{3+})$ -saturated montmorillonite. This inflection observed during titration of  $\text{K}^+$ -saturated montmorillonite reinforces the previous assumption that the increased total titer of  $(\text{H}^+ - \text{Al}^{3+})$ -saturated montmorillonite in AN compared to  $\text{H}_2\text{O}$  may have been due to pH-dependent sources of acidity.

### CONCLUSIONS

The present study indicates that the acidic properties of montmorillonite may be drastically altered in organic solvent systems. These acidic properties may be used to advantage in studies of clays, e.g., the possible determination of edge-site acidity. The observed salt-induced hydrolysis of  $\text{Al}^{3+}$ -saturated montmorillonite has implications concerning possible chemical reactions and/or alterations of clay in organic solvent systems.

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