TITRATION OF pH-DEPENDENT SITES OF KAOLINITE IN WATER AND SELECTED NONAQUEOUS SOLVENTS

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Abstract—K-saturated kaolinite was titrated in 13 different solvents with tetrabutylammonium hydroxide using a combination electrode for potentiometric determination. The titer of base required to reach the final potentiometric endpoint was dependent on the solvent and increased according to the following solvent order in both the presence and absence of excess neutral salt: methanol $\leqslant$ water $<$ ethanol $\leqslant$ 1-propanol $<$ 1-butanol $<$ 2-propanol $<$ DMF $<$ t-butanol $<$ DMSO $<$ pyridine $\leqslant$ acetonitrile $\leqslant$ methylethyl ketone $<$ acetone. With the protic solvents, titratable acidity increased according to decreasing dielectric constant of the solvent and increasing size and/or branching of the aliphatic constituent. The largest titratable acidities were obtained in the dipolar aprotic solvents with negligible basic character (e.g., acetonitrile, acetone, methylethyl ketone). These results are discussed in terms of solvent properties, solvation characteristics of ions in the solvents, and acid-base behavior of crystalline edge sites.

Key Words—Acidity, Kaolinite, Solvents, Titration.

INTRODUCTION

In a previous study, Loeppert et al. (1977) titrated K-saturated kaolinite in both acetonitrile and water and observed that the titer of base required to reach the final potentiometric end point was greater in the organic solvent. Since constant charge sites of the mineral were occupied by K^+, acidic species which were titrated were assumed to originate predominantly from pH-dependent edge sites. The larger titers in acetonitrile were attributed to: (1) pH-dependent sites for which a quantitative end point was not obtained in water due to the acid-base properties of this solvent, and (2) an increased surface acidity in acetonitrile. Mitra and Kapoor (1969) and Kapoor (1972) titrated acidified nontronite in water and several nonaqueous solvents and obtained larger titers of base at the final end point as well as more complex titration curves in the organic solvents. They attributed the larger titers in the organic solvents to weakly acidic pH-dependent sites. In an earlier study, Fripiat et al. (1960) used high frequency conductimetric titrations in ethylenediamine-benzene and acetone-benzene solvent mixtures to investigate the surface acidity of montmorillonite, kaolinite, cracking catalyst, and silica gel.

The objective of this study was to investigate the effect of solvent on titration of acidic crystalline edge sites of K-saturated kaolinite.

MATERIALS AND METHODS

The 13 solvents used in this study are shown in Table 1 along with some of their physical and chemical properties. All organic solvents were spectroquality and were stored over 3 Å molecular sieves prior to use. The

presence of acidic impurities was checked by titrating 20 ml of solvent with 0.01 N tetrabutylammonium hydroxide.

Tetrabutylammonium hydroxide titrant, approximately 0.01 N, was prepared by diluting 5 ml of 25% tetrabutylammonium hydroxide to 500 ml with spectroquality 2-propanol and was standardized with primary standard benzoic acid in methanol.

Kaolinite, ultrafine hydrite grade, was obtained from the Georgia Kaolin Company. The $<2.0\ \mu$m clay fraction was washed twice for 5 min with 0.1 N HCl and was leached immediately with deionized water in a large Büchner funnel following each treatment with HCl. This procedure was performed to remove amorphous Al-sesquioxide coatings from the clay surface. K-saturation was accomplished by three 10-min mechanical shakings of the clay with 0.1 N KCl. The suspension was centrifuged and the supernate discarded after each washing. The K-saturated clay was desalted by successive 10-min washings with deionized water until the supernate gave a negative test for Cl^-. The clay was subsequently freeze-dried, stored at 0°C, and equilibrated over P_2O_5 in a desiccator for 18 hr prior to titration.

Titration equipment and procedures have been described previously (Loeppert et al., 1977). A Radiometer combination electrode with porous plug liquid junction was used for all potentiometric determinations. Solvent (25 ml) previously dried over 3 Å molecular sieves was added to a 0.3 g clay sample and allowed to equilibrate for 24 hr in a N_2 atmosphere prior to titration. Excess salt, tetraethylammonium iodide, previously dried over P_2O_5, was added 5 min prior to the start of the titration to give a 0.1 M solution. The sample was agitated with a mechanical stirrer for a 5 min period as dry N_2 was bubbled through the suspension. Titrations were then performed with dry N_2 passed continuously over the suspension which was agitated with a me-

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Table 1. Properties of selected solvents used in this study.[1]

Solvent	ϵ[2]	Potential Range[3] mv	pks[2]
water	78.3	500	14.00
methanol	32.6	650	16.7
ethanol	24.3	—	19.1
1-propanol	20.1	—	19.4
1-butanol	17.1[4]	—	21.6[4]
2-propanol	18.3	1000	20.8
t-butanol	11.6[4]	1200	—
DMF	36.7	1300	18.0(20°C)
DMSO	46.7	1200	33.3
acetonitrile	36.0	1500	28.5
acetone	20.7	1550	—
MEK	—	750	—
pyridine	12.3	1050	—

[1] All values listed were obtained at 25°C unless otherwise noted.
[2] Obtained from values tabulated by Bates (1973).
[3] Obtained from Fritz (1973).
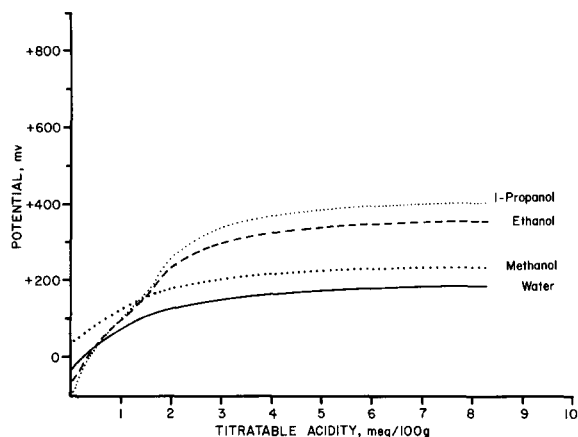[4] Obtained from values tabulated by King (1973).

Fig. 1. Titration of 0.30 g of P_2O_5-dried K-saturated kaolinite in 25 ml of water and selected protic solvents with 0.01248 N tetrabutylammonium hydroxide in the presence of excess neutral salt.

chanical stirrer. Titratable acidities (Table 2) were reported as the total quantity of base added at the final end point (Δ potential/Δ volume of base)$_{max}$ observed during titration of the clay.

RESULTS AND DISCUSSION

Titrations of K-saturated kaolinite in water and methanol resulted in sloping titration curves with no noticeable end points (Figure 1), compared to titrations in each of the other solvents which produced noticeable inflections (Figures 1–4) and required significant titers of base to reach the final end points (Table 2). The quantity of base required was dependent on the solvent and increased in the following order in both the absence and presence of excess neutral salt: methanol $\leq$ water < ethanol $\leq$ 1-propanol < 1-butanol < 2-propanol < dimethylformamide (DMF) < t-butanol < dimethyl-

sulfoxide (DMSO) < pyridine $\leq$ acetonitrile $\leq$ methylethyl ketone (MEK) < acetone. Since the clay was pretreated to remove amorphous coatings from the surface prior to saturation with K^+ and since the constant charge sites of the mineral were saturated with K^+, the acidic species which were titrated were assumed to originate predominantly from pH-dependent sites at the crystalline clay edges. This acidity would originate from exposed Al and Si atoms at the edges of octahedral and tetrahedral sheets, respectively. With the sample in an aqueous environment, the coordination spheres of these exposed atoms are completed by strongly bound H_2O and OH^-. Solvation characteristics of exposed atoms in nonaqueous systems would be much more complex, although the abundant literature concerning solvation of ions in aqueous, organic, and mixed solvent systems may provide clues which will allow us to hypothesize concerning solvation properties at the clay surface.

Table 2. Titratable acidity of K-kaolinite in selected solvents in the presence of excess neutral salt (tetraethylammonium iodide).

Solvent	Titratable acidity[1]
	meq/100 g
water	0.00 (0.00–0.00)
methanol	0.00 (0.00–0.00)
ethanol	1.46 (1.45–1.47)
1-propanol	1.68 (1.47–1.78)
1-butanol	2.01 (1.96–2.06)
2-propanol	2.58 (2.52–2.69)
DMF	2.88 (2.79–2.97)
t-butanol	3.36 (3.32–3.40)
DMSO	3.63 (3.60–3.66)
pyridine	3.86 (3.71–4.00)
acetonitrile	4.04 (3.90–4.13)
methylethyl ketone	4.16 (4.13–4.18)
acetone	4.30 (4.26–4.33)

[1] Values given in parenthesis are the range of three replications.

Table 3. Classification scheme for solvents.

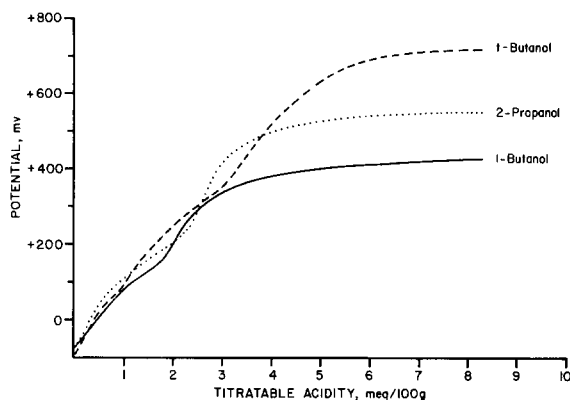| Major class	Subdivision	Group	Solvents[1]
Nonpolar		A	hexane, benzene
Protic	aqueous	B1	water (78.3)
	$\epsilon > 30$	B2	methanol (32.6)
	$\epsilon < 30$	B3	ethanol (24.3)
			1-propanol (20.1)
			2-propanol (18.3)
			1-butanol (17.1)
			t-butanol (11.6)
Dipolar aprotic	basic	C1	DMSO
			DMF
			pyridine
	very weakly basic	C2	acetone
			methylethyl ketone
			acetonitrile

[1] Dielectric constants are given in parenthesis.

Fig. 2. Titration of 0.30 g of P_2O_5-dried K-saturated kaolinite in 25 ml of selected protic solvents with 0.01248 N tetrabutylammonium hydroxide in the presence of excess neutral salt.

Fig. 4. Titration of 0.30 g of P_2O_5-dried K-saturated kaolinite in 25 ml of selected very weakly basic dipolar aprotic solvents with 0.01248 N tetrabutylammonium hydroxide in the presence of excess neutral salt.

Four possible conditions of solvation may exist in the nonaqueous solvent: (1) Al or Si atoms at the crystalline clay edges may remain solvated with water, (2) edge sites may become desolvated and exist as unsolvated Lewis acid sites, (3) edge sites may become solvated by the organic solvent, or (4) water completing the hydration sphere of ions at the edge sites may be polarized to a greater extent resulting in increased hydrolysis and decreased positive charge character and/or increased negative charge character of the edge sites. Intermediates or combinations of these four conditions may also exist.

The effect of solvent on potentiometric titration and acid-base behavior of K-saturated kaolinite can be evaluated by examining the properties of the solvents. Solvents may be classified and compared according to physical or chemical properties (e.g., dielectric constant, viscosity, autoprotolysis constant, H-bonding character, solubility parameter, solvating ability, etc.).
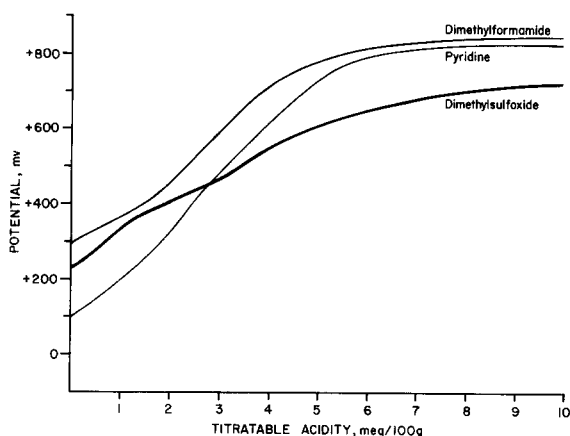

Fig. 3. Titration of 0.30 g of P_2O_5-dried K-saturated kaolinite in 25 ml of selected basic dipolar aprotic solvents with 0.01248 N tetrabutylammonium hydroxide in the presence of excess neutral salt.
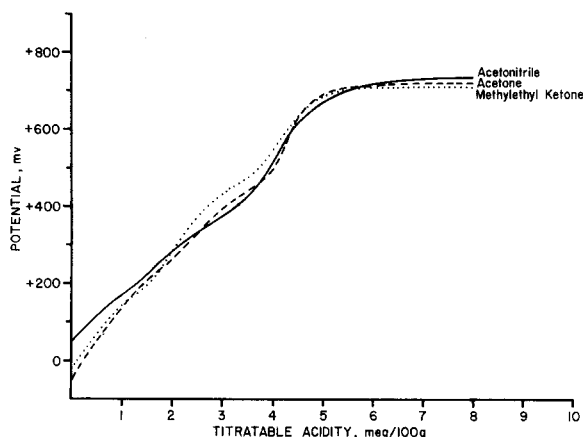
Each of the above-listed properties would influence reactions at the clay surface.

Numerous solvent classification schemes have been devised (Fritz, 1973; King, 1973; Kolthoff, 1974). For our purposes, we shall divide the solvents into three general groupings (Table 3): (1) nonpolar or weakly polar, (2) protic, and (3) dipolar aprotic. The protic solvents are further subdivided according to dielectric constant and the dipolar aprotic solvents according to relative basicity.

Protic solvents

The titratable acidity determined in the protic solvents decreased according to the following solvent order: t-butanol > 2-propanol > 1-butanol > 1-propanol ≥ ethanol >methanol = H_2O (Table 2, Figures 1, 2). This sequence follows the same general order of decreasing dielectric constant and size and/or branching of the C chain. In a previous paper, Loeppert et al. (1977) speculated that the low titers of K-saturated kaolinite in water may be partially attributed to the acidic character of this solvent which would prevent a quantitative end point during potentiometric titration. Methanol is a stronger acid than water under some conditions (Hine and Hine, 1952). The acidic character of water and methanol may account for the smaller titratable acidity in these solvents than in the other solvents. The aliphatic alcohols have been shown to decrease in relative acidity according to the order: methanol > 1-propanol > 2-butanol > t-butanol (Brown and Rogers, 1957). Therefore, higher alcohols, due to their weaker acidic character, may be more desirable than water or methanol for titration of weak acids. Also, the higher alcohols have larger autoprotolysis constants and wider working potential ranges than the lower alcohols (Table 1).

Nuclear magnetic resonance (NMR) studies have shown that Al^{3+} ions assume octahedrally coordinated

structures in aqueous systems, with six water molecules in the primary hydration spheres (Connick and Fiat, 1963). On the contrary, in ethanol (Grasdalen, 1971) and 1-propanol (Grasdalen, 1972) the solvation number for Al^{3+} decreased to four. The Al^{3+} ion was tetrahedrally coordinated by the ligand O atoms with no competition from Cl^- ions for solvation shell sites and with ligand exchange apparently occurring via exchange of the entire alcohol molecule. In methanol, Al^{3+} ion maintains a solvation number of 6 (Grasdalen, 1972). Exposed Al at the crystal edge of kaolinite is in an octahedral symmetry. It is likely that the higher alcohols would be unable to stabilize these edge octahedrally coordinated atoms to the same degree as the lower alcohols due to the tendency of the higher alcohols to tetrahedrally coordinate Al^{3+} ions in solution. Based on this reasoning, it follows that acidity of the edge sites would increase with the size of the aliphatic constituent of the coordinating alcohol molecules since the larger molecules would be less likely to satisfy the imposed octahedral coordination. The observed titratable acidity followed this same trend and increased with the size of the aliphatic constituent of the solvating alcohol.

The titers of base required to reach the final observable end points in the various protic solvents may be attributed to (1) the acidic properties of the solvents which prevent sharp end points and (2) the basic properties of the solvents which stabilize atoms or hydrated atoms at crystalline edges. Even though the titrations follow expected behavior, the determination of relative influence of the above factors will require further study.

Basic dipolar aprotic solvents

Larger titratable acidities were obtained in the dipolar aprotic solvents with basic properties, solvent group C1, than in each of the protic solvents, except t-butanol (Table 2, Figures 1–3). NMR studies by Fratiello et al. (1967), Orlander et al. (1969) and Thomas and Reynolds (1970) demonstrated that DMSO successfully competes with water for solvation of Al^{3+} ions and that Al^{3+} ions exist as $Al(DMSO)_6{}^{3+}$ ions in anhydrous systems and as $Al(DMSO)_n(H_2O)_{6-n}{}^{3+}$ ions in mixed solvent systems. Similarly, Fratiello et al. (1967) have shown that amides can successfully compete with water for solvation of ions. Coordination of amides to ions at the clay surface occurs via the $C=O$ group (Tahoun and Mortland, 1966). Because of the octahedral coordination of Al^{3+} ions in DMSO and DMF, it is conceivable that these solvents may replace water in the coordination spheres of Al ions at the edges of kaolinite. Thomas and Reynolds (1970) presented evidence that bonding water molecules donate more charge to the central Al^{3+} ion in the solvated $Al(DMSO)_n(H_2O)_{6-n}{}^{3+}$ ion than do bonding DMSO molecules. Therefore, since exchange of DMSO for water

does occur, it is likely that acidic properties of Al^{3+} ions at the crystalline clay edges would be altered.

The negligible acidic character and the basic properties of DMF and DMSO make these solvents suitable for the titration of weak acids (Fritz, 1973). These properties along with a probable change in the acidic character of the pH-dependent edge sites would account for the larger titratable acidity of K-saturated kaolinite in the basic dipolar aprotic solvents than in water.

The formation of interlayer complexes of DMSO and DMF with kaolinite have been well documented (Olejnik et al., 1970; Theng, 1974). Therefore, it is likely in this study that the kaolinite samples were at least partially expanded during titration. Expansion may have affected titrations, especially if new acidic sites were exposed. Titrations in each of the solvents of this group resulted in sloping curves with end points very difficult to determine. Due to the above factors, the utility of these solvents for the titration of weakly acidic pH-dependent edge sites of clays is doubtful.

Very weakly basic dipolar aprotic solvents

The largest titratable acidites were obtained with the very weakly basic dipolar aprotic solvents (Table 2, Figure 4). Each of the solvents previously discussed, except t-butanol, has been shown to solvate Al^{3+} ions in anhydrous and in mixed aqueous systems. The solvents in this class, however, will not solvate Al^{3+} ions (Supran and Sheppard, 1967) or Mg^{2+} ions (Matwiyoff and Taube, 1968; Green and Sheppard, 1972) in mixed aqueous solvent systems as long as the water content is great enough to fill the primary solvation shells of the ions present. Parfitt and Mortland (1968) found that acetone was adsorbed to the clay surface of Ca^{2+} or Mg^{2+} montmorillonite by outer sphere coordination to the metal ion via bridging through directly coordinated water molecules. Similarly, Kohl and Taylor (1961), following IR studies, concluded that diethylketone was bound to the clay surface by H-bonding between the $C=O$ group of the ketone and the OH group of the broken edges of the clay. Acetone (Green and Sheppard, 1972) and acetonitrile (Supran and Sheppard, 1967) will, however, solvate ions in anhydrous solvent systems. The studies by Sheppard and co-workers have shown that Al^{3+} ions maintain an octahedral coordination in the anhydrous and aqueous-organic mixed solvent systems of acetonitrile or acetone.

At the edge sites of clay, two possible conditions may exist: (1) the solvation sphere of atoms at the crystalline edge sites may be completed by water molecules, or (2) the water molecules at the edge sites may have been removed as the clay was dried over P_2O_5. In the latter case, the solvation sphere of Al^{3+} at the crystalline edge sites would be partially filled by the organic solvent molecule and the acidic properties of these sites would be altered.

It was observed by Shirvington (1967) that hydrolysis of hydrated $AlCl_3$ was promoted in acetonitrile to produce ion paired halogen acids and Al-hydroxyl complexes. Protons were produced from dissociation of water and not solvent molecules. According to Sharp (1972), water is depolymerized at very low concentrations in acetonitrile and is polarized by ions. As the water content of the system is raised, increasing structural factors are superimposed on the polarization effect. The greater titratable acidity of K-saturated kaolinite in acetonitrile compared to water may be at least partially attributed to polarization of water associated with Al at the crystalline edge sites and a resulting stronger surface acidity. These polarization reactions are somewhat similar to the polarization reactions on 2:1 swelling clays discussed by Mortland and Raman (1968).

Hydrated $AlCl_3$ was dried over P_2O_5 in a vacuum and was shown to retain six water molecules per Al^{3+} ion. Also, K-kaolinite dried over P_2O_5 and K-kaolinite equilibrated at 20% relative humidity required similar quantities of base to reach the final potentiometric end points in acetonitrile and in acetone. These observations provide indirect evidence that Al atoms at crystalline edge sites remain hydrated, in which case the sites would have a stronger acidic character in a very weakly basic aprotic solvent than in water.

The weakly acidic character of the group C2 solvents make them excellent media for the titration of very weak acids (Fritz, 1973; Loeppert et al., 1977). This factor along with the increased surface acidity accounts for the significantly greater titratable acidity in acetonitrile, acetone, or methylethyl ketone than in water.

KCl-extractable Al, extracted at pH 3.0 in water was determined on clay samples which were previously titrated to the potentiometric end point in acetone or in acetonitrile. Total equivalents of extractable Al^{3+} accounted for less than 4% of the total equivalents of base added during titration of the clay in the organic solvent. This small quantity of Al dissolved from the clay surface would have a negligible influence on the larger titers in acetone or acetonitrile compared to water. Also, treatment of K-saturated kaolinite with acetone or acetonitrile for 24 hr in the presence or in the absence of excess neutral salt did not result in acidic decomposition products of acetone or acetonitrile, as determined by titrations of salt extracts and residual clay. It was concluded, therefore, that the acidic component measured was due to surface properties of the kaolinite.

It is interesting to note that the titers obtained in the dipolar aprotic solvents with very weakly basic character, group C2 (Figure 4), are greater than the titers obtained in the solvents of group C1 (Figure 3). This phenomenon may be attributed to the solvation properties at the crystalline edge sites and deserves further study.

ACKNOWLEDGMENTS

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Резюме- Каолинит,насыщенный К,был титрован в тринадцати различных растворителях с гидроокисью тетрабутиламмония с использованием комбинированного электрода для потенциометрического определения. Титр основания,необходимый для достижения окончательной потенциометрической границы,зависел от растворителя и возрастал согласно следующему порядку растворителей в присутствии и отсутствии избыточной нейтраной соли: метанол≤вода<этанол≤1-пропанол<1-бутанол<2-пропанол<Т-бутанол<диметилсульфоксид<пиридин≤ацетонитрит≤метилэтилкетон<ацетон. С протонными растворами титрационная кислотность возрастала в соответствии с уменьшением диэлектрической постоянной растворителя и возрастанием размера и/или разветвлением алифатического компонента. Наибольшие титрационные кислотности были получены в дипольных апротонных растворителях с незначительным основным характером.(т.е. ацетонитрил,ацетон,метилэтилкетон). Эти результаты обсуждаются в отношении свойств растворителей, характеристик сольватации ионов,кислотно-основного поведения некоторых частей кристаллических граней.

Kurzreferat- Ein mit Kalium gesättigtes Kaolinit wurde in dreizehn verschiedenen Lösungsmitteln mit Tetrabutylammoniumhydroxyd titriert,indem eine Kombinationselektrode für potentiometrische Bestimmungen benutzt wurde. Die Menge von Alkali,die nötig war,um den potentiometrischen Endpunkt zu erreichen,war vom Lösungsmittel abhängig und nahm in der folgenden Lösungsmittelreihenfolge zu,sowohl in Anwesenheit wie auch in Abwesenheit eines Überschusses an neutralen Salzen:Methanol≤ Wasser< Äthanol≤ 1-Propanol< 1-Butanol< 2-Propanol< DMF< t-Butanol< DMSO< Pyridin≤ Acetonitril≤ Methyläthylketon< Aceton.Mit den protischen Lösungsmitteln nimmt die titrierbare Azidität mit abnehmender Dielektrizitätskonstante des Lösungsmittels und mit zunehmender Länge und/oder Verzweigung des aliphatischen Anteils zu.Die höchsten titrierbaren Aziditäten wurden in den dipolaren,aprotischen Lösungsmitteln mit unbedeutendem basischen Charakter (z.B. Acetonitril,Aceton,Methyläthylketon) erhalten.Diese Resultate werden hinsichtlich der Eigenschaften der Lösungsmittel,Solvatationscharakteristiken der Ionen in den Lösungsmitteln und Säure-Basen Benehmen der kristallinen Randstellen diskutiert.

Résumé-Une kaolinite saturée de K a été titrée dans treize solvants différents avec de l'hydroxide de tétrabutylammonium utilisant une électrode de combinaison pour la détermination potentiométrique.Le titre basique nécessaire pour parvenir au point potentiométrique final dépendait du solvant,et augmentait,à la fois en la présence et l'absence d'un excès de sel neutre,dans l'ordre de solvants suivant:méthanol ≤ eau < éthanol ≤ 1-propanol < 1-butanol < 2-propanol < DMF < t-butanol < DMSO < pyridine ≤ acétonitrile ≤ méthyléthyl cetone < acétone.Pour les solvants protiques,l'acidité titrable augmentait selon la constante diélectrique décroissante du solvant,et selon la taille et/ou le branchement croissant du constituant aliphatique.Les plus grandes acidités titrables étaient obtenues dans les solvants dipolaires aprotiques à caractère basique négligible(c.à.d. acétonitrile, acétone,méthyléthyl cetone).Ces résultats sont discutés selon les proprétés des solvants,les caractéristiques de dissolution des ions dans les solutions,et le comportement vis à vis des acides et des bases des sites de bords de cristaux.