THE RELEASE OF ALUMINUM FROM ALUMINOSILICATE MINERALS. II. ACID-BASE POTENTIOMETRIC TITRATIONS

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Abstract—Acidified suspensions of Al-saturated kaolinite, montmorillonite, mica, illite, and biotite in 10^{-3} M $NaNO_3$ were potentiometrically titrated with 0.1 N NaOH and 0.1 N HNO_3 in succession in a CO_2-free nitrogen atmosphere. The resulting curves were compared with those for $Al(NO_3)_3$ solutions of similar Al concentration in the supernatant solution and corrected for Al in the entrained solution in the clay.

Base titrations of Al ions adsorbed on all the minerals, except montmorillonite, showed two pH inflections separated by a buffering range. With montmorillonite, there were three pH inflections similar to those for Al in solution. The first inflections in the titration of suspensions occurred at lower pHs and were less pronounced than for Al in solution. These represent the titration of H_3O^+ sorbed during the pretreatment. The buffering by adsorbed Al ions is also less than that by Al in solution.

The OH^- used up by adsorbed Al ions between the first and last inflections was equal to, or slightly greater than, the CEC of the minerals, except for mica where it was more than twice the CEC, because new interlayer surfaces were formed during the acid pretreatment. Acid titration curves of Al ions in the adsorbed and solution states showed hysteresis when related to the base titration curves. The use of two titration speeds (3 and 0.3 pH units/hr) only slightly affected the titration curves of the minerals suggesting that the observed effects were not caused by lack of equilibrium with added base or acid.

Key Words—Aluminum, Biotite, Buffer, Illite, Kaolinite, Mica, Montmorillonite

INTRODUCTION

The existence of partially hydrolyzed Al ions on the surface of acid soils and clays was suggested by several authors from the study of the composition of the extracts with various salt solutions (Bache, 1974; Dalal, 1975; Bache and Sharp, 1976a, 1976b; Smith and Emerson, 1976; Cabrera and Talibudeen, 1978) from the composition of the solution in equilibrium with these materials (Chakravarti and Talibudeen, 1961) and from the adsorption of Al from solution (Brown and Newman, 1973).

Using potentiometric titration, Low (1955) determined the amount of Al^{3+} in a H-Al-bentonite with different proportions of H/Al on its surface. He found that the pH of $Al(OH)_3$ precipitation in bentonite suspension was higher than in free solution and attributed this to the lower activity of Al ions in suspension because of electrostatic interaction with the clay. Schwertmann and Jackson (1963, 1964) found three buffer ranges in the pH titration curve of aged H-Wyoming bentonite and H-vermiculite, and attributed these, in order of ascending pH, to exchangeable H^+, exchangeable Al^{3+}, and basic Al compounds formed in the presence of these negatively charged clays. The third buffer range increased greatly on aging the H-saturated clay and was comparable to the third buffering range observed in

aged, partially neutralized $AlCl_3$ solutions. Smith and Emerson (1976) observed that potentiometric titration curves of kaolinite were not helpful in trying to decide the forms of Al present although they showed that some of it was as Al^{3+}. Pyman *et al.* (1976) reported that the apparent hydrolysis constants of Al calculated from base titration curves of Al-bentonite were smaller than those of the Al ions in solution.

The titration curves of Al in solution depend on Al concentration, ionic strength, temperature, titration speed, method of titrant injection, etc. (Frink and Sawhney, 1967; Vermeulen *et al.*, 1975; Stol *et al.*, 1976). From a theoretical treatment of the base titration of dilute $AlCl_3$ solutions, Turner (1968a, 1968b) predicted different shapes of titration curves depending on the Al species assumed to be present in solution. It seems then that the kind of Al species formed in solution during titration depends very much on experimental conditions and that adsorbing surfaces in suspensions modify this.

The present paper examines titration curves of Al adsorbed on Al-saturated minerals and compares them with the titration curves of Al in solution under similar experimental conditions.

MATERIALS AND METHODS

Minerals

The relevant properties of the minerals used in this work are listed in Table 1; (for a fuller description, see Cabrera and Talibudeen, 1978).

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Table 1. Description of minerals.

Mineral	Particle-size μm	CEC meq/1000 g
Kaolinite A (St. Austell)	0.5–0.25	76
Kaolinite B (St. Austell)	2.5–1.5	32
Montmorillonite (Upton)	0.2–1	733
Mica (Muscovite)	<1	124
Illite (Fithian No. 35)	<1	237
Biotite (Ontario)	<50	47

Potentiometric titration of Al-saturated minerals and $Al(NO_3)_3$ solutions

Weighed samples of mineral were treated with 10 ml of 0.1 N $Al(NO_3)_3$ solution adjusted to pH 3 in polypropylene centrifuge tubes. After shaking overnight, the tubes were centrifuged and the supernatant solution rejected. This treatment was repeated three times to ensure that the concentration and pH of the final supernatant were those of the added solution. The Al-saturated minerals with entrained $Al(NO_3)_3$ solution were shaken intermittently for 1 hr with 50 ml of 10^{-3} M $NaNO_3$ and centrifuged. Twenty-five milliliters of the clear supernatant were taken out. The suspension and the supernatant ('control') each were mixed with 25 ml of 10^{-3} M $NaNO_3$ solution and saturated with CO_2-free nitrogen for 1 hr, and 0.1 N HNO_3 was added slowly over ca. 24 hr to bring the pH to approximately 2. When the pH remained steady for 1 hr after adding the acid, 'suspension' and 'control' were titrated to pH 11 with 0.1 N NaOH and then back to pH 2 with 0.1 N HNO_3. CO_2-free nitrogen gas was bubbled throughout to prevent CO_2 absorption from the air. The temperature was kept constant at $25 \pm 2°C$.

To help interpret the titration curves of the Al-saturated minerals, solutions of $Al(NO_3)_3$ containing 0.499 and 1.000 meq Al^{3+} in 50 ml and 25 ml of 10^{-3} M $NaNO_3$ were also titrated after adding acid to bring the pH to approximately 2. (The final concentrations of these solutions were then 2.9×10^{-3} M and 1.1×10^{-2} M, respectively.)

The titrations were done on a Radiometer automatic titrator (model Copenhagen TTT2b) coupled to an Autoburette ABU12b and a Titrigraph SBR3. Mean speeds of 3 pH units/hr and 0.3 pH units/hr were used on both acid and base titrations with standardized 0.1 M HNO_3 and 0.1 M NaOH.

RESULTS AND DISCUSSION

Titration curves of $Al(NO_3)_3$ solutions

The base titration curves of acidified aluminum nitrate solutions (Figure 1) showed three inflection points separated by two plateaus whose exact locations were found by means of the differentiated curves. The first inflection point determines the neutralization equivalence of the excess H_3O^+ initially present, the second

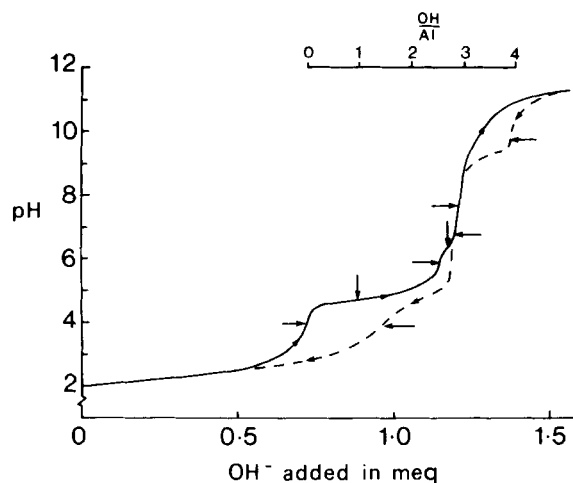Figure 1. Base (———) and acid (– – –) titration curves of acidified 2.9×10^{-3} M $Al(NO_3)_3$ in 10^{-3} M $NaNO_3$. Titration speed 0.3 pH units/hr. Horizontal and vertical arrows mark inflection points and plateaus, respectively.

is associated with the formation of a solid phase, and the third determines the total neutralization of the Lewis acid Al^{3+} (see also Vermeulen et al., 1975). These titration characteristics changed only slightly with titration speed.

The total Al^{3+} titrated (i.e., the difference of OH^- used between the first and third inflections) was 3.5% less than the total Al^{3+} taken initially, which is attributed to experimental error. However, Vermeulen et al. (1975) found by microelectrophoretic measurement that the Al hydroxide particles formed during the titration are positively charged up to pH 10, which suggests that the Al^{3+} ions may not have been fully titrated at pH 7.4.

The OH/Al ratios calculated on the basis of the total Al in solution initially are given in Table 2 for the two Al concentrations (mean of two titration speeds) and in Figure 1 for the dilute solution at a titration speed of 0.3 pH units/hr. The pH values at the inflection points and the plateaus, and the OH/Al ratios at each pH were smaller for the more concentrated Al solution (see also Stol et al., 1976). The second inflection and plateau became less pronounced and finally disappeared as the initial Al concentration was decreased below 5.7×10^{-4} M. This was also reported by Frink and Sawhney (1967) for 10^{-4} M solutions, and for 10^{-2} M solutions at high titration speeds, and by Stol et al. (1976) for 5×10^{-5} M Al solution and for any Al concentration when alkali was added dropwise to the surface of the solution without continuous stirring, creating locally 'higher-than-mean' concentrations of OH ions. The occurrence of this second inflection and plateau was related to the existence of positively charged Al-hydroxy polymers in partially neutralized, concentrated Al solutions.

Table 2.　Characteristics of the base and acid titration curves of 2.9×10^{-3} M and 1.1×10^{-2} M $Al(NO_3)_3$ in 10^{-3} M $NaNO_3$.

	2.9×10^{-3} M						1.1×10^{-2} M					
	pH_b	pH_a		$(OH/Al)_b$	$(OH/Al)_a$		pH_b	pH_a		$(OH/Al)_b$	$(OH/Al)_a$	
	mean of two speeds	speed 1	speed 2	mean of two speeds	speed 1	speed 2	mean of two speeds	speed 1	speed 2	mean of two speeds	speed 1	speed 2
1st inflection	3.94	3.82	3.97	0	0.72	1.49	3.70	3.76	3.60	0	0.34	2.22
1st plateau	4.65	—	—	0.95	—	—	4.44	—	—	0.89	—	—
2nd inflection	5.85	—	—	2.16	—	—	5.50	—	—	2.49	—	—
2nd plateau	6.25	—	—	2.71	—	—	6.10	—	—	2.66	—	—
3rd inflection	7.44	6.78	6.70	2.92	2.90	2.80	7.30	7.85	6.67	2.87	3.04	2.91
3rd plateau	—	—	—	—	—	—	—	—	—	—	—	—
4th inflection	—	9.60	9.72	—	3.81	3.90	—	10.22	10.35	—	4.29	3.74
Standard Error	±0.08	—	—	±0.03	—	—	±0.05	—	—	±0.02	—	—

Note: Subscripts a and b refer to the acid and base titrations, respectively.

The acid titration curves (Figure 1) showed hysteresis when related to the base titration curves, more so at the titration speed 0.3 pH units/hr than at 3 pH units/hr (Table 2), presumably because the titration with NaOH at the slower speed caused larger and more crystalline nuclei of $Al_2O_3 \cdot nH_2O$ to form which reacted more slowly during the reverse acid titrations. The second inflection in the base titration did not occur in the acid titration curve, and the first and third inflections occurred at slightly lower pH values (Figure 1 and Table 2). The amount of acid added between these inflections was less than expected from the total Al^{3+} in solution initially, more so at the slower titration speed. The inflection at about pH 4 was less pronounced than in the base titration curve and at the end of the acid titration (i.e., pH 2), the solution was still slightly turbid. This suggests that the precipitate formed during the base titration had aged considerably, resisting subsequent dissolution during acid titration, and more so at the slower titration speed (see above).

In the acid titration curve, another inflection occurred between pH 9.5 and 10.5 when the ratio OH/Al was <4 (Figure 1 and Table 2); this did not appear in the base titration curves. This inflection is caused by the reaction of the aluminate ions, AlO_2^-, with H^+ to form $Al_2O_3 \cdot nH_2O$. The theoretical OH/Al ratio of 4 was not reached because, at the end of the base titration (pH 11), all the Al had not been converted to the AlO_2^- form, and the solution was still turbid.

Titration curves of Al-saturated minerals

The base titration curves of acidified suspensions of Al-saturated minerals showed, in general, two inflections separated by a plateau, except in montmorillonite which had three inflections and two plateaus resembling those of the concentrated Al solutions (Figure 2 and Table 3). The pH values at which inflections and plateaus occurred were the same, or only slightly different, using titration speeds of 3 and 0.3 pH units/hr.

The inflections and plateaus can be attributed to the same causes as with the base titration curves of Al solutions (see previous section). The titration includes

Table 3.　Characteristics of the base titration curve of acidified Al-saturated minerals in 10^{-3} M $NaNO_3$.

		1st inflection pH	1st plateau pH	2nd inflection pH	2nd plateau pH	3rd inflection pH	meq OH^- consumed per 1000 g of mineral
Kaolin A	Fast	3.75	4.37	—	—	7.30	79
	Slow	3.90	4.60	—	—	7.00	88
Kaolin B	Fast	3.95	4.50	—	—	7.25	40
	Slow	3.95	4.55	—	—	7.15	47
Montmorillonite	Fast	3.50	4.17	4.75	5.75	7.60	739
	Slow	3.50	4.17	4.70	5.70	7.25	728
Mica	Fast	3.37	4.50	—	—	6.00	393
	Slow	3.37	4.50	—	—	6.00	400
Illite	Fast	3.87	4.30	—	—	6.50	240
	Slow	3.87	4.37	—	—	6.50	242
Biotite	Fast	4.10	4.60	—	—	6.13	42
	Slow	5.45	6.60	—	—	7.31	36

Fast = 3 pH units/hr; Slow = 0.3 pH units/hr.
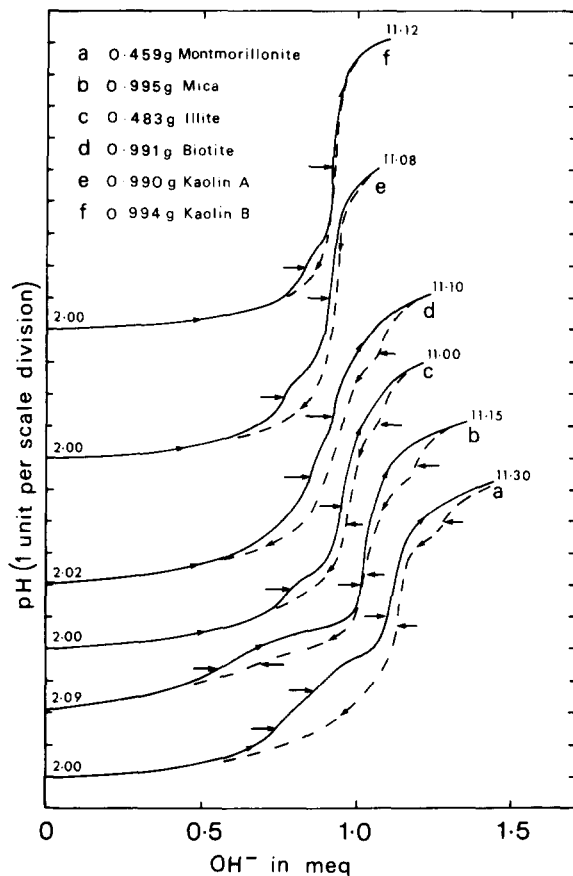
Figure 2. Base (——) and acid titration curves (– – –) in 10^{-3} M $NaNO_3$ of acidified Al saturated montmorillonite, mica, illite, biotite, kaolin A, and kaolin B. Titration speed is 0.3 pH units/hr, except for biotite at 3 pH units/hr. Initial and final pH values are indicated on the curves; horizontal arrows mark the inflection points.

adsorbed Al ions and the free Al in the entrained solution, estimated from the 'control.' The OH^- used by the adsorbed Al ions was calculated by difference (Table 3).

The OH^- used in titrating the adsorbed Al (Table 3) was almost equal to the CEC of most minerals (Table 1). The slight excess for kaolin, illite, and biotite is accounted for by the pH-dependent negative charge developed from pH 6 onwards. For mica, the OH^- used was more than twice its CEC, presumably because of the dissolution of Al from the mineral matrix in the previous treatment with 0.1 M HNO_3 to pH 2 creating new interlayer surfaces, and subsequent base-titration of this Al (see also Cabrera and Talibudeen, 1978). This phenomenon may be the initial step in the formation of chloritized micas in soils (de Villiers and Jackson, 1967a, 1967b).

The first inflection in the base titration curves of the Al-saturated mineral suspensions (Figure 2) is less pro-

nounced and occurs at lower pH values than in those for $Al(NO_3)_3$ solutions of similar Al concentration, except in biotite (cf. Tables 2 and 3). It would seem from this that adsorbed Al is more acidic than Al in solution, the opposite to what is expected because the activity of adsorbed Al ions is less than in free solution (Low, 1955). However, in the pretreatment with acid to bring the suspension to pH 2, the ratio of sorbed H_3O^+ to sorbed Al^{3+} ions is about 10:1, so it is more likely that the first inflection represents the pH at which mostly the sorbed H_3O^+ is titrated. If so, the inflections corresponding to the titration of sorbed H_3O^+ and Al^{3+} ions will be fully distinguishable only if the ratio of the equilibrium constants for the two reactions is $>10^4$ (Vogel, 1961) and measurable concentrations of both ionic species are present. Schwertmann and Jackson (1963, 1964) found that the first inflection shifts to higher pH values with increasing time of ageing of H-bentonite and H-vermiculite suspensions (i.e., with progressive changes from H-clay → H-Al-clay → Al-clay).

The plateaus in the base titration curves of Al-saturated minerals are less pronounced than those of the corresponding curves for Al in solution. In the latter, the existence of hydroxy Al polymers can be detected only by the shape of the curve (i.e., second inflection and plateau) above a limiting concentration of Al. Rich (1970) observed that the second inflection and plateau of the base titration curves of Al in solution disappeared when K-montmorillonite was added to the system. Therefore, little can be said, in a quantitative sense, about the nature of adsorbed Al ions from such potentiometric titration. However, the observation of the more complex buffering of adsorbed Al than of Al in solution points to its resistance to reaction with added OH^- ions because of the strong binding of Al^{3+} and to the existence of hydroxy-polymeric Al (Cabrera and Talibudeen, 1978) on mineral surfaces, which therefore titrate at higher pH values.

The acid titration curves of the adsorbed Al (as with Al in solution) show hysteresis relative to the base titration curves and an extra inflection at pH 9–10. Changing the titration speed alters the curves only slightly, unlike the titration of Al in solution. The first and second inflections are difficult to distinguish from each other and the third inflection is observed at pH 6–7. However, no precise interpretation can be given for these inflections from this work.

ACKNOWLEDGMENTS

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Резюме—Ацилированные суспензии насыщенных Al каолинита, монтмориллонита, слюды, иллита, и биотита, в 10^{-3} M $NaNO_3$ были последовательно потенциометрически титрованы с 0,1 N NaOH и 0,1 N HNO_3 в азотной атмосфере, свободной от CO_2. Результирующие кривые сравнивались с кривыми для растворов $Al(NO_3)_3$ с такой же концентрацией Al как в отстоявшемся растворе и корректировались за Al в захваченном растворе с глине.

Основные титры ионов Al, адсобированные всеми минералами, за исключением монтмориллонита, показывали два перегиба pH, разделенные буферным диапазоном. Что касается монтмориллонита, то здесь были три перегиба, подобных перегибам для Al в растворе. Первые перегибы в титре суспензий появлялись при низких значениях pH и были менее выражены, чем перегибы для Al в растворе. Они представляют титры H_3O^+, сорбированного в течение предварительной обработки. Буферное действие адсорбированных ионов Al также слабее по сравнению с Al в растворе.

OH^-, использующийся адсорбированными ионами Al между первым и последним перегибами, был равен или несколько выше катионной обменной способности минералов, за исключением слюды, где он более чем в два раза превышал его катионную обменную способность, потому что образовались новые межслойные поверхности во время предварительной кислотной обрабртки. Кривые кислотного титрования ионов Al в адсорбированном и растворенном состояниях показывали гистерезис, когда относились к кривым основного титрования. Использование двух скоростей титрования (3 и 0,3 pH единиц/ч только незначительно воздействует на кривые титрования минералов, показывая, что наблюдавшиеся эффекты не были вызваны отсутствием равновесия с добавленными основанием или кислотой.

Resümee—Angesäuerte Suspensionen von mit Al gesättigten Kaolinit, Montmorillonit, Glimmer, Illit, und Biotit in 10^{-3} M $NaNO_3$ wurden nacheinander mit 0,1 N NaOH und 0,1 N HNO_3 in einer Kohlendioxyd freien Atmosphäre potentiometrisch titriert. Die resultierenden Titrationskurven wurden mit denen für $Al(NO_3)_3$ Lösungen mit ähnlichen Al-Konzentrationen in der überstehenden Flüßigkeit verglichen und korrigiert für Al in den eingeladenen Lösungen im Ton. Als Al-Ionen, adsorbiert auf allen Mineralien mit Ausnahme von Montmorillonit, mit Basen titriert wurden, zeigten sich zwei pH-Inflektionen, welche durch ein Pufferbereich getrennt waren. Mit Montmorillonit gab es drei pH-Inflektionen, die denen von Al in Lösung gleichen. Die ersten Inflektionen in der Titrationen von Suspensionen findet bei niedrigen pH Werten statt und sind weniger ausgeprägt als für Al in Lösung. Diese repräsentieren die Titration von H_3O^+, welches während der Vorbehandlung adsorbiert wurde. Adsorbierte Al-Ionen puffern weniger als Al in Lösung. Das OH^-, welches von den adsorbierten Al-Ionen zwischen den ersten und letzten Inflektionen verbraucht werden, entsprach oder war etwas höher als das CEC der Mineralien mit Ausnahme des Glimmer, für den es mehr als zweimal seines CEC war, weil neue Zwischenschichtflächen während der säurevorbehandlung geformt worden. Säuretitrationskurven von Al-Ionen im adsorbierten und Lösungszustand zeigte Hysteresis, wenn man sie auf die Alkalititrationskurven bezieht. Die Benutzung von zwei Titrationsgeschwindigkeiten (3 und 0,3 pH Einheiten/h) hatten nur wenig Einfluß auf die Titrationskurven, was andeutet, daß die beobachteten Effekte nicht durch Mangel eines Gleichgewichts mit zugefügter Base oder Säure verursacht wurden.

Résumé—Des suspensions acidifiées dans 10^{-3} M $NaNO_3$ de kaolinite, de montmorillonite, de mica, d'illite, et de biotite saturés d'Al ont été potentiométriquement titrées avec 0.1 N NaOH et 0.1 N HNO_3 en succession, dans une atmosphère nitrogénée sans CO_2. Les courbes résultantes ont été comparées à celles de solutions d'$Al(NO_3)_3$ de concentration Al semblable dans la solution surnageante et corrigées pour Al dans la solution entraînée dans l'argile. Des titrages basiques des ions Al adsorbés sur tous les minéraux sauf la montmorillonite, ont montré 2 inflexions de pH séparés par une région tampon. Pour la montmorillonite, il y avait 3 inflexions de pH semblables à celles pour l'Al en solution. Les premières inflexions dans les titrages des suspensions ont survenu à de plus bas pH et étaient moins prononçés que dans le cas de l'Al en solution. Celles-ci représentent le titrage de H_3O^+ sorbé pendant le prétraitement. L'effet de tampon produit par les ions d'Al adsorbé est aussi moins élevé que celui d'Al en solution. L'OH^- utilisé entre les premières et dernières inflexions par les ions d'Al adsorbés était égal à ou un peu plus élevé que la capacité d'échange de cations (CEC) des minéraux, sauf dans le cas du mica, où il était plus de deux fois plus élevé que son CEC parceque de nouvelles surfaces interfeuillet ont été formées pendant le prétraitement acide. Les courbes de titrage acide des ions Al dans les états adsorbés et en solution ont montré une hystérésis lorsque mis en relation avec les courbes de titrage basique. L'emploi de deux vitesses de titrage (3 et 0.3 pH unités/h) n'a affecté que très peu les courbes de titrage des minéraux suggérant que les effets observés n'étaient pas causés par un manque d'équilibre dû à l'addition de base ou d'acide.