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RELATION BETWEEN DUAL ACIDITY AND
STRUCTURE OF H-MONTMORILLONITE

By Alfred M. Pommer

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

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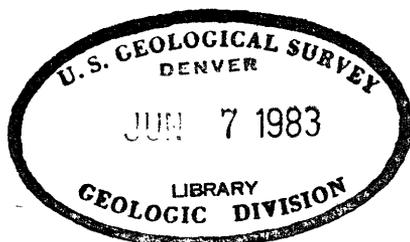
Alfred M. Pommer

March 1962

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RELATION BETWEEN DUAL ACIDITY AND STRUCTURE OF H-MONTMORILLONITE

by

Alfred M. Pommer

ABSTRACT

Potentiometric studies with hydrogen-sensitive and cation-sensitive glass electrodes supplemented by chemical determinations and X-ray diffractions on a hydrogen-montmorillonite prepared from A.P.I. Reference Clay No. 23 (Chambers, Ariz.) indicate that the clay behaves as a mixture of two acids, resulting from the presence of two types of exchange sites, interlayer and edge, both occupied by hydrogen ions. The interlayer sites, which hold the hydrogen ions less tightly, cause the stronger acid function, and the edge sites, which form stronger hydrogen bonds, are responsible for the weaker acid function.

Correlation of these data with information from the literature indicates that in the case of beidellites the pattern is reversed and the interlayer positions represent the weaker acid function. Application of Eiseman's theory of atomic selectivity to the clay leads to the prediction that the stronger acid sites are more likely to hold cesium preferentially. This has bearing upon the problem of waste disposal of radioactive cesium-137.

INTRODUCTION

Garrels and Christ (1956), using original data of Marshall and Bergman (1942) for the titration of the clay mineral (beidellite) in the Putnam silt loam soil, have shown that the neutralization curve of pH plotted against concentration of potassium hydroxide appears similar to that of two independent clay acids. They termed the two substrates the C⁻ (center or interlayer) site and the E⁻ (edge) site. Hauser (1955) has published titration curves of bentonite which show the dibasic character of this material very strikingly. Thompson^{1/} has reviewed and summarized the extensive literature in this field.

^{1/} Thompson, A. C., 1956, Acidic properties of bentonite. Ph.D. Thesis, State College of Washington, Pullman, 101 p.

The picture is complicated by the fact that hydrogen clays spontaneously alter to hydrogen-aluminum clays. The literature pertaining to this phenomenon has been recently summarized by Coleman and Craig (1961). Of great importance in this respect is the finding of Low (1955) that in bentonites the initial inflection point or break in the curve represents the point at which the titration of exchangeable hydrogen is completed and the titration of exchangeable aluminum begins. This leads immediately to the question whether there is a conflict between the findings of Garrels and Christ and those of Low. It is intended here to propose a model capable of accomodating both of these concepts and to report on experimental work which, it is hoped, will eventually lead to a resolution of the problem.

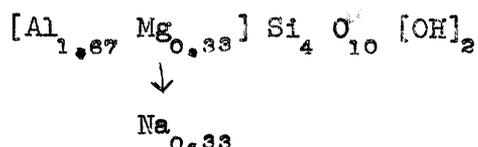
ACKNOWLEDGMENTS

Special thanks are due to Dorothy Carroll, who contributed greatly to this work by performing a considerable portion of the laboratory work, by making calculations, and by teaching me much clay mineralogy. The discussions of R. O. Fournier and E-an Zen were very helpful, and I am also grateful to them for their help and instruction in the use of the X-ray diffractometer. Thanks are also due to T. Tamura, Oak Ridge National Laboratories, for his help in reviewing the paper.

The study was supported by the Division of Reactor Development, U. S. Atomic Energy Commission.

IMPLICATIONS OF MONTMORILLONITE STRUCTURE

Ross and Hendricks (1945) give the following idealized formula for montmorillonite:



In this simplified formula the aluminum and magnesium are coordinated octahedrally and the silicon is tetrahedrally coordinated. The mineral may be represented by a sandwichlike structure (figure 1).

The tetrahedral layer is essentially silica and is electrically neutral in this idealized structure. The octahedral layer would be hydrated alumina and also electrically neutral if there were no magnesium present. However, the substitution of the bivalent magnesium for the trivalent aluminum in this layer causes a charge deficiency which is neutralized by cations entering exchange positions on the surface of the material, and the cation-exchange capacity of the clay results from this charge deficiency. The clay is an insulator and the charge deficiency may be considered distributed over its surface according to the laws of electrostatics. As may be seen by inspection of figure 1, octahedrally coordinated layers are exposed in the "edge" positions. Elsewhere they are covered by an insulating layer of tetrahedral silica. It follows that the charge density in the interlayer positions must

be less than that in the edge position, because the charge is attenuated by the silica interposed between the surface of the octahedral unit and the surface of the clay.

The implications of this concept in terms of the acid strength of a hydrogen clay are simple and straight forward. Hydrogen ions in the edge positions are held by a relatively strong electrostatic field, ionized with difficulty, and the part of the acid represented by these positions must be weaker than the part represented by the interlayer positions. At the interlayer positions the field is attenuated, the hydrogen ions are more readily ionized, and the acid is stronger than at the edge positions.

In the decay of a hydrogen clay to a hydrogen-aluminum clay the alumina of the octahedral unit releases aluminum ions which then occupy exchange positions, replacing hydrogen ions. Inspection of figure 1, in conjunction with the electrostatic concept presented here, makes it reasonable to assume that the aluminum can be released from the octahedral unit only at the edge positions, because this unit has a surface only at the edges. It is then likely that, to the extent that sites are available, the aluminum ions occupy these sites. The forces holding the aluminum to the edge sites are stronger than the attenuated forces at the interlayer positions and the aluminum remains in place. Hence the exchangeable aluminum is the E^- positions and the hydrogen in the C^- positions. If such a clay is titrated, it should behave as a dibasic acid, the first acid representing H^+ in C^- positions, and the second acid Al^{+3} in E^- positions. This model essentially accommodates the concepts of Low (1955) and Garrels and Christ (1956). Although it is possible to introduce aluminum interlayers in montmorillonite by treatment with $AlCl_3$ solutions, this results in a product with an interplanar basal spacing³ of 14A. (Sawhney, 1960). The X-ray data on titrated clays presented later in this paper show that this does not occur under the experimental conditions discussed here.

EXPERIMENTAL DATA

Experimental Plan

It is known (Barshad, 1950) that the interplanar basal spacing of montmorillonite varies with the cation in the exchange position, and that this variation is related to the degree of hydration in the interlayer position. It is difficult to see how the type of cation in the edge position or its degree of hydration could affect the (001) spacing of a clay the same way. Accordingly, it might be expected that the change in this spacing during the replacement of H^+ (or Al^{+3}) with Na^+ in a clay should depend on the type of position affected by the exchange. It was decided to investigate this aspect.

Discontinuous or "bottle" titrations (see p. 14) were used for reasons discussed elsewhere (Pommer, 1960) and an attempt was made to correct for the effect of atmospheric CO_2 on pH for reasons discussed by Carroll (1960). Unfortunately it was not possible in this work to follow the change in exchangeable aluminum in the clay, as it was desired to keep the whole sample in the solution for a long time to complete the bottle titration, and then to use it for X-ray determinations including ethylene glycol treatment and firing.

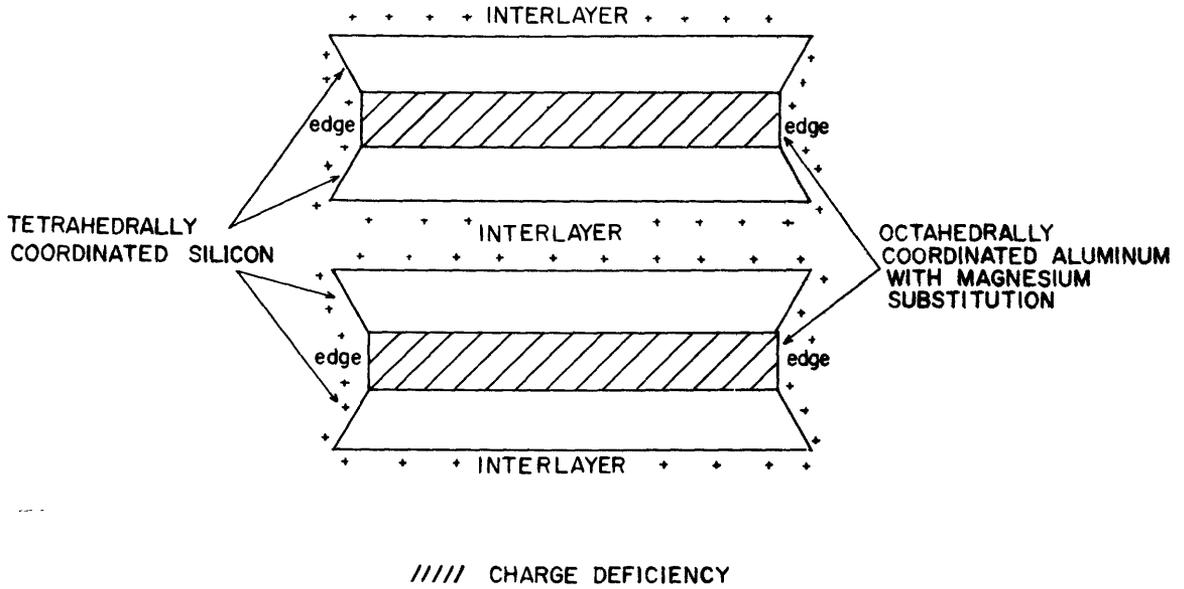


FIGURE 1.—SIMPLIFIED MONTMORILLONITE STRUCTURE

Material used

A sample of montmorillonite from Chambers, Arizona, (A.P.I. Reference Sample No. 23) was obtained from Ward's Natural Science Establishment. This reference sample has been described by Kerr and Kulp (1949). The clay contained 2.4 volume percent quartz and 0.6 percent other impurities (Dorothy Carroll, written communication, 1960). Table 1 shows a comparison of analytical results obtained on this clay by this laboratory and those published by Kerr and others (1950). It can be seen that the montmorillonite studied here is not identical with the sample reported on by the American Petroleum Institute Project; however, the differences as shown in the clay formulas are not significant for the purpose of this investigation. X-ray diffraction studies on a nonoriented slide of the original material and on an oriented slide of the H-clay disclosed no significant abnormalities. A total cation exchange capacity determination by saturation with ammonium acetate and Kjeldahl distillation (modification of the procedure of Association of Official Agricultural Chemists, 1950) yielded a total base-exchange capacity of 104 meq/100g (Dorothy Carroll, written communication). The clay was converted to the hydrogen (H) form by the method of Aldrich and Buchanan (1958) as modified by Dorothy Carroll, who made the preparation as outlined here.

Preparation of the H-form

A sample of montmorillonite was crushed to pass a 230-mesh (0.06 mm) sieve and a 1 percent suspension was made in distilled water. Sufficient HCl was added to make the suspension 1 N. The suspension was placed in a 1-liter cylinder and shaken in an end-over-end shaker for about one hour. The montmorillonite was removed from the acid solution by repeated centrifugation and washing until a negative chloride test with AgNO_3 showed that all the acid had been removed. The quartz impurity was separated during centrifugation and discarded. The sample was finally dried at about 60°C, finely ground, and stored in a glass vial until required. The exchangeable cations remaining on the clay after its conversion to the hydrogen form were determined (Dorothy Carroll, analyst). They were in meq/100 g (milliequivalents per 100 grams): Ca 11.5, Mg 16.7, Na 5.7, and K 0.6. In addition to the exchangeable hydrogen ions there were 34.5 meq/100 g of other exchangeable cations; from the original total exchange capacity of 120.0 (obtained by addition of the exchangeable cations of the original clay) we can estimate the exchangeable hydrogen ions of this clay as 85.5 meq/100 g. Almost all the potassium and more than 85 percent of the calcium was replaced by hydrogen, whereas the magnesium and the sodium were almost completely retained during the process. The role of exchangeable aluminum will be discussed later. As the hydrogen clay decayed, some exchange positions originally occupied by hydrogen ions became filled with aluminum ions. As this section is concerned with how good a hydrogen clay was produced by the treatment originally, the exchangeable aluminum is immaterial here.

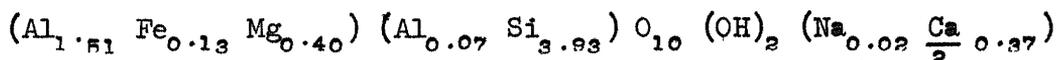
Table 1.--Comparison of material used with original
clay reference sample (API No. 23)

	Original sample ^{a/} (in weight percent)	Material used ^{b/} (in weight percent)
SiO ₂	49.91	53.4
Al ₂ O ₃	17.20	15.9
Fe ₂ O ₃	2.17	1.5
FeO	.26	< .05
MgO	3.45	4.5
CaO	2.31	2.2
Na ₂ O	.14	.11
K ₂ O	.28	.28
H ₂ O	23.47	21.6
TiO ₂	.24	.20
MnO	.04	.10
C	Trace	--
CO ₂	--	< .05
	(in meq/100g)	(in meq/100g)
Exchangeable Ca	--- ^{c/}	87.5 ^{d/}
Exchangeable Mg	--- ^{c/}	18.2 ^{d/}
Exchangeable Na	--- ^{c/}	5.9 ^{e/}
Exchangeable K	--- ^{c/}	8.4 ^{f/}
Total exchange capacity	147.5	120.0 ^{g/}

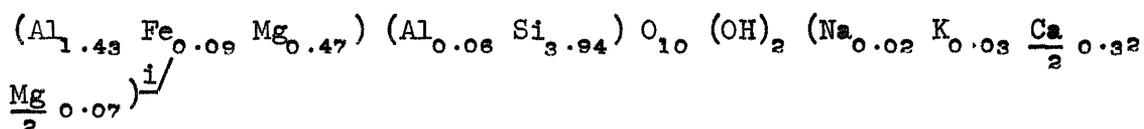
Table 1.--Continued

Table 1.--Comparison of material used with original
clay reference sample (API No. 23)

Formula of original sample^{a/}.



Formula of material used (corrected for quartz impurity)^{h/}



^{a/} Kerr, P. F. and others, 1950.

^{b/} Elmore, P. L. D., Barlow, I. H., Botts, S. D., and Chloe, G. W., analysts. No corrections for impurities were made.

^{c/} Not reported.

^{d/} Brannock, W. W., analyst.

^{e/} Budinsky, J. W., analyst.

^{f/} Carroll, Dorothy, analyst.

^{g/} Calculated sum of exchangeable cations. Exchange capacity determined by ammonium extraction was 104 meq/100 mg (Dorothy Carroll, analyst).

^{h/} Dorothy Carroll, Written communication (1960).

^{i/} The charge deficiency is -0.474 in the tetrahedral layer, and -0.055 in the octahedral layer, for a total of -0.529. The exchangeable cations neutralizing the charge, on the other hand, total 0.433 charge units.

Titration with NaOH

A discontinuous titration was made using small hydrogen-montmorillonite samples (65 mg) to which increments of 0.1 N NaOH were added. Each 65 mg sample was weighed into a separate weighing bottle and sufficient water was added to make a constant volume. The increments were 0.02 ml for samples 2 through 13 and 0.04 ml for samples 14 through 37. The largest volume of NaOH was in sample 37 which contained 1.20 ml. The total volume for all samples was 6.20 ml. Sample 1 contained only montmorillonite with water. Reagent blanks without clay were run for samples 1, 6, 12, 18, 24, 30, and 37 to measure the effect of CO₂ absorption. All samples were shaken gently after being prepared and allowed to stand 1 day before pH readings were taken. The concentration of montmorillonite was a little more than 1 percent. The increments of NaOH were added by an automatic microtitrator. Results are summarized in table 2.

Analysis of filtrates

The solutions in contact with the samples were removed by centrifugation and repeated washing in distilled water. The samples were returned to the weighing bottles and kept for X-ray examination. The filtrates were made up to 100 ml in volumetric flasks. Sodium and aluminum were determined in separate aliquots.

The titration was arranged so that the total exchange capacity of the montmorillonite in the H-form would be taken up at about sample 24 (0.68 ml 0.1 N NaOH, table 2). It was expected that the montmorillonite would absorb all the sodium added to it up to the equivalence point. Sodium in the filtrates was determined by flame photometer, with the results given in table 3. Sodium activities were measured in the solutions above the montmorillonite samples with a special Beckman sodium electrode. The millivolt readings are also given in table 3.

Aluminum in the filtrates was determined with alizarin red-S by the rapid method of Shapiro and Brannock (1956, p. 34). The aluminum found is given in table 4. This determination was made to see whether aluminum was released from the montmorillonite during the titration.

The aluminum values in table 4 are quite high for the more alkaline solutions. This is so because the solutions were in contact with the clay for almost four months prior to filtering. This was necessary to provide time for the 115-day reading considered desirable in a discontinuous titration. In order to obtain correlative analytical results bearing on the decomposition of the clays replicate runs of samples 10, 20, and 30 were made, filtered after 7 and 12 days, respectively, and analyzed for alumina by L. Shapiro by methods similar to those described by Shapiro and Brannock (1956). As before, 65-mg samples were used, and total Al₂O₃ in the solutions ranged from 0.06 to 0.11 mg. No trend was apparent, and it seems reasonable to state that, although there was significant decomposition of the clays exposed to more concentrated sodium hydroxide solutions over a longer time, at the time of the pH and glass

electrode readings taken during the first two weeks, the clay may be considered as essentially intact, provided no new solid phase formed. No crystalline phase was apparent on X-ray diffraction.

pH readings

The neutralization of the acid montmorillonite was measured by pH readings made with a Beckman Model GS-meter using a glass electrode. The readings were made in the supernatant solutions in contact with the montmorillonite samples that had settled to the bottom of the weighing bottles. The bottles were kept covered at all times except when making pH determinations. Clay in contact with electrodes will cause irregular pH values. These irregularities have been ascribed generally to the "suspension effect." This is discussed elsewhere (Pommer, 1961). Except for the most acid solutions no difficulty was experienced in getting the clay to settle, and the shape of the curves indicated that the slight turbidity involved in those few reaction mixtures did not cause a detectable error.

Presentation of potentiometric and analytical data

Two separate series of determinations were run at different times. The results of the first series are shown in tables 2-4, and those of the second series in tables 5-6.

Table 2.--Titration of montmorillonite (Chambers, Ariz.) with 0.1 N NaOH
(65 mg samples in a total volume of 6.20 ml)

Time after mixing	1 day	2 days	3 days	6 days	Average ^{a/}	48 days ^{b/}	50 days	115 days	
Temperature at time of pH measurement	25°C	24°C	25°C	25°C		29°C	26°C	25°C	
pH readings									
Sample NaOH (ml)									
1	nil	4.05 ^{x/}	4.40	4.60	4.55	4.51	4.55	4.80	4.95
2	.02	4.60 ^{x/}	5.22	5.08	5.15	5.15	5.10	5.35	5.30
3	.04	5.60	5.30	5.22	5.50	5.40	4.75	5.15	5.03
4	.06	5.70	5.70	5.29 ^{x/}	5.75	5.71	5.20	5.45	5.58
5	.08	5.90	5.93	5.91	5.89	5.90	5.45	5.95	5.70
6	.10	6.20	6.20	6.05 ^{x/}	6.00 ^{x/}	6.20	5.70	6.01	5.75
7	.12	6.30 ^{x/}	6.20	6.12	6.19	6.17	6.22	6.10	5.85
8	.14	6.40 ^{x/}	6.02	5.90	5.90	5.94	5.20	5.95	5.75
9	.16	6.35	6.40	6.40	6.23 ^{x/}	6.38	6.35	6.39	6.02
10	.18	6.40	6.32	6.45	6.35	6.38	6.50	6.45	6.12
11	.20	6.60	6.70	6.50	6.49	6.57	6.60	6.58	6.20
12	.22	6.65	6.70	6.58	6.48	6.60	6.65	6.55	6.30
13	.24	6.70	6.85 ^{x/}	6.65	6.58	6.64	6.70	6.80	6.38
14	.28	7.05 ^{x/}	6.75	6.70	6.75	6.73	6.80	6.90	6.51
15	.32	7.40 ^{x/}	6.70	6.80	6.90	6.80	6.90	6.95	6.60
16	.36	7.70 ^{x/}	6.85	7.08	7.20	7.04	7.35	7.40	7.10
17	.40	8.25 ^{x/}	7.37	7.50	7.50	7.45	7.80	7.80	7.35

Table 2.-- Continued

Table 2.--Titration of montmorillonite (Chambers, Ariz.) with 0.1 N NaOH
(65 mg samples in a total volume of 6.20 ml)

Time after mixing	1 day	2 days	3 days	6 days	Average ^{a/}	48 ^{b/} days	50 days	115 days	
Temperature at time of pH measurement	25°C	24°C	25°C	25°C		29°C	26°C	25°C	
pH readings									
Sample NaOH (ml)									
18	.44	9.15 ^{x/}	7.95	7.95	8.05	7.98	7.95	8.40	7.75
19	.48	9.50 ^{x/}	8.65	8.25	8.21	8.37	8.25	8.29	7.90
20	.53	9.85	9.10	8.59	8.50	9.01	8.90	8.15	8.00
21	.56	10.05	9.40	9.10	8.65	9.30	8.60	8.40	8.25
22	.60	10.13	9.60	9.40	8.80	9.48	8.60	8.62	8.33
23	.64	10.25	9.65	9.42	8.85	9.54	8.50	8.70	8.48
24	.68	10.30	9.80	9.62	9.15	9.71	8.63	8.65	8.48
25	.72	10.40	10.15	9.85	9.25	10.13	8.90	8.88	8.60
26	.76	10.60	10.40	9.85	9.60	10.11	8.95	8.90	8.70
27	.82	10.73	10.30	10.02	9.75	10.20	8.85	8.98	8.80
28	.86	10.70	10.50	10.11	9.65	10.24	8.90	9.01	8.82
29	.90	10.85	10.75	10.40	9.85 ^{x/}	10.66	8.95	9.00	8.88
30	.94	11.02	10.85	10.55	10.20	10.65	8.92	9.02	8.92
31	.98	11.00	10.79	10.60	10.10 ^{x/}	10.79	8.91	8.95	8.91
32	1.06	11.15	11.02	10.88	10.70	10.93	8.95	9.10	9.00
34	1.10	11.35	11.25	10.98	10.80	11.09	9.10	9.10	9.05

Table 2.--Continued

Table 2.--Titration of montmorillonite (Chambers, Ariz.) with 0.1 N NaOH
(65 mg samples in a total volume of 6.20 ml)

Time after mixing	1 day	2 days	3 days	6 days	Average ^{a/}	48 ^{b/} days	50 days	115 days	
Temperature at time of pH measurement	25°C	24°C	25°C	25°C		29°C	26°C	25°C	
pH readings									
Sample NaOH (ml)									
35	1.14	11.30	11.00	11.10	10.90	11.07	9.10	9.15	9.08
36	1.16	11.20	11.05	10.91	10.60 ^{x/}	11.05	9.10	9.10	9.05
37	1.20	11.40	11.15	11.01	10.85	11.10	9.05	9.16	9.11
38 ^{c/}	1.20	11.70	11.65	11.61	11.65	11.65	9.45	9.50	9.30

^{a/} The average was made up of the readings for the first four figures, but only those not differing by more than half the difference between the highest and the lowest reading for any sample were used to calculate the average. This value is plotted in figure 2, and was published by Pommer and Carroll, 1960.

^{b/} Dilutions to constant volume (6.20 ml) made 1 day prior to this reading.

^{c/} Sample 38 contained no clay sample, only 1.20 ml 0.1 N NaOH.

^{x/} Reading omitted from calculation of average in column 7.

Table 3.--First series--A comparison of readings, in millivolts (as determined by calomel and sodium-sensitive glass electrodes), with sodium values determined by flame photometry (Pommer, 1960).

Sample	pH	Na ^a / (millimoles per liter)	Electrode reading (millivolts)
1	4.80----	0.53	89
2	5.30----	.55	109
3	5.25----	.60	104
4	5.80----	.55	120
5	6.00----	.55	120
6	6.10----	.69	120
7	6.15----	.70	122
8	6.00----	.70	104
9	6.40----	.76	118
11	6.55----	.70	118
12	6.65----	.90	118
13	6.70----	.98	118
14	6.80----	1.4	116
15	7.00----	1.8	113
16	7.40----	2.0	104
17	7.60----	2.4	91
19	8.25----	2.4	69
20	8.35----	2.5	61
21	8.50----	3.5	53
22	8.60----	3.8	51
23	8.60----	4.2	45

Table 3.--Continued

Table 3.--First series--A comparison of readings, in millivolts (as determined by calomel and sodium-sensitive glass electrodes), with sodium values determined by flame photometry (Pommer, 1960).

Sample	pH	Na ^{a/} (Millimoles per liter)	Electrode reading (millivolts)
24	8.65----	4.2	42
25	8.75----	4.8	38
26	8.80----	5.7	35
27	8.90----	6.4	31
28	8.90----	7.0	31
29	8.75----	7.0	31
30	9.05----	7.8	24
31	9.05----	7.2	25
32	9.10----	8.8	22
34	9.10----	9.1	20
35	9.05----	11	18
36	9.20----	11	18
37	9.20----	11	15
38	9.45----	19	7

^{a/} Dorothy Carroll, analyst.

Table 4. First series--Al₂O₃ found in filtrates from the titration of H-montmorillonite with 0.1 N NaOH (Carroll, 1960)

[65 mg samples in a total volume of 6.2 ml]

Sample	NaOH added (ml)	Al ₂ O ₃ (mg)
1-----	nil	0.06
2-----	0.02	nil
3-----	.04	.06
4-----	.06	nil
5-----	.08	nil
6-----	.10	nil
7-----	.12	.25
8-----	.14	.37
9-----	.16	.50
10-----	.18	.82
11-----	.20	.99
12-----	.22	.99
13-----	.24	1.75
14-----	.28	2.75
15-----	.32	4.13
16-----	.36	3.92
17-----	.40	3.69
18-----	.44	.87
19-----	.48	2.32
20-----	.52	2.87

Table 4.--Continued

Table 4.--First series--Al₂O₃ found in filtrates from the titration of
H-montmorillonite with 0.1 N NaOH (Carroll, 1960)
 [65 mg samples in a total volume of 6.2 ml]

Sample	NaOH added (ml)	Al ₂ O ₃ (mg)
21-----	.56	3.53
22-----	.60	3.95
23-----	.64	3.11
24-----	.68	3.95
25-----	.72	3.95
26-----	.76	3.11
27-----	.82	2.99
28-----	.86	2.39
29-----	.90	4.31
30-----	.94	3.53
31-----	.98	3.05
32-----	1.06	4.19
34-----	1.10	4.31
35-----	1.14	5.38
36-----	1.16	4.84
37-----	1.20	5.26

Table 5.--Second series--Titration of montmorillonite^a with 0.1 N NaOH^b with provision for reaction blanks^c

Sample	NaOH added	Meg Na/100g 100 mg clay	pH value after number of days indicated			Na electrode reading after number of days indicated (-mv)		Na in ^d filtrate (ppm)		
			1	2	5	7	12			
1	nil		4.05	4.45	5.10	4.25	5.10	107	96	1.0
2	0.02	3.08	4.55	4.75	4.75	4.80	4.80	125	122	.7
3	.04	6.16	5.20	5.00	5.15	4.90	4.71	127	126	.5
4	.06	9.24	5.51	5.30	5.10	5.20	4.80	129	133	.6
5	.08	12.32	5.45	5.40	5.15	5.15	4.95	125	126	.7
6	.10	15.40	5.61	5.55	5.20	5.30	4.95	125	131	.7
7	.12	18.48	5.78	5.80	5.80	5.85	5.65	124	131	.7
8	.14	21.56	5.85	5.75	5.50	5.55	5.20	122	122	.7
9	.16	24.64	5.73	5.90	5.72	5.65	5.40	122	122	1.0
10	.18	27.72	6.15	6.05	5.78	5.80	5.45	122	129	.9
11	.20	30.80	6.70	6.15	5.85	6.00	5.50	118	122	.8
12	.22	33.88	6.32	6.20	5.80	5.90	5.50	122	124	.8
13	.24	36.96	6.82	6.75	6.15	6.30	5.90	111	122	1.0
14	.28	43.12	7.50	6.70	6.15	6.35	5.75	109	116	1.0
15	.32	49.28	7.65	6.55	6.25	6.50	5.90	107	115	1.0
16	.36	55.44	8.08	6.60	6.30	6.50	6.00	100	111	1.6
17	.40	61.60	8.50	6.85	6.55	6.70	6.25	100	107	2.0
18	.44	67.76	8.65	7.15	6.80	6.85	6.60	93	98	2.1
19	.48	73.92	9.15	7.80	7.05	7.10	6.90	87	89	2.4
20	.52	80.08	9.15	7.95	7.25	7.40	7.20	78	78	2.4
21	.56	86.24	9.25	8.05	7.50	7.60	7.45	73	75	3.6
22	.60	92.40	9.65	8.80	7.75	7.75	7.55	71	69	3.7
23	.64	98.56	9.85	9.05	8.05	8.05	7.80	67	67	4.1
24	.68	104.72	9.85	9.15	8.35	8.35	8.25	62	60	4.9
25	.72	110.88	10.05	9.38	8.83	8.58	8.20	60	58	5.2
26	.76	117.04	10.00	9.60	9.25	9.02	8.40	58.1	56	4.7

Table 5.--Continued

Sample	NaOH added	Meq Na/100g 100 mg clay	pH value after number of days indicated				Na electrode reading after number of days indicated (-mv)			Na. in ^d / filtrate (ppm)
			1	2	5	7	12	7	12	
27	.80	123.20	10.30	9.60	9.30	9.10	8.45	56.3	53	5.6
28	.84	129.36	10.50	9.95	9.51	9.30	8.75	52.7	49.1	7.1
29	.88	135.52	10.60	10.00	9.63	9.40	8.90	50.9	45.5	7.2
30	.92	141.68	10.65	10.38	9.95	9.80	9.45	50.2	45.5	7.2
31	.96	147.84	10.65	10.30	9.80	9.65	9.15	45.4	40.0	8.9
32	1.00	154.00	10.78	10.48	10.11	9.90	9.55	46.5	41.8	10.0
33	1.04	160.16	11.00	10.51	10.35	10.20	9.90	45.4	38.2	10.2
34	1.08	166.32	11.00	10.68	10.45	10.25	10.05	41.8	36.4	12.4
35	1.12	172.48	11.05	10.80	10.60	10.35	9.85	40.0	32.8	12.4
36	1.16	178.64	11.15	10.85	10.71	10.45	10.10	38.2	32.8	13.4
37	1.20	184.80	11.18	10.88	10.75	10.45	10.15	38.2	30.9	13.3

a/ Sample from Chambers, Arizona

b/ 60-mg samples in total volume of 6.20 ml.

c/ Shown in table 6.

d/ Dorothy Carroll, analyst.

Table 6.--Second series--pH values of solutions to which increments of 0.1 N NaOH were added (Carroll, 1960)

[Total volume of each is 6.2 ml]

	NaOH added (ml)	NaOH micromoles in solution	pH values after number of days indicated					Difference in pH in 11 days
			1	2	5	7	12	
1a	0.02	0.32	7.60	6.40	6.10	6.10	6.05	1.55
6a	.10	1.61	9.85	9.50	7.80	7.45	7.20	2.65
12a	.22	3.54	10.50	10.30	9.75	9.15	8.00	2.50
18a	.44	7.10	11.00	10.95	10.90	10.60	9.70	1.30
24a	.68	10.96	11.50	11.35	11.40	11.35	11.35	.15
30a	.92	14.83	11.75	11.58	11.52	11.65	11.65	.10
38	1.20	19.35	11.85	11.65	11.75	11.75	11.85	nil

Semilogarithmic plotting of titration curves

Sillen (1959) has discussed the literature, theory, and application of the logarithmic diagram with a master variable, a very useful graphic presentation of equilibrium data which was originally presented by Bjerrum (1914). The application of this technique to acid-base equilibria has been illustrated by Sillen (1959). Essentially it involves the equivalent of plotting titration curves semilogarithmically, the volume being entered on the logarithmic axis. Such plots were found useful previously (Pommer and Breger, 1960a, 1960b; Pommer and Carroll, 1960; Pommer, 1960; Carroll and Pommer, 1960) in producing reasonable straight lines if the values obtained in discontinuous titrations were thus treated. The nearness of the points of intersection of these lines to the equivalence points was verified in most cases by Gran's method (1952). The plotting method may be expected to be effective for the reasons given below.

If increments of a strong base solution are added to an aqueous neutral salt solution, the hydroxyl ion concentration of the solution is a linear function of the titrant volume, and hence the solution pH is a linear function of the logarithm of the titrant volume. The only requirement is that the initial volume be large enough to assume constant volume, this situation applies at the end of most acid-base titrations. If acid is present, the change in pH as a function of the logarithm of volume of base added may be linear under some conditions, as when the hydrogen ion concentration due to free acid is negligible. Under these conditions the slope of this portion of the linear titration curve will be less. This is typical of most acid-base titrations before the end point is reached. Hence, semilogarithmic plotting of titrations can indicate end points; it can also yield dissociation constants of weak acids.

Evaluation of electrode data

Plots of pH and Na electrode data on the first series have been presented previously. Originally the average of the first four pH readings was plotted semilogarithmically (Pommer and Carroll, 1960) and these values were then compared with sodium-sensitive electrode readings (Pommer, 1960). As table 2 shows a lowering of pH with time, it was felt that, in addition to the aging of the clay, carbon dioxide absorption might play a part. Carroll (1960) has discussed some implications of this factor. Because the effect of carbon dioxide upon pH values in the first run could not be determined from the available data, the experiment was repeated.

The results of the second titration are presented in figures 2 and 3. Here line A represents the curve on the day after mixing, (the alternate A' line indicates equivocal indications of a second end point), line B one week later, and lines D and E represent the titration curves of the reagent blanks on these days. It may be observed that, whereas line A shows two equivalence points, the problematic second equivalence point has been lost in line B. A pronounced shift to the left from A to B and D to E shows the lowering of pH owing to CO₂ absorption from the air. All bottles received the same handling at all times, and for this reason it appeared that NaOH solutions of identical pH should exhibit the same acid shift, whether or not

65 mg of clay were suspended in them. A corrected curve was made, adjusted for the effects of CO_2 absorption. This was done graphically by taking a point at B, going down vertically to the intersection with E, then horizontally to the right (to counteract the shift to the left caused by CO_2 absorption) to the intersection with D, then up vertically to the ordinate of the original point on line B. This point was plotted and the procedure repeated until line C was constructed. It may be noted that D and E join at a pH of 5.6, a not too unreasonable value for distilled water saturated with 10^{-4} atmospheres of CO_2 ; below pH 5.6 lines B and C are therefore identical. In the linear plot the lines join at pH 5.0, an experimentally determined value. It was decided not to use this point in the semilogarithmic plot for two reasons: The proper ordinate for the experimental point would be located at minus infinity; also the adopted procedure illustrates that the plotting method has limitations. The difference of 0.6 pH units is not excessive for such an unbuffered system. Comparison of A and B then gives the overall effect of standing upon the titration, whereas a comparison of A and C shows the effect on standing with the CO_2 absorption effect removed.

Figure 4 shows the corrected curves derived from the linear and semilogarithmic plots and shows them to be similar enough to indicate the validity of both plots for the purpose. The line derived from the semilogarithmic plot appears to be slightly better at the lower end. In this connection it should be noted also that in figures 2 and 3 line C crosses line A. This is physically unreasonable and is probably caused by the inadvertent CO_2 uptake of sample 18a. This sample contained twice as much NaOH as sample 12a and its pH was only 0.1 units higher. Also, when plotted semilogarithmically, the pH of NaOH solutions at different concentrations should fall on a straight line. Inspection of curve D, figure 2, indicates that the point identified as 18a on table 6 deviates from the straight line by 0.15 pH unit and should be at pH 11.15 if the line were straight. This is almost at the place where the buffering capacity of the solution is at a maximum and indicates, therefore, considerable CO_2 absorption, owing to a technical accident. The overcorrection probably does not affect the position of the endpoints or the conclusions presented; however, it makes impossible an evaluation of the second pK and an interpretation of Henderson-Hasselbalch plots (Pommer and Carroll, 1960).

The results show that more blank solutions are required in a run to cancel out the effects of possible technical accidents. However, the graph clearly shows the advantage of the procedure.

Figures 5 and 6 compare the value of the first series previously published (Pommer and Carroll, 1960) to the experimental and corrected value of the second series. Although the consistency of the experimental pH values of both series is clearly shown in tables 2 and 5, figure 6 summarizes strikingly the effect of using a titration curve from average pH values compared to titration curves not corrected for CO_2 absorption as they change with time. The figure also points out the difference between the two series not accounted for by the changed procedure. For instance, curve I should remain in the area bounded by A and B, as the averaging procedure used in its construction should yield an intermediate value. However, it crosses line A in the region where the sodium concentration is higher. The reason for this discrepancy is not known, but a possible explanation is that the CO_2 uptake of the system in the first

series was much less. This might explain the remarkable similarity of curves I and C in figure 6.

Experimental details for the measurement of sodium by cationic-sensitive electrodes (first series) have been reported elsewhere (Pommer, 1960, 1961). Figure 7 compares flame photometric and potentiometric sodium values of the first series and figure 8 compares the potentiometric data of both series with sodium values from flame photometry of the second series. A complete enumeration of all sodium data is presented in tables 3 and 5. As the determination of sodium by cation-sensitive electrodes is relatively new, these data are given to indicate the powers and limitations of the electrode used.

It can be concluded that the clay takes up virtually all the sodium added during neutralization of the "first" acid and that it continues to take up a considerable fraction of the sodium added during the neutralization of the "second" acid. In the region of overtitration some sodium may be taken up, either by physical absorption or possibly by exchange for residual calcium in the hydrogen clay,

It is of interest to note that the second segment of the sodium electrode curve in figure 8 is less steep than the third. Although this is physically unreasonable, it is to be expected in view of the abnormality of the response of the sodium electrode in clay titrations in this region discussed elsewhere (Pommer, 1961).

X-ray diffraction studies

X-ray diffraction procedure

Oriented aggregate mounts on glass slides were made of the montmorillonite samples that had been titrated. The clay suspensions were allowed to dry at room temperature. X-ray diffraction patterns were made of the (001) d spacing in order to show the change in this spacing from the H-form montmorillonite to that in which the interlayer exchange positions were filled with sodium. Copper $K\alpha$ radiation was used throughout, and the chart was run at 1° per minute. Some of the slides were also treated at 35 percent humidity in a desiccator. Others were treated with ethylene glycol, and a few were heated. Slide preparation was done by Dorothy Carroll.

Presentation of data

The X-ray data are presented in tables 7 and 8. Essentially, as the hydrogen in the clay is replaced by sodium, there is a systematic change in the (001) spacing completely in line with what might be expected in the light of Barshad's (1950) data. This change is most pronounced if the patterns are taken at room temperature and humidity. It is lessened if the slides are pretreated at 35 percent humidity, and totally obliterated, if they are treated with glycol, or if they are fired. This is as must be expected. It is, however, important to note that almost the entire change in (001) spacing appears to take place during the neutralization of the "first" acid. This is precisely the result to be predicted from the concept of interlayer versus edge sites of Garrels and Christ (1956) in the light of Barshad's (1950) findings concerning the effect of the cations upon interplanar spacing. The data furnish experimental indications that the neutralization of the "first" acid is related to the exchange of Na^+ for H in interlayer positions and that the neutralization of the second acid is related to the exchange of Na^+ for H^+ in positions which are not interlayer positions. Presumably these positions are edge sites.

The relation of interplanar spacing to the type of exchangeable cation can be utilized in an attempt to determine the position of some of the cations. It will be recalled that the clay used in this work had not been completely converted to the hydrogen form and that it contained 28 meq/100 g of bivalent cations (Ca and Mg) and about 6 meq/100 g univalent alkali, cations (Na and K) in addition to about 90 meq/100 g hydrogen ions. It is now of interest to determine whether the exchangeable alkali and alkaline earth cations are located in interlayer or edge positions. Because the edge positions exhibit lower acidity and hold hydrogen ions more tightly, it may be predicted that hydrogen ions will first replace other cations in these positions, and that the remaining exchangeable ions most likely will be found in interlayer positions.

This hypothesis may easily be supported by the following consideration. A pure hydrogen montmorillonite has an interplanar basal spacing of 14.5 Å (Barshad, 1950) whereas the values of the hydrogen montmorillonite used in this work tend to be slightly higher (tables 7 and 8). Similarly as the spacing of the sodium montmorillonite produced by titration tends to be slightly more than the 11.9 Å for magnesium and calcium montmorillonite, respectively, increased spacing for hydrogen or sodium clay containing some of these cations is to be expected, provided these cations are in interlayer positions where they can affect the d spacing.

An evaluation of the interlayer expansion in montmorillonite by Barshad (1949) showed that, in a montmorillonite containing one layer of water, the thickness of the unit cell may be expected to be $10.16 + 2.76 = 12.92$ Å, if the centers of the oxygens of the water molecules are vertically above and below the centers of the oxygens of the lattice. If, however, the water molecules form tetrahedra with the bases of the linked silica tetrahedra of the lattice, the interplanar basal spacing would be $10.16 + 1.78 = 11.94$ Å, a value closely comparing with the value of 11.9 Å for sodium montmorillonite, a monomolecular layer of water being associated with sodium in the interlayer position (Barshad, 1950). According to the same author (Barshad, 1950) a dimolecular water layer is associated with hydrogen, calcium, or magnesium

ions in the interlayer positions of montmorillonite at normal temperature and humidity, and Barshad (1949) considers the thickness of a montmorillonite with two water layers under various assumptions. The values for hydrogen, calcium, and magnesium montmorillonite given here fit best the value of $10.16 + 1.78 + 2.76 = 14.70$ A, a value expected when the water molecules form tetrahedra at the water-oxygen interface but are vertically above each other at the water-water interface. A change from a pure hydrogen montmorillonite to a pure sodium montmorillonite then would be expected to produce a decrease of 2.76 A in interplanar basal spacing.

It is now desirable to calculate the expected decrease in interplanar basal spacing, if the hydrogen clay used in this work is titrated with a sodium hydroxide solution. For clarity, all the assumptions made are summarized below:

- a. The remaining exchangeable alkali and alkaline earth cations are in interlayer positions.
- b. Only cations in interlayer positions affect this spacing.
- c. Water molecules form tetrahedra with the bases of the linked silica tetrahedra of the lattice, but in the case of two layers the water molecules are vertically above each other at the water-water interface.
- d. As the determination of interplanar basal spacings by X-ray diffraction is essentially an averaging procedure, replacement of a fraction, f , of all cations causing expansion by two molecular layers of water by cations causing expansion by only one such layer will cause a decrease in the thickness of the unit cell amounting to $2.76 \times f$.

If the hydrogen clay used here has a total exchange capacity of 120 meq/100 g, and the remaining alkali ions on the clay total 6 meq/100 g, there are 114 meq/100 g ions causing expansion by two molecular layers of water. Of these, the calcium and magnesium are not replaced during the titration, and the exchangeable hydrogen ions which are replaced then amount to $114 - 28$ or 86 meq/100 g. The fraction, f , then is $86/114$ or 0.754, and the expected decrease in interplanar basal spacing is 0.754×2.76 or 2.08 A.

As can be seen in tables 7 and 8, there is considerable spread in the \underline{d} spacings. This may be expected in view of the sensitivity of the clay to atmospheric humidity changes, and also in view of the difficulty in having to work at very low angles of incidence. The hydrogen clays, having essentially two molecular water layers on C^- positions, are more sensitive to variations in humidity, and it may be observed that the sequence of decreasing \underline{d} spacings with increasing sodium content of the clay is more often disturbed in the high-hydrogen region. For this reason the decrease in the four series at room temperature and humidity shown in tables 7 and 8 was determined by taking the difference between the highest and the lowest rather than the first and the last member of each series. These decreases in interplanar spacings, in angstroms, amount to 2.10, 1.85, 2.17, and 1.85, or $1.99 + 0.29$ A, a value well compatible with the expected decrease in \underline{d} spacing of 2.08 A. Therefore, the X-ray data furnish a reasonable indication that the remaining exchangeable cations on the hydrogen clay used in this work were in interlayer positions.

It must be borne in mind that the explanation of the change in d spacings by Barshad is not necessarily correct. Other interpretations may be found in the literature. It is important to note that this does not necessarily affect the validity of the argument, because the numerical values appear to be correct. In view of the high standard deviation of the data reported here, not too much confidence should be placed in their interpretation. All the information supports the trend of reasoning, but does not prove it uniquely by any means. It must also be pointed out that the columns in tables 7 and 8 indicating the calculated Na in the clay are based on the assumption that the clay was not decomposed during the run. As table 4 shows, this is clearly not true for the samples with higher numbers. In view of the fact that data on dissolved silica were not available, corrections could not be made. The numerical sodium values indicate that the error is not unreasonably high, because the values go as high as 82.2 meq/100 g, a value easily within experimental error of the expected value of 90 meq/100 g (Pommer and Carroll, 1960).

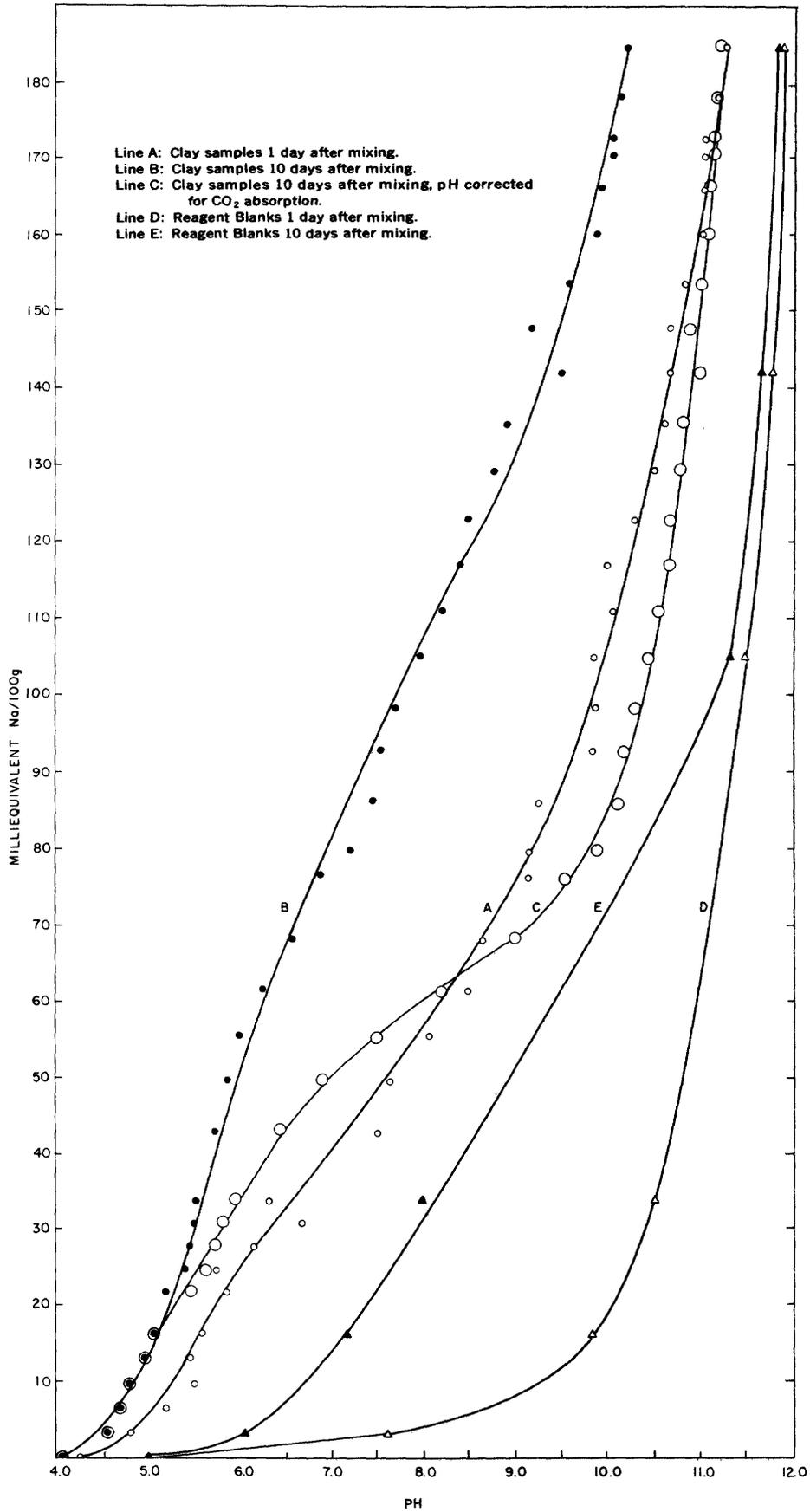


FIGURE 2.—SECOND SERIES—PLOT OF pH FOR THE TITRATION OF H-MONTMORILLONITE WITH SODIUM HYDROXIDE (WITH CORRECTION FOR CARBON DIOXIDE ABSORPTION).

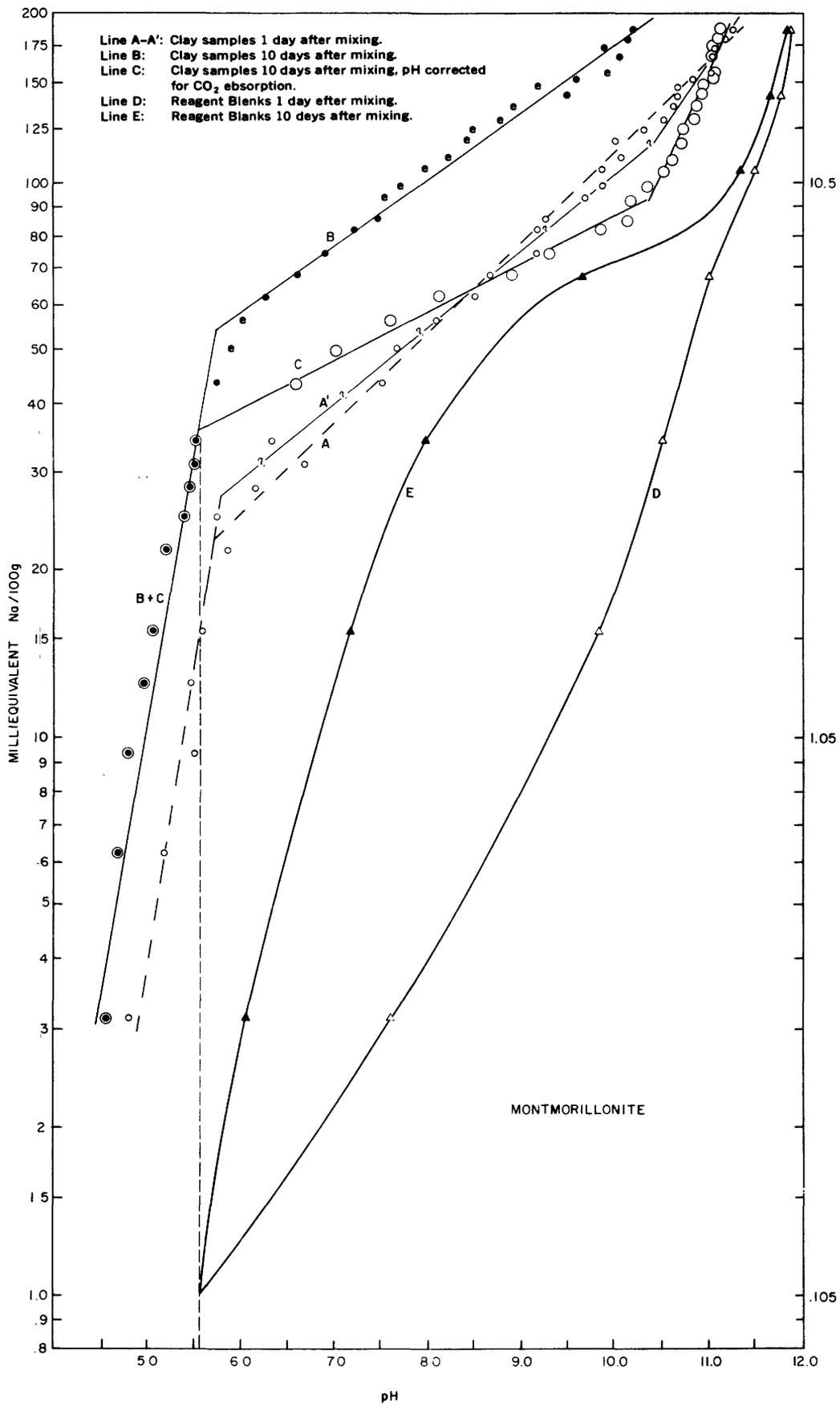


FIGURE 3.—SEMILOGARITHMIC PLOT OF pH FOR THE TITRATION OF H-MONTMORILLONITE WITH SODIUM HYDROXIDE (WITH CORRECTION FOR CARBON DIOXIDE ABSORPTION)

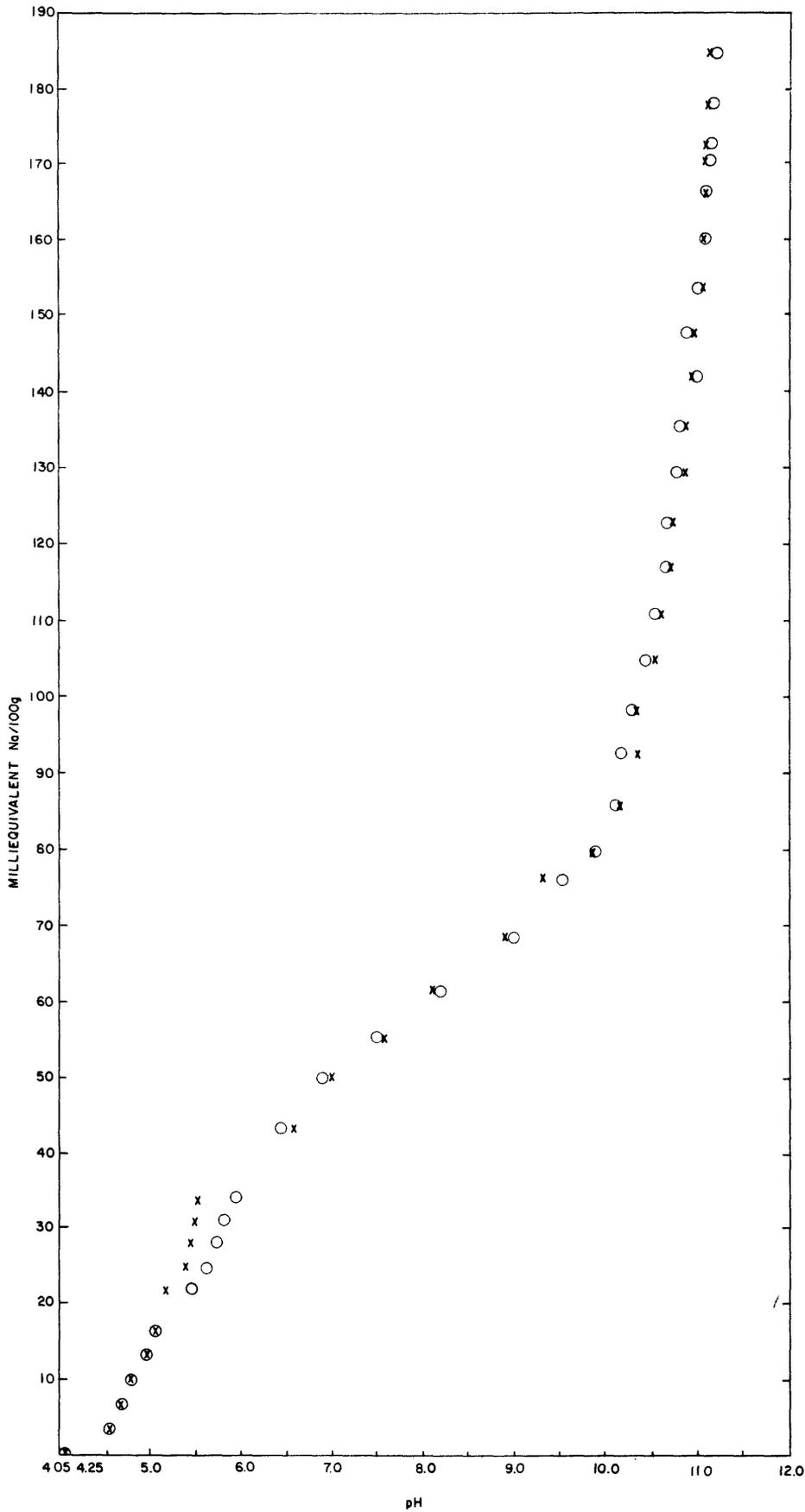


FIGURE 4.—COMPARISON OF A CORRECTED pH TITRATION CURVE CONSTRUCTED FROM A SEMILOGARITHMIC PLOT (x-x-x) WITH ONE CONSTRUCTED FROM A LINEAR PLOT (o-o-o-o). (FOR PURPOSES OF CLEARNESS THE POINTS OF THE CURVES ARE NOT CONNECTED BY LINES.)

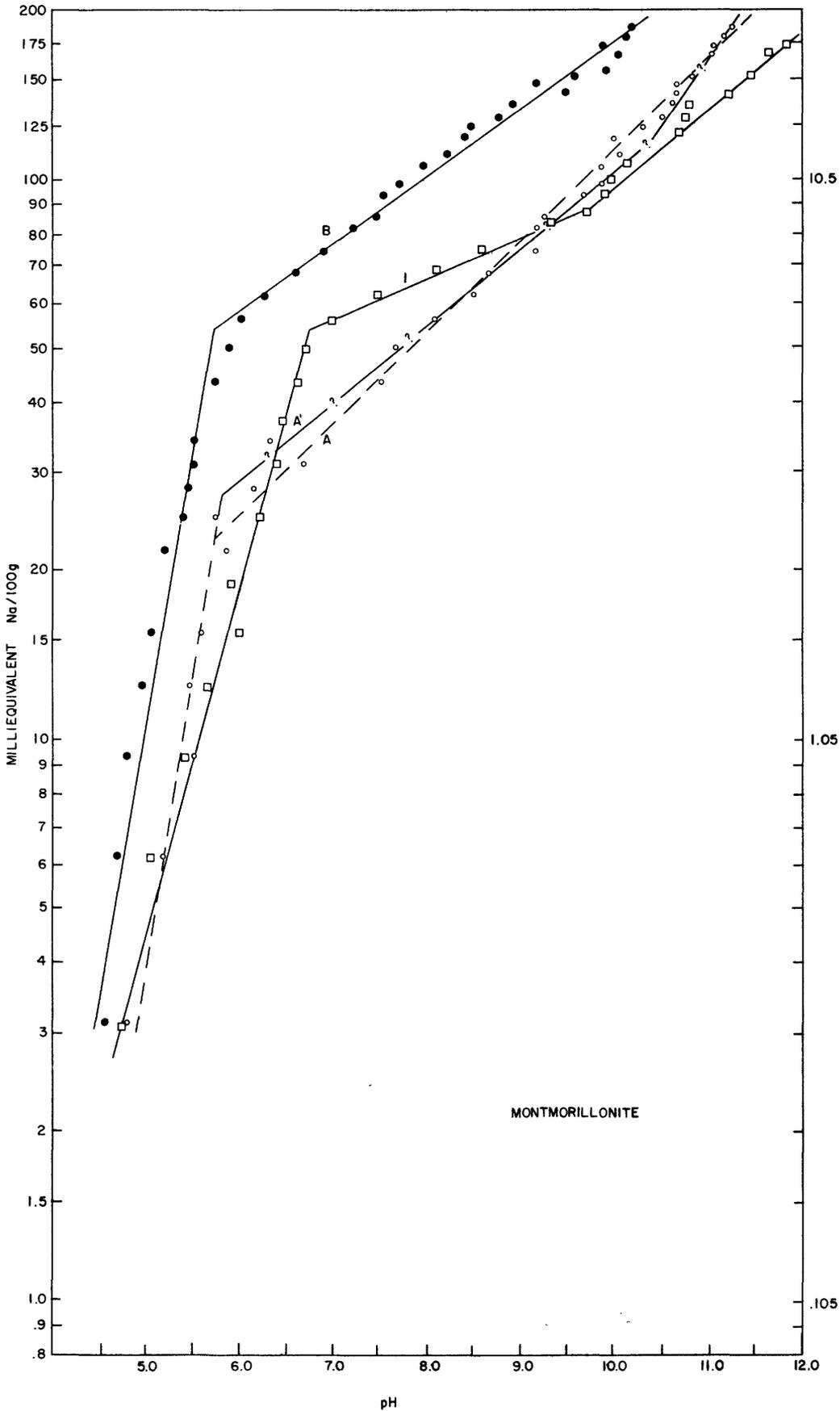


FIGURE 5.—COMPARISON OF EXPERIMENTAL pH DATA OF FIRST SERIES (1) AND SECOND SERIES (LINES A AND A' AND B SAME AS SHOWN IN FIGURE 3). THE ALTERNATE A AND A' LINES SHOW THAT THE SECOND INFLECTION POINT IS BASED ON EQUIV. OCAL EVIDENCE.

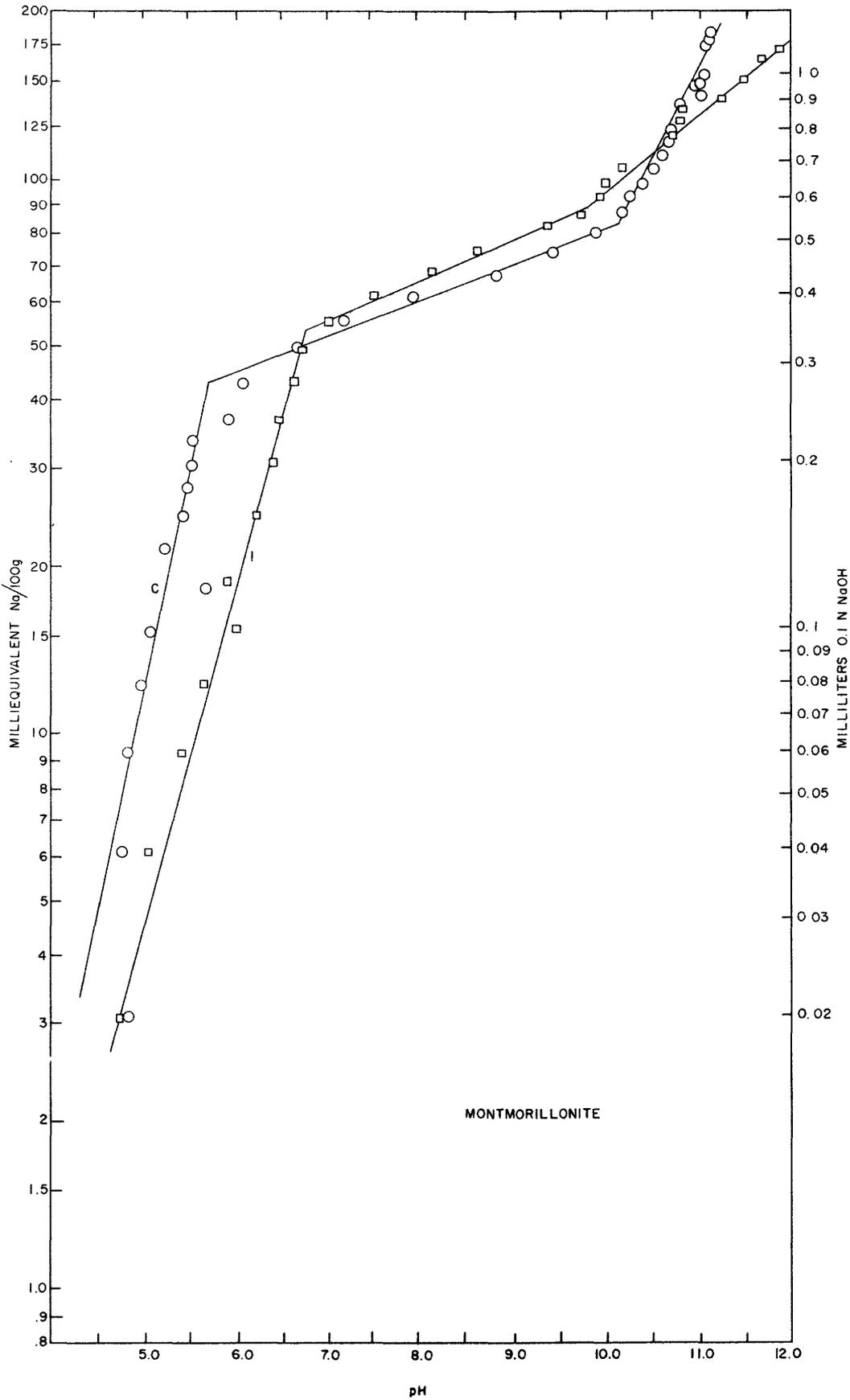


FIGURE 6.—COMPARISON OF pH CURVE OF FIRST SERIES BASED ON AVERAGING OF FOUR DETERMINATIONS WITH (LINE 1) THE pH CURVE OF SECOND SERIES AFTER CORRECTION FOR CO₂ (LINE C).

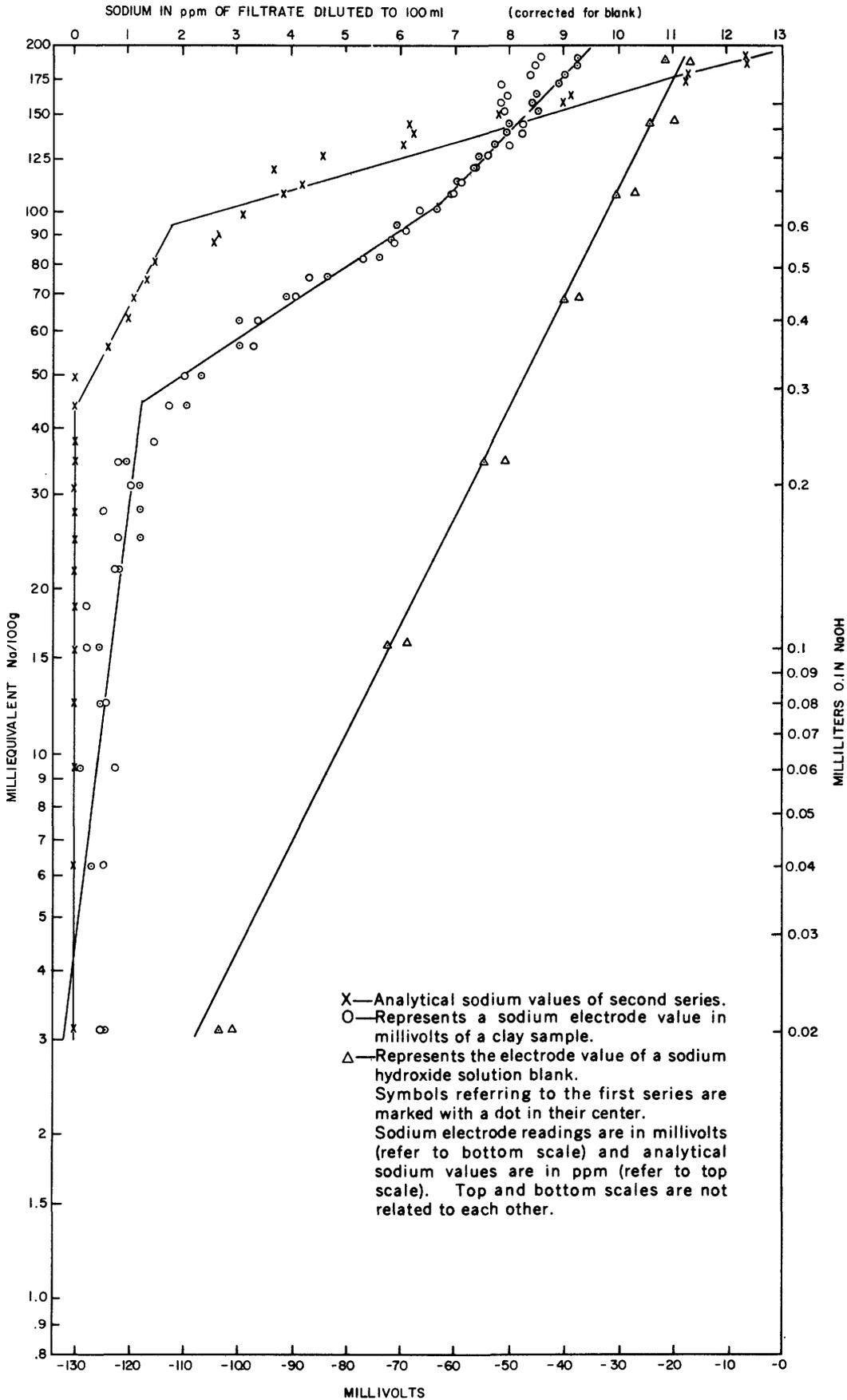


FIGURE 8.—COMPARISON OF SODIUM ELECTRODE READINGS POOLED FOR BOTH SERIES WITH ANALYTICAL SODIUM VALUES OF THE SECOND SERIES.

Table 7. --X-ray diffraction data on montmorillonite specimens recovered after discontinuous titration (first series)

[Cu K α radiation, 1° per min]

Sample	Na added (meq/100g)	Na taken up by clay (meq/100g)	\bar{d} (001) A ^{b/}	\bar{d} (001) A ^{c/}	\bar{d} (001) A ^{d/}	\bar{d} (001) A ^{e/}
Neutralization of first clay acid						
1	0	0	14.73	14.48	16.99	14.26
2	3.1	3.1	---	14.48	---	14.26
3	6.2	6.2	---	14.48	---	---
4	9.3	9.3	13.92	---	16.67	14.03
5	12.3	12.3	---	14.85	---	14.48
6	15.4	13.9	---	14.37	---	14.26
7	18.4	16.9	---	---	---	14.26
8	21.6	20.0	13.39	---	---	13.81
9	24.6	23.1	13.39	14.26	---	13.60
10	27.7	---	13.81	14.37	16.67	13.81
11	30.8	29.3	13.19	---	---	13.39
12	33.9	30.8	13.39	---	---	13.39
13	37.0	32.3	12.99	---	---	13.39
14	43.1	33.9	13.29	13.59	16.67	13.19
			12.62	---	---	13.19
Neutralization of second clay acids						
15	49.3	37.0	12.81	13.81	---	---
16	55.4	40.0	12.45	---	---	13.00
17	61.6	43.1	12.53	13.59	16.67	13.00
18	67.8	53.9	12.27	13.57	---	13.00
19	73.9	55.4	12.45	13.49	16.67	12.63
20	80.1	61.6	12.45	13.55	---	12.63
21	86.2	72.4	---	13.59	---	12.81

Table 7.--Continued

Table 7.--X-ray diffraction data on montmorillonite specimens recovered after discontinuous titration (first series).

[Cu K α radiation, 1° per min]

Sample	Na added (meq/100g)	Na taken up by clay (meq/100g)	\bar{d} (001) A ^{b/}	\bar{d} (001) A ^{c/}	\bar{d} (001) A ^{d/}	\bar{d} (001) A ^{e/}
22	92.4	75.5	12.63	---	---	12.63
23	98.6	63.1	---	13.49	16.83	---
24	104.7	69.3	---	---	---	12.81
25	110.9	69.3	---	---	---	---
26	117.0	66.2	12.63	---	---	12.63
27	123.2	66.2	---	---	---	---
28	129.4	66.2	---	---	---	---
29	135.5	72.4	---	---	---	12.63
30	141.7	72.4	---	---	---	12.63
31	147.8	77.0	---	---	---	12.63
32	154.0	73.9	---	13.55	---	12.63
33	160.2	---	---	---	(f)	12.63
34	166.3	83.2	---	13.59	---	12.81
35	172.5	80.1	---	---	---	---
36	178.6	81.6	---	---	---	---
37	184.8	86.2	12.36	---	16.83	12.63

Overtitration

Table 7.---Continued

Table 7.---X-ray diffraction data on montmorillonite specimens recovered after discontinuous titration (first series).

- a/ Calculated from analysis for Na in the filtrate (Dorothy Carroll, analyst).
- b/ Allowed to dry on slide at room temperature and humidity (Dorothy Carroll, written communication).
- c/ Same as b/ but kept at humidity of 35 percent for 24 hours.
- d/ Same as b/ but treated with ethylene glycol at 60° C.
- e/ Allowed to dry on slide at room temperature and humidity (on different day than b)
- f/ After ethylene glycol treatment this sample was fired at 300° C for 2.5 days; it had a (001) spacing of 10.16A.

Table 8.---X-ray diffraction data on montmorillonite specimens recovered after discontinuous titration (second series).

[Cu K α radiation, 1° per min]

Sample	Na added (meq/100g)	Na taken up by clay (meq/100g)	$\frac{a}{d}$ (001) A ^{b/}	$\frac{b}{d}$ (001) A ^{b/}	$\frac{c}{d}$ (001) A ^{c/}
Neutralization of first clay acid					
1	0	0	14.98	-----	16.99
2	3.1	3.1	14.98	14.23	(a)-----
3	6.2	6.2	14.73	14.48	-----
4	9.3	9.3	14.73	14.26	16.99
5	12.3	12.3	14.73	14.03	-----
6	15.4	15.4	14.26	13.60	-----
7	18.4	18.4	14.26	13.81	-----
8	21.6	21.6	14.26	14.03	-----
9	24.6	24.6	14.03	13.81	-----
10	27.7	27.7	14.23	13.81	16.99
11	30.8	30.8	14.03	13.81	-----
12	33.9	33.9	13.81	13.60	-----
13	37.0	37.0	13.81	13.39	16.99
14	43.1	43.1	13.81	13.39	-----
Neutralization of second clay acid					
15	49.3	49.3	13.60	13.39	-----
16	55.4	52.4	13.39	13.19	16.99
17	61.6	55.4	13.39	13.00	-----
18	67.8	60.1	13.19	12.81	-----
19	73.9	64.7	-----	-----	-----
20	80.1	70.8	13.00	12.80	16.99
21	86.2	67.8	-----	-----	-----

Table 8.--Continued

Table 8.--X-ray diffraction data on montmorillonite specimens recovered after discontinuous titration (second series)

[Cu K α radiation, 1° per min]

Sample	Na added (meq/100g)	Na taken a/ up by clay (meq/100g)	\bar{d} (001) A ^{b/}	\bar{d} (001) A ^{b/}	\bar{d} (001) A ^{c/}
22	92.4	73.9	12.63	12.63	16.99
23	98.6	78.5	-----	-----	-----
24	104.7	78.5	-----	-----	-----
25	110.9	83.2	-----	-----	-----
26	117.0	92.4	12.81	12.63	-----
27	123.2	92.4	-----	-----	-----
28	129.4	89.3	12.81	12.63	-----
29	135.5	93.9	-----	-----	-----
30	141.7	101.6	12.81	12.63	-----
31	149.8	95.5	-----	-----	-----
32	154.0	93.9	-----	-----	-----
33	160.2	100.1	-----	-----	-----
34	166.3	90.9	-----	-----	16.99
35	172.5	97.0	12.81	12.63	-----
36	178.6	97.0	-----	-----	-----
37	184.8	103.2	-----	-----	16.99

Overtitration

Table 8.--Continued

- a/ Calculated from analysis for Na in the filtrate (Dorothy Carroll, analyst).
- b/ Allowed to dry on slide at room temperature and humidity. Determinations made on different days.
- c/ Same as b/ but treated with ethylene glycol at 60° C.
- d/ After ethylene glycol treatment this sample was fired at 300° C for 2.5 days; it has a (001) spacing of 10.40 A.

Determination of exchangeable aluminum in hydrogen clay

For the purpose of determining the probable maximum spontaneous alteration of the hydrogen clay to hydrogen-aluminum clay, a sample was stored in a closed vessel under air for 2 years, extracted by the method of Low (1955) and the aluminum in the extract was determined by the method of Shapiro and Brannock (in press). The exchangeable aluminum in the hydrogen montmorillonite was 47 meq/100 g (Leonard Shapiro, analyst).

DISCUSSION

Total acidity of the clay

The total acidity of the hydrogen clay can be evaluated from the last "break" in the titration curve. This gives, from pH measurements, 90 meq/100 g (Pommer and Carroll, 1960). The pH curve was constructed by taking the average of four pH readings taken over a period of 10 days, "outlying" values being eliminated by a statistical procedure; another pH curve, corrected for CO₂ absorption as explained previously, yielded a total acidity of 84 meq/100 g (fig. 3, line C). From a plot of analytical sodium values in the filtrates (fig. 8), the total acidity is 93 meq/100 g; a plot of sodium electrode readings gives a very questionable endpoint at about 100 meq/100 g (fig 8). If the total cation-exchange capacity is calculated at 120 meq/100 g by summing the exchangeable cations (table 1) and the exchangeable cations actually found on the hydrogen clay are subtracted from this value (34.5 meq/100 g, Pommer and Carroll, 1960), the difference of 86 meq/100 g gives the total acidity. Disregarding the very questionable "break" in the sodium electrode curve of figure 8, a series of four determinations done by four different approaches gives a total acidity of 88 ± 7 meq/100 g clay.

The "first" acid

Although the quality of the data varies significantly, it is not difficult to determine a reasonable value. Here the pH curves are not good, owing to the CO₂ absorption effect. The value obtained by simply averaging a series of pH measurements obtained over a period of time, 50 meq/100 g (Pommer and Carroll, 1960), is considerably higher than the 35 meq/100 g obtained from figure 3, using the graphical correction for CO₂ absorption. The limitations of the data obtained here have been discussed. The best values are probably obtained from the sodium values (figure 8). These are 44 meq/100 g for the analytical sodium values and 45 meq/100 g obtained from the X-ray diffraction spacings of the first series, both at room humidity and at a humidity of 35 percent. However, these values could not be reproduced satisfactorily in the second series.

The "second" acid

The difference between the average total acidity and the best values of the "first" acid is 44 meq/100 g; individual segments of this portion of the curve range from 40 to 49 meq/100 g in the pH and analytical sodium curves. If, in accordance with the theory of Low (1955) and the considerations proposed in the section of implications of montmorillonite structure the exchangeable aluminum (47 meq/100 g) is assigned to the second acid, a very consistent pattern is obtained which indicates that the experimental evidence produced in this work supports the postulates presented here. The results also are consistent with those reported in the literature. Typical values for the two acids are given by Bradfield (1931) as 45 and 50 meq/100 g; by Thompson as 41 and 43 meq/100 g; and by Hauser and Colombo (1954) as 42 and 43 meq/100 g.

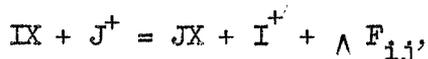
Thompson, A. C., 1956, Acidic properties of bentonite: State College of Washington, Pullman, Ph.D. Thesis, 101 p.

Montmorillonite and the problem of ionic specificity

Eisenman (1961) has shown that the anionic field strength of the protoplasmic and membrane components of living cells governs the sequence and magnitude of specificity among the alkali metal cations and hydrogen ion. He has explained that in biological material this field strength is controlled by the energy interactions between the nearest neighbor to the cations, usually oxygen, as modulated by the next adjacent atom, usually carbon or phosphorus. In clays a generally similar mechanism must be involved, but here the relations between the oxygen atoms must be controlled by silicon and aluminum.

In montmorillonite, however, a rather unique situation is found. The anionic field strength with respect to exchangeable cations is a function of the charge deficiency. As montmorillonite has two types of exchange sites which can be distinguished by different charge densities, anionic field strength in the interlayer and edge sites is different, and for this reason the selectivity for alkali ions in these two types of sites may be expected to be different. It will be recalled from figure 1 and preceding discussion that the anionic field strength in the interlayer positions is significantly lower than that of the edge positions.

The selectivity rule of Eisenman (1961) is based on the assumption that with increasing negative electrostatic field strength the least strongly hydrated cation is the first to be desolvated. In brief, it can be presented as follows. For a typical cation exchange reaction,



where IX and JX represent a solid ion exchanger in an unspecified state of hydration which does not change during the reaction, and I^+ and J^+ are dilute

aqueous ions, the Gibbs free energy change, ΔF_{ij} is a function of K_{ij} , the equilibrium constant of the reaction, and hence related to the ease of dehydration and absorption of an ion in solution by the exchanger. The anionic field strength in turn is a function of the anionic radius r_- , which also, in an oxyanion, is a function of the acid dissociation constant pK_a . Figure 9 summarizes Eisenman's calculations. The selectivity orders are indicated by vertical regions which are marked by Roman numerals. In this figure, the cation most strongly selected from water by the anionic "site" is the lowest on the chart.

Puri and Ashgar (1938) have pointed out that, if soil acidoids are treated with different bases, the characteristic shape of the titration curve is maintained with every base, although different amounts of alkali are required to produce a particular pH value with various ions. These authors also pointed out that this was in agreement with observations made on weak acids such as phosphoric acid, that the actual course of the titration curve depends on the nature of alkali used, although the end point must be reached with the same amount of alkali, but at a different pH, in every case.

If Eisenman's theory is applied to a montmorillonite with approximately the structure shown in figure 1, it can be predicted that the characteristic shape of the titration curve will not be maintained if this material is titrated with different alkalis.

Montmorillonite and beidellite

Beidellite has been defined as a member of the montmorillonite group in which there is substantially no magnesium present and in which trivalent aluminum replaces quadrivalent silicon in the tetrahedral unit (Ross and Hendricks, 1945). This results in a clay where the entire charge deficiency resides in the tetrahedral unit.

This clay and the type of montmorillonite represented in figure 1 form the end members of a solid solution series, which subsumes montmorillonites and beidellites; these derive their designation from whatever end member they more closely represent. It can be seen (table 1), however, that the montmorillonite used here approximates the theoretical charge relations of figure 1 satisfactorily.

Figure 10 represents a simplified beidellite structure, representing, however, an actual situation. There are charge deficiencies in both units and no statement is made on the illustration concerning their relative amounts. This is necessary to avoid classification difficulties in the middle of the series. For instance, taking the montmorillonite-beidellite series of Ross and Hendricks (1945), sample 44 is a clay from Beidell, Colo., a beidellite, with a charge deficiency of 0.36 in the tetrahedral unit and 0.08 in the octahedral unit, whereas sample 45, a clay from Embudo, N. Mexico, has a charge deficiency of 0.43 in the tetrahedral unit and 0.72 in the octahedral unit.

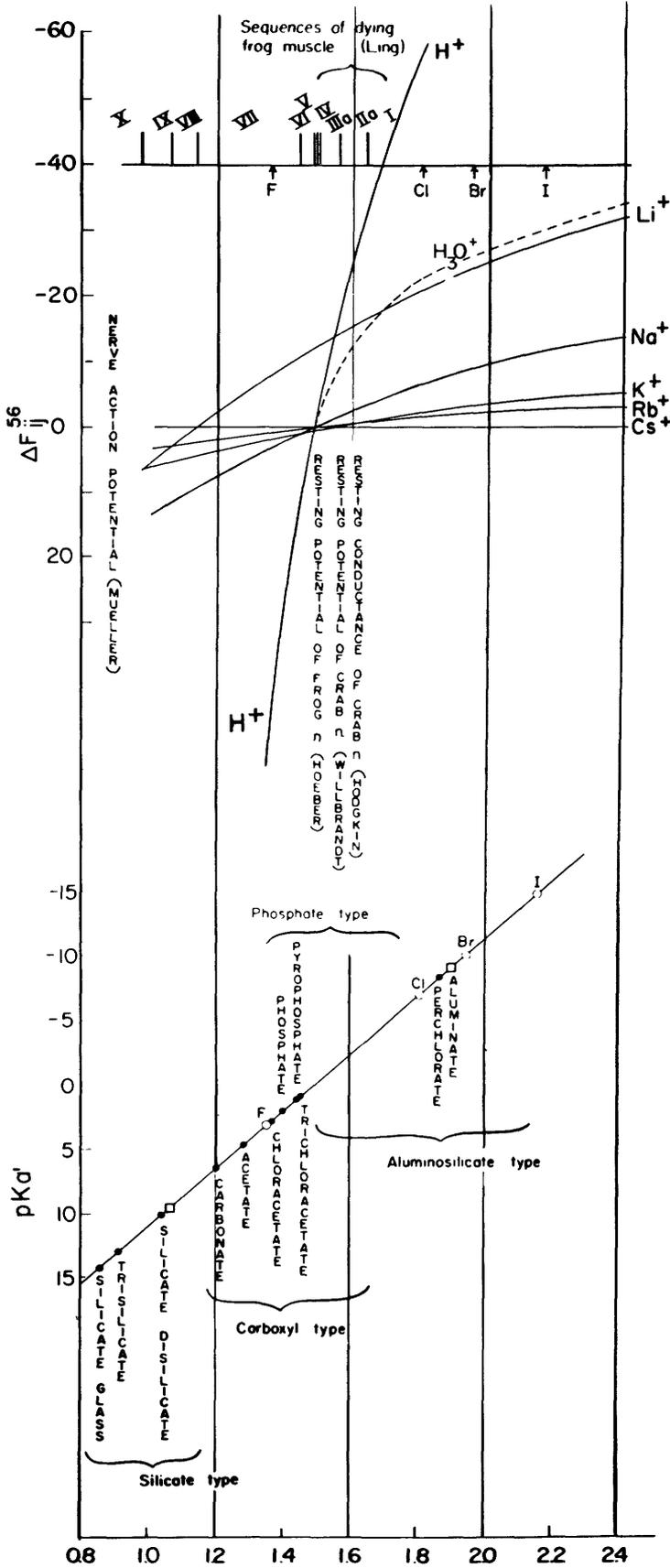


FIGURE 9.—THE RELATIONSHIP BETWEEN THE ACID DISSOCIATION CONTACT pK_a , THE ANIONIC RADIUS r , FOR OXY—ANIONS WHETHER IN FREE SOLUTIONS OR POLYMERIZED, INCLUDING THE LOCATION OF BIOLOGICAL PHENOMENA BY THEIR SPECIFIC SEQUENCE (EISENMAN 1961).

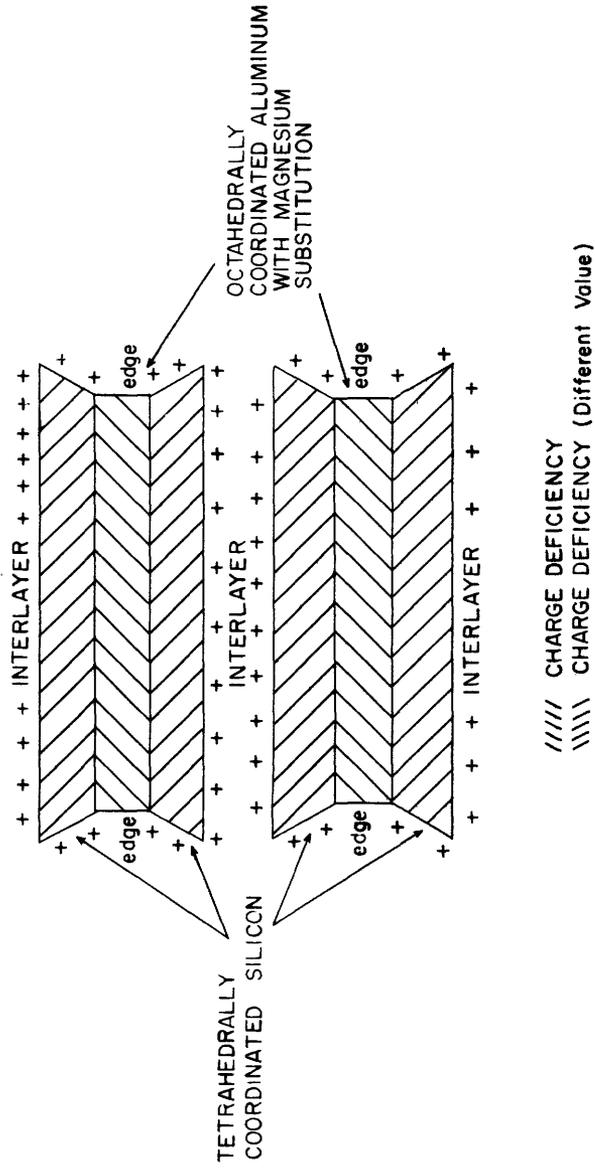


FIGURE 10.—SIMPLIFIED BEIDELLITE STRUCTURE.

This clay is clearly more aluminum than the Beidell clay and should be classified as beidellite; still, the charge deficiency relations between the two types of layers are reversed. Foster (1954) states that the charge of beidellite is predominantly in the tetrahedral layer. Some modern authors object to the term beidellite (Grim, 1953, p. 40); however, as a true beidellite has been described (Weir and Greene-Kelly, 1962) it is not desirable to replace this term by another expression in this discussion.

The actual charge deficiencies of the beidellite of the Putnam soil are -0.64 charge per unit on the tetrahedral layer and -0.20 charge per unit on the octahedral layer. The charge relations support the argument that the more strongly bonded hydrogen ions occupy the interlayer positions, as the charge density on the layer bounding the clay is stronger; hence, in disagreement with the interpretation of Garrels and Christ (1956), the interlayer acid is the weaker of the two substrates and the edge acid is stronger.

In this connection it becomes apparent that the charge deficiencies of the two beidellite units do not differ as much from each other as those of a relatively ideal montmorillonite. For this reason, if hydrogen beidellites of the Putnam type are titrated with different alkalis, it may be expected that their titration curves will show a similar relation to each other as the soil acidoids of Puri and Ashgar (1938). Putnam beidellite and a Wyoming montmorillonite have been titrated under similar conditions with KOH (Marshall and Bergman, 1942) and NaOH (Marshall and Krinbill, 1942), and the titration curves, plotted on a semilogarithmic basis, are presented in figure 11 for bentonite (montmorillonite) and in figure 12 for Putnam beidellite. As predicted, the curves for Na^+ and K^+ titrations do not resemble each other in the case of the bentonite, but are similar for the Putnam beidellite titration.

Blackmon (1958) calculated constants for the conversion of cation from the C exchange site to the E exchange site for beidellite and bentonite from the data of Marshall and Bergman (1942) and Marshall and Krinbill (1942), and reported, for beidellite, the logarithm of the exchange constant for conversion from the C to the E position to be -1.1 for potassium and -1.5 for sodium, and, for bentonite, these values as -0.5 for potassium and -1.4 for sodium. As he neglected to take into account the charge relations of beidellite, the logarithms of the constants must be multiplied by (-1) to yield a compatible picture. If this is done, however, it can be seen that the relative strength with which sodium and potassium are bound to these respective sites is similar in beidellite, but quite different in bentonite. All this is consistent with the general postulate that in beidellite the selectivity of both types of exchange positions for sodium and potassium does not differ very much, but that this is not true for bentonites.

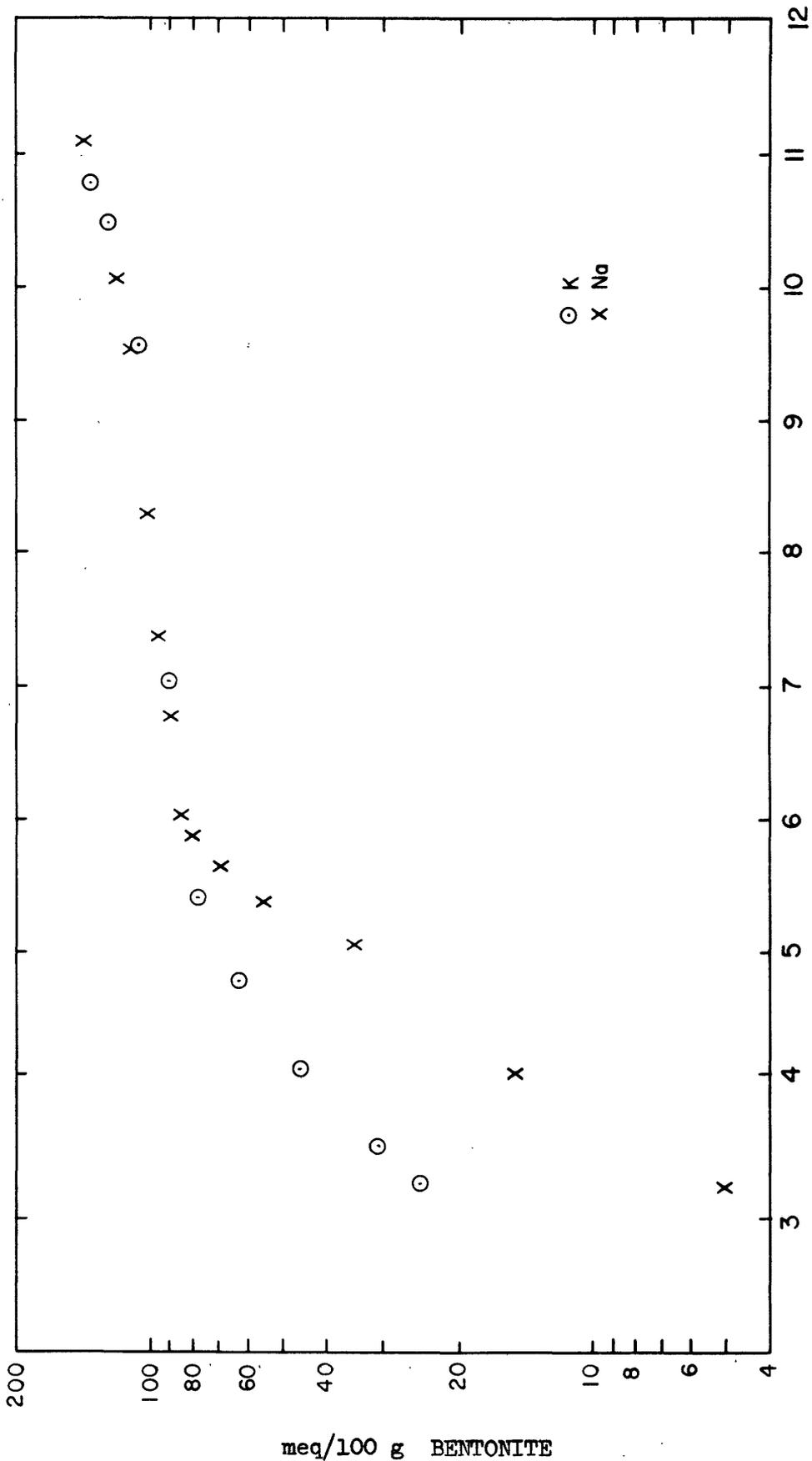


FIGURE 11.—SEMILOGARITHMIC PLOT OF TITRATION OF BENTONITE WITH NaOH (DATA BY MARSHALL AND KRINBILL, 1942) AND KOH (DATA BY MARSHALL AND BERGMAN, 1942).

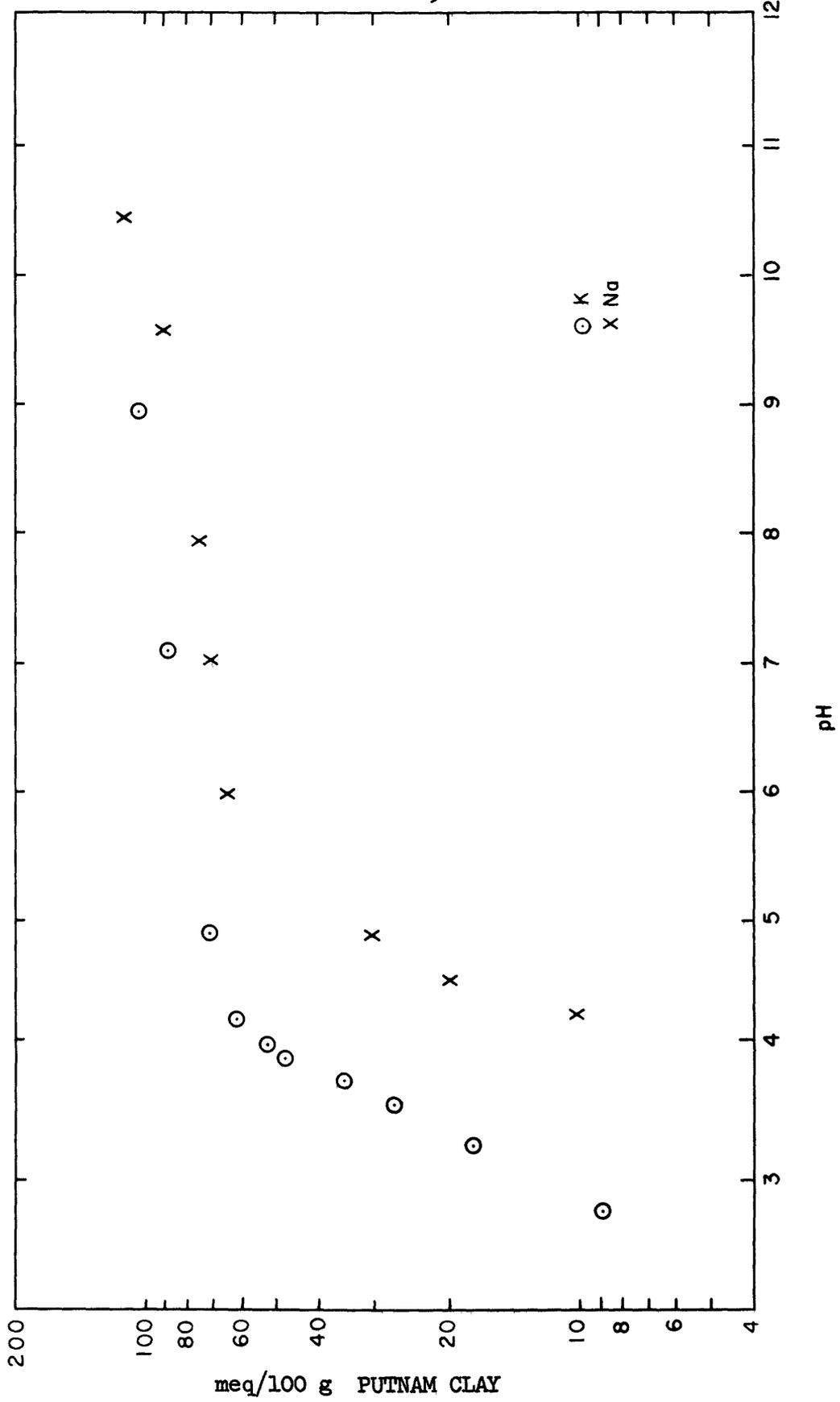


FIGURE 12.—SEMILOGARITHMIC PLOT OF TITRATION OF PUTNAM BEIDELLITE WITH NaOH (DATA BY MARSHALL AND KRINBILL, 1942) AND KOH (DATA BY MARSHALL AND BERGMAN, 1942).

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Relation of alkali ion selectivity of clay to radioactive waste disposal

Among the alkali ions considered in the selectivity rule of Eisenman (1961) is cesium. The radioisotope of this element Cs^{137} is a product of nuclear fission which, on account of its long half life, is especially troublesome in the environmental contamination by radioactive fallout (Schulz, Overstreet, and Barshad, 1960) and in radioactive waste (Glueckauf, 1961). A brief review of nuclear technology including references to the literature on radioactive waste has recently been presented by Tomlinson (1961); among others, Theis (1956) and Barker (1958) have discussed the problem of radioactive waste.

A site of low anionic field strength is most likely to select cesium over other alkali metals. In other words, those clays or clay sites which form strong clay acids are the best cesium-binders. Among clays examined by Tamura and Jacobs (1960) "illite" was the most effective for cesium sorption, and, as shown by Carroll and Pommer (1960), hydrogen "illite" after aging forms a very strong acid. Eisenman (1961) has determined the anionic field strength of some materials including clay minerals. Among the materials listed, in decreasing order of cesium selectivity, are kaolin, Utah bentonite, Putnam clay, and montmorillonite. Eisenman's prediction, made from the anionic field strength, that feldspar should prefer rubidium over sodium, is in accordance with the experimental findings of Hechter and others (1959). Eisenman's findings also lead to the prediction that the two clay acids of the montmorillonite used here will differ in their cesium-binding property. Tamura and Jacobs (1961) find that heating of bentonites improves their selectivity for cesium, though the exchange capacity of this material, which consists almost entirely of montmorillonite, drops considerably. As it is likely that heating causes some of the exchangeable cations to migrate into the interior of the lattice, and to neutralize a portion of the charge deficiency, the loss in exchange capacity is easily understood. As the lessening of the charge deficiency decreases the anionic field strength, an increase in cesium selectivity is also expected and found.

It appears that clays of high-exchange capacity and low-charge density would be ideal for cesium sorption. Although in natural material those two requirements are somewhat but not altogether incompatible, synthetic ceramics could be made which contain only porous material of low-charge density and a large surface.

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