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## **CATION-EXCHANGE PROPERTIES OF SOME ACID SOILS OF CALIFORNIA**

**P. F. PRATT and F. L. BAIR**

**UNIVERSITY OF CALIFORNIA • BERKELEY, CALIFORNIA**

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## **CATION-EXCHANGE PROPERTIES OF SOME ACID SOILS OF CALIFORNIA<sup>1</sup>**

**P. F. PRATT<sup>2</sup> and F. L. BAIR<sup>3</sup>**

MOST SOIL acidification experiments are conducted in laboratory or greenhouse over short periods of time, and there is always some uncertainty concerning the application of the data to the field where soils are acidified over a much longer period. Thus, the data presented in this report, part of a study of acid soil samples from the field, provide a background against which to compare the results of short-term experiments.

This report is not intended to be a complete survey of acid soils of California because too few samples have been included. But there are a sufficient number to provide a wide range in such properties as clay and organic C content, cation-exchange capacity (CEC), clay mineral content and pH. The samples also represent a variety of acid soils found in central and southern California. Cole (1949)<sup>4</sup> reported the acidity and alkalinity of soils of California that had been previously surveyed.

### **SOIL SAMPLES**

Data on county location, pH, clay and organic C contents of 31 samples are presented in table 1. The clay content was measured by a pipette method and the organic C by a modified Walkley-Black method (Pratt *et al.* 1957). With the exception of samples 27, 29 and 31, all were taken from the surface soil of cultivated fields or from the A<sub>1</sub> horizon of undisturbed soils. Samples 27, 29 and 31 were taken from the horizon immediately below the plow layer of the same soils as samples 26, 28 and 30, respectively. All samples were air-dried and then ground to pass a 2 mm screen. Subsamples ground to pass a 60-mesh screen were used where small portions were taken for analysis. Sixteen of the samples were taken from central California and fifteen came from Kern and San Diego counties.

Data on the relative abundance of various minerals in the clay fractions of a number of soils are presented in table 2. The clay in twelve of these samples was dominantly illite and montmorillonite, and in seven samples there were mixtures, with montmorillonite constituting only a small portion.

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<sup>1</sup> Submitted for publication March, 1962.

<sup>2</sup> Associate Professor of Soil Sciences and Associate Chemist in the Experiment Station, Riverside.

<sup>3</sup> Laboratory Technician, Department of Soils and Plant Nutrition, Riverside.

<sup>4</sup> See "Literature Cited" for citations referred to in the text by author and date.

Data on percentage of water at saturation, and soluble cations in the saturation extract are presented in table 3. Fifteen of the samples contained more than 40 meq total cations per liter and of these fifteen, eight contained more than 80 meq per liter. Thus, about half of the samples can be classified as of medium to high salinity. All of these were from irrigated fields, with the ex-

TABLE 1  
COUNTY LOCATION, pH, CLAY AND ORGANIC C CONTENTS  
OF SOIL SAMPLES

Soil No.	Location	pH*	Clay	Organic C
	<i>County</i>		<i>Per cent</i>	<i>Per cent</i>
1.	San Diego.....	5.8	8.9	0.5
2.	San Diego.....	6.0	5.6	0.4
3.	San Diego.....	4.0	10.9	0.7
4.	San Diego.....	6.0	5.3	1.4
5.	San Diego.....	5.0	4.6	0.4
6.	San Diego.....	6.3	32.3	1.4
7.	San Diego.....	5.2	4.8	0.5
8.	San Mateo.....	4.4	8.9	0.8
9.	Napa.....	3.6	43.2	3.4
10.	Napa.....	4.1	49.3	3.7
11.	Lake.....	5.7	41.8	3.4
12.	Lake.....	5.6	28.3	3.2
13.	Sonoma.....	5.7	53.0	2.2
14.	Marin.....	5.8	51.2	1.8
15.	Marin.....	5.4	18.3	2.6
16.	San Mateo.....	4.5	12.1	1.6
17.	San Mateo.....	5.4	15.6	1.9
18.	San Mateo.....	5.4	17.0	2.1
19.	San Mateo.....	4.7	18.9	2.0
20.	San Diego.....	7.0	11.3	0.8
21.	Kern.....	5.2	7.8	0.3
22.	Kern.....	6.4	9.5	0.2
23.	Kern.....	4.9	10.6	0.4
24.	Kern.....	5.3	10.2	0.2
25.	Kern.....	5.1	62.0	3.5
26.	Kern.....	4.7	64.5	3.7
27.	Kern.....	4.0	56.7	2.8
28.	San Joaquin.....	5.8	47.3	14.8
29.	San Joaquin.....	5.6	45.1	15.1
30.	San Joaquin.....	5.2	25.4	9.5
31.	San Joaquin.....	5.2	21.4	0.4

\* At 1-1 dilution with water.

ception of numbers 9 and 10 taken from areas in Napa County which were influenced by salt water intrusion from San Pablo Bay. All other samples, collected from nonirrigated areas, were of low salinity. The data illustrate the fact that, although most acid soils are nonsaline, those that are irrigated can become highly saline.

Values of 0.5 ppm Al and 10 ppm Mn were used as diagnostic criterion for Al and Mn toxicity for sensitive plants; six soils were found to have toxic Al concentrations and thirteen soils toxic Mn concentrations. Compared with acid soils of the humid regions of eastern USA, having pH values of between 4 and 5, the soluble Al values presented in table 2 are relatively low. For example, Pierre *et al.* (1932) found 1.0 to 27.2 ppm Al in the soil solution of soils having pH values near 4.5, Magistad (1925) found 16 to

96 ppm Al in soil solutions for soils having pH values of 4.0 to 4.5, and Schmehl *et al.* (1950) found that a Mardin silt loam with pH 4.75 had 1.9 ppm Al in the displaced solution of the untreated soil and 10 ppm Al when gypsum was added.

TABLE 2  
RELATIVE ABUNDANCE OF CLAY MINERALS FOUND IN THE  
CLAY FRACTIONS OF A NUMBER OF ACID SOILS

Sample No.	Effective size fraction	Per cent of total clay	Mineral composition							
			Mi	Vm	Mt	Chl	Kl	Qt	Fl	Am
	<i>Microns</i>									
3.....	2.0-0.2	48	XX	..	XX	..	XX	XX	X	..
	<0.2	52	X	..	XXX	..	X	X	..	..
5.....	2.0-0.2	57	XX	..	XX	..	XX	XX	X	..
	<0.2	43	X	..	XXX	..	X	X	..	..
6.....	2.0-0.2	29	XXX	..	X	..	X	XXX	X	..
	<0.2	71	XX	..	XXX	..	X	X	..	..
8.....	2.0-0.2	79	X*	..	..	X*	X	XXX	X	..
	<0.2	21	..	..	..	..	..	..	..	XXX
9.....	2.0-0.2	51	X	..	XXX	X	XX	XX	X	..
	<0.2	49	X	..	XXX	..	X	X	..	..
10.....	2.0-0.2	53	X	..	XXX*	X*	X	XX	X	..
	<0.2	47	..	..	XXXX	..	..	X	..	..
11.....	2.0-0.2	57	..	..	..	..	X	..	..	XXXX
	<0.2	43	..	..	..	..	X	..	..	XXXX
12.....	2.0-0.2	67	..	..	..	X	X	X	..	XXX
	<0.2	33	..	..	..	..	X	..	..	XXX
14.....	2.0-0.2	46	X	..	XXX*	X*	XX	X	X	..
	<0.2	54	X	..	XXX	..	X	X	..	..
15.....	2.0-0.2	46	X	XX	..	X	X	XX	X	..
	<0.2	54	..	XX	X	..	..	..	..	..
16.....	2.0-0.2	57	X	X	..	..	X	XX	X	X
	<0.2	43	..	..	..	..	XX	..	..	X
17.....	2.0-0.2	43	X	X	..	..	..	..	..	..
	<0.2	57	..	..	X	..	..	..	..	..
18.....	2.0-0.2	37	XX	..	..	..	X	XXX	X	..
	<0.2	63	..	..	..	..	XX	..	..	X
22.....	2.0-0.2	57	XXX	..	XXX	..	X	X	X	..
	<0.2	43	X	..	XXX	..	X	X	..	..
23.....	2.0-0.2	64	XXX	..	XX	..	X	X	..	..
	<0.2	36	X	..	XXX	..	..	X	..	..
25.....	2.0-0.2	47	X	..	XXXX	..	X	X	X	..
	<0.2	53	X	..	XXXX	..	X	X	..	..
28.....	2.0-0.2	61	X	..	XXX	..	XX	X	X	..
	<0.2	39	..	..	XX	..	X	..	..	X
29.....	2.0-0.2	62	..	..	XXX	..	X	X	..	..
	<0.2	38	X	..	XX	..	X	..	..	..
30.....	2.0-0.2	59	X	..	XXXX	..	XX	X	X	..
	<0.2	41	..	..	XXX	..	..	..	..	..

\* Interstratified

Legend:

Mi = mica (illite)  
Vm = vermiculite  
Mt = montmorillonite  
Chl = chlorite  
Kl = kaolinite  
Qt = quartz  
Fl = feldspar  
Am = amorphous

X = detectable  
XX = moderate  
XXX = abundant  
XXXX = predominant



## EXCHANGEABLE CATIONS

Data on exchangeable cations, including exchange acidity extracted by unbuffered *N* KCl and by buffered (pH 8.2) BaCl<sub>2</sub>-triethanolamine (TEA) following the KCl extraction, as well as CEC are presented in table 4. The exchangeable Ca, Mg, Na and K represent the amounts extracted by neutral

TABLE 3  
WATER CONTENT AT SATURATION AND CATIONIC CONCENTRATIONS  
OF SATURATION EXTRACT OF SOILS

Soil No.	Water content	Ca	Mg	Na	K	Al		Mn		Total cations
	Per cent	meq/l				meq/l	ppm	meq/l	ppm	meq/l
1	24	12.8	9.7	14.7	0.4	ND*	ND	0.38	10.8	38.0
2	22	9.6	4.4	3.9	2.6	ND	ND	0.19	5.2	20.7
3	28	55.0	31.4	31.1	12.8	0.56	5.0	5.7	158.0	136.6
4	21	3.3	1.8	3.2	1.9	ND	ND	0.14	3.8	10.3
5	22	34.7	27.8	34.2	3.4	0.02	0.2	1.7	46.4	101.8
6	47	0.9	0.8	6.3	0.3	ND	ND	ND	ND	8.3
7	26	27.3	8.6	7.8	5.6	0.01	0.1	2.0	55.2	51.3
8	25	6.0	2.8	2.2	1.9	0.08	0.7	0.63	17.2	13.6
9	72	16.9	46.4	51.2	2.0	12.0	108.0	1.2	33.8	129.7
10	70	10.0	29.4	88.8	1.2	0.36	3.2	0.60	16.6	130.4
11	81	1.6	1.5	1.5	0.1	ND	ND	ND	ND	4.7
12	44	1.8	0.6	0.6	0.7	ND	ND	0.09	2.6	3.8
13	61	0.4	1.0	2.1	0.4	ND	ND	ND	ND	3.9
14	58	0.5	1.0	1.0	0.3	ND	ND	ND	ND	2.8
15	34	1.8	1.6	1.9	0.1	0.01	0.1	ND	ND	5.4
16	29	37.7	24.7	12.1	7.9	0.1	0.9	0.87	24.0	83.4
17	37	0.5	0.5	1.7	0.1	0.02	0.2	ND	ND	2.8
18	35	0.7	0.8	1.3	0.2	0.01	0.1	ND	ND	3.0
19	39	13.3	14.1	8.6	1.0	0.01	0.1	0.54	14.8	37.5
20	28	9.7	5.7	8.2	2.9	ND	ND	ND	ND	26.5
21	23	37.2	12.8	7.3	1.7	0.01	0.1	0.54	14.8	59.5
22	21	32.2	12.4	5.8	0.8	ND	ND	0.29	7.9	51.5
23	22	53.7	18.6	9.6	1.8	0.02	0.2	2.0	56.0	85.7
24	20	31.1	5.5	2.5	0.8	0.01	0.1	0.7	20.4	40.6
25	85	23.3	5.2	12.9	0.8	0.01	0.1	0.16	4.4	42.4
26	83	30.0	6.9	9.2	1.2	0.01	0.1	0.21	5.7	47.5
27	81	27.8	15.4	8.5	0.6	0.19	1.7	0.22	6.0	52.7
28	114	41.2	13.9	16.7	0.7	ND	ND	0.11	3.1	72.6
29	120	9.0	2.8	7.0	0.3	ND	ND	ND	ND	19.1
30	69	89.8	76.0	127.2	0.8	0.02	0.2	0.58	16.0	294.4
31	46	43.2	36.0	76.5	0.4	0.01	0.1	0.18	5.2	156.3

\* Not determined.

*N* NH<sub>4</sub>OAc minus the quantities in the saturation extract. The CEC was determined as the amount of Ba adsorbed from a buffered-BaCl solution at pH 8.0.

The acidity displaced by *N* KCl solution was used as an estimate of the acidity exchangeable at the pH of the soil, and that extracted by BaCl<sub>2</sub> buffered at pH 8.2 as a measure of the pH-dependent acidity. The exchange acidity was only a few tenths meq per 100 g in most soils whereas the pH-dependent acidity ranged from 2.4 to 37 meq per 100 g. Soils 3, 9, 10 and 27, the only ones with any appreciable exchange acidity, contained 1.0, 9.8, 3.2

and 2.0 meq per 100 g, respectively. The Al determined in the KCl extracts of these soils was 0.8, 7.8, 2.5 and 1.4 meq per 100 g, respectively. These data suggest that if any appreciable exchange acidity develops in a soil, most of it can be accounted for by measuring the exchangeable Al. Data collected on two soils acidified in a greenhouse experiment show the same trend; at pH

TABLE 4  
EXCHANGEABLE CATIONS, INCLUDING EXCHANGE ACIDITY EXTRACTED  
BY *N* KCl AND BY BaCl<sub>2</sub>TEA, TOTAL CATIONS AT pH OF THE SOIL  
AND AT pH 8.2, CEC AT pH 8, AND pH OF THE SOIL

Soil No.	Ca	Mg	Na	K	Exchange acidity*	Total cations at pH of soil	pH dependent acidity (pH 8.2)†	Total cations to pH 8.2	CEC at pH 8.0	pH‡
	meq/100 g									
1	2.9	1.3	0.3	0.2	0.1	4.8	2.4	7.2	7.8	5.8
2	2.0	0.7	0.2	0.3	0.2	3.4	1.9	5.3	8.4	6.0
3	3.9	0.9	0.3	1.3	1.0	7.4	6.4	13.8	12.8	4.0
4	2.8	1.0	0.2	0.5	0.1	4.6	2.6	7.2	10.7	6.0
5	1.6	1.1	0.2	0.3	0.2	3.4	2.3	5.7	6.8	5.0
6	7.5	6.5	1.6	0.8	0.2	16.6	4.8	21.4	21.4	6.3
7	2.4	0.7	0.2	0.8	0.2	4.3	3.6	7.9	7.2	5.2
8	0.8	0.3	0.1	0.4	0.8	2.4	5.7	8.1	7.1	4.4
9	3.1	5.8	1.4	0.9	9.8	21.0	23.9	44.9	46.2	3.6
10	4.1	8.0	3.5	1.1	3.2	19.9	21.8	41.7	43.0	4.1
11	12.4	5.8	0.8	0.5	0.2	19.7	17.6	37.3	39.0	5.7
12	9.6	1.3	0.3	1.7	0.2	13.1	19.1	32.2	32.2	5.6
13	5.8	15.0	1.1	1.5	0.2	23.6	11.0	34.6	36.4	5.7
14	8.7	14.0	0.9	1.3	0.2	25.1	10.4	35.5	37.1	5.8
15	7.7	4.0	0.4	0.2	0.2	12.5	13.1	25.6	24.8	5.4
16	2.4	0.7	0.4	0.7	0.5	4.7	7.5	12.2	15.2	4.5
17	2.1	2.0	0.3	0.1	0.6	5.1	8.6	13.7	13.9	5.4
18	4.5	2.6	0.3	0.2	0.3	7.9	9.9	17.8	17.2	5.4
19	5.2	2.6	0.2	0.4	0.3	8.7	8.8	17.5	18.4	4.7
20	7.7	2.8	0.4	0.9	0.1	11.9	1.4	13.3	11.2	7.0
21	4.8	1.4	0.2	0.4	0.2	7.0	2.8	9.8	9.1	5.2
22	5.6	1.5	0.2	0.2	0.1	7.6	1.2	8.8	7.8	6.4
23	8.5	1.0	0.1	0.3	0.3	10.2	3.0	13.2	8.9	4.9
24	9.4	0.5	0.4	0.3	0.2	10.8	3.4	14.2	8.8	5.3
25	23.7	2.1	2.4	1.4	0.3	29.9	16.1	46.0	48.0	5.1
26	28.4	1.8	0.7	1.5	0.4	32.8	17.3	50.1	48.0	4.7
27	69.1	0.7	0.9	0.7	2.0	73.4	19.8	93.2	34.8	4.0
28	48.8	3.5	2.1	1.0	0.2	55.6	33.0	88.6	87.0	5.8
29	45.1	3.4	1.1	0.8	0.2	50.6	37.0	87.6	86.0	5.6
30	24.8	1.1	4.2	0.5	0.2	30.8	26.3	57.1	57.1	5.2
31	12.0	1.1	2.6	0.1	0.4	16.2	6.6	22.8	24.4	5.2

\* Extracted by *N* KCl solution.

† Extracted by BaCl<sub>2</sub>-TEA solution at pH 8.2 following the KCl extraction.

‡ At 1-1 dilution with water.

values of 3.4 and 3.5 the exchange acidities were 5.2 and 5.1 meq per 100 g and the exchangeable Al values were 4.6 and 4.4 meq per 100 g, respectively.

The sum of the exchangeable cations, including the pH-dependent acidity, greatly exceeded the CEC at pH 8.0 for soil No. 27. A qualitative test showed that gypsum was present in this soil. There was also rather poor agreement between the sum of the cations and CEC for several soils with CEC values of about 10 or less meq per 100 g, but for all other soils these two values were in excellent agreement.

The relations between pH and base saturation (saturation with the cations Na, K, Ca and Mg) as per cent of the total exchangeable cations at the pH of the soil, and as per cent of total cations to pH 8.2 are presented in figure 1. If the sum of the cations at the pH of the soil is used as a reference point, all the soils were, for all practical purposes, base-saturated at pH values of 5 and above. But, if the sum of the total cations to pH 8.2 is used, all soils were

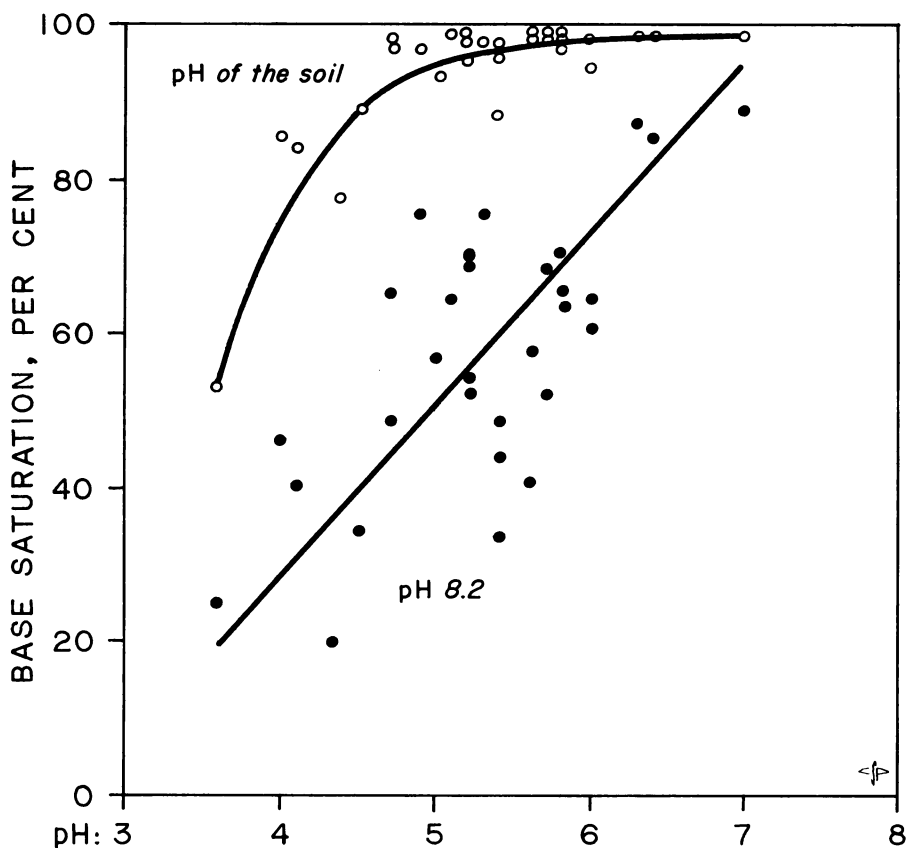


Fig. 1. Relations between pH and base saturation as per cent of the CEC at the pH of the soil and base saturation as per cent of the CEC at pH 8.2.

unsaturated. There is a closer relationship between base saturation and pH when the sum of exchangeable cations at the pH of the soils is considered than when the sum of the cations at pH 8.2 is taken as a reference point.

The linear correlation between exchangeable Na ratio (exchangeable Na/CEC-exchangeable Na) and the SAR ( $\text{Na}/\sqrt{\text{Ca} + \text{Mg}}$  with the concentrations expressed in mmole/l) of the saturation extract was 0.89, with a regression equation of  $Y = 0.023 + 0.0098 X$ . Corresponding values given in Agriculture Handbook No. 60 (1954) of the U. S. Salinity Laboratory are  $r = 0.923$  and  $Y = -0.0123 + 0.01475X$ . While the regression equations differ to some extent, the data given here and that presented by the Salinity

Laboratory are similar over the relatively narrow range of SAR values (0.6 to 20) in this report. The CEC values used in calculating the exchangeable Na ratio were assumed to be the sum of the total exchangeable cations at the pH of the soil as listed in column 7 of table 4.

The exchange constant for the reaction  $\text{Mg-soil} + \text{Ca}^{++} \rightleftharpoons \text{Ca-soil} + \text{Mg}^{++}$  was calculated from data on the saturation extract and the exchangeable

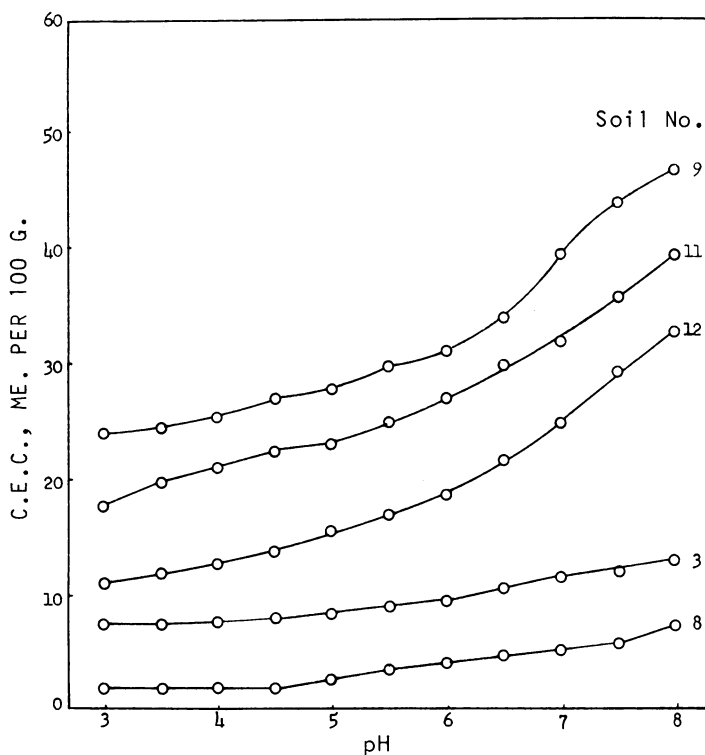


Fig. 2. Relations between cation-exchange capacity and pH for five soils.

cations. The constant averaged 1.76 with a range of values from 1.18 to 2.52. The data indicate that considerable error might be involved in calculating exchangeable Mg and Ca by using an average exchange constant and the saturation extract data, as was done by Pratt and Harding (1957) and Mc-Colloch *et al.* (1957); however, the relative values calculated for various samples of the same soil might be reliable.

### CATION-EXCHANGE CAPACITY

Recent investigations (Schofield 1950 and Coleman *et al.* 1959) have shown that soils and clays have a pH-dependent component of the CEC. In order to measure this pH-dependent component, and also to verify that the sum of the cations at the pH of the soil represents the capacity to adsorb cations at that pH, a method was developed for measuring the CEC over a pH range from 3 to 8.



**Method.** A 2.5-g sample of soil was washed with 25-ml portions of a buffer solution until the pH was constant. The buffer solution contained 18.5 g  $\text{Ba}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ , 80 g  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , 2.18 g p-nitrophenol, and 7.5 ml of triethanolamine per liter and was adjusted to pH values of 3 to 8 with HCl. The sample was then washed with four 25-ml portions of 0.5*N*  $\text{BaCl}_2$  solution containing 2 ml of the appropriate buffer per 100 ml of  $\text{BaCl}_2$  solution and adjusted to the pH of the buffer by adding TEA or HCl. The excess salt was

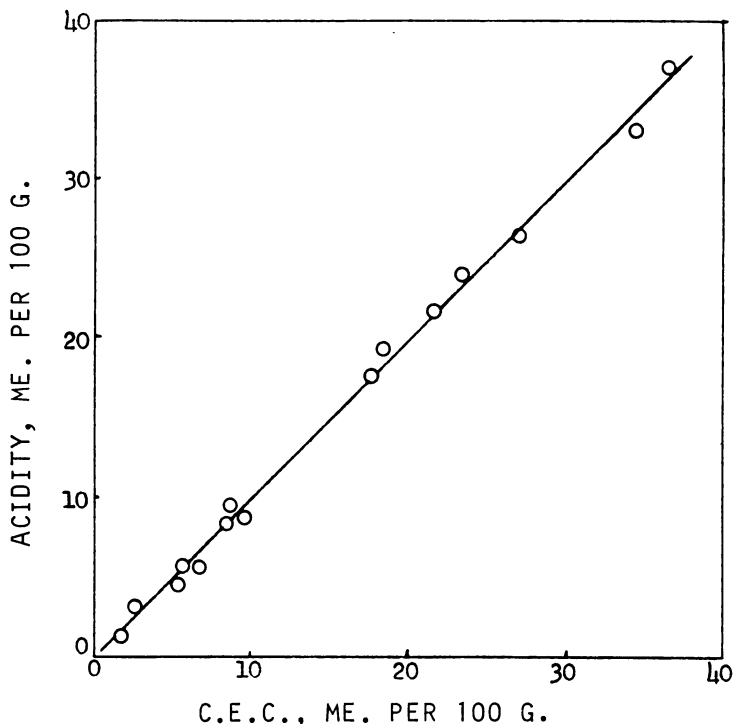


Fig. 3. Relation between pH-dependent acidity and pH-dependent cation-exchange capacity as measured by the difference in cation-exchange capacity at pH 8.2 and at the pH of a 1 to 5 suspension of soil in *N* KCl.

removed by washing with methyl alcohol and the alcohol was removed by heating the sample in a water bath. The adsorbed Ba was replaced with neutral *N*  $\text{NH}_4\text{OAc}$  solution and the Ba determined flame-photometrically. The CEC was calculated from the Ba in the  $\text{NH}_4\text{OAc}$  extract.

**Results.** The relations between the CEC and pH for five soils are shown in figure 2. Similar data, obtained on nine other soils, are not presented because the curves obtained had the same characteristics as those in figure 2. Data on some soils showed a continuous change in CEC with change in pH while data on others showed a constant value between pH 3 and 4.5 with increases as the pH increased from 4.5 to 8.0.

If the reduction in CEC obtained as the pH decreased is a result of association of  $\text{H}^+$  ions with exchange radicals such that the radicals no longer

carry a negative charge, one should be able to obtain, independently, a measure of the pH-dependent CEC by measuring the  $H^+$  ions displaced by a salt solution buffered at the higher pH value. This means that the difference in CEC between pH 8.2 and the pH of the soil suspended in *N* KCl solution should be equivalent to the pH-dependent acidity as measured by extraction with  $BaCl_2$ -triethanolamine (at pH 8.2) following extraction with KCl. Data in figure 3 show this to be the case for the 15 soils. The agreement between the two values indicates that they are estimates of the same thing, i.e., the change in CEC with change in pH.

TABLE 5  
CEC AT pH 8.0, pH-DEPENDENT CEC OF SOIL AND OF CLAY SEPARATED FROM THE SOIL, AND CONTRIBUTION OF CLAY AND ORGANIC C TO THE pH-DEPENDENT CEC OF THE SOIL

Soil No.	CEC at pH 8	pH-dependent CEC of soil	pH-dependent CEC of clay	Contribution of clay to pH-dependent CEC of soil*	Contribution of organic C to pH-dependent CEC of soil	pH-dependent CEC of organic C
	meq/100 g		meq/100 g clay	meq/100 g soil		meq/100 g
3.....	12.8	5.7	17.0	2.4	3.3	470
6.....	21.4	6.6	11.2	3.6	3.0	210
8.....	7.1	5.3	13.0	1.2	4.1	380
9.....	46.2	22.4	13.9	6.0	16.4	480
10.....	43.0	20.6	13.9	6.8	13.8	370
11.....	39.0	21.6	16.7	7.0	14.5	430
12.....	32.2	21.3	24.2	6.8	14.5	450
17.....	13.9	8.6	13.0	2.0	6.6	280
22.....	7.8	2.5	13.0	1.2	1.3	650
23.....	8.9	2.5	13.0	1.4	1.1	280
28.....	87.0	47.4	20.5	9.7	37.7	260
29.....	86.0	48.1	18.6	8.8	39.3	260
30.....	57.1	33.0	16.8	4.3	28.7	300
Average...	....	....	15.8	...	....	370

\* Assuming the clay and organic C contributed independently to the pH-dependent cation-exchange capacity of the soil.

Table 5 presents data for the CEC of the soil at pH 8, the pH-dependent CEC (difference between pH 8 and pH 3) of the soil, and of the clay separated from the soil, and the contribution of clay and organic C to the pH-dependent CEC of the soil. It is assumed that the clay and organic C contribute independently, an assumption that may not be justified but allows a calculation of the relative effects of clay and organic matter on the pH-dependent CEC of the soil. Per unit weight of material, the organic C contributes about 24 times more than the clay.

Russell (1950) presented data showing that a montmorillonite clay had a CEC of 95 meq per 100 g in the pH range of 2.5 to 6 but the value increased to 100 meq per 100 g at pH 7.0. The pH-dependent CEC for a montmorillonite clay, as determined by the method used for this paper, was 97, 102, and 104 meq per 100 g for pH 3, 7 and 8, respectively. The pH-dependent cation-exchange capacity to pH 7 was 5 meq per 100 g, which is nearly the same value as reported by Russell.

The pH-dependent CEC (pH 3 to 8) of clays separated from the soils used in this study varied from 11.2 to 24.2 meq per 100 g; however, 8 of the 15 values were between 13 and 15 meq. If Schofield's (1950) data for a clay subsoil are extrapolated to pH 8, the calculated pH-dependent CEC of the clay in the soil is about 15 meq per 100 g. This figure is based on a clay content of 60 per cent calculated from the ratio of the CEC of the clay to that of the soil. Thus, the pH-dependent CEC or the relation between CEC and pH of clays, as measured by the method herein described, agrees well with data from other sources.

## SODIUM-CALCIUM EXCHANGE EQUILIBRIA

Because a number of the acid soils collected contained large amounts of Na and Ca salts, a measurement of the effect of pH on relative adsorption of Na and Ca was considered desirable. The specific information wanted concerned the change in ratio of Na adsorption to Ca adsorption as the CEC decreased with decrease in pH.

The double-layer equation derived by Eriksson (1952) has been used by Bolt (1955) and Bower (1959) to study the adsorption of Na and Ca ions from salt solutions. The equation, which is based on the Poisson-Boltzmann differential equation, shows the charge fraction of monovalent to total ions in the diffuse double-layer of a plate-like exchanger as a function of the concentration of monovalent and divalent ions in the solution. The equation as simplified by Bolt (1955) is:

$$\Gamma_1/\Gamma = \frac{r}{\Gamma \sqrt{\beta}} \sinh^{-1} \frac{\Gamma \sqrt{\beta}}{r + 4v_c \sqrt{c_2}}$$

where  $\Gamma$  is the surface charge density of the exchanger in meq per  $\text{cm}^2$ ,  $\Gamma_1/\Gamma$  is, in the use of the equation, the fraction of surface charge that is neutralized by monovalent cations,  $r = c_1/\sqrt{c_2}$  (mole/l) $^{\frac{1}{2}}$  where  $c_1$  and  $c_2$  are the molar concentrations of the monovalent and divalent cations, respectively,  $\beta = 1.06 \times 10^{15}$  cm/mmole at 25° C and  $v_c = 1$ .

To calculate data for the theoretical curves shown in figures 4, 5 and 6, actual values for  $\Gamma$  and  $r$  were put into the equation and  $\Gamma_1/\Gamma$  values were obtained. The data were then recalculated in terms of  $\Gamma_1/\Gamma - \Gamma_1$  or  $\text{Na}_{\text{ad}}/\text{Ca}_{\text{ad}}$  and SAR or  $\text{Na}/\sqrt{\text{Ca}}$ , (mmoles/L) $^{\frac{1}{2}}$ . In figure 5 the  $\Gamma$  for the soil was multiplied by 2.1 to obtain an adjusted  $\Gamma$  that was put into the equation. The value 2.1 was obtained by measurements of the departure of the theoretical data from the experimental data.

Bolt (1955) found that this double-layer equation adequately described the equilibrium of a Na-Ca-illite in solutions of NaCl and  $\text{CaCl}_2$  when the determined value of surface charge density was multiplied by 1.2, and Bower (1959) found agreement between the equation and experimental data for four soils and two clays when the surface charge densities were multiplied by 1.4. A recent report by Lunin and Batchelder (1961) showed that the ratio of Na adsorbed to Ca adsorbed increased with decrease in pH of soils.

Coleman *et al.* (1959) have shown that at pH values of 5 and above, soils have only small amounts of acidity exchangeable with neutral salts, i.e., soils with pH 5 and above are essentially base-saturated, but they increase in basic

cation adsorption as a result of increase in CEC with increase in pH. Thus, if the double-layer equation applies at pH 8, it should apply equally well at any other pH within the range of 5 to 8 if the surface charge density appropriate to the pH of equilibrium condition is used.

**Methods.** Buffers for pH 5, 6, 7 and 8 were prepared. Each buffer contained 0.71 g of  $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ , 2.18 g of p-nitrophenol and sufficient NaCl to give the desired Na concentration. Before dilution to 1.0 liter the pH was adjusted to the desired values by adding triethanolamine or acetic acid. The  $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  added was sufficient to give 4.0 mmoles Ca per liter, and buffers were prepared for Na concentrations of 40, 80, 120, 160 and 200 mmoles per liter for each pH value.

A 2.5 g or 5.0 g sample of soil was washed 4 times with a 25 ml portion of the appropriate buffer solution. The 4 washings were always sufficient to bring the pH of the soil suspension to the pH of the buffer. The soil sample was then washed with 25 ml portions of a diluted buffer solution containing the same Ca and Na concentrations as the concentrated buffer solution. This solution, containing only 2 per cent as much of the buffering reagents and adjusted to the same pH as the buffer, was used to displace most of the buffer reagents from the soil, maintaining at the same time the desired pH. Washing with the diluted buffer was continued until equilibrium was indicated by the same Ca and Na concentrations in the wash solution as in the original solution. Equilibrium was attained by 10 washings in most cases, but some soils with high CEC required 13 washings.

After equilibrium was attained the sample was washed with  $\text{NH}_4\text{OAc}$ , and the Ca, Na and Cl in the  $\text{NH}_4\text{OAc}$  extract were determined. The Na was determined flame-photometrically. The Ca was titrated with versenate following oxidation of the  $\text{NH}_4\text{OAc}$  in the muffle furnace, and the Cl was titrated with standard  $\text{Hg}(\text{NO}_3)_2$  following an  $\text{H}_2\text{O}_2$  oxidation of the  $\text{NH}_4\text{OAc}$  in the presence of a small amount of CaO to prevent loss of Cl.

The adsorbed Na and Ca were determined as the total in the  $\text{NH}_4\text{OAc}$  minus the correction for quantities present as Cl salts. The proportions of Na and Ca present as Cl salts were assumed to be the same as in the final washing with replacement solution.

The Na-Ca equilibria, with the use of a Ca concentration of 0.004 *M* with variable Na concentrations, were measured on ten soils. In addition, the Na-Ca equilibria, with the use of 0.10 *M* and 0.20 *M* Na with variable Ca concentrations, were measured on one soil.

Surface area measurements were made by ethylene glycol retention (Bower and Goertzen, 1959). The CEC values used to obtain the surface charge density were obtained by the method described previously.

**Results.** Figures 4 and 5 present relations among the ratio of adsorbed Na to adsorbed Ca, Na and Ca in solution and pH of the solution of soils 8 and 12, respectively. The solid lines in the figures represent the theoretical relations, as calculated from the double-layer equation, and the circles represent experimental data.

With soil 8, the double-layer equation satisfactorily predicted the ratio of adsorbed Na to Ca at all four pH values. At an SAR value of 100 the ratio of Na to Ca in the adsorbed state increased from 0.89 at pH 8 to 2.42 at pH 5.



The actual values for surface charge density were used in the double-layer equation and no factor such as that used by Bolt (1955) and by Bower (1959) was necessary. Soil 3 was similar to 8 in that the equation predicted the experimental data without using a correction factor for the surface charge density.

The experimental data on soil 12 agreed with the equation when the surface charge density was multiplied by 2.1. However, the same correction was

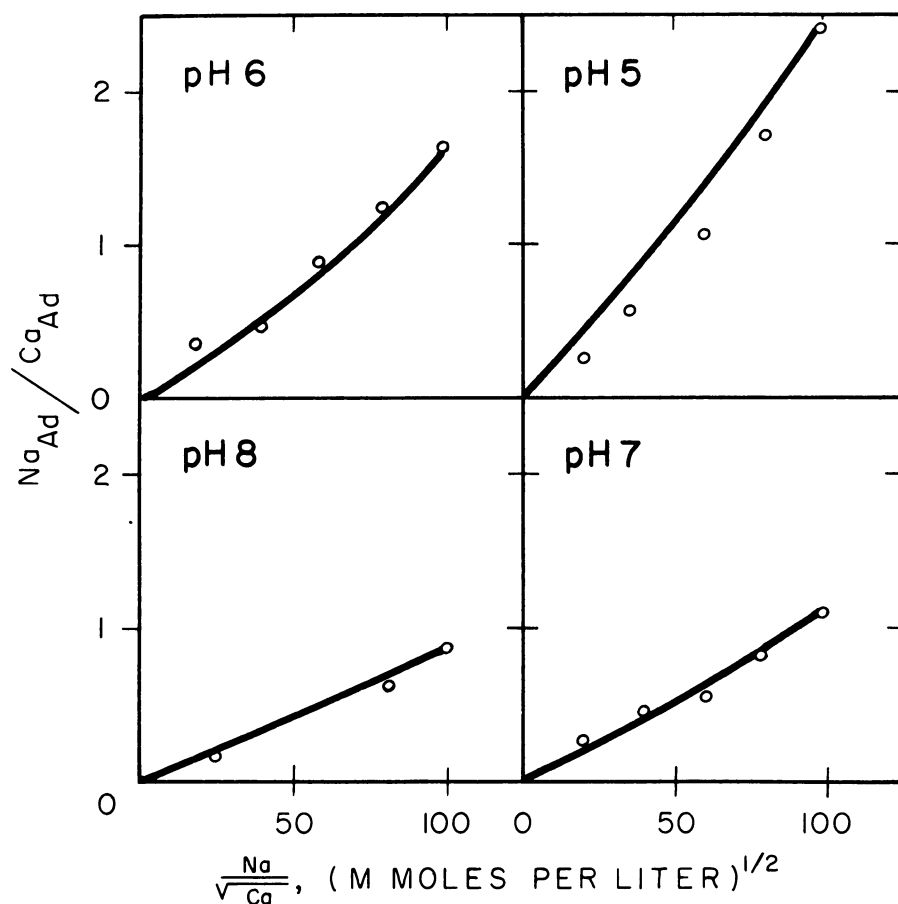


Fig. 4. Relations among the ratio of adsorbed Na to adsorbed Ca, Na and Ca in solution and pH of the solution for soil 8. Solid lines represent the theoretical relations and the circles represent experimental data.

needed at all four pH values, and thus the equation predicted the relative change in Na to Ca ratios with change in surface charge density associated with variations in pH. The agreement of the experimental data with the theoretical line was essentially independent of the total concentration of Na and Ca in solution. The data obtained with use of a high constant concentration of Na and a variable Ca concentration fit the line, as well as those ob-

tained with use of a low constant Ca concentration and a variable Na concentration.

Data on 7 other soils were similar to those in figure 5 in that the equation and the experimental data agreed well when the surface charge densities were multiplied by an appropriate factor. Thus, with ten soils on which detailed data were obtained, the theoretical equation predicted the relative

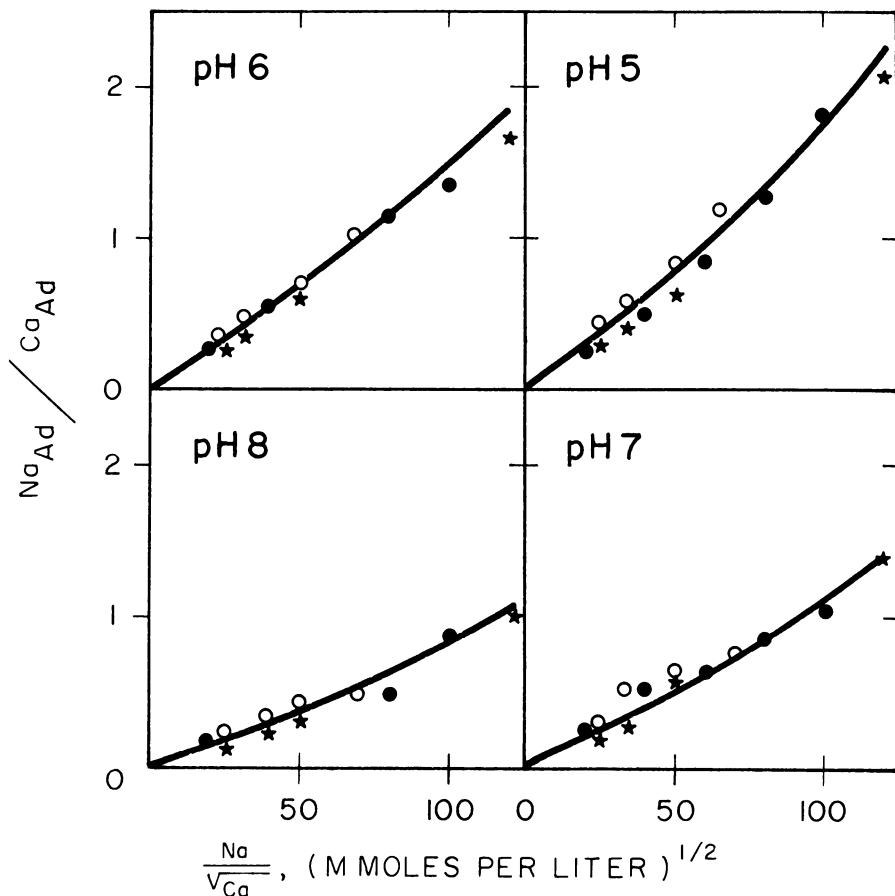


Fig. 5. Relations among the ratio of adsorbed Na to adsorbed Ca, Na and Ca in solution and pH of the solution for soil 12. The lines represent the theoretical relations, the solid circles represent data for 0.004 M Ca with variable Na concentrations, the open circles represent data for 0.10 M Na with variable Ca concentrations, and the stars represent data with 0.20 M Na and variable Ca concentrations.

change in ratio of Na to Ca adsorption with change in pH over a range of pH values from 5 to 8 inclusive.

The relations between the ratio of adsorbed Na to adsorbed Ca and the surface charge density for seven soils are presented in figure 6. The equilibrium solutions (fig. 6) had SAR values of 100; data on three other soils were so similar to those shown that they were omitted to avoid confusion.

The curve for each soil is of the same type as the theoretical curve but is displaced, to the left, by a constant.

Data on exchangeable Na and Ca and relative amounts of adsorbed Na and Ca, in relation to pH of an equilibrium solution containing an SAR of 100 for five soils, are presented in table 6. With four of the soils, the amount of adsorbed Na decreased as the pH increased, but with soil 13 it increased

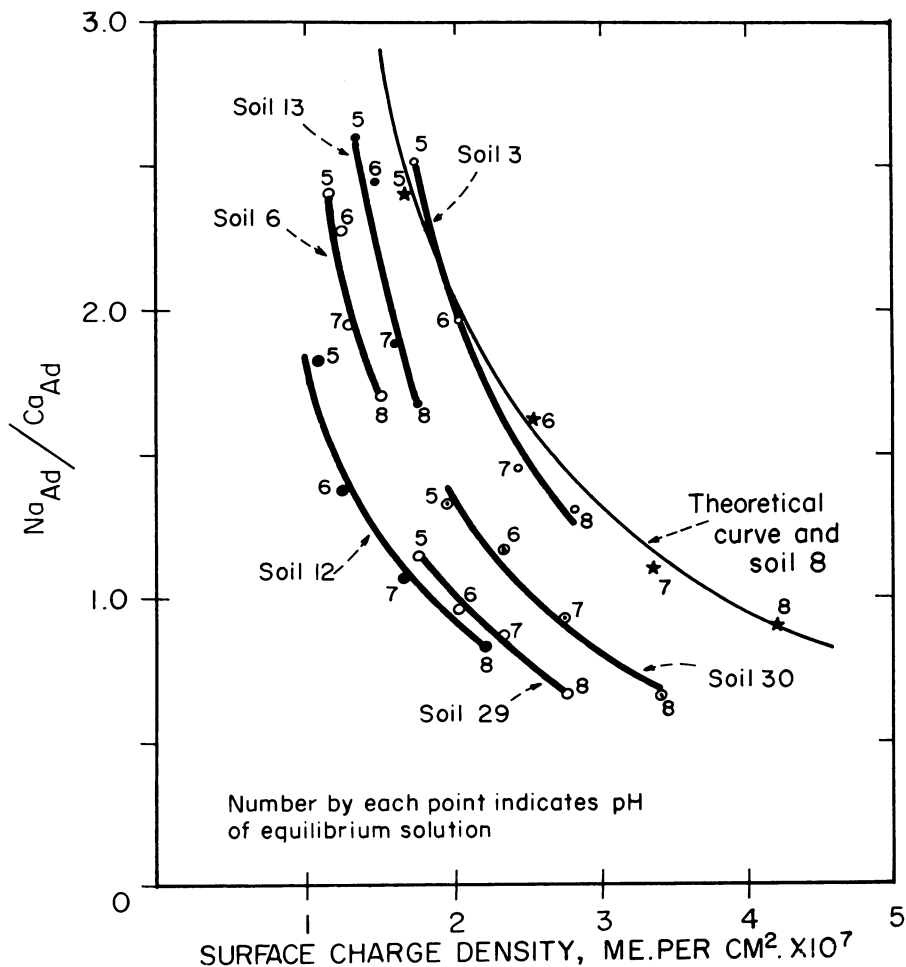


Fig. 6. Relations between the ratio of adsorbed Na to adsorbed Ca and the surface charge density for seven soils. The equilibrium solution had an SAR of 100.

slightly. In all cases the adsorbed Ca decreased with decrease in pH, to a greater degree than Na. Thus, as the pH decreased with a loss in CEC, the reduction in Ca was greater than the reduction in Na adsorption.

The double-layer equation as presented by Bolt (1955) seems to describe, satisfactorily, the relative change in the ratio of Na to Ca adsorption, with change in pH of equilibrium solutions containing Cl salts of these two cations.

The method of measuring relative CEC with change in pH also seems to be valid. However, the large variation in correction factors for the surface charge density, necessary to make the experimental data agree with the equation, suggest that something is either inherently wrong with one or both of the experimental determinations leading to the values of surface charge density, or that the soils have rather wide differences in the specificity with which they adsorb Ca vs. Na ions.

TABLE 6  
EXCHANGEABLE Na AND Ca AND RELATIVE ADSORPTION OF Na AND Ca  
IN RELATION TO THE pH OF AN EQUILIBRIUM SOLUTION  
CONTAINING AN SAR OF 100

Soil	pH	Exchangeable		Relative adsorption	
		Na	Ca	Na	Ca
		<i>meq/g</i>			
3	8.....	0.075	0.047	100	100
	7.....	0.058	0.037	77	79
	6.....	0.057	0.026	76	55
	5.....	0.048	0.018	64	38
8	8.....	0.024	0.029	100	100
	7.....	0.017	0.020	71	69
	6.....	0.019	0.011	79	38
	5.....	0.018	0.007	75	24
12	8.....	0.118	0.147	100	100
	7.....	0.112	0.101	95	69
	6.....	0.098	0.076	83	52
	5.....	0.087	0.051	74	35
19	8.....	0.090	0.090	100	100
	7.....	0.078	0.072	86	80
	6.....	0.079	0.056	88	62
	5.....	0.073	0.039	81	43
13	8.....	0.194	0.104	100	100
	7.....	0.210	0.095	108	91
	6.....	0.210	0.085	108	82
	5.....	0.207	0.076	107	73

The method of measuring the CEC was found to give CEC values in agreement with the sum of the exchangeable cations in the soils used in this study; therefore, there seems to be nothing inherently wrong in this determination.

The surface area data used were averages of three different determinations. Although there were variations among these, the magnitude of the variations was of the order of 10 per cent departure from the mean, and could not account for the range in correction factors needed. Thus, the analytical error in the surface area determination is not at fault. There is a possibility, however, that included in the surface area were various types of surfaces which contributed little or nothing to the CEC of the soil. Various minerals of the clay fraction such as quartz, feldspar and amorphous oxides of Fe, Al and Ti would probably contribute to the surface area without adding much to the



CEC. Also, certain organic colloids might behave in a similar manner. This would mean that the surface charge is not uniformly distributed on the total surface area but is confined to certain surfaces. Thus, the correction factor would seem to adjust the average surface charge density to the surface areas on which it exists.

Since the specificity with which Ca vs. Na is adsorbed is directly related to the surface charge density, the explanation for the correction factors, as

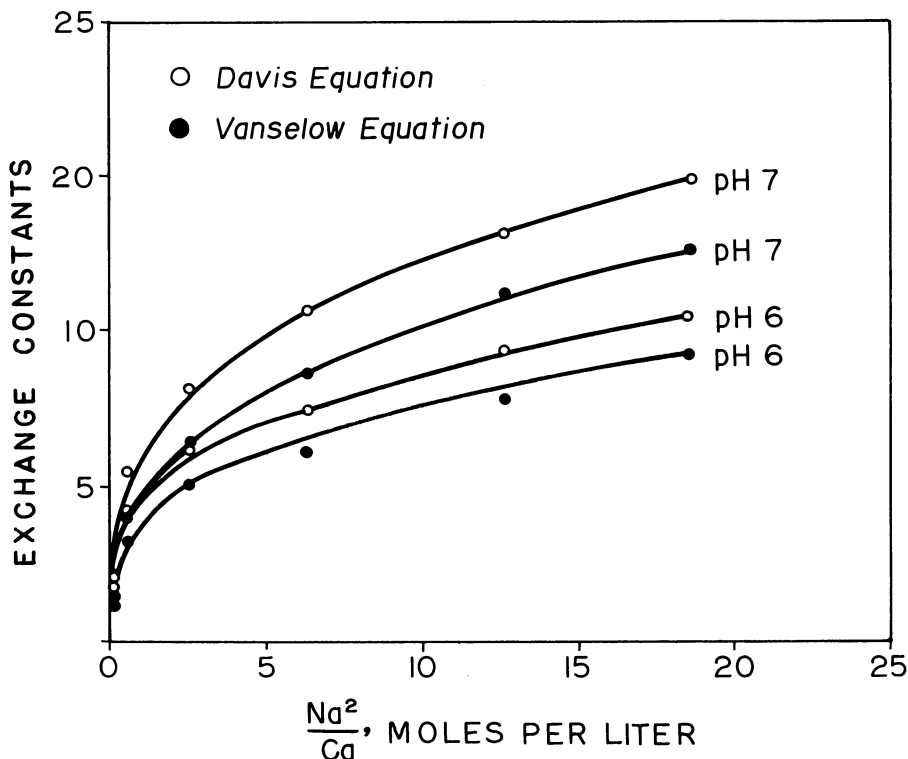


Fig. 7. Relations between the apparent exchange constant calculated from Vanselow's and Davis' equations and the solution phase concentration of Na and Ca at pH values of 6 and 7 for soil No. 12.

given, may explain all of the variations in such specificity. On the other hand, the specificity of adsorption of Ca vs. Na might be related to the chemical nature of the negative charge on some of the exchangers in the soils, and not to the surface charge density. The underestimation of the surface charge density of the exchangers because of materials that contribute to surface area, but not to CEC, as well as the specific nature of the negative charges, not related to surface charge density, probably influence the value of the correction factors necessary to make the double-layer equation agree with the experimental data.

The data on soil 12 at pH values of 6 and 7 were used to calculate constants for the exchange equations of Vanselow (1932) and of Davis (1950a, 1950b)

as used by Krishnamoorthy and Overstreet (1950). The results are presented in figure 7. Obviously, the exchange reaction according to either of these equations does not give a constant. The  $K$  values vary with change in cation concentrations in solution and with change in pH. This lack of a constant is in agreement with the statement by Krishnamoorthy and Overstreet (1950) that a constant cannot be obtained in a reaction when two or more exchange materials are involved.

Since most soils are mixtures of two or more exchange materials and since all equations similar to those of Vanselow (1932) and Davis (1950*a*, 1950*b*) do not apply to these mixtures, the double-layer equation developed by Eriksson (1955), which does show some agreement with data obtained on soils, would seem to be the more useful one to apply to soil systems.

## SUMMARY

Data are presented on the soluble cations, exchangeable cations, cation-exchange capacity, pH-dependent cation-exchange capacity and Na-Ca exchange equilibria of a number of acid soils of central and southern California.

About half of the soils collected were of medium to high salinity. About 20 per cent of the samples contained greater than 0.5 ppm Al in the saturation extract and about 40 per cent had greater than 10 ppm Mn. At pH values of 5 and above there was very little exchange acidity extracted by  $N$  KCl solution. Most of the acidity was pH-dependent and was extracted by a  $BaCl_2$  solution buffered at pH 8.2. At pH values below 5 some soils contained considerable exchange acidity which was largely accounted for by measuring exchangeable Al. For most soils the sum of the exchangeable cations, including the pH-dependent acidity, was equal to the CEC measured by Ba adsorption at pH 8.0.

All soils and clays contained a pH-dependent component of the CEC. The decrease in CEC with decrease in pH was found to be equal to the gain in pH-dependent acidity. The contribution of organic matter to the pH-dependent CEC was much greater than that of the clay. The CEC measured at the pH of the soil was a close estimate of the exchangeable cations plus exchange acidity extracted by KCl solution.

The ratio of adsorbed Na to adsorbed Ca increased with decrease in pH; as the CEC decreased with reduction in pH, the exchangeable Ca decreased more than exchangeable Na. The relative change in the ratio of adsorbed Na to Ca was predicted by an exchange equation based on the Poisson-Boltzmann differential equation. For a good agreement between the exchange equation and the experimental data the surface charge density had to be multiplied by a factor which was specific for each soil. These factors varied from 1.0 to 2.1.

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