Clays and Clay Minerals, Vol. 27, No. 2, pp. 87–90, 1979.

CATION-EXCHANGE BEHAVIOR OF CLAYS AND SYNTHETIC ALUMINOSILICA GELS[1]

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(Received 16 May 1978)

Abstract—Cation-exchange capacities determined by methylene blue adsorption (CEC MB) and by the amount of K displaced from a K-saturated clay by NH_4 (CEC $K//NH_4$) correlate closely in five soil clays from Pennsylvania, but differ greatly in two soil clays with a large content of amorphous material. CEC MB was found to provide a more precise distinction between montmorillonite and vermiculite than CEC $K//NH_4$. Synthetic aluminosilicate gels showed CEC $K//NH_4$ > CEC Ca/Mg > CEC MB, but no relation to the behavior of the two soil clays with a large content of amorphous material was found.

Key Words—Amorphous Material, Ca/Mg, $K//NH_4$, Methylene Blue, Montmorillonite, Vermiculite.

INTRODUCTION

It is well known that the cation-exchange reaction of clays is stoichiometric. The capacity value, being different in magnitude among clay mineral types, has been used as a means of characterization of a given mineral or mineral group. Alexiades and Jackson (1965) used the cation-exchange capacity as measured by the amount of Ca displaced from a Ca-saturated clay by Mg at room temperature (CEC Ca/Mg) and the cation-exchange capacity as measured by the amount of K displaced from a clay saturated with K and heated to 110°C by NH_4 (CEC $K//NH_4$) in calculating the amount of smectite and vermiculite components. In recent quantitative studies by the authors (Chu *et al.*, 1977), cation-exchange capacity determined by methylene blue adsorption (Hang and Brindley, 1970), along with CEC Ca/Mg and CEC $K//NH_4$, was used in part to calculate clay components. This paper compares the values obtained by these techniques for soil clays and describes the response of standard clay and synthetic aluminosilicate gels.

MATERIALS AND METHODS

Seven soil clays (<2 μm) were used (Table 1). The clays were separated from the soil after the removal of organic matter by NaOCl (Anderson, 1963). Free iron oxides were then removed from the clays by the citrate-dithionite-bicarbonate method (Mehra and Jackson, 1960). Standard mineral samples were obtained from Ward's Natural Science Establishment, Inc. and included montmorillonite from Upton, Wyoming, and vermiculite from Transvaal, South Africa. The montmorillonite was crushed to <30 mesh, and the vermiculite was treated with boiling NaCl solution to remove interlayer K. The <2-μm fractions were then separated and used. All soil and standard clays were saturated with sodium and washed free of salts.

Aluminosilica gels were prepared from 0.5 m $AlCl_3 \cdot 6H_2O$ and 0.5 M $Na_2SO_3 \cdot 9H_2O$ solutions. Two large burettes were used to deliver these reagents simultaneously into 500 ml of deionized water being stirred by a blender. The proportional amounts of 0.5 M $AlCl_3 \cdot 6H_2O$ and 0.5 M $Na_2SO_3 \cdot 9H_2O$ added for different gels were 1:9, 3:7, 1:1, and 7:3; a total of 500 ml was added. The pH of the suspension was then immediately adjusted to 7.0 by addition of 1:1 HCl or 6 N NaOH. After transfer to centrifuge tubes, the products were washed free of chloride ($AgNO_3$ test) with deionized water, ethanol, and finally with acetone. The gels were dried at room temperature and powdered by mortar and pestle. Analysis of the four gels by the technique of Medlin *et al.* (1969) gave $Al_2O_3/(Al_2O_3 + SiO_2)$ percentages of 9.5, 27.1, 46.5, and 66.4.

Cation-exchange capacity was determined by methylene blue (MB) adsorption (Hang and Brindley, 1970) and by the Ca/Mg and $K//NH_4$ method of Alexiades and Jackson (1965). Data presented represent an average of duplicates for all determinations.

RESULTS AND DISCUSSION

Cation-exchange capacities of the soil clays as determined by various methods are presented in Table 2. CEC MB of the five soil clays from Pennsylvania correlated closely with CEC $K//NH_4$, $r = 0.88$. The amounts of vermiculite calculated by the method of Alexiades and Jackson (1965), using either CEC $K//NH_4$ or CEC MB, were similar to the estimated value by X-ray powder diffraction analysis of oriented samples of the five soil clays from Pennsylvania (Tables 1 and 2). For the Groveton and Paxton soil-clay samples, however, CEC Ca/Mg and CEC $K//NH_4$ are similar, while CEC MB is considerably lower. The quantity CEC Ca/Mg − CEC $K//NH_4$, as used by Alexiades and

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[1] Authorized for publication as Paper No. 5512 in the journal series of the Agricultural Experimental Station, The Pennsylvania State University.

Table 1. Source and selected mineral composition of the soil clays.

Soil number[1]	Soil series	Horizon	Sample composition (wt %) Montmorillonite[2]	Vermiculite[2]	Amorphous material[3]	$\frac{Al_2O_3}{Al_2O_3 + SiO_2{}^4} \times 100$
S65 Pa 20-6-4	Titusville	Bxlg	30	10	7.5	46.0%
S65 Pa 28-12-2	Duffield	B1	30	5	6.1	49.0
S61 Pa 32-52-3	Cavode	B22	15	10	2.5	32.5
S64 Pa 26-11-5	Purdy	B23	10	5	4.7	49.3
S64 Pa 14-15-2	Berks	B2	0	5	4.4	46.9
S75 NH 4-1-2	Groveton	B21	0	20	16.6	62.0
S75 Ct 7-1-1	Paxton	Ap	0	25[5]	25.6	63.3

[1] Pa = Pennsylvania; NH = New Hampshire; Ct = Connecticut.

[2] Estimated semiquantitatively by X-ray powder diffraction analysis.

[3] Determined by 0.5 N NaOH dissolution (Hashimoto and Jackson, 1960).

[4] Composition of the amorphous material.

[5] Interstratified vermiculite-chlorite.

Jackson, indicates that little or no vermiculite is present in these two samples. When CEC Ca/Mg − CEC MB is used, the results are more consistent with those found by X-ray powder diffraction analysis. Since amorphous material commonly contributes significantly to the cation-exchange capacity, a large content of material soluble in 0.5 N NaOH in both the Groveton (16.6%) and the Paxton (25.6%) clays may be a factor in the difference between CEC K//NH_4 and CEC MB for these two samples.

CEC Ca/Mg and CEC MB are almost identical for the montmorillonite used, but differ greatly for the standard vermiculite (Table 3). With vermiculite, CEC MB is much closer to CEC K//NH_4. This behavior may be explained if the nature of the methylene blue molecule is considered. The relatively large methylene blue cation, 17.0 × 7.6 × 3.3 Å (Hang and Brindley, 1970), can be accommodated within the interlayer space of a highly expanded montmorillonite but can not be adsorbed into the interlayer space of a vermiculite which has only limited layer expansion. For vermiculite, CEC MB essentially measures the externally exposed cation-exchange sites. The somewhat higher value of CEC K//NH_4 when compared to CEC MB may indicate that some fixed K near the edges of the particles is being displaced by NH_4. The difference in CEC Ca/Mg and CEC K//NH_4 for the montmorillonite suggests either that it contains some vermiculite layers, or that some of the montmorillonite layers can fix potassium. CEC MB for the montmorillonite favors the latter interpretation. If this is accepted, then CEC MB gives rise to a more precise distinction between smectites and vermiculites than does CEC K//NH_4.

Table 2. Cation-exchange capacities of the soil clays.

Soil series	Cation-exchange capacity (meq/100 g) Ca/Mg	K//NH_4	MB
Titusville	52.2	36.9	39.3
Duffield	40.2	33.0	34.4
Cavode	32.2	22.2	22.6
Purdy	19.3	15.9	16.2
Berks	14.7	10.9	9.1
Groveton	58.4	58.6	18.5
Paxton	54.3	51.7	16.0

Cation-exchange data for the synthetic gels (Table 4) show CEC K//NH_4 > CEC Ca/Mg > CEC MB. This behavior is different from that of the soil and standard clay in which CEC Ca/Mg should be greater or equal to CEC K//NH_4. According to van Reeuwijk and de Villiers (1968), the replacing power of the cations against K adsorbed on their gels, which are similar compositionally to those of Table 4, is NH_4 > Na > Ca > Mg. This sequence follows the lyotropic series, and fixation of the cation is not restricted to K. In other words, any cation could be fixed against the exchange of a weaker replacer. Thus, the lower value of CEC Ca/Mg could be due to Ca-fixation against the exchange by Mg. Evidence of this is found when comparable Ca-saturated gels are exchanged by K (CEC Ca/K, Table 4). Analysis of the gels after determining CEC Ca/Mg also reveals that Ca is retained. The total Ca adsorbed (CEC Ca/Mg plus Ca retained in gel) is very close to CEC K//NH_4. If this gel-like material is present in the soil clay, CEC Ca/Mg should be decreased while CEC K//NH_4 would not be affected.

In an attempt to relate the cation-exchange behavior of Groveton and Paxton soil clays to the synthetic gels, Ca-saturated clays were exchanged with K. No difference was found between CEC Ca/K and CEC Ca/Mg.

Table 3. Cation-exchange capacities of the standard clays.

Sample	Cation-exchange capacity (meq/100 g) Ca/Mg	K//NH_4	MB
Montmorillonite, Upton, Wyoming	81.0	62.3	80.2
Vermiculite, Transvaal, South Africa	175.0	23.3	16.1

Table 4. Cation-exchange capacities and Ca-fixation of the aluminosilica gels.

Gel composition $\frac{Al_2O_3}{Al_2O_3 + SiO_2}$	Cation-exchange capacity (meq/100 g)				Ca fixed against exchange by Mg[1] (meq/100 g)
	Ca/Mg	K//NH_4	MB	Ca/K	
9.5%	40.7	133.6	20.6	n.d.	94.4
27.1%	90.1	360.5	17.8	n.d.	253.8
46.5%	39.3	117.8	5.7	115.6	89.1
66.4%	4.2	10.5	0	9.4	7.1

n.d. = not determined.

[1] After CEC Ca/Mg determination, gels were reacted with 3 N HCl and Ca was determined in the supernatants.

The composition of the amorphous material in these two clays indicates that their contribution to CEC values would be small if the amorphous material were similar to the synthetic gels. It is uncertain, therefore, how the similarity of CEC Ca/Mg and CEC K//NH_4 is related to the amorphous material content in Groveton and Paxton soil-clay samples. It should be emphasized, however, that for samples with a high content of amorphous material, caution should be exercised in the determination of vermiculite and montmorillonite using the method of Alexiades and Jackson (1965). A modified method has been proposed by Rengasamy *et al.* (1975), in which amorphous material is removed prior to the determination of cation-exchange capacities. For some soil clays, a treatment with 0.5 N NaOH could alter the nature of exchange sites. Gains in calculated vermiculite of the samples studied vary from 0 to 25%. Since no difference was found between X-ray patterns of the soil clays before and after the 0.5 N NaOH treatment, the modified method is questionable for general application. In conclusion, CEC MB may provide for a better distinction between smectite and vermiculite minerals than does CEC K//NH_4. Furthermore, caution should be exercised when a considerable amount of amorphous material is present if cation-exchange capacities are used to characterize the clay components in soil clays.

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Резюме—Катионные обменные способности, определенные с помощью адсорбции метилена синего (КОС МС) и с помощью определения объема K, выделенного из насыщенной K глины при взаимодействии с NH_4 (КОС K//NH_4), хорошо коррелируются для пяти почвенных глин из Пенсильвании, но сильно отличаются для двух почвенных глин с большим содержанием аморфного материала. Было обнаружено, что КОС МС обеспечивает более точное различение между монтмориллонитом и вермикулитом, чем КОС K//NH_4. Синтетические алюминосиликатные гели показали, что КОС K//NH_4 > КОС Ca/Mg > КОС МС, но не было найдено отношения к поведению двух почвенных глин с большим содержанием аморфного материала.

Résumé—Les capacités d'échange de cations déterminées par l'adsorption du bleu de méthylène (CEC MB) et par la quantité de K déplacée d'une argile saturée de K par NH_4 (CEC K/NH_4) sont très proches dans cinq argiles de sol de Pennsylvanie, mais sont très différents dans deux argiles de sol contenant beaucoup de matière amorphe. Il a été trouvé que CEC MB procurait une distinction plus précise entre la montmorillonite et la vermicullite que CEC K/ $/NH_4$. Des gels synthétiques d'aluminosilice montraient CEC/ $/NH_4$ > CEC Ca/Mg > CEC MB, mais il n'a été trouvé aucune relation avec le comportement des deux argiles de sol contenant beaucoup de matière amorphe.

Resümee—In fünf Erden aus Pennsylvania sind die Kationenaustauschkapazitäten, welche via Methylenblauadsorption (CEC MB) und durch den Anteil von Kalium, in einem K-gesättigten Ton durch NH_4 ersetzt (CEC K/ $/NH_4$), bestimmt wurden, untereinander sehr ähnlich, aber unterscheiden sich sehr in zwei Erden, die viel amorphes Material enthalten. CEC MB zeigte einen präziseren Unterschied zwischen Montmorillonit und Vermiculit als CEC K/ $/NH_4$. Synthetische Aluminosilikatgele zeigten CEC K/ $/NH_4$ >CEC Ca/Mg >CEC MB, aber keine Verbindung zu dem Verhalten der zwei Erden mit dem hohen Gehalt an amorphen Material.