CATION EXCHANGE BETWEEN MIXTURES OF CLAY MINERALS AND BETWEEN A ZEOLITE AND A CLAY MINERAL*

by

PATRICK J. DENNY and RUSTUM ROY

Pennsylvania State University, University Park, Pa.

ABSTRACT

The electron microprobe has been used to analyse mixtures of fine-grained silicates such as clay minerals in order to determine directly how cations distribute themselves between mixtures of two fine-grained ion-exchanging materials in pure water and in dilute solutions.

Cation distributions have been determined for mixtures of:

(a)   a zeolite, faujasite, and the clay mineral in an Arizona bentonite;
(b)   the clay mineral in an Arizona bentonite and hectorite; and
(c)   three synthetic beidellites of varying charge density.

Distributions have been found for varying ratios of Ca to K ions in the suspensions. The results for the faujasite–bentonite mixture show complex behavior and exhibit curves with maxima and minima. For the system bentonite–hectorite most of the Ca goes to the montmorillonite in the bentonite.   For the mixture of synthetic beidellites, the results are rather confusing but it appears that the calcium is more associated with the beidellite with the highest exchange capacity. In all these systems, hydrolysis takes place and the hydronium ion plays a part in determining the equilibrium.

INTRODUCTION

MANY studies of cation exchange equilibria have been made between single ion-exchanging minerals and cations in solution. Little experimental evidence exists on how two or more cations distribute themselves in mixtures of two types of inorganic cation-exchangers, such as a clay mineral and a zeolite. One problem in obtaining such information has been the difficulty in separating the two crystalline phases for analysis. Recent work (Denny and White) with the electron microprobe has shown a way of overcoming this difficulty.

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It has been shown that the electron probe can analyse particles in the 1–10-micron size-region to give elemental ratios such as Ca/Si. Although the elemental ratios show variations from particle to particle of ± 35 per cent for synthetic zeolites and ± 10 per cent for clay minerals, means of large numbers of particles give reproducible values. In the present work, the technique has been extended to investigate elemental ratios in separate components of a fine grained mixture.

Such work using mixtures of ion-exchanging minerals should make possible a direct comparison of bonding energies of cations between two or more species of exchangers. If the supply of cations in solution is limited, then the equilibrium distribution of cations between the two exchangers will depend on which of the two exchangers is more strongly bonded to a particular cation. If exchanger A and B are both more strongly bonded to cation X than to cation Y, and exchanger A is more strongly bonded to X than exchanger B, then A will contain most of cation X, leaving exchanger B richer in cation Y.

In the present work as a starting point the distribution of a divalent and a univalent cation was studied between a wide range of exchangers as follows:

(a)   a zeolite and a clay mineral;

(b)   one dioctahedral and one trioctahedral clay mineral;

(c)   a series of synthetic beidellites of varying surface charge.

EXPERIMENTAL PROCEDURES

Materials

The Arizona bentonite from Chambers, Arizona, was supplied by the Filtrol Corporation and was stated to consist of 94.4 per cent "pure montmorillonite" with the main impurities being quartz and feldspars. X-ray diffraction showed the presence of a small amount of quartz but no other impurities. Occasionally particles having Ca/Si ratios corresponding to quartz or Ca-feldspar were detected with the electron probe but these readings were neglected. The compositions was: SiO_2, 66.92; Al_2O_3, 19.85; Fe_2O_3, 2.25; MgO, 6.98; Ca, 3.21, Na_2O, 0.10; K_2O, 0.18; and the cation exchange capacity was given as 133 meq/100 g. The C.E.C. was redetermined by saturating the material with calcium chloride, followed by washing, and analysis of the calcium content. This gave a C.E.C. of 137 meq/100 g.

The hectorite from Hector, California, was obtained from the National Lead Company and was stated to have a C.E.C. of 82.7 meq/100 g. A redetermination of the C.E.C., as with the Arixona bentonite, gave a value of 95 meq/100 g. This latter value was the one assumed when mixing the components. An examination by X-ray diffraction showed no detectable impurities. The synthetic zeolite, faujasite, was obtained from the Linde Company as molecular sieve 13X, and was found to have a C.E.C. of about 450 meq/100 g. Analysis of the calcium-exchange form gave a composition of $CaO.Al_2O_3.2.45SiO_2$.

The three synthetic beidellites were synthesized as described by Koizumi and Roy (1959). X-ray diffraction indicated the presence of beidellite as the only crystalline species present. Electron microprobe investigations of the calcium-exchange products showed the crystalline beidellites in the products to have C.E.C.'s of 86, 111, and 140 meq/100 g and to contain material with little or no calcium present, presumably uncrystallized gel or material of low C.E.C. This lowered the overall C.E.C.'s to values of 45, 72 and 74 meq/100 g respectively. These products are referred to as the 1/2 N, 1 N, and 2 N beidellites respectively (referring to the gels from which they were crystallized). Electron microscopy verified the presence of a beidellite and a gel-like material.

The monocationic end members of these species were made by exchanging them with excess of potassium and calcium chloride solutions at room temperature. The products were filtered and washed and the process was repeated four or five times. The products were then dried at room temperature or 40°C. This low drying temperature was used to avoid any possible potassium fixation.

X-ray spectrochemical analysis of these monocationic end members gave Ca/Si and K/Si elemental ratios as shown in Table 1.

Table 1.—Ca/Si and K/Si Atom Ratios for Monocationic End Members

Material	Ca/Si	K/Si
Arizona bentonite	0.065	0.126
Hectorite	0.055	0.101
Faujasite	0.404	0.78
1/2 N beidellite	0.043[1]	0.063[1]
1 N beidellite	0.057[1]	0.095[1]
2 N beidellite	0·076[1]	0.145[1]

[1]For beidellite crystals only in synthetic product.

These atom ratios are taken to represent complete saturation of the ion-exchange material with cations and are used in calculating the fraction of ion-exchange sites filled by a particular cation.

Conditions of Ion-exchange

The ratios of calcium to potassium ions in the total mixture were varied by weighing out different amounts of the monocationic end members to give the desired ratios. In the cases where solutions were used, the initial ratio of the ions in solution was also varied to give the desired result. All the exchanges were between calcium and potassium ions. Sodium ion exchanges may have been desirable, but at the time the electron probe could not handle sodium analyses.

The following suspensions were shaken, and are referred to in the text by the designations below.

System 1. *Faujasite and Arizona bentonite.*—(a) 1 meq of Arizona bentonite and 1 meq of faujasite in 40 ml of solution containing a total of 2 meq of calcium and potassium chlorides at 20°C for 2 days. (b) As in (a) except that suspensions were shaken at 81°C for 2 days. (c) 1 meq. of Arizona bentonite and 1 meq. of faujasite in 40 ml of pure water (i.e. with no cations in solution) at 20°C for 3 days.

System 2. *Arizona bentonite and hectorite.*—1 meq of the Ca- and K-exchanged forms of each, in varying ratios, at 20°C for 4 days, with 40 ml water only.

System 3. *Mixture of beidellites.*—A mixture of equal weights (0.200 g) of each calcium and potassium end member of the three synthetic beidellites, with 40 ml of pure water at 20°C for 7 days.

In order to see if equilibrium was reached in the times allowed, a series of suspensions, of 1 meq Ca–faujasite and 1 meq K–Arizona bentonite in 40 ml of water, were shaken for varying periods from 40 min. to $2\frac{1}{2}$ days. The equilibrium was also approached from the opposite direction by starting with Ca–bentonite and K–faujasite.

In another experiment to see if exchange could take place easily under conditions where the supply of water was limited, 1 meq each of monocationic Ca–faujasite and K–bentonite were mixed with 1 ml of water to give a thick paste which was dried out at about 45°C for $4\frac{1}{4}$ hr and left to stand at room temperature for several days.

Sampling and Analysis

In the earlier runs (systems 1 a and b) the suspension was filtered as rapidly as possible, washed to remove any excess salts, and dried at about 40°C. However, it was considered that this sampling technique was quite likely to alter the equilibrium obtained in suspension . Therefore, runs of systems 1 c, 2 and 3 were sampled by placing a drop of diluted suspension on the sample holder and allowing it to evaporate to dryness at room temperature. This method could only be used when the exchangers were shaken with pure water.

The mixtures were analysed on an A.R.L. electron microprobe as described elsewhere (Denny and White). The electron back scatter image on the oscilloscope was not clear enough to distinguish between the

faujasite and the bentonite single crystals. However, this could be over-come by using the third channel on the probe. For systems 1(b), 1(c) and 3, the three channels available were used to measure Ca, K, and Si. Only two channels were available during the time that system 1(a) was examined; these were used to measure Ca and K. The ratio of Ca and K to Si is sufficiently different in the case of a zeolite and clay to enable the readings for the faujasite and bentonite to be differentiated unequivocally. Also, if the beam current is kept constant, the absolute peak heights for the Ca and K also give a good indication of the species being analysed. This was used to differentiate between the faujasite and bentonite for system 1(a). For system 2, the three channels were used to measure Ca, K and Al. The ratio of either exchange cation to Al was used to distinguish between hectorite and montmorillonite since hectorite contains very little aluminum.

The K/Si ratios obtained for the faujasite are not as accurate as those for the clay minerals since large potassium evaporation occurs in the electron beam. The potassium evaporation is not nearly so serious, and is usually negligible in the clay minerals owing to their smaller thickness.

It was assumed that the Ca/Si atoms ratios (Table 1) for the monocationic end members represented complete filling of the exchange positions by the cations in the clay mineral or zeolite. The Ca/Si and K/Si ratios for the components in the equilibrated mixtures were obtained from the electron probe analyses as described above. The percentage of exchange positions filled by a particular exchange cation can then be calculated from these atom ratios.
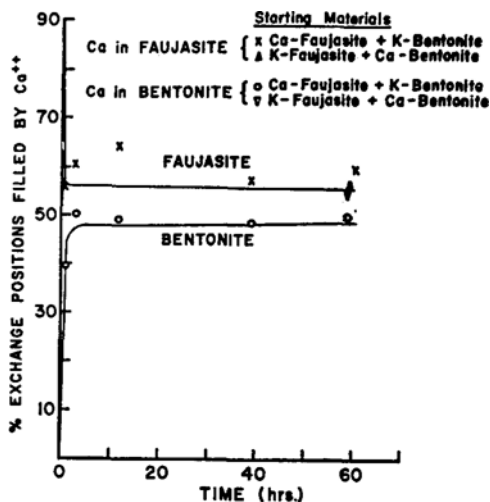

FIGURE 1.—Exchange with time between K^{ex}–bentonite and Ca^{ex}–faujasite in water at 20°C.

Results and Discussion

The results for the kinetics of exchange between Ca–faujasite and K–bentonite in water only are shown in Fig. 1. The rate of exchange is rapid, being almost complete in 40 min, the minimum time allowed. Almost the same equilibrium point was reached when the equilibrium was approached from the opposite direction as is also shown on Fig. 1. It has been shown (Marshall, 1954) that clay minerals are slightly ionized in solution and so the exchange can take place through a solution mechanism. The zeolite, faujasite, has a very open structure (Barrer, Bultitude and Sutherland, 1957) and so exhange can be rapid in this mineral.

TABLE 2.—EQUILIBRIA FOR SYSTEM 1A

Initial Ratios $\dfrac{\text{Total Equivs. Ca}}{\text{Total Equivs. K}}$	Equilibrium Ratios $\dfrac{\text{Equivs. Ca}}{\text{Equivs. K}}$	
	Faujasite	Bentonite
3.0	9.56	2.52
1.5	5.12	1.45
1.0	2.76	0.86
0.67	1.75	0.48
0.33	0.11	0.11

It is interesting to note that exchange can also be rapid in the moist state. Thus, in the case where 1 meq each of monocationic Ca–faujasite and K–bentonite were mixed with 1 ml of water to give a thick paste, on analysis it was found that a great deal of exchange had taken place and it is likely that the mixture has reached equilibrium. In the final products, the percentage exchange positions filled by calcium ions were 64 and 38

TABLE 3.—EQUILIBRIA FOR SYSTEM 1B

Initial Ratios $\dfrac{\text{Total Equivs. Ca}}{\text{Total Equivs. K}}$	Equilibrium Ratios $\dfrac{\text{Equivs. Ca}}{\text{Equivs. K}}$	
	Faujasite	Bentonite
3.0	41.2	6.22
1.5	10.5	3.10
1.0	5.75	2.00
0.33	2.19	1.06

and by potassium ions 19 and 59 in the faujasite and Arizona bentonite respectively.

For the systems 1(a) and (b), where faujasite and Arizona bentonite were shaken with dilute solutions containing $CaCl_2$ and KCl, the ratios of equivalents of calcium to potassium in both the solid phases at equilibrium are given in Tables 2 and 3 respectively. The ratios are plotted against the initial ratio of total equivalents of calcium to potassium in the suspension (including solid and solution) in Fig. 2. It can be seen that the
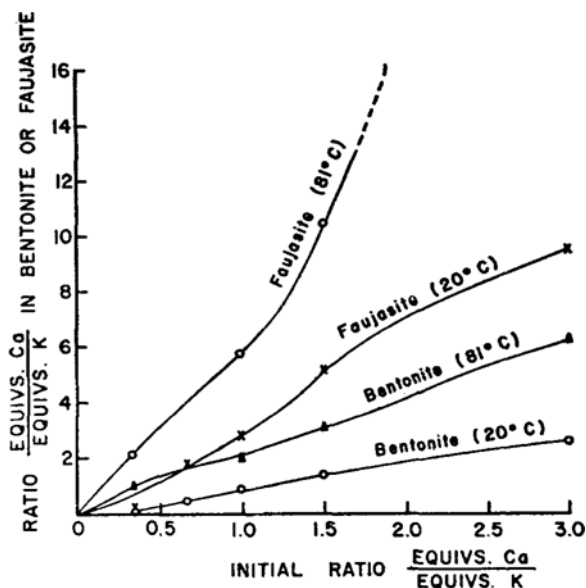

Figure 2.—Equilibria for system Ca–K–Arizona bentonite–faujasite + solution $CaCl_2$ + KCl at 20°C and 81°C.

faujasite has the greater ratio of calcium to potassium ions and that this ratio is greater at the higher temperature. Thus, at 20°C for an initial ratio of 1 the ratio of equivalents Ca to K in the mixed suspension is 2.76 and 0.86 for the faujasite and bentonite respectively. Under the same conditions, it was found that with faujasite or bentonite alone the equilibrium ratios were 1.65 and 1.11. Thus the faujasite takes up calcium at the expense of the bentonite, leaving the bentonite richer in potassium, although bentonite itself has a greater affinity for calcium than for potassium ions.

For system 1 b and 1 c, the Ca/Si and K/Si ratios can be calculated and used to find the percentage of exchange positions occupied by calcium or potassium ions. Unfortunately, at the time the system 1 a was analysed the third (Si) channel was not available on the electron probe and only

Ca/K ratios could be obtained. The percentages of Ca and K in the faujasite and bentonite for systems 1 b and 1 c are given in Tables 4 and 5 respectively. In Figs. 3 and 4 these percentages are plotted against the initial ratios of the total equivalents of Ca to K in the suspension.

Table 4.—Equilibria for System 1b

Initial Ratio Total Equivs. Ca Total Equivs. K	% Exchange Positions Filled by Ca++		% Exchange Positions Filled by K++	
	Faujasite	Bentonite	Faujasite	Bentonite
3.0	75	49	1.8	7.8
1.5	58	56	5.5	18
1.0	63	76	11	38
0.33	45	46	21	43

As can be seen from Figs. 3 and 4, the percentages of exchange positions filled by calcium ions in both the faujasite and bentonite show maxima at about a ratio of 1.0. These maxima are surprising and cannot be explained easily. Repeat experiments gave the same results. Also, for these systems if the total number of exchange positions filled by both calcium and

Table 5.—Equilibria for System 1c

Initial Ratio Total Equivs. Ca Total Equivs. K	% Exchange Positions Filled by Ca++		% Exchange Positions Filled by K+	
	Faujasite	Bentonite	Faujasite	Bentonite
3.0	47	37	25	40
1.5	34	32	25	50
1.0	56	51	25	55
0.67	43	26	—	—
0.50	42	22	22	61
0.33	29	14	19	56

potassium ions in each species is calculated, it is found that a large percentage of the exchange positions are left unaccounted for. It can only be concluded that these positions are filled by hydronium ions. Hence, in these suspensions where the concentration of cations is small or zero, considerable hydrolysis takes place and the hydronium ions play an important role in determining the equilibrium. The percentage of hydrolysis in the systems 1(b) and 1(c) are given in Tables 6 and 7 respectively. For
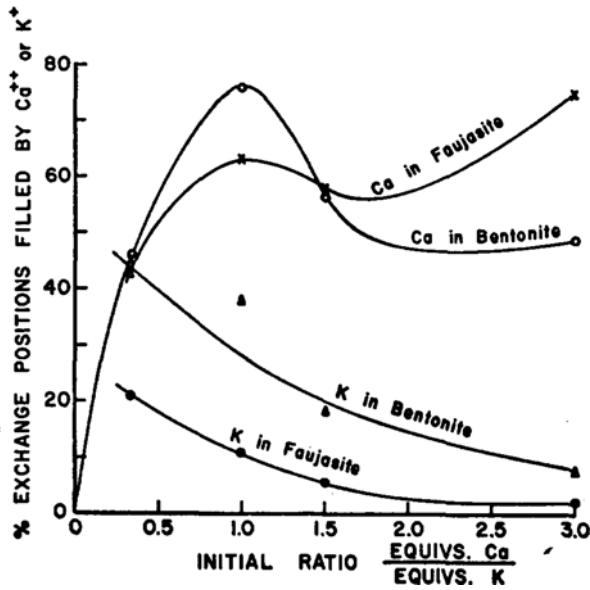
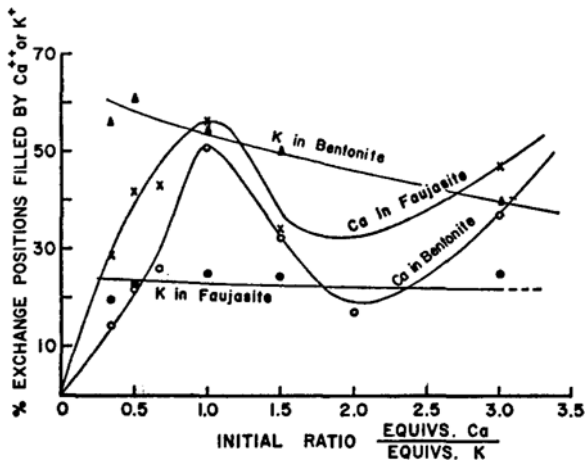FIGURE 3.—Equilibria for system Ca–K–Arizona bentonite–faujasite + solution $CaCl_2$ + KCl at 81°C.

FIGURE 4.—Equilibria for system Ca–K–Arizona bentonite–faujasite + water only at 20°C.

system 1(c) where no excess ions were present in solution, a mass balance can be made using Table 5. It can be seen that hydrolysis of both calcium and potassium ions takes place. As is to be expected, most of the hydrolysis is of calcium ions in the suspensions rich in calcium and most by potassium in the suspensions rich in potassium ions. Also, it is apparent that the

TABLE 6.—HYDROLYSIS IN SYSTEM BENTONITE AND FAUJASITE AND SOLUTION AT 81°C (SYSTEM 1B)

Initial Ratio $\dfrac{\text{Equivs. Ca}}{\text{Equivs. K}}$	% Hydrolysis in Faujasite	% Hydrolysis in Bentonite
3.0	24	44
1.5	37	26
1.0	26	0
0.33	34	11

affinity for hydronium ions is a function of the ratios of calcium to potassium in the bentonite and faujasite. This is also apparent from the mean free bonding energy curves of Marshall *et al.* (Marshall, 1954) for clay minerals. The mean free bonding energies of calcium and potassium depend on the relative saturation of the Arizona bentonite with these and hydrogen ions. The maxima and minima observed for Ca in Figs. 3 and 4 are no doubt caused by the presence of hydronium ions in the system.

TABLE 7.—HYDROLYSIS IN SYSTEM BENTONITE AND FAUJASITE AND WATER ONLY AT 20°C (SYSTEM 1c)

Initial Ratio $\dfrac{\text{Equivs. Ca}}{\text{Equivs. K}}$	% Hydrolysis in Faujasite	% Hydrolysis in Bentonite
3.0	28	23
1.5	41	18
1.0	19	0
0.67	—	—
0.50	36	17
0.33	52	30

For the suspension using hectorite and Arizona bentonite in water, the results are given in Table 8 for the Arizona bentonite. Only Ca/K ratios could be found for the hectorite since it contains little or no aluminum and Al was used on the third channel of the electron probe.

The percentage of the exchange positions filled by Ca and K in the

TABLE 8.—EQUILIBRIA FOR HECTORITE AND ARIZONA BENTONITE (SYSTEM 2)

Initial Ratio Equivs. Ca / Equivs. K	% Exchange Position Filled in Bentonite by:	
	Ca	K
3.0	80	23
2.0	89	18
1.5	78	20
1.0	82	19
0.5	51	29

bentonite are shown in Fig. 5. As can be seen, the percentage Ca in the bentonite rises rapidly as the Ca content of the system is increased until about 80 per cent of the positions are filled. After this, no further Ca adsorption takes place over the range studied. Thus it appears that the affinity of Arizona bentonite for calcium ions is large until 80 per cent saturation is reached. At this point, the bonding energy for Ca must fall rapidly. This is supported by the work of Marshall *et al.* (Marshall, 1954) for Arizona bentonite. The mean free bonding energy curves, which Marshall gives for Ca in Arizona bentonite, when K is the accompanying cation, is falling rapidly when 80 per cent saturation is reached with calcium.
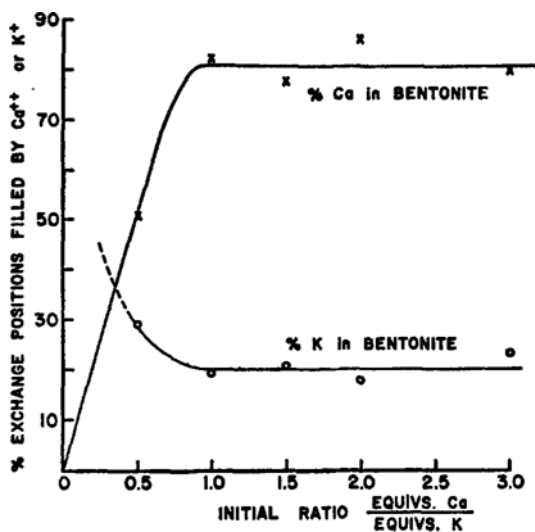

FIGURE 5.—Equilibria for system Ca–K–Arizona bentonite–hectorite + water at 20°C.

From Table 8 it can be seen that all the exchange positions in the Arizona bentonite are filled and, therefore, no hydrolysis takes place. Since no ions were initially present in solution, a mass balance can be made and the expected ratios of equivalents of Ca to K in the hectorite can be calculated. These are given in Table 9 where they are compared

TABLE 9—CA/K RATIOS IN HECTORITE (SYSTEM 2)

Initial Ratio Equivs. Ca / Equivs. K	Ratio Equivs. Ca to K in Hectorite	
	Calculated	Experimental
3.0	2.6	6.9
2.0	1.1	—
1.5	0.70	2.3
1.0	0.26	2.0
0.5	0.16	1.82

with the experimentally determined ratios. Table 9 shows that the experimentally determined Ca/K ratios are in every case considerably greater than the calculated ones. This means that hydrolysis has taken place in the hectorite and also that it is largely the potassium ions that have hydrolyzed.

The results for the mixture of synthetic beidellites are rather confusing. In Fig. 6 the ratio of Ca to K for each particle in the equilibrated mixture
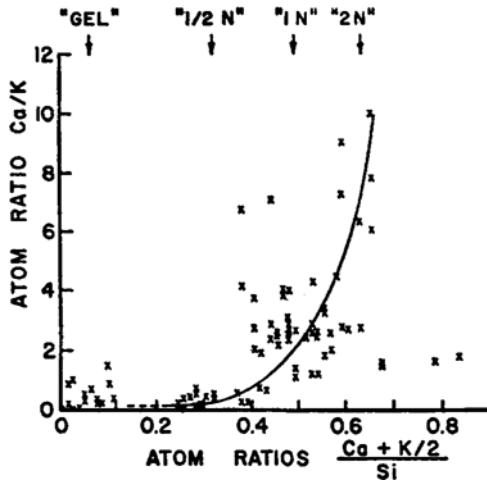

FIGURE 6.—Equilibria for mixture of synthetic beidellites.

is plotted againat the ratio of the total Ca and K to Si, i.e., against the apparent C.E.C. of the crystal. The readings should be expected to fall into three well-defined sets. However, they are far more scattered than was to be expected from readings on the monocationic end members of the beidellites. However, a general picture seems to emerge and three (or four if the material of very low C.E.C. is included) sets of readings can possibly be distinguished as indicated by the arrows in Fig. 6. The ratio of Ca to K seems to increase as the C.E.C. of the beidellite increases. Thus the beidellite with the higher surface charge has a greater affinity for Ca than the lower C.E.C. material. The percentages of the ion exchange positions filled by Ca in the three biedellites, 1/2 N, 1 N and 2 N, are 35, 70 and 75 per cent respectively. The corresponding values for K are 44, 14 and 6 per cent. Thus in this system some hydrolysis (about 20 per cent) has taken place. Also, it can be concluded that the greater the surface charge on the beidellite, the greater is the bonding energy.

CONCLUSIONS

In general, the bonding energies in clays are greater for divalent than for monovalent cations (Marshall, 1954) and the same probably holds for zeolites. Thus, in a suspension of two clay minerals, the material which accepts most of the calcium has the greater bonding energy for cations.

In the suspensions containing faujasite and bentonite, the Ca/K ratios are greater for faujasite than for bentonite. This is largely because the bentonite has a greater affinity for potassium over all the conditions studied, however, thus lowering the Ca/K ratio. The amount of calcium taken up by these two species is roughly comparable (Figs. 3 and 4). Of all the clay minerals, Arizona bentonite has perhaps the greatest bonding energies for both monovalent and divalent cations (Marshall, 1954) and the bonding energy for faujasite thus appears to be high and comparable to Arizona bentonite.

For the suspensions containing hectorite and Arizona bentonite, most of the calcium is contained in the bentonite which, therefore, has the higher bonding energies. In hectorite (trioctahedral) the charge is on the central octahedral layer whereas in Arizona bentonite (dioctahedral) the charge is partially on the octahedral and partially on the tetrahedral layers.

In the mixture of beidellites most of the calcium goes to the material with the higher charge density. Two possible factors which may influence bonding energies are the charge density, and the position of this charge in the tetrahedral or octahedral layer. Which factor is most important is an open question, but from the study of the biedellites, which all have the same structure with the charge on the silica layers, it can be said that the bonding energies are greater for the material with the greater charge density.

In all these systems studied, hydrolysis of the clay minerals and zeolites occurs and the hydronium ion plays an important part in determining the equilibrium. Measurements of the pH developed is probably necessary for a fuller understanding of the equilibria in these systems containing very low concentrations of salts in solution.

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