CATION-EXCHANGE CONSTANTS FOR CLAYS FROM ELECTROCHEMICAL MEASUREMENTS*

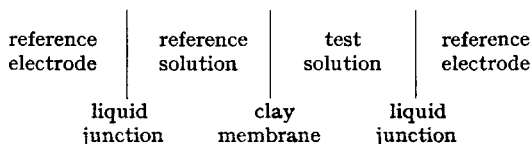*by*

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ABSTRACT

Ion exchange constants for various cations adsorbed on clays were determined using compacted-clay samples as membrane electrodes and theory for the membrane response of glass electrodes. The electrochemical cell used is conventionally written:

reference electrode	reference solution	test solution	reference electrode
liquid junction	clay membrane	liquid junction	

A static electrical potential is developed between the reference electrodes. The potential is a function of the cation species and of the cation activities in the two solutions and is given by an adaptation of the Nernst equation. From measurements of the electrical potential, the free energy of reactions or exchange constants for a series of reactions between various cation species were obtained. These determinations indicate that compacted clays prefer monovalent over divalent cations.

Some exchange constants were determined for the same clays in a non-compacted state. Not only the magnitude but also the order of cation selectivity changed for the same clay when determinations were made in the dispersed state and compared with those obtained by electrochemical means using compacted clay.

INTRODUCTION

THE exchange capacity and exchange constants of a clay are generally determined with the clay sample in a dispersed state. The purpose of this paper is to show that exchange constants may be determined for clay in a compacted state by making electrochemical measurements.

Exchange constants for compacted clay samples were obtained by utilizing the similarities of compacted clay cakes to glass electrodes. Above a certain compaction pressure, compacted clays behave as membrane electrodes. A static electrical potential is developed across a membrane

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electrode in response to the difference in chemical potential of cation species between two solutions in contact with, and on opposite sides of, the membrane. The potential is given by equations which have been developed for the response of glass electrodes. From these equations together with potential measurements, exchange constants were determined.

The results show that for clays in the compacted state monovalent cations are preferred over divalent. This is the reverse of the sequence generally reported for dispersed clay systems. It was also found that in the compacted state montmorillonite prefers Na^+ over H^+ but in a dispersed state H^+ is preferred over Na^+. These results indicate that a simple ion-exchange model to explain cation selectivity is inadequate; the physical state of the clay (and, hence, of the exchange site) apparently affects cation selectivity. Work is in progress to determine monovalent:divalent selectivity for the same clay in the dispersed and compacted states.

Previous Work and Acknowledgments

Many previous investigations of the use and theory of mineral electrodes have been made. In a series of papers C. E. Marshall and colleagues (1939, 1941, 1942a, b, c, d and 1948) discussed the preparation and theory of operation of zeolite and heat-treated clay electrodes. Wyllie (1948) measured a 59 mV potential across a shale which separated two solutions with a ten-fold difference in activity of NaCl.

This investigation was part of the author's doctoral dissertation (Hanshaw, 1962) conducted at Harvard University under the supervision of Professor Robert M. Garrels. The author gratefully acknowledges the advice, encouragement, and constructive criticism of Professors R. M. Garrels and Raymond Siever of the Department of Geological Sciences, Harvard University. He also wishes to thank Harold W. Olsen and William Back, U.S. Geological Survey, for their critical review and discussions of the manuscript.

THEORY

Origin of Potential

One theory of the response of a hydrogen-ion-sensitive glass electrode (Wright, 1959) is that the two surfaces of the glass behave as hydrogen electrodes whereas the interior glass framework acts simply as a high-resistance connector between the two surface phases. Eisenman (1962) suggests that the phase boundary potential of a glass electrode is caused by the cation species distributing itself between the glass phase and aqueous solution phase according to its chemical affinity for these two phases and that this therefore approximates an ion-exchange equilibrium. In like manner, the compacted clay is presumed to develop an electrical

potential owing to the tendency for ion exchange between the external solution and the surface of the clay. In fact, Eisenman (1962) suggests that the pores of a clay membrane may be crudely analogous to an intricately infolded glass–electrode surface.

When equilibrium of cations is achieved at a solution: clay interface then:

$$\mu^*_i = \overline{\mu^*}_i \tag{1}$$

where μ^*_i is the electrochemical potential of the ith cationic species in free solution and the barred quantity refers to the membrane phase. From this fundamental concept it is possible to show that when a cation-sensitive membrane separates two solutions which contain the same cation species at different activities the potential developed is given by:

$$E = C + \frac{RT}{z_i F} \ln \frac{a_{i\alpha}}{a_{i\beta}} \tag{2}$$

where E is the Volta or measured potential in millivolts, C is the collected asymmetry potential, R is the gas constant, T is temperature in °K, z_i is the valence of the ith cation species, F is the Faraday, and $a_{i\alpha}$ and $a_{i\beta}$ represent the activity of the ith cationic species in solutions α and β respectively. Equation (2) is the usual expression of the Nernst equation. It states that if compacted clay behaves as a membrane electrode it should exhibit a 59 mV change in potential for every ten-fold change of mono-valent cation activity in solution α if solution β is maintained at a constant reference composition.

Selectivity of Clays from Electrochemical Measurements

Several authors (Nikolskii, 1937; Eisenman *et al.*, 1957; Garrels *et al.*, 1962) have suggested that the response of a glass electrode may be represented by an ion-exchange reaction. It has been postulated that the potential of a clay membrane may be treated in an analogous manner. The following treatment is essentially that of Nikolskii (1937) and of Eisenman (1962) for glass electrodes that presumably behave as ion-exchange membranes.

Consider a membrane which initially has all its exchange sites filled with cation A^+. One side of the membrane is in contact with a reference solution of constant composition. If the other side of the membrane is put in contact with a solution which contains B^+ cations there will be a tendency for the exchange of ions between the solution and the membrane until equilibrium is attained. The reaction may be characterized by the expression:

$$A\overline{X} + B^+ = B\overline{X} + A^+ \tag{3}$$
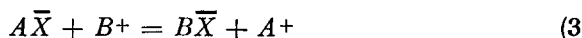
where $\overline{X}$ represents an exchange site with a charge of minus one. The equilibrium constant, K_{AB}, is:

$$K_{AB} = \frac{a_{BX} \ \ a_{A^+}}{a_{AX} \ \ a_{B^+}} \tag{4}$$

Walton (in Nachod, 1949) showed that the ratio of the activities of BX to AX fits the empirical expression:

$$\frac{a_{BX}}{a_{AX}} = \left(\frac{N_{BX}}{N_{AX}}\right)^q = \left(\frac{m_{BX}}{m_{AX}}\right)^q$$

where N represents the mole fraction of each species, m represents concentration, and q is an empirically derived number. For most ion exchangers, q lies between 0.8 and 2.0 (a few substances have a q as high as 5) whereas for clays, q commonly ranges between 0.8 and 1.1 (Walton, in Nachod, 1949). For glass electrodes in common use, q is generally between 0.85 and 1.3 although Eisenman (1962) reports q values for glasses as high as 5.

Using fundamental thermodynamic relationships Eisenman *et al.* (1957) showed that the electrical response of two monovalent cations competing for a glass electrode surface is given by the empirical equation:

$$E = C + \frac{RT}{F} \ln \ (a_{A^+}^{1/q} + K_{AB}^{1/q} \ a_{B^+}^{1/q})^q \tag{6}$$

For the case where q is unity, equation (6) reduces to Nikolskii's expression:

$$E = C + \frac{RT}{F} \ln \ (a_{A^+} + K_{AB} \ a_{B^+}) \tag{7}$$

Because q's for the clays used do not depart markedly from one, equation (7) was used in this study to characterize the electrode response of compacted clays to mixed electrolyte solutions.

Garrels *et al.* (1962) have shown that if the reaction for monovalent: divalent ion exchange is written as:

$$A_2\overline{X}_2 + B^{++} = BX_2 + 2A^+ \tag{8}$$
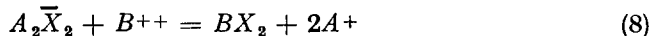
then using arguments similar to those of Eisenman *et al.* (1957) a membrane electrode that responds to both monovalent and divalent cations follows the expression:

$$E = C^1 + \frac{RT}{2F} \ln \ (a_{A^+}^{2/q} + K_{AB}^{1/q} \ a_{B^{++}}^{1/q})^q \tag{9}$$

When q is near unity the following expression may be used:

$$E = C^1 + \frac{RT}{2F} \ln \ (a_{A^+}^2 + K_{AB} \ a_{B^{++}}) \tag{10}$$

Under the same set of conditions various cation species do not have the same replacing power on an ion exchange substance. The sequence and magnitude of ease of substitution of one ionic species for another is termed

selectivity (also specificity or replaceability). The selectivity of a particular cation species on a clay may be determined from electrochemical measurements in either of the following manners: (1) By a comparison of the activity of the two cation species at the same Volta potential measured separately against the same reference solution or ; (2) by the titration of a solution which contains one cation species with a second cation species.

From the Nernst relationship (equation (2)) we see that if the solution on one side of the membrane is a reference solution of constant composition then equation (2) reduces to:

$$E = C + \frac{RT}{F} \ln a_{A^+} \tag{11}$$

In equation (7) if $a_{B^+} = 0$ then the expression reduces to equation (11) also. Equation (11) represents the change of e.m.f. with change of activity of a cation species in the test solution. A different activity of B^+ is generally required to achieve the same static electrical potential as a given amount of A^+ (with respect to the same reference solution). The constant difference between the amount of A^+ and B^+ needed to achieve the same electrical potential is given by:

$$K_{AB} = \frac{a_{A^+}}{a_{B^+}} \tag{12}$$

Eisenman (1962) has shown that K_{AB} is a thermodynamic equilibrium constant (exchange constant). It follows from equation (12) that if K_{AB} is less than one then the membrane prefers A^+ over B^+ by that amount. That is, it would require less a_{A^+} than a_{B^+} in a test solution to attain the same potential. Eisenman (1962) calculates K_{AB} by a comparison of the potentials developed by the same activity of each cation species in separate test solutions. An alternate approach is to compare activities required to achieve the same potential. The latter method and equation (12) were used in this study to calculate selectivity between monovalent: monovalent or divalent: divalent cation species. The comparison may be made accurately only where both slopes are ideal (i.e. Nernst).

Similarly, the exchange constant for monovalent: divalent comparison at the same potential is given by:

$$a_{A^+}^2 = K_{AB} \, a_{B^{++}} \tag{13}$$

When $K_{AB} = 1$ (i.e., when the exchanger is not selective toward either species) then $a^2_{A^+} = a_{B^{++}}$. The exponential 2 is significant because it means that in solutions less concentrated than 1 M the contribution of the monovalent ion to the e.m.f. is much less than the divalent ion contribution when $a_{A^+} = a_{B^{++}}$. In solutions more concentrated than 1 M when $a_{A^+} = a_{B^{++}}$, then the exchanger will be largely occupied by A^+.

Much confusion has arisen in the literature concerning the effect of concentration and valency on the exchange constant. Govindan and

Krishnaswamy (1958) state that in concentrated solutions of monovalent A^+ and divalent B^{++} cations present at the same concentration a certain resin is more selective to A^+, whereas in dilute (0.05 N) the resin prefers the B^{++} ion. These authors suggest that the value of the equilibrium "constant" is not constant but is concentration-dependent. This is not necessarily the case; the problem can be resolved by an examination of equation (13) which shows that upon dilution a_A^2+ decreases much more rapidly than a_B++. Thus the results reported by Govindan and Krishnaswamy are predicted by equation (13) provided that K is constant.

Eisenman (1962) has pointed out that the relation among selectivity constants is given by:

$$K_{AB} = \frac{K_{CB}}{K_{CA}} \tag{14}$$

Equation (14) may be used to cross-check individual exchange constants or to calculate new ones without doing the experimental work.

EXPERIMENTAL EQUIPMENT AND METHODS

Apparatus

A clay compaction press was built capable of compacting samples to 5000 psi and, while a load was maintained, electrochemical properties of solutions placed in contact with the two sides of the clay sample were measured. The equipment was designed in such a way that the solutions on opposite sides are electrically insulated from each other. A system of filters was required that would inhibit the flowage of clay at high pressure and yet allow for easy passage of solvent and solute. These requirements resulted in the apparatus shown schematically in Fig. 1.

As shown in Fig. 1 both the hydraulic piston and the confining steel cylinder are insulated from the stand which holds the apparatus. The confining cylinder is fitted with a Nylatron GS liner (The Polymer Corp. of Penn., Reading, Penn.) on top of which is attached a lucite solution container. The detachable piston head is perforated with 0.050 in. diameter holes for passage of solution. The bottom-nut screws onto the outside of the confining cylinder and is made of stainless steel as is the piston head, piston, and filter retainer ring which are the only parts of the apparatus other than plastic to touch solutions. The steel bottom-nut contains a series of 0.050 in. diameter holes over which is placed successively a coarse (0.016 in. holes) perforated metal disc, a fine (0.0015 in. holes) perforated metal disc (both obtained from Perforated Products, Inc., Boston, Mass.) and a Millipore filter (pore size = 1.20 microns, Millipore Filter Corp., Bedford, Mass.). The perforated metal discs provide mechanical strength for the fragile Millipore filter. All three filters are attached to the bottom-
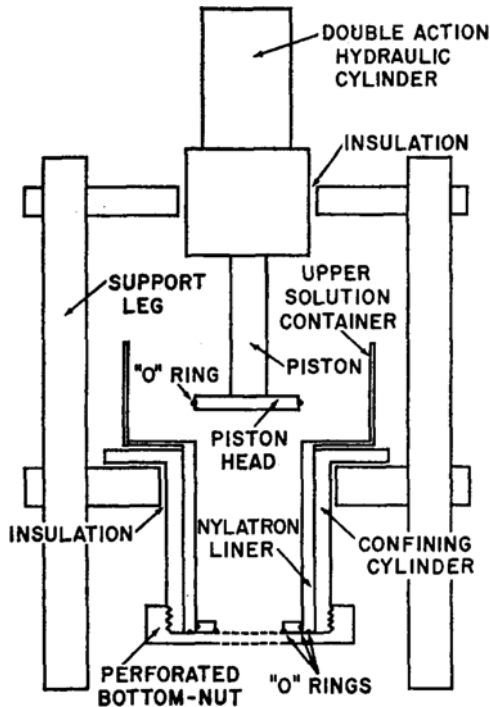
FIGURE 1.—Cutaway diagram of compaction press.

nut by means of a stainless steel retainer ring. For perfect fluid seals, "O"-rings are used as indicated in Fig. 1. The same series of filters is used just below the permeable piston head (i.e., Millipore filter next to the clay sample).

Experimental Procedure

Clay samples.—Two clays were used throughout the study: (1) A montmorillonite provided by the National Lead Co. of Texas and, (2) an illite. API standard No. 7. Prior to being used in the squeezer the dispersed clays were put into a sodium form by conventional means.

Loading the press.—After the perforated screens and Millipore filter had been secured to the bottom-nut the nut was screwed tightly to the confining cylinder. Approximately 10 g of clay paste was placed in the cylinder and then a Millipore filter, fine screen and coarse screen were put in the cylinder in that order. The perforated piston head was placed over the top of the cylinder and the clay was then compacted to the desired

pressure by means of a Blackhawk hydraulic pump fitted with a pressure gauge. The compacted clay cake was approximately 1 cm thick.

Electrochemical measurements.—In Fig. 2 the direct analogy between a glass electrode and a clay membrane electrode is shown. The compaction
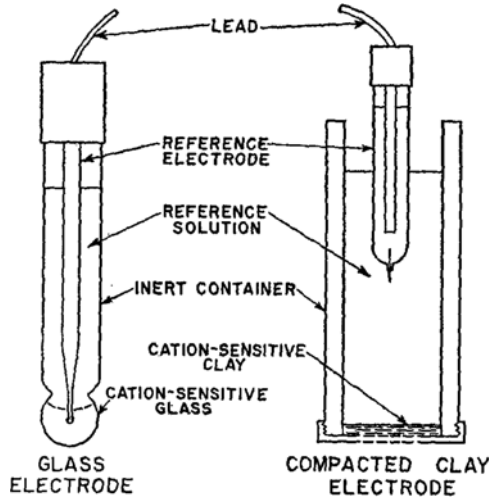

FIGURE 2.—Analogy between glass electrode and compacted clay membrane electrode.

press, when loaded with a sample of compacted clay, becomes a clay membrane electrode. A reference solution (0.1 M NaCl) is placed in the upper solution container and a test solution is put in contact with the lower side of the clay membrane. Electric stirrers keep the solution in each container well mixed. A saturated calomel reference electrode is placed in each solution. The electrochemical cell thus obtained is conventionally written:

reference electrode	reference solution	test solution	reference electrode
liquid junction	clay membrane	liquid junction	
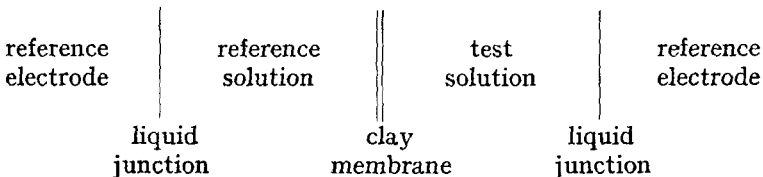
Reading from the left, the reference electrode, reference solution, and clay membrane are analogous to a glass electrode (see Fig. 2); the right-hand reference electrode is the other half of the cell, identical to the reference electrode normally used with a glass electrode. The leads from the two reference electrodes were connected to a Keithley Electrometer. Figure 3 shows the experimental set-up diagrammatically. The bias potential is

used to balance the potential developed across the clay membrane in order to use the electrometer as a null detector thus making use of its most sensitive scale.
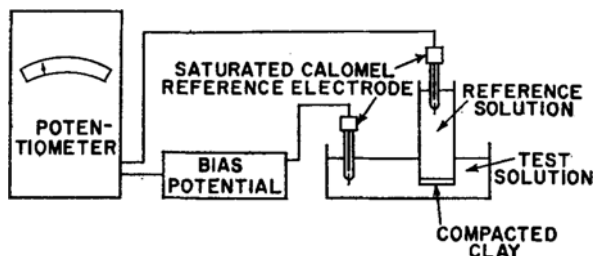

FIGURE 3.—Schematic diagram of experimental equipment.

Temperature variations.—No attempt was made to control temperature variations of the equipment during this investigation. Diurnal variations are slight and the seasonal range of temperature in the laboratory varies from 22° to 30°C. When values for R, T, and F are substituted into the Nernst equation, at 25°C the RT/F portion is equal to 59; at 22°C it is 58.4 and at 30°C it is 60. These values represent the slope of the Nernst equation when E is plotted against log a_i. The slight departure from the slope at 25°C is within the limit of experimental accuracy.

Electrochemical measurements.—The one measurement basic to an interpretation of the electrode response of a compacted clay cake is the rate of change of electrical potential with change of cation activity in the test solution. Thus membrane response may be defined as $(\delta E/\delta pJ)_{T,P}$ where E is the potential and $pJ = -\log a_J$ (a_J is the activity of cation species J in the test solution). This fundamental measurement was made for the clay samples at different compaction pressures and with various cations and anions in the test solution.

A small asymmetry potential was commonly measured across the compacted clay when identical solutions were on either side. The same effect is commonly observed with glass electrodes. No attempt is made to explain its origin.

EXPERIMENTAL RESULTS

Effect of Pressure on Membrane Response

In order to examine the effect of pressure on membrane response a sample of clay was compacted to some predetermined pressure; when the cation activity in the test solution was changed, the slope of the membrane response, $(\delta E/\delta pJ)_{T,P}$, was determined at that compaction pressure.

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A family of curves for $(\delta E/\delta p\mathrm{Na})_{T,P}$ at various pressures is plotted in Fig. 4 for illite. As the compaction pressure is increased the response approaches the ideal (Nernst) response of 59 mV potential change for a ten-fold change in Na^+ activity in the test solution. At some pressure
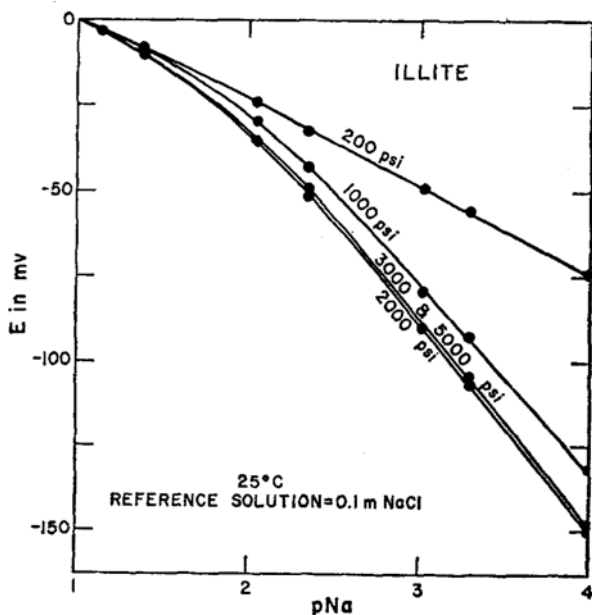

FIGURE 4.—Effect of compaction pressure on membrane response of Na-illite.

between 1000 and 2000 psi the slope becomes ideal at activities of Na^+ less than 0.01 M. For ease of comparison the asymmetry potential is reduced to zero by adding a numerical quantity of equal magnitude but opposite sign to the asymmetry potential. Therefore, all curves pass through zero potential at an activity of Na^+ of 0.1 M in the test solution. Montmorillonite responded ideally at a slightly lower pressure than illite presumably owing to the higher exchange capacity of montmorillonite.

Even at high pressure the membrane response or slope decreases with increasing Na^+ activity (Fig. 4). This phenomenon is caused by ionic leakage at high ionic strength and will be discussed more fully below.

Effect of Anion Species on Membrane Response

A sample of illite was compacted to 5000 psi and a 0.1 M NaCl reference solution was placed in the upper solution chamber. Test solutions containing a single sodium compound at various activities were prepared.

The compounds used were NaCl, NaNO$_3$, Na$_2$SO$_4$, and NaOH. The results (Fig. 5) indicate that the sodium response of the clay is essentially independent of anionic species in the test solution. All curves were corrected to zero potential at a Na$^+$ activity of 0.1 M. The slight difference between the four curves is probably within the limit of experimental error.
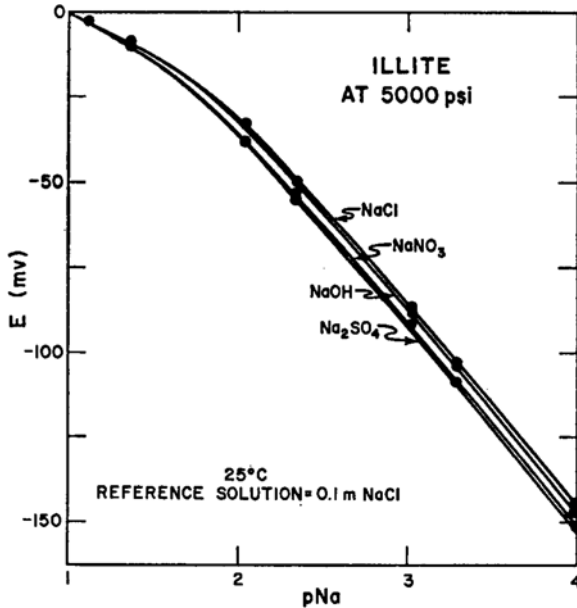

FIGURE 5.—Effect of anion species on membrane response as function of Na+ activity.

Effect of Cation Species and Concentration of Test Solution on Membrane Response

Test solutions of various activities of a cationic species were put in contact with the lower membrane surface and the potential was measured. The chloride salt of each cation was used. These experiments were done with only one cation species in the test solution at a time. The results, using illite compacted at 5000 psi, are shown in Fig. 6 (Na$^+$ and K$^+$), Fig. 7 (Ca^{++}), and Fig. 8 (Mg^{++}). Membrane response to hydrogen ion was investigated but it was found that the potential was not stable, expecially at low pH.

The membrane electrode response of montmorillonite was investigated in like manner. Results are plotted as the solid curve on Fig. 9 (Na$^+$ and K$^+$), Fig. 10 (H$^+$), Fig. 11 (Ca^{++}), and Fig. 12 (Mg^{++}). With H$^+$, a stable potential was developed when the pH was greater than 2.8; at lower pH the potential was not stable.
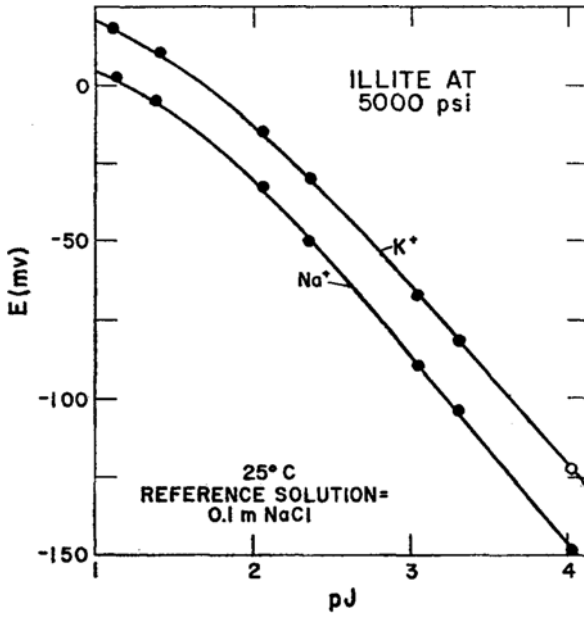
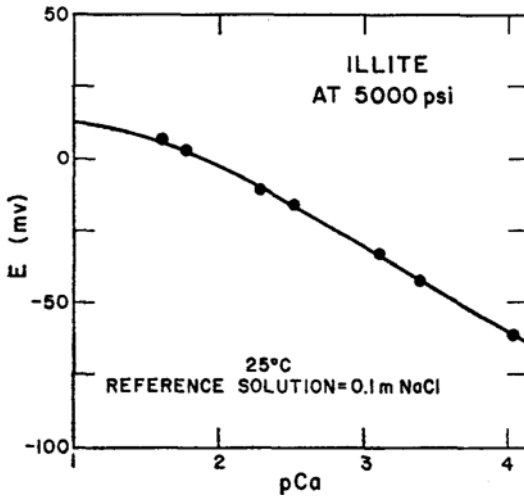FIGURE 6.—Membrane response of compacted illite to changes of Na+ or K+ activity in test solution.

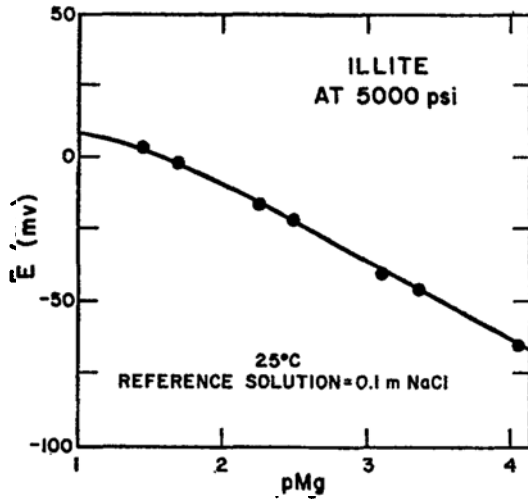FIGURE 7.—Membrane response of compacted illite to change of Ca++ activity in test solution.

FIGURE 8.—Membrane response of compacted illite to change of Mg++ activity in test solution.

FIGURE 9.—Membrane response of compacted montmorillonite to changes of Na+ or K+ activity in test solution.

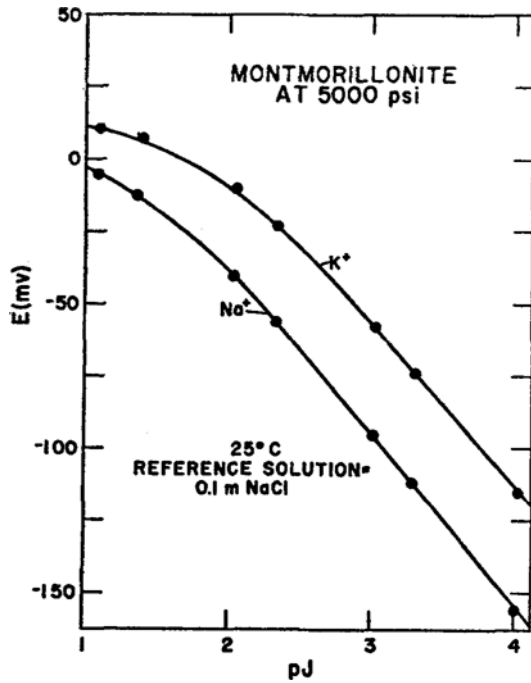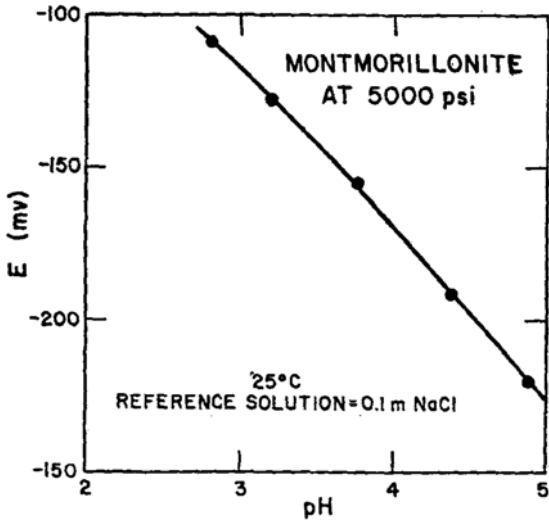FIGURE 10.—Membrane response of compacted montmorillonite to change of H^+ activity in test solution.
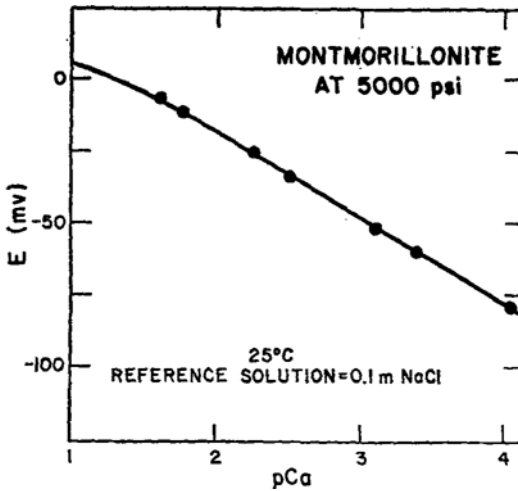

FIGURE 11.—Membrane response of compacted montmorillonite to change of Ca^{++} activity in test solution.
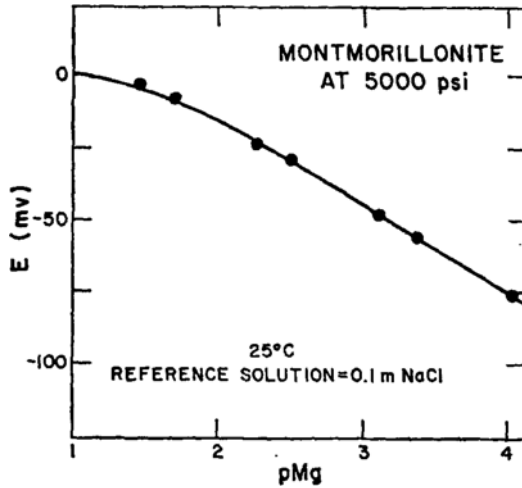
FIGURE 12.—Membrane response of compacted montmorillonite to change of Mg^{++} activity in test solution.

Test solutions with a pJ greater than 4 were not used because of the difficulty of reproducing solutions of low concentration. Also, when monovalent cations were used, it was observed that H$^+$ present in the water used to make up the test solutions interfered with the membrane response to the monovalent cation when pJ was greater than 4.

Decrease in membrane response.—Various workers have noted that in test solutions more concentrated than about 0.1 N the measured potential is less than predicted by the Nernst equation. This decrease in membrane response indicates ionic leakage into and across the membrane at high ionic strength. Similar results were noted during the present investigation.

In Figs. 6 through 12 the slope is not constant but decreases when test solutions in which cation activities are more concentrated than about 0.01 M are used. The reason for the slope decrease is qualitatively apparent from an inspection of the mathematical expression of the Teorell–Meyer–Siever theory:

$$\overline{m}_j = -\frac{\overline{X}_-}{2} + \sqrt{\frac{X^2_-}{4} + \frac{a^2_\pm}{\gamma^2_\pm}} \tag{15}$$

where $\overline{m}_j$ is the concentration of anion species j in the membrane pore, X_- is the moles of negative sites per liter of pore volume (related to the ion-exchange capacity), $a_\pm$ is the mean activity of a dissolved salt, and $\gamma_\pm$ is the mean activity coefficient of that salt in the pores of the membrane. Equation (15) shows that as the concentration of the solution outside the membrane is increased, the concentration of anions admitted into the

micellar solution increases almost twice as rapidly. Thus at very low external ionic strength anions are essentially restricted from the membrane; the transport number of anions in the membrane approaches zero. However, anions are not excluded from the membrane at high external concentration according to the TMS theory, and both cations and anions diffuse across the membrane. In other words, the membrane leaks. Apparently the key factor controlling anion leakage (and, therefore, membrane response) is the concentration of anions within the membrane micellar solution.

Selectivity of Compacted Clays

The sequence of selectivity or order of preference of a compacted clay for a number of cationic species was determined in two ways. The simplest method is to compare the curves of e.m.f. vs. pJ. An alternate method is to titrate a test solution which initially contains only one cation species with known amounts of a second cation species and observe the change of potential as the activity of the second cation is increased.

Selectivity by comparison of activities.—In general, different cation species in separate test solutions will not produce the same electrical potential when the two species have the same activity. In other words, when compared to the same reference solution, different activities of two

TABLE 1.—EXCHANGE CONSTANTS FOR ILLITE COMPACTED AT 5000 PSI

Exchange Reaction	Column A	Column B	Column C		Column D
	K from comparison of activities at same emf (Figs. 6–8)	K from electro-chemical titrations (per (Figs. 13, 14)	q near initial solution response	q near titrant ion response	Comparison of K's by equation (14)
Monovalent: monovalent					
$Na\overline{X}+K^+$	2.5	2.8	0.7	0.9	2.5
$Na\overline{X}+H^+$	—	0.22	0.9	0.8	0.25
$H\overline{X}+K^+$	—	11.2	0.9	0.8	12.7
Divalent: monovalent					12.6
$Ca\overline{X}_2+2\,Na^+$	12.6	12.6	0.9	0.9	79
$Ca\overline{X}_2+2\,K^+$	79	—	—	—	99
Divalent: divalent					
$Ca\overline{X}_2+Mg^{++}$	0.63	0.63	0.8	0.9	—

cation species in the two test solutions are required to achieve the same electrical potential. The exchange constant for theoretical reaction between the two species and the clay can be obtained by comparing the cation activities necessary to achieve the same potential. For the determination of monovalent:monovalent or divalent:divalent cation exchange constants equation (12) was used; equation (13) was used to determine monovalent:divalent exchange constants. Values for the exchange constants calculated in this manner from Figs. 6 through 12 are recorded in column A of Table 1 for illite and column A of Table 2 for montmorillonite.

As an example, Fig. 6 shows that to achieve a potential of 100 mV pNa must be 3.25 in the test solution whereas a pK of only 3.65 is required in a separate test solution of K^+ to attain the same potential. From equation (12) pK_{NaK} is 0.4 or K_{NaK} is 2.5 (see Table 1, column A).

TABLE 2.—EXCHANGE CONSTANTS FOR MONTMORILLONITE
COMPACTED AT 5000 PSI

Exchange Reaction	Column A	Column B	Column C		Column D
	K from comparison of activities at same emf (Figs. 9–12)	K from electro-chemical titrations (per Figs. 13, 14)	q near initial solution response	q near titrant ion response	Comparison of K's by equation (14)
Monovalent: monovalent					
$Na\overline{X}+K+$	4.7	5.0	0.7	0.7	5.0
$Na\overline{X}+H+$	0.56	0.5	0.7	0.7	0.53
$H\overline{X}+K+$	8.9	8.9	0.9	0.8	8.4
Divalent: monovalent					
$Ca\overline{X}_2+2\,Na+$	40	40	1.1	0.8	32
$Ca\overline{X}_2+2\,K+$	630	795	1.1	0.8	800
					1000
$Ca\overline{X}_2+2\,H+$	5	—	—	—	—
Divalent: divalent					
$Ca\overline{X}_2+Mg++$	1.3	1.4	0.8	0.8	—

Selectivity by titration.—The second method for the electrochemical determination of exchange constants involves the presence of two cation species in the test solution at the same time. The membrane electrode is first put in contact with a test solution containing a single cation species at a known activity. A static electrical potential is thus developed. The test solution is then titrated with a second cation species; the potential

increases with changing slope as the titration continues until the activity of titrant becomes large enough so that the electrode responds only to the titrant cation.

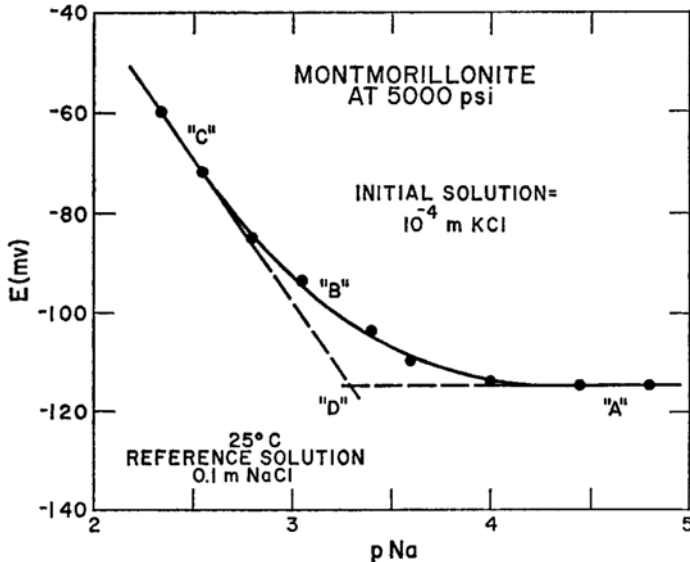Figure 13 is a typical curve obtained in this manner for montmorillonite

FIGURE 13.—Membrane response of compacted montmorillonite upon titration of NaCl solution into a test solution initially containing 10^{-4} M KCl.

compacted at 5000 psi. That portion of the curve marked "A" represents the stable potential for a 10^{-} M K^+ solution. The "B" portion of the curve corresponds to a mixed electrode response characterized by equation (6) where $q = 0.7$. The "C" part of the curve represents the membrane response to Na^+ only. If this part of the curve is projected to its intersection with the extension of the "A" part, the point of intersection, "D", is the theoretical point where the electrode is occupied equally by each cation species. The exchange constant may be determined directly from equation (12).

Figure 14 represents a monovalent:divalent exchange reaction. The value of q (equation 9) is not constant for the mixed-ion response portion of the curve but varies from 1.1 near that portion where the exchanger is largely occupied by Ca^{++} to 0.8 where K^+ is the predominant ion on the exchanger . The exchange constant is determined in a manner analogous to that outlined above by using equation (13).

Exchange constants determined by titration are reported in column B of Table 1 for illite and column B of Table 2 for montmorillonite. In
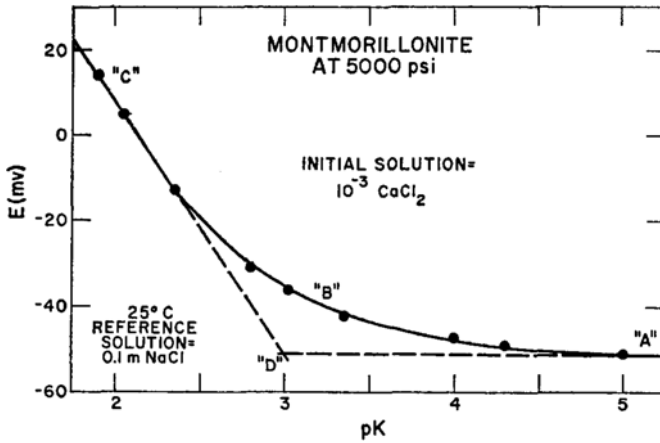
FIGURE 14.—Membrane response of compacted montmorillonite upon titration of KCl solution into a test solution initially containing 10^{-3} M CaCl$_2$.

column C of these tables is listed the q determined for each end of the mixed-ion response portion of the titration (see "B" portion of curves on Figs. 13 and 14). The experimental data for the determinations of selectivity are presented in Tables 3 (illite) and 4 (montmorillonite). A comparison of column A and B in either Table 1 or 2 indicates that the two methods of determining selectivity are essentially in agreement. Column D,

TABLE 3.—EXPERIMENTAL DATA ON ELECTROCHEMICAL DETERMINATION OF SPECIFICITY OF ILLITE COMPACTED AT 5000 PSI

Initial solution pK=3.02 E= −63 mV		Initial solution pH=3.0 E= −124 mV		Initial solution pH=3.0 E= −126 mV		Initial solution pCa=4.0 E= −59 mV		Initial solution pCa=3.1 E= −32 mV	
pNa	E in mV	pNa	E in mV	pK	E in mV	pNa	E in mV	pMg	E in mV
5.0	−63	5.0	−123	5.0	−124	5.0	−59	4.35	−32
4.4	−63	4.45	−121	4.4	−119	4.30	−59	4	−32
4.0	−63	4.0	−116	4.0	−112	4.0	−58	3.85	−31
3.6	−62	3.55	−106	3.75	−104	3.35	−54	3.45	−30
3.4	−61	3.3	−97	3.55	−94	3.05	−50	3.10	−27
2.8	−56	3.05	−87	3.02	−67	2.7	−44	2.5	−18
2.35	−45	2.9	−79			2.35	−35	2.25	−13
2.05	−34	2.55	−59			2.05	−24	1.9	−5
1.9	−28					1.7	−8	1.7	+1
1.7	−15					1.45	+1		
1.45	−5								

TABLE 4.—EXPERIMENTAL DATA ON ELECTROCHEMICAL DETERMINATION OF
SPECIFICITY OF MONTMORILLONITE COMPACTED AT 5000 PSI

| Initial solution pK=4 $E=-115$ mV		Initial solution pH=4 $E=-168$ mV		Initial solution pH=3 $E=-118$ mV		Initial solution pCa=3.1 $E=-52$ mV		Initial solution pCa=3.1 $E=-51$ mV		Initial solution pCa=3.1 $E=-52$ mV	
pNa	E in mV	pNa	E in mV	pK	E in mV	pNa	E in mV	pK	E in mV	pMg	E in mV
4.8	−115	5.0	−166	5.0	−118	5.0	−52	5.0	−51	4.5	−52
4.45	−115	4.8	−164	4.4	−113	4.45	−52	4.3	−49	4.0	−51
4.0	−114	4.45	−160	4.0	−106	4.0	−51	4.0	−47	3.85	−50
3.6	−110	4.0	−148	3.8	−102	3.6	−50	3.35	−42	3.45	−47
3.4	−104	3.8	−138	3.55	−93	3.05	−46	3.02	−36	3.1	−42
3.05	−94	3.6	−127	3.3	−80	2.8	−44	2.8	−31	2.7	−36
2.8	−85	3.4	−117	3.02	−62	2.55	−40	2.35	−13	2.5	−31
2.55	−72					2.35	−35	2.05	+5	2.25	−26
2.35	−60					2.05	−26	1.9	+14		
						1.7	−13				
						1.45	−4				

Tables 1 and 2, shows a range of selectivity constants calculated using equation (14). Constants calculated from equation (14) are in fair agreement with those obtained from experiments and serve as a check on the accuracy of experimental work.

Table 1 indicates that compacted illite prefers in the following order, the cations which were studied:

$$K^+ > Na^+ > H^+ > Ca^+ \geq Mg^+$$
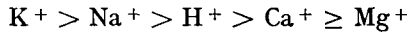
For compacted montmorillonite, Table 2 shows the selectivity of cations to be:

$$K^+ > Na^+ > H^+ > Mg^{++} \simeq Ca^{++}$$
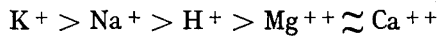
R. M. Garrels (written communication) has been studying the selectivity of silicate electrodes (micas and feldspars) and reports a sequence of selectivity which is in essential agreement with the compacted clay results. Part of his sequence is:

$$H^+ > K^+ > Na^+ > Ca^{++} > Mg^{++}$$
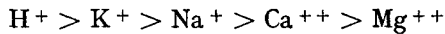
Garrels also reports that hydrogen ion acts strangely with these electrodes. too. In all probability, at low pH, H^+ reacts chemically with tektosilicates, micas, or clays rather than undergoing a simple ion-exchange reaction.

Significance and determination of q.—The quantity q in equations (5), (6) and (9) is directly analogous to an activity coefficient; that is, it records the deviation of a solution from ideality. If q is unity then the solution is ideal. If q is not equal to one but is constant during a reaction then the solution is termed regular; if q varies during a reaction then the solution is termed non-regular.

When an ion exchange substance reacts with two cation species, A^+ and B^+, in an aqueous solution then the exchange material may be considered a binary solid solution with pure end members $A\overline{X}$ and $B\overline{X}$. If the solid solution is non-ideal then values of q will be needed to describe precisely the experimental results.

Values for q were determined experimentally by solving equations (6) and (9) for a variety of q's and fitting the experimental curves to the calculated ones. Column C of Tables 1 and 2 indicate that during many titration reactions q varies by as much as 0.3. This indicates that the membrane electrode is reacting as a non-regular solid solution. However, the exchange constants determined in the two ways as described in the preceding sections above are in good agreement. It would seem, therefore, that the non-regular behavior of the clay toward two cations present at the same time does not adversely affect the results.

Potential Developed for a Mixed Electrolyte Solution

Equations have been developed (Garrels *et al.*, 1962) to describe the

response of a membrane electrode to several cation species of different charge. If we take the ideal case where q is unity then the general equation for a mixture of n species of monovalent and divalent cations takes the general form (modified after Garrels *et al.*, 1962):

$$E_{A\cdots J} = C_A + \frac{RT}{2F} \ln \sum_{J=A}^{n} \left(K_{AJ} \, a_{J}z_{+} \right)^{2/z} \tag{16}$$

where J is any cation from A to n. For a solution containing Na$^+$, K$^+$, and Ca^{++} equation (16) becomes:

$$E_{NaKCa} = C_{Na} + 29.5 \log \left(a^2_{Na^+} + K^2_{NaK} \, a^2_{K^+} + K_{NaCa} \, a_{Ca^{++}} \right) \tag{17}$$

To test this expression a solution which contained 10^{-3} M Na$^+$, K$^+$, and Ca^{++} was put in contact with a montmorillonite membrane compacted at 5000 psi. The reference solution was 0.1 M NaCl. From Table 2, column A, the value of K^2_{NaK} is 22 and the value of K_{NaCa} is 0.025; the value of C_{Na} is $59 \times 3 - 95 = +82$ mV. Putting these values into equation (17) and solving for E gives $E = -49$ mV. The e.m.f. measured experimentally was -53 mV. The agreement with theory is excellent when we consider that the assumption was made that q is unity; from column C, Table 2 we see that q is not unity for the reactions considered. Also it is not strictly correct to assume that K_{NaK} is independent of the presence of Ca^{++} or that K_{NaCa} is independent of K$^+$ under conditions where q is not unity.

It should be borne in mind that K$^+$ provides most of the e.m.f. measured; Ca^{++} provides about one-twentieth of the response and Na$^+$ a negligble amount. A better test of equation (16) would be to use a test solution of such composition that the contribution of each ionic species to the e.m.f. is approximately the same.

Selectivity of Clays in Dispersed State

As pointed out by Eisenman (1962) a glass may be discerning for a particular cation species owing to the "anionic field strength" of the negative sites within the glass framework. Although the sequence of selectivity is controlled by this parameter, the magnitude of the selectivity is controlled by the number of water molecules in the vicinity of a negative-site: cation interaction. The magnitude of the exchange constant decreases as the number of water molecules increases. Walton (in Nachod, 1949) has pointed out a similar characteristic of cation-exchange resins and clays, i.e. the membrane pore is a highly aqueous or water swollen environment and the more hydrated the environment the less an exchanger will distinguish among species.

From the above discussion we would predict that the order of selectivity should remain constant regardless of the physical state of the exchanger but that the more aqueous the environment the less the magnitude of

selectivity. To test this hypothesis the selectivity of montmorillonite in a dispersed form was studied.

Montmorillonite was put in a sodium form and a weighed amount of the dried clay was put into a measured volume of water; aliquots of KCl were added to the clay suspension. The amount of Na^+ released into solution was determined after addition of K^+. When Na^+ release became insigni-cant it was assumed that all the exchange sites were occupied by K^+. The selectivity is the ratio of the activity of K^+ to Na^+ in solution when half of the Na^+ has been released from the exchanger. The selectivity determined in this manner is 1.2 which indicates that dispersed montmorillonite prefers K^+ over Na^+ to a lesser extent than does compacted montmorillonite.

If the same experiment is run using H^+ rather than K^+ as the titrant the exchange constant indicates that H^+ is preferred over Na^+. The results of these two experiments indicate that not only the magnitude but also the order of selectivity is dependent upon the environment in which the experiments are done.

A change in *magnitude* of the exchange constant is predicted by Eisenman and Walton when the physical environment of reaction is modified but a change of order is not predicted. The reasons why the same clay prefers Na^+ over H^+ in a compacted state and H^+ over Na^+ in a dispersed state are not known. The results of these series of experi-ments indicate that the environment of exchange reactions must be clearly stated whenever such work is reported. The results also seem to indicate that a simple ion-exchange model to explain cation selectivity is inadequate.

Laboratory work is in progress to clarify further the effect of physical state on the selectivity of clays.

SUMMARY

Compacted clay cakes behave as membrane electrodes at high compac-tion pressure and low ionic strength of test solution. Experimental evidence shows that under these conditions the Nernst equation is obeyed. Failure of the membrane electrodes at low pressures and/or high ionic strength is consistent with the TMS theory and the concept of anionic transport through the membrane under these conditions.

Exchange constants of compacted clays were determined in two ways. The results of the two methods are in essential agreement and indicate that the compacted clays show some selectivity for monovalent cations over divalent; the exchange constant for exchange between one cation species and the next most preferred species is not large.

The validity of the electrochemically determined exchange constants is further established by the fact that the calculated and experimentally measured electrical potential were in excellent agreement for a three

cation solution. The fact that Garrels reports monovalent over divalent cation preference for silicate electrodes lends further credence to these results. Whereas glass electrodes can be made which exhibit a high degree of selectivity for a particular cation species, the clay membranes studied so far are not highly specific.

Exchange constants were determined for the montmorillonite in a dispersed state. In the compacted state montmorillonite prefers Na$^+$ over H$^+$ whereas in the dispersed state the order is reversed. This reversal requires further study. In a monovalent:divalent exchange, because the activity of the monovalent cation is squared, the divalent ion will be the prevalent species on the clay if the concentrations of the two species are low, provided that the exchange constant is not large. If the concentration of the two species is increased by the same amount or if the exchange constant is very large, then the monovalent cations may be the prevalent species on the exchanger. This investigation has demonstrated that the order of selectivity can vary according to the state of the system. This fact should be taken into account when studies are made of the exchange constants of clays.

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