POTENTIOMETRIC, ELECTRICAL CONDUCTANCE AND SELF–DIFFUSION MEASUREMENTS IN CLAY–WATER SYSTEMS*

by

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ABSTRACT

Potentiometric measurements using commercially available cationic glass electrodes, electrical conductance and self-diffusion measurements of cations and water were made in electrolyte-free 3–5 per cent Li, Na, K, Cs, Ca and Sr bentonite–water systems and bi-ionic systems with varying ratios of K and Ca. Activation energies for conductance in the homoionic clays were calculated using the Arrhenius equation.

The agreement between cation mobilities measured by diffusion and conductance indicates that the underlying mechanism is essentially the same for the two processes. But the activation energies for ion movement determined for conductance measurements do not explain the observed reduction in mobility. Only two clays, Li and Cs, gave values significantly higher than for the measured solution conductance and only the Cs clay gave a value higher than those calculated for ion conductance at infinite dilution.

Increasing Ca saturation in K-Ca clays from 1 to 99 per cent increased the self-diffusion coefficient or mobility of K by a factor of about 1.7 and Ca by a factor of about 30 reflecting the effect of the predominate accumulation of the divalent cation in regions of highest negative potential. The reduction in activity of monovalent cations calculated from the potentiometric measurements, although of the same order of magnitude, was consistently less than the corresponding reduction in mobility in both the homoionic and bi-ionic clays. This difference became greater with increasing mobility of K in the bi-ionic clays.

INTRODUCTION

THE energy of activation for ion movement which may be regarded as the magnitude of the energy barrier an ion must surmount in going from one position to the next (Oster and Low, 1963; Glasstone, Laidler and Eyring, 1941, p.518) has been used to evaluate the factors involved in determining cation mobilities in clays (Lai and Mortland, 1961, 1962;

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Oster and Low, 1963; Dutt and Low, 1961; Low, 1962). Since our technique for determining diffusion coefficients is not well suited for temperature-dependence measurements, the activation energies for cation movement in homoionic clays have been determined from electrical conductance measurements. Diffusion and electrical conductance measurements were made in homoionic and bi-ionic clays to establish that the relationship (Spiegler and Coryell, 1953)

$$D = \frac{1000 \ kRT}{c \ Z \ F^2} \tag{1}$$

holds indicating that the underlying mechanism is the same for the two processes. In equation (1) D is the diffusion coefficient, k the specific conductance and the rest of the symbols have their usual meaning.

Self-diffusion of water and e.m.f.'s using cationic glass electrodes were measured to obtain additional information about the processes controlling cation movement and of the expected variations as the cation species is varied.

EXPERIMENTAL PROCEDURE

Preparation of the Clay

The $<0.2\mu$ fraction of bentonite was separated from a sample of Volclay obtained from the American Colloid Company. A 0.4 per cent suspension was passed through an OH^- saturated amberlite 1RA–400 anion exchange column. The clay was then passed through an H^+ saturated Dowex–50 cation exchange column and saturated with the desired cation by passing it directly into a similar column saturated with the appropriate cation. It was then run through a recharged cation saturated column to assure complete conversion to the desired form and concentrated using Pasteur–Chamberlain filter candles. This method kept the clay in the acid form only a few hours and assured only one equivalence of the counter ion on the clay. The cation saturation was determined experimentally to be 90 ± 2 meq per 100 g for all cations studied and the pH of the concentrated clay (4–6 per cent by volume) was about 5.0–5.5. The homoionic clays were diluted to the desired concentration with distilled water. The bi-ionic clays were prepared by mixing the appropriate amounts of the two clays and diluting with distilled water.

Determination of Diffusion Coefficients

The method of determining the self-diffusion coefficient has been described previously (Bloksma, 1957; Gast, 1962). Determinations were made at five different time intervals using five repetitions for each determination

for all cations except K which was limited to four time intervals due to the short half-life of the isotope. Thus twenty observations were used in calculating the K diffusion coefficients and twenty-five for all others. Diffusion coefficients of K and Ca in the bi-ionic clays were determined simultaneously using K^{42} and Ca^{45}. Tritium was used for measuring self-diffusion rates of water.

Potentiometric Measurements

Potentiometric measurements were made using the Beckman 38137 Cationic Electrode in conjunction with a saturated calomel electrode with fiber junction. The e.m.f.'s were determined using a Beckman Model 76 Expanded Scale pH Meter which was calibrated using known activities of the desired cation in chloride solution. The theoretical 59.2 mV per ten-fold change in activity was observed for K and Na. The mV response for equal changes in Li or Cs activity, although reproducible, were less than 59.2 mV and decreased as the activities decreased. Adjusting the instrument to read zero for cation activities of 0.1 moles per liter, the mV response for three successive ten-fold changes in activity were 58, 57 and 52 mV for Li and 56, 45 and 33 for Cs. The e.m.f. measured in a homoionic Ca clay indicated that the contribution of Ca was insignificant when determining K activities in bi-ionic K and Ca clays.

Assuming the glass to act as an ideally permselective membrane for cations and no liquid junction potential, the cation activity can be calculated from the measured e.m.f. using the Nernst equation (Helfferich, 1962, p.375; Spiegler, 1953).

$$E = \frac{RT}{ZF} \ln \frac{A_1}{A_2}$$

The cation activities were calculated from the total e.m.f. of the cell using this formula; recognizing that any liquid junction effects will be included. This value was divided by the total concentration of the cation to give what will be referred to as an activity coefficient, a/c, or after Marshall (1951), a fraction active.

Electrical Conductance Measurements

Electrical conductance measurements were made using a Hewlett Packard Model 200 CS oscillator in conjunction with a Leeds and Northrup No. 1553 shielded ratio box and 4755 A-C Decade Resistance Box. A No. 1185 variable air capacitor was used to compensate for the conductivity cell. This provided a means of measuring conductivities from 20 to 600,000 cps. The null point was determined using a General Radio Company type 1232–A tuned amplifier and null detector up to 200,000 cps; above

this frequency an oscilliscope was used. A conductivity cell with a cell constant of about 0.15 and a ground glass fitted thermometer was used and set in a double water bath to control temperatures to at least $\pm$ 0.1 degrees. The cell constant decreased by about 2 per cent over the range 20 to 600,000 cps with over 1 per cent of this variation occurring at < 200 cps. The variation in conductivity of the clay with frequency is shown in Fig. 1 for 3 per cent clays. After the apparent initial increase below 200
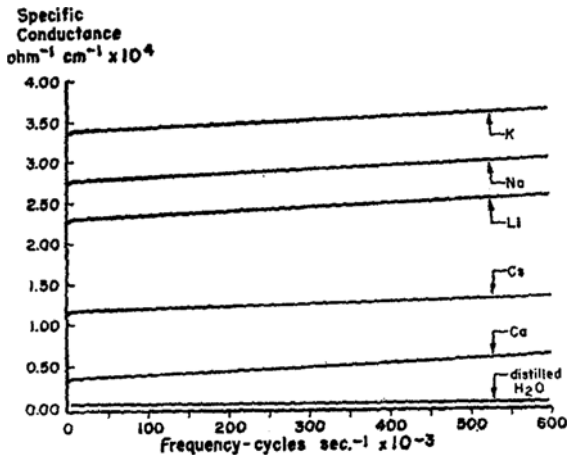

FIGURE 1.—Specific conductance vs. a.c. frequency for 3 per cent homoionic bentonite clays and distilled water.

cps which is probably due to cell constant variation, there is a gradual and consistent increase over the entire frequency range with no obvious plateaus or significant changes in rate of increase. The total increase in conductivity was approximately the same regardless of the saturating cation making the relative increase much greater for the low conductivity clays such as Ca or Cs compared to Na, K, or Li clays. Conductivity values to be compared with diffusion measurements were calculated from measurements at 200 cps to minimize the frequency effect on conductivity and cell constant. The value is well within 1 per cent of the true d.c. conductance value which theoretically should be compared with diffusion measurements. Temperature dependence of conductance was determined on two separate samples of the homoionic clay. The first was at three and the second at five temperature levels ranging from 25 to about 62°C.

RESULTS AND DISCUSSION

Homoionic Clays

The results of potentiometric, conductance, and diffusion measurements in homoionic clays are given in Table 1. As described previously, the total reduction in cation activity due to the presence of the clay is expressed as the activity coefficient (a/c), where a represents the measured cation

TABLE 1.—ACTIVITY COEFFICIENTS, TRANSMISSION FACTORS FOR SELF-DIFFUSION OF CATIONS AND WATER, AND TRANSMISSION FACTORS FOR CONDUCTANCE OF CATIONS IN BENTONITE–WATER SYSTEMS AT 25°C*

Cation	% Clay by volume	a/c	D_{clay}/D_{H2O} cation	$\lambda_{clay}/\lambda_{H2O}$	D_{clay}/D_{H2O} (H_2O)
Li	3.5	0.205	—	0.260	0.67
Na	3.0	0.202	0.140	0.211	0.63
K	3.5	0.210	0.156	0.193	0.61
Cs	3.0	0.079	0.041	0.055	0.67
Ca	3.5	—	0.054	0.033	0.68
Sr	3.5	—	—	0.009	
Sr	5.0	—	0.024	0.012	

* Values are reliable within two or three units in the last figure given.

activity calculated from the total e.m.f. of the cell and c the total concentration of the given cation. The reduction in mobility is expressed in the transmission factors for diffusion (Porter *et al.*, 1960), D_{clay}/D_{H2O}, and conductance, $\lambda_{clay}/\lambda_{H2O}$, where D_{clay} and λ_{clay} are the measured diffusion coefficients and specific conductances in the clay system and D_{H2O} and λ_{H2O} are the values in aqueous solution at infinite dilution. This method of presenting the data was chosen because it not only provides a means of making relative comparisons between the different measurements but also reflects the total effect of the clay.

The transmission factor for the self-diffusion of water was about 0.65 and essentially uniform for all cation species. This is intermediate between the values of 0.57 for sulfate and 0.75 for chloride reported previously (Gast, 1963).
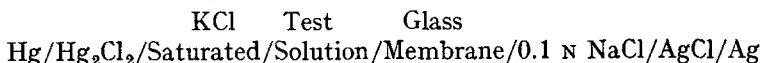
Dutt and Low (1962) in studying deuterium oxide diffusion in Wyoming bentonite found that the diffusion coefficients varied with the exchangeable cation in the order K>Li>Na. The respective transmission factors calculated from their data would be 0.61, 0.23 and 0.20 in 29 per cent K, 23 per cent Li and 31 per cent Na clays. They concluded that "either the steric effect of the clay particles or an increased viscosity in the adsorbed

water has reduced the diffusion coefficient of D_2O in the clay systems. Further, the nature of the adsorbed cation must influence either or both of these factors." We did not observe the variations with exchangeable cations probably because of the low clay concentrations used. Since the transmission factors vary between Cl^-, H_2O and $SO^=_4$ something other than steric hindrance must be involved in at least the latter two cases as they are both lower than Cl^-.

Variations in the transmission factors for diffusion and conductance follow similar patterns between cation species. The total reduction in mobility due to the presence of the clay is of the same order of magnitude for both indicating that the underlying mechanisms are essentially the same. The higher values for conductance than diffusion observed for the monovalent cations have been explained as being due to electro-osmosis or convection conductivity (Spiegler and Coryell, 1953) which is due to a displacement of the free charge of the double layer (Overbeek, 1952, p.235). The clay particles probably do not move in our systems but even though they are fixed with respect to the apparatus their Hittorf transference numbers are not zero, because electro-osmosis drives the solvent through the plug (Overbeek, 1953). Therefore the measured conductance is higher than that calculated from diffusion by equation (1). The transmission co-efficient then would be greater for conductance than diffusion for when self-diffusion takes place in an ion exchanger no electro-osmosis occurs.

Roughly speaking the contribution due to electro-osmotic movement is proportional to the free charge of the double layer (Overbeek, 1952, p.235) and as would be expected from double layer theory the effect is much greater for monovalent than divalent cations. In fact the transmission factors for conductance of divalent cations are less than those for diffusion. The differences are relatively small, however, and may be due to a summation of errors including limited experimental accuracy and uncertainties in calculating values for conductance in solution.

The theory of membrane potentials and their use in determining cation activities has recently been discussed by Helfferich (1962) with an excellent review of the literature. Briefly the cationic glass electrode consists of a sodium alumino-silicate glass bulb filled with 0.1 N NaCl solution into which is immersed a Ag–AgCl electrode. Using this with a saturated KCl–calomel half-cell with fiber type salt bridge the measuring cell is (Bower, 1959)

$$\text{KCl} \quad \text{Test} \quad \text{Glass}$$
$$Hg/Hg_2Cl_2/\text{Saturated}/\text{Solution}/\text{Membrane}/0.1 \text{ N NaCl}/AgCl/Ag$$

Assuming the electrode potential of the calomel electrode is zero in both the calibrating solution and the clay paste, the membrane potential and the e.m.f. of the cell are equal. The membrane potential can be considered as consisting of the two "Donnan" potentials at the interfaces between the membrane and solutions and the diffusional potential within the mem-

brane (Sollner, 1950; Helfferich, 1962, p.374). For ideally permselective membranes the equation for the membrane potential reduces to the Nernst equation (Helfferich, 1962, p.375; Marshall, 1948) which has been used to calculate single ion activities in clay suspensions (Marshall, 1951).

The activity coefficients, a/c, were essentially constant for Li, Na, and K but were lower for Cs. The accuracy for Cs might be questioned due to the deviation from the theoretical potentials in the standard solution. However, the values were reproducible in both the standard solutions and clays. The reductions in activity are of the same order of magnitude as the reductions in mobility. This is not surprising, for as Overbeek (1953) has shown these potentials are dependent on ion mobilities. The a/c values generally agree better with the transmission factors for conductance than for diffusion. Marshall and Krinball (1942) also found a close correspondence between activity and conductance measurements. In order to evaluate the significance of those differences using the relationships given by Overbeek (1953), a knowledge of the mobilities of all components of the system and of the composition of the equilibrium dialyzate is required. The clay systems studied, which are essentially free of excess electrolyte, would have an equilibrium dialyzate very low in concentration. These concentrations were not determined experimentally and the uncertainties in calculating them would be large. This makes any attempt to use this approach in quantitatively explaining the differences between the potentiometric, conductance and diffusion data largely speculative. But as Marshall (1956) has pointed out, it is possible that the liquid junction potential at
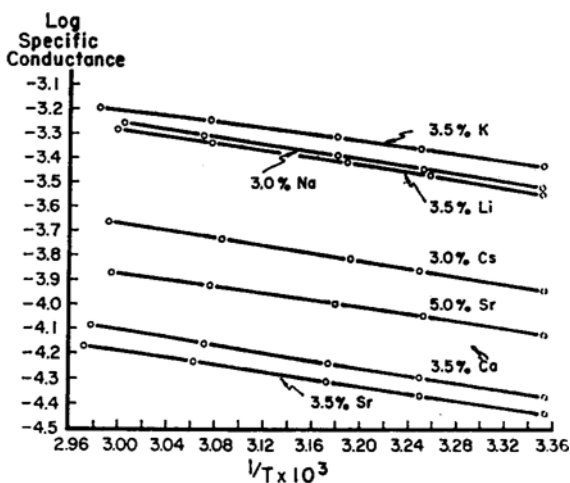

FIGURE 2.—Temperature dependence of specific conductances.

the KCl junction of the calomel electrode is significantly different from zero in clay systems as concentrated as these.

The temperature dependence of the conductance measurements plotted as the negative logarithm of the specific conductance against the reciprocal of the absolute temperature are shown in Fig. 2 for five temperatures ranging from 25 to about 62°C. The results give essentially a straight line for all clays. Activation energies for conductance calculated from the slope of the lines using the Arrhenius equation (Glasstone, 1946, p.1088) are given in Table 2 for two replications. Also the values determined for conductance in dilute (about 0.01N) chloride solutions of the respective cations and those calculated for ion conductance at infinite dilution

TABLE 2.—Activation Energies for Electrical Conductance in Clays, Dilute Chloride Solutions and Ions at Infinite Dilution

Cation	% Clay by volume	Activation energy—cal mol^{-1}				
		Clay–water systems			Dilute chloride solutions	Ions at infinite dilution*
		Rep. 1	Rep. 2	Ave.		
Li	3.5	3660	3630	3645	3480	3990
Na	3.0	3410	3510	3460	3400	3690
K	3.5	3170	3190	3180	3240	3330
Cs	3.0	3790	3700	3750	3190	3210
Ca	3.5	3580	3380	3480	3440	3720
Sr	3.5	3480	3290	3400	3400	3720
Sr	5.0	3340	3300	3320		
"H"	3.0			2450		2500

* Calculated from data given by Glasstone (1942—p. 56) with the exception of Cs which was calculated from data of Robinson and Stokes (1955, p.454).

(Glasstone, 1942, p.61) are given. Conductance for replicate one were only determined over the range 25 to about 42°C. So for comparison purposes the values for replicate two were calculated using the data from Fig. 2 for the same temperature range. The specific conductances were generally reproducible to within 5 per cent.

Only two clays, Li and Cs, gave activation energies significantly higher than for the measured solution conductance and only the Cs clay gave a value higher than those calculated for ion conductance at infinite dilution. It is interesting that the activation energies for "H+" or acid clay and the calculated value for conductance of H+ at infinite dilution have essentially the same low value. The calculated values for ion conductance, like those given by Wang (1952) for tracer diffusion of ions in infinitely dilute aqueous solutions, increase with the size of the hydrated ion from Cs to Li and

approach that for self-diffusion of pure water. He interpreted this increase as indicating that the activation mechanism involves the activation of the immediately surrounding solvent water molecules to get out of the way of the tracer ion. This line of reasoning would explain the value for Li being higher than Na and K, especially in view of the evidence presented by Low (1961) for the increased viscosity of water near clay surfaces. But it does not explain the high value for Cs nor the low values for Na, K, Ca and Sr. The values for Ca and Sr which show the greatest reduction in mobility are no higher than those measured for solution conductance and are lower than those calculated for ions at infinite dilution.

Oster and Low (1963) in determining the activation energies for ion movement in thin water films on montmorillonite by electrical conductance found that the values decreased as the water content increased. At their high water content which would be 7.5–10 water layers in the clay surface compared to about 800 in ours, the activation energies were in the order Na$>$Li$>$K, all being in the range of 4.0–4.3 kcal. Our values for monovalent cations are in the order Cs$>$Li$>$Na$>$K. They conclude that the lower activation energies for "high" water content compare to those at medium and low contents are likely due to a less coherent water structure of the water and the absence of appreciable ion–oxygen interaction. While it is expected that the effect of both these factors will diminish as the water content is increased, the fact remains that the mobilities of the cations are reduced and that those showing the largest reduction have among the lowest activation energies.

So with the possible exception of Cs the reduction in mobility apparently cannot be explained by an increase in the activation energies for electrical conductance as determined here. As Rosenqvist (1963) has pointed out, the activation energies probably include the temperature dependence of other processes than ion movement alone and are really "apparent" values. He suggested one possible explanation of the high values often observed for diffusion and electrical conductance in clays would be a "melting off" of the outer layers of water near the clay surfaces which have a more ordered water structure. The activation energies for ion movement in these regions would appear to be very high. This effect is not apparent in our systems as our values are generally lower than would be expected, possibly because ions are not concentrated in the layers where this "melting off" occurs. Cs might be an exception where this explanation would apply. In addition any temperature dependence of the electro-osmosis process would be included in the calculated activation energies for conductance. Since both diffusion and conductance reflect essentially the same reductions in mobility it does not seem that the temperature dependence of this process should mask that for ion movement. This is especially true for Ca and Sr where the electro-osmotic effect is not detectable by our measurements.

Bi-ionic Clays

The transmission factors for H_2O, K and Ca and activity coefficients for K in 3.5 per cent bentonite clays with varying ratios of K : Ca are given in Fig. 3. The confidence limits put on the a/c values were calculated assuming a precision of $\pm$ 1 mV in the e.m.f. measurements. The transmission factor for H_2O are between 0.575 and 0.675 with no particular
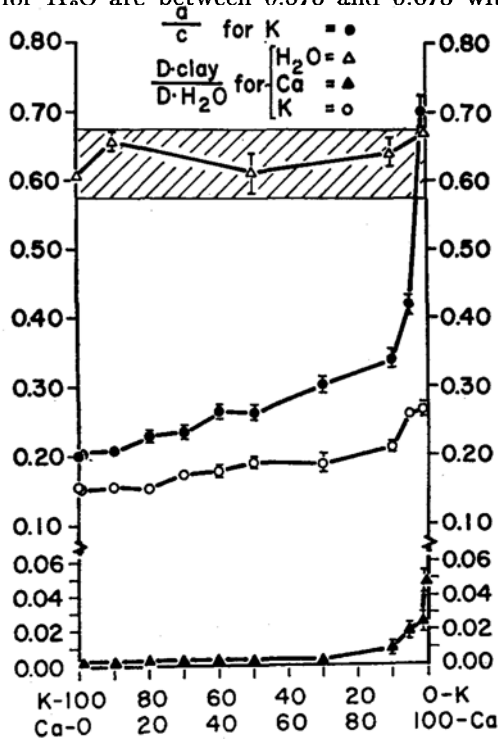

FIGURE 3.—Transmission factors, D_{clay}/D_{H2O}, for self-diffusion of K, Ca, and H_2O and activity coefficients for K, a/c, in 3.5 per cent bentonite--water systems with varying K:Ca ratios.

pattern to the variation. As in the homoionic clays, there variations are intermediate between those for $SO_4^=$ and Cl^+ reported previously, and show no significant variation with the K : Ca ratio.

The transmission coefficients, and hence the mobility, increased by a factor of 1.7 for K and over 30 for Ca on increasing Ca from 1 to 100 per cent. The precision of the Ca diffusion measurements was limited at Ca saturations below 70 per cent for the rate of Ca movement was so slow that the total transfer between the half cells due to diffusion was of the

same order as that due to mixing on formation of the boundaries by the shearing process. The confidence limits which range from about 30 to 70 per cent of the calculated value are all within the area enclosed by the symbols representing the individual values. It is emphasized that the variations in K and Ca mobility were a result of mixing the homoionic clays in the given proportions only and that the K and Ca diffusion coefficients were determined simultaneously eliminating possible variations due to experimental techniques and conditions. These changes in mobility reflect the predominate accumulation of divalent over monovalent cations in regions of highest negative surface potential (Overbeek, 1962, p.176).

As in the homoionic clays, the activity coefficient for K was consistently higher than the transmission coefficient for diffusion. Comparison with conductance measurements could not be made since the relative contributions of K and Ca to the electrical conductance cannot be distinguished. While values for both K activity and diffusion increased with increasing Ca saturation, the rate of increase was greater for activity. When the specific conductance calculated from the diffusion coefficient using equation (1) is plotted against that calculated from K activities a linear relationship is observed (Fig. 4), illustrating again the dependence of the potentiometric measurements on cation mobilities predicted by Overbeek (1953).

The specific conductance was calculated from the K activities by a procedure similar to the procedure given by Marshall and Krinball (1942). The KCl concentration corresponding to the K activity was obtained by
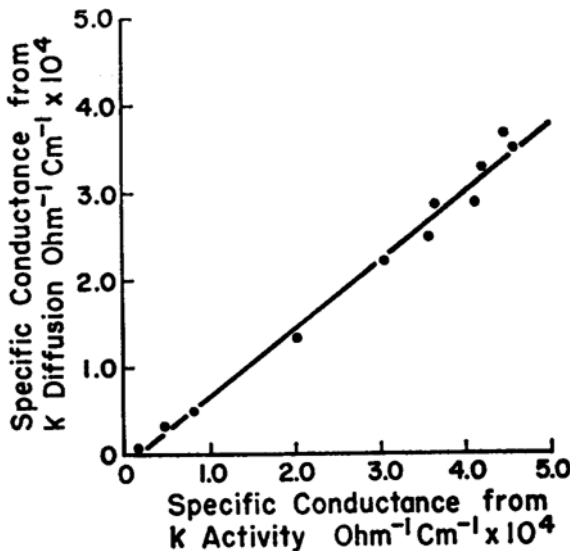

FIGURE 4.—Specific conductance calculated from K diffusion vs. that calculated from K activity in 3.5 per cent bentonite–water systems with varying K:Ca ratios.

plotting the specific conductance of KCl vs. concentration. The specific conductance for the measured K activity was then taken to be one-half this value. As they pointed out, this involves the uncertainties of using cation activities as concentrations. The slope of the line is 0.78 which might be considered a proportionality constant between K mobilities and activities in these systems. Again there is insufficient information concerning the equilibrium dialyzates to attempt quantitatively to explain the significance of this relationship between the results of potentiometric and diffusion measurements.

Figure 5 shows specific conductances calculated for equivalent concentrations of K and Ca in solution and those measured and calculated from the self-diffusion coefficients of K and Ca in the bi-ionic clays. In comparison
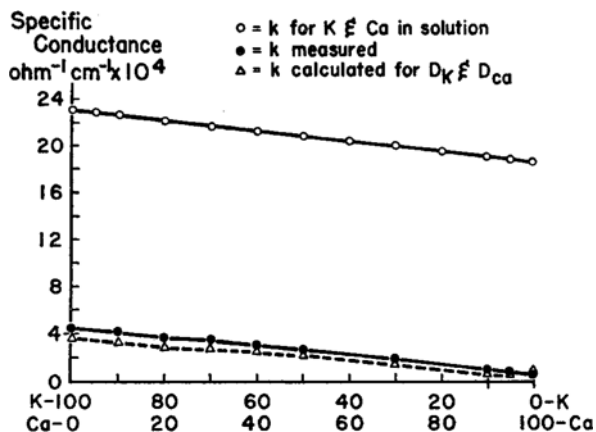

FIGURE 5.—Comparison of specific conductance values calculated for K and Ca in solution with those measured and calculated from self-diffusion coefficients in 3.5 per cent bentonite–water systems with varying K:Ca ratios.

with the total reduction in mobility due to the presence of the clay, the difference between the measured values and those calculated from diffusion are small and are probably due to convection conductivity or electro-osmosis. Thus it can be concluded that the two methods agree closely and both accurately reflect the cation mobilities in the clay systems.

Finally the variation in self-diffusion with varying degrees of base saturation with Na obtained by mixing Na and acid clays is given in Fig. 6. The diffusion coefficient decreased as the Na content increased up to about 90 per cent base saturation. This has immediate implications to the results reported here in that it indicates that the diffusion rates are not sensitive to small variations in base saturation in the higher ranges. The pH of the clays, about 5.0–5.5, suggest something less than 100 per cent base satura-

tion even though they have about 90 meq of exchangeable cations per 100 g of clay which is about the exchange capacity.
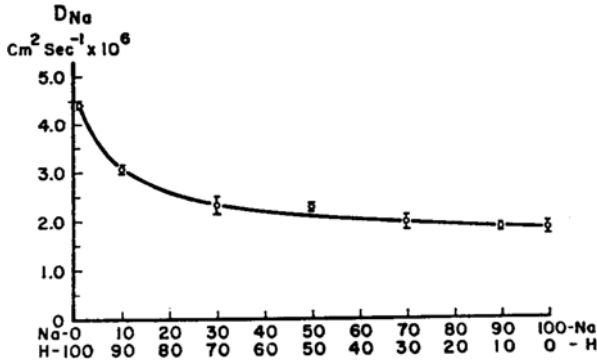

FIGURE 6.—Self-diffusion coefficients of Na in 3 per cent bentonite–water systems with varying Na:H ratios.

CONCLUSIONS

The agreement between cation mobilities measured by diffusion and electrical conductance indicates the underlying mechanism is the same for the two processes. But the activation energies for ion movement determined from conductance measurements do not explain the observed reductions in mobility. From this it can be concluded that either (1) the reductions in mobility are not due to an increase in activation energy for the processes which determine the rate of ion movement or (2) the observed activation energies do not accurately represent the processes involved in ion movement. Of the two, the latter is of course most probable in view of the existing theoretical and experimental evidence in the literature.

The observed reductions in mobility can be associated with the preference of the clay for certain cations in ion exchange equilibrium and with the cation distributed predicted by electric double layer theory. But it does not seem, at the present time at least, that these associations can explain the forces actually involved in controlling cation mobilities in clays.

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