

# THERMODYNAMIC, QUASITHERMODYNAMIC, AND NONTHERMODYNAMIC METHODS AS APPLIED TO THE ELECTROCHEMISTRY OF CLAYS<sup>1</sup>

*By*

C. EDMUND MARSHALL

University of Missouri, Columbia, Missouri

## ABSTRACT

The consequences of a nonhomogeneous charge distribution in clay systems are first examined. The mean ionic activity is shown to be a geometrical rather than an arithmetical average. Potentiometric methods of measurement, with (quasithermodynamic), and without (thermodynamic) liquid junctions are compared. The latter give chemical potentials of soluble molecular species or ratios of mean activities; neither of these affords a characterization of single cations in relation to clay surfaces. The quasithermodynamic method, like conductance measurements, affords data which can be interpreted directly in terms of single ions. The two are compared for dilute and more concentrated clay systems by using the ratio: "Cation conductivity/total conductivity of clay systems." For dilute systems this ratio varies slowly and smoothly with concentration and with degree of saturation. High concentrations give an abnormally high value. Cataphoresis results are shown to be in agreement with conductance and potentiometric data for dilute clay systems.

## INTRODUCTION

The relation of the surface properties of clays to their structural chemistry represents a central problem whose solution would be of immense benefit to colloid chemistry and to every aspect of clay technology. The study of clay-water systems by the methods which physical chemists have applied to colloidal systems as well as to true solutions constitutes the major part of this problem. We shall here take up the particular contributions which different methods provide towards its solution. They readily fall into three groups.

Thermodynamic methods include: (1) the colligative properties—vapor pressure lowering, depression of freezing point, etc.—which measure the chemical potential of the water; (2) methods which measure or make use of the chemical potentials of molecular species other than water; (3) measurements of energy transformations in clay systems.

The term "quasithermodynamic" is here used for methods based on electrochemical cells with liquid junctions. Combinations of such measurements may result in the cancelling of liquid junction effects and hence in the provision of strictly thermodynamic data. Granted certain assumptions, the quasithermodynamic methods unlike the strictly thermodynamic ones, enable direct conclusions to be drawn regarding individual ions in their relations to clay surfaces.

The term "nonthermodynamic" concerns evidence from conductance experiments, as well as theoretical relationships derived for model systems. Conductance data can be interpreted only in terms of the properties of individual charged particles. Hence they provide direct evidence on dissociating surfaces.

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In what follows, the use of colligative properties will not be discussed in detail. Emphasis will be placed on the comparison of measurements on Donnan systems with potentiometric determinations of ionic activities and with conductance measurements.

Three assumptions are usually made in the discussion of Donnan equilibria: (1) that the charge distribution in the colloidal system is homogeneous, as in a true solution; (2) that dissociation of the colloid is complete; (3) that the total volume of the system remains constant. None of these assumptions is essential.

In clay systems it is certainly evident that the charge distribution is far from uniform. The exchange cations form atmospheres or envelopes about the platy or elongated particles. This has important consequences. Consider a sodium-clay system in presence of sodium chloride. The chemical potential of the latter as a molecular species must be everywhere the same: that is, at different distances from the surfaces of the clay particles it remains constant. Hence, its effect on the chemical potential of the water must also be the same. But the water layers near the clay surfaces are also affected by the latter. Hence, on a micro scale the osmotic pressure varies from point to point. If the colloidal system is separated by a permeable membrane from the true solution of sodium chloride with which it is in equilibrium, then the membrane osmotic pressure represents the difference between the mean of the variable osmotic pressures on the colloid side and the constant osmotic pressure on the solution side. In order to maintain a constant volume on the colloid side a hydrostatic pressure equal to this mean membrane osmotic pressure must be applied.

According to Guggenheim, the electrochemical potential of an ion must also be everywhere the same in a system at equilibrium. If we consider two points, I and II, at different distances from the charged clay surfaces, we shall have, using Alexander and Johnson's (1949) application to colloidal systems,

$$\begin{aligned} \mu_{Na}^I + zF\psi^I &= \mu_{Na}^{II} + zF\psi^{II} \\ \mu_{Cl}^I - zF\psi^I &= \mu_{Cl}^{II} - zF\psi^{II} \end{aligned}$$

where  $\mu^I$  and  $\mu^{II}$  are the chemical potentials and  $\psi^I$  and  $\psi^{II}$  the electrostatic potentials of the respective ions at points I and II,  $Z$  is the ionic valency (here  $Z = 1$ ), and  $F$  the Faraday. Since the electrostatic potentials vary from point to point, it is evident that the chemical potentials of individual ions must also vary. Thus for each clay—water system there will be a certain mean chemical potential for each ionic species, which is the space average of the individual values. This implies that if we are to define a mean ionic activity  $a$  for the system it must be done as follows:

$$\ln \bar{a}_{Na} = n_1 \ln a_{Na}^I + n_2 \ln a_{Na}^{II} + n_3 \ln a_{Na}^{III} \dots$$

where  $n_1 + n_2 + n_3 \dots = 1$

Hence  $\bar{a}_{Na} = (a_{Na}^I)^{n_1} \cdot (a_{Na}^{II})^{n_2} \cdot (a_{Na}^{III})^{n_3} \dots$

and similarly for the chloride ion. Thus the activities cannot be treated additively like concentrations in true solution. Potentiometric determinations will always give the geometrical mean activity. If we denote the clay—water

system by the symbol  $A$  and the Donnan equilibrium NaCl solution by  $B$  then we have

$$RT \ln \frac{\bar{a}_{\text{Na}}^A}{\bar{a}_{\text{Na}}^B} = zF(\psi_A - \psi_B) = RT \ln \frac{\bar{a}_{\text{Cl}}^B}{\bar{a}_{\text{Cl}}^A}$$

In the true solution  $B$  the arithmetical and geometrical mean activities will be practically indistinguishable and readily calculated from total concentrations and known activity coefficients. Hence if the membrane potential ( $\psi_A - \psi_B$ ) can be measured, the geometrical mean ionic activity of the colloidal system  $\bar{a}_{\text{Na}}^A$  or  $\bar{a}_{\text{Cl}}^A$  can be determined.

The suspension effect in clay systems involves simply the setting up of a Donnan system without membrane, the constraint on the colloid being provided by a centrifugal or gravitational field or by gel coherence. The potential difference ( $\psi_A - \psi_B$ ) is usually measured by the insertion of calomel electrodes with saturated KCl junctions. It is assumed that the liquid junction potentials are close to zero. The assumption is usually accepted for dilute true solutions, but in recent years there has been considerable discussion as to whether this is the case for colloidal systems, (Jenny and others, 1950; Marshall, 1951; Mysels, 1951; Marshall, 1952; Eriksson, 1951; Babcock and Overstreet, 1953; Mysels, 1953; Peech, Olsen, and Bolt, 1953; Marshall, 1953), particularly clays and exchange resins. Unfortunately, according to Overbeek (1953) this question can hardly be decided by simple experimentation. The present position is that indirect evidence strongly favors the validity of these assumptions for dilute colloidal systems, but not for such concentrated ones as beds of exchange resins. As far as clay systems are concerned, it seems safe to draw conclusions for "dilute" sols from potentiometric determination using liquid junctions. What is meant by "dilute" will be discussed later.

### APPLICATIONS OF POTENTIOMETRIC METHODS

The relationship of strictly thermodynamic and quasithermodynamic methods can well be approached through consideration of a cell containing three electrodes. Suppose we have a clay system containing silver and hydrogen ions. We insert into it three separated electrodes: (a) a metallic silver electrode, (b) a hydrogen electrode (platinum with  $\text{H}_2$  at atmospheric pressure), (c) a calomel half cell with suitable liquid junction, such as a mixture of potassium and ammonium nitrates instead of KCl. The combination of the silver and hydrogen electrodes involves no liquid junction.

The potential difference between them is given by the thermodynamically

valid equation:  $E_{\text{cell}} - E_{\text{Ag}}^{\text{std}} = \frac{RT}{nF} \ln \frac{\bar{a}_{\text{Ag}}}{\bar{a}_{\text{H}}}$ . The potential difference between

the calomel and the silver electrode is  $E_{\text{Ag}}^{\text{std}} + E_{\text{cal}}^{\text{std}} + \frac{RT}{nF} \ln \bar{a}_{\text{Ag}}$ ; and that

between the calomel and the hydrogen,  $E_{\text{cal}}^{\text{std}} + \frac{RT}{nF} \ln \bar{a}_{\text{H}}$ . In this case  $E_{\text{cal}}^{\text{std}}$  can be evaluated, since when  $\bar{a}_{\text{H}} = 1$  for true solutions the second term

vanishes. This is equivalent to the use of the conventional standard state of the ion in question as the basis of reference, combined with the assumption that the liquid junction potential at the calomel electrode bridge is close to zero.

We may now consider an alternative formulation of the thermodynamic quantity  $E_{\text{cell}} - E_{\text{Ag}}^{\text{std}}$ . Since  $p_{\text{H}} + p_{\text{OH}} = \log_{10} K_w$

$$\text{we can write } E_{\text{cell}} - E_{\text{Ag}}^{\text{std}} = 1364 [\log_{10} \bar{a}_{\text{Ag}} + \log_{10} K_w - p_{\text{OH}}]$$

upon evaluation of the constants at 25°C.

$$\begin{aligned} \text{Hence } E_{\text{cell}} - E_{\text{Ag}}^{\text{std}} &= 1364 [\log_{10} \bar{a}_{\text{Ag}}^2 \cdot \bar{a}_{\text{OH}} + \log_{10} K_w] . \\ &= 1364 [\log_{10} \bar{a}_{\text{Ag}} \cdot \bar{a}_{\text{OH}} + 14.08] . \end{aligned}$$

Thus the potential measurement is in linear relationship with the chemical potential of the molecular species AgOH. This is true at every point. In this way a strictly thermodynamic titration curve emerges, by combination of the two sets of quasithermodynamic measurements. However, use of this thermodynamic chemical potential of the molecular species AgOH, automatically removes us from the direct measurement of surface properties. Changes in the latter are now to be interpreted, not directly, but indirectly through their effects on the chemical potential of this soluble molecular species. What is needed for structural interpretation is the relation between the silicate surface and the individual ions which balance its charge. This can be obtained by the quasithermodynamic route, which, however, involves plausible but not strictly proved assumptions.

The relationship of the thermodynamically valid quantity to the quasithermodynamic pH and p cation can be seen in Figure 1 in which all three are given. The quantity  $p\text{H} - p_{\text{Na}}$  or  $\log_{10} \frac{\bar{a}_{\text{Na}}}{\bar{a}_{\text{H}}}$  cannot be interpreted in terms of the surface and the individual ions. Variations in slope cannot even be explained when the corresponding case for an electrolyte like HCl is placed on the same diagram. On the other hand if the cations are taken singly then their mean free bonding energies are easily computed, and variation in this quantity can be linked with many aspects of the chemistry of clay surfaces. An alternative procedure, which will be discussed later, is to translate the quasithermodynamic quantities into activities and then to compare them with conductance measurements.

This discussion has been introduced in order to make clear the deep-seated dilemma by which we are faced in the use of potentiometric methods. If a ratio of ionic activities such as  $\bar{a}_{\text{Na}}/\bar{a}_{\text{H}}$  will suffice for our purposes then strictly thermodynamic methods can be used. As we shall see later, they need not be potentiometric. Under certain conditions analytical data on Donnan equilibria will provide the same information. However, when we inquire regarding surface dissociation, the situation for a single cation is already complicated enough. It needs to be clarified before functions of pairs of cations or chemical potentials of soluble molecular species can receive interpretation.

We can now take up three other types of potentiometric measurement which have been used in clay systems. Davis (1955) has successfully employed the

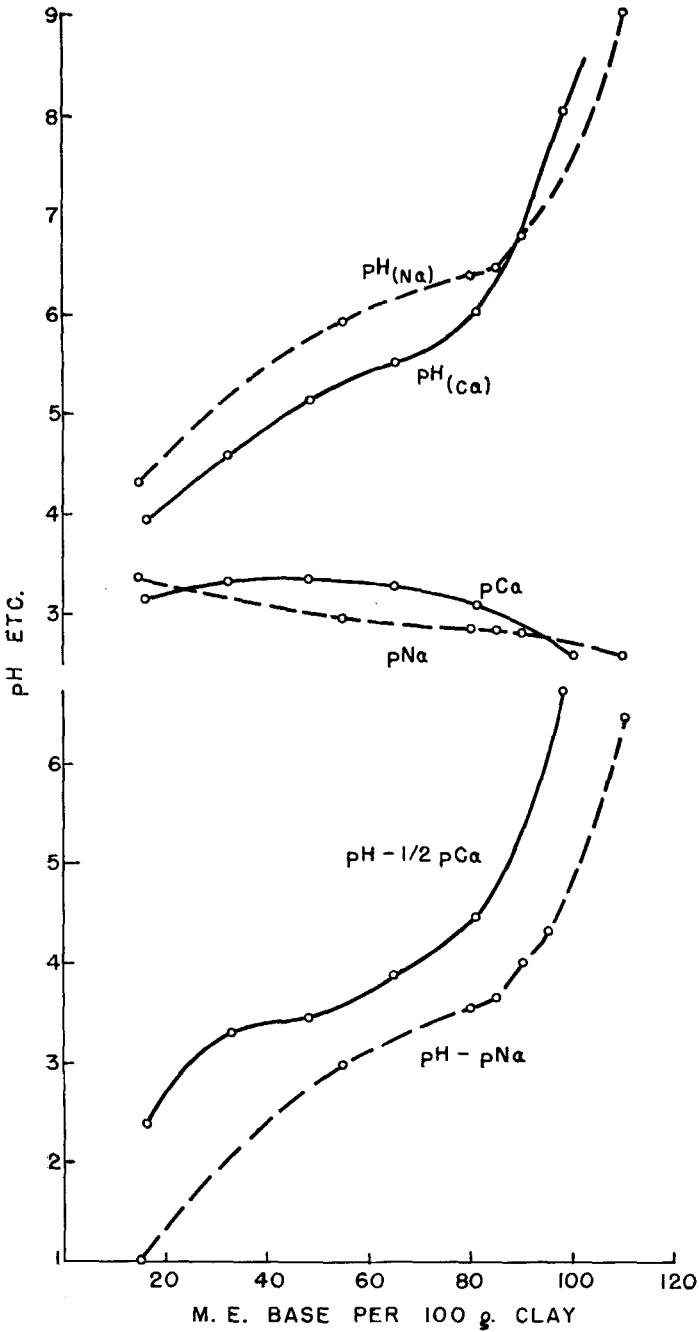


FIGURE 1.—Logarithmic functions in the titration of 1 percent Wyoming bentonite with sodium hydroxide and calcium hydroxide.

cell : Ag, AgCl | Clay system + chloride | membrane electrode, which effectively measures the chemical potential of the sodium, potassium or other chloride in the clay system. Using the same molecular proportions of water, salt and clay in each case and varying the nature of the salt to correspond with the cation on the clay, the chemical potential of KCl in presence of K clay was found to be significantly different from that of NaCl in presence of Na clay. How are these facts to be interpreted? It is a natural but nonthermodynamic step to say that the Na clay is dissociated to a different degree than the K clay and hence affects differently the chemical potential of the corresponding salt. Such conclusions were found to be in agreement with the quasithermodynamic measurements obtained over a period of years by the present author and co-workers.

Another method of deducing the chemical potentials of molecular species or activity ratios in the clay-water system employs tertiary electrodes, which operate through the ionic equilibrium set up by two sparingly soluble salts which share a common ion. Thus Russell and Cox (1950) employed the lead, lead oxalate, calcium oxalate chain as a calcium electrode, combining it with the glass electrode in order to determine  $\sqrt{a_{Ca}/a_H}$  or with the silver-silver chloride electrode to obtain  $\sqrt{a_{Ca} \cdot a_{Cl}}$ . The accuracy and reproducibility of such combinations has so far remained considerably below those of membrane electrode systems, but in favorable circumstances there is no evident obstacle to high precision. One factor which may have affected the results is possible adsorption by the clay of the anion common to the two salts. Certainly this might be expected with fluoride and phosphate, whose salts with divalent atoms are sometimes used in tertiary electrode chains.

Mukherjee and Marshall (1951) employed the cell,



This has two liquid junctions between saturated KCl and dilute salt solutions and hence is not a strictly thermodynamic arrangement. However, silver-silver chloride electrodes could be used directly, and from the measured potentials, strictly thermodynamic conclusions could be drawn. Such a cell measures the free energy change of the reaction  $K^+ + Na \text{ clay} = Na^+ + K \text{ clay}$ , plus the difference in chemical potential of the salts in the two dilute chloride solutions. The latter is a known quantity; hence the difference in free energy of adsorption of K and Na on the clay can be derived. (In the original derivation it was tacitly assumed that entropy differences would be negligible and that the results could be expressed as differences in differential heats of adsorption of the cations. The free energy formulation is preferable, particularly when ions differing widely are to be compared.) The experiments must be set up in such a way that there will be no liquid junction potential in the interior of the plug. Examination of the Donnan conditions through application of the Teorell-Meyer and Sievers theory indicates that for this to obtain, both  $C_1$  and  $C_2$  must be small compared with  $\bar{a}_{Na}$  and  $\bar{a}_K$  in the plug. Under these circumstances when the same salt is present on both sides of the plug the total potential difference should follow the Nernst equation.

Although successful experiments could be carried out only with highly concentrated clay-water systems enclosed in medium-bore glass capillaries, the

free energy differences for Na and K were found to be very similar to those deduced from quasithermodynamic titration-curve data on dilute systems.

*Analytical Determinations Through the Donnan Equilibrium*

Consider a clay system containing a variety of exchange cations (K, Na, Ca, Mg, H, etc., System I) in equilibrium with a solution of the chlorides of these cations (System II). The chemical potentials of the species KCl, NaCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, HCl, etc., must be the same at all points. Since the chloride ion is common to all it is then easy to show that

$$[\bar{a}_K/\bar{a}_{Na}]^I = [a_K/a_{Na}]^{II}; [\bar{a}_K/\sqrt{\bar{a}_{Ca}}]^I = [a_K/\sqrt{a_{Ca}}]^{II}$$

and similarly for other possible ratios. The values in II can be determined with a fair degree of accuracy by analytical methods combined with knowledge of the activity coefficients for the salt mixtures under investigation. Hence the same ratios for the clay-electrolytes are established. If now the concentration of the soluble anion in the outer system is sufficiently reduced, it becomes negligible in the clay system in comparison with the mean colloidal anion concentration. Thus the analytical determinations upon the outer solution define the corresponding mean cationic activity ratios for the colloidal system.

The application of this principle was foreshadowed by the work of the Mattson group (Mattson 1929, Wiklander 1951) which was at first mainly directed towards finite exchanges involving the  $K/\sqrt{Ca}$  ratio, and by that of Bray (1942) on small exchanges. The establishment of its thermodynamic significance apparently began with the work of Teräsvoori (1930) and was completed by Schofield and Taylor (1955) and their associates (Aslyng, 1954). The results are expressed by the latter on the -logarithmic scale. The quantity ( $pH - \frac{1}{2}p_{Ca}$ ) is termed the lime potential. Other important quantities used in the investigation of soil systems are ( $p_K - \frac{1}{2}p_{Ca}$ ) and  $\frac{1}{2}p_{Ca} - \frac{1}{2}p_{Mg}$ . Woodruff (1955) has also evaluated small exchange experiments through the thermodynamic approach, and has expressed the results directly in terms of free energy. Thus

$RT \ln a_{II}/\sqrt{a_{Ca}} = 1364 \log_{10} a_{II}/\sqrt{a_{Ca}}$  is evaluated in calories per equivalent and termed free energy of exchange. The present author prefers to describe this quantity merely as the difference in free energy status of the two ions, the standard state being the point of reference in each case. The use of the energy scale greatly simplifies comparisons in different systems and for different purposes.

The experimental procedure for this type of work is very simple. The exchange system is treated with a dilute salt solution, the proportions of the two being so chosen that lowering of the salt concentration causes no change in the various ratios as determined in the filtrate, ultrafiltrate, or supernatant liquid. Two conditions are thereby fulfilled: (I) that the diffusible anion concentration is sufficiently low in the colloidal system; (II) that no appreciable change occurs in the exchange system as a result of the reaction.

Since the various activity ratios can be determined by this thermodynamic analytical procedure, it is only necessary to establish one cation activity in the clay system by the quasithermodynamic potentiometric method in order to obtain all of them. In this way both the thermodynamic and the quasithermodynamic information for systems containing several exchange cations can be made

available. The method was first applied by Schuffelen and Loojes (1942) who set up Donnan equilibria and in addition determined the pH of colloidal nutrient media used in plant cultures.

### CONDUCTIVITY DETERMINATIONS

The simple interpretation of conductance measurements on colloidal systems is based on the arithmetical additivity of contributions from the charged species. The comparison of potentiometric and conductometric data for the same colloidal system has led to the discovery that although the two are always in agreement as regards order of magnitude, there are certain cases in which the calculated conductivity of the cation determined potentiometrically somewhat exceeds the measured conductivity of the whole system. Many colloidal acids, including a number of clay systems, show this anomaly. The author (Marshall, 1949) has offered a qualitative explanation in terms of the shielding effect which the outer parts of the ionic atmosphere can exert upon the conductance of the inner parts. In such comparisons of conductometric and potentiometric data, the fact that one is dealing with different kinds of averages should also be borne in mind; but the effect is in the opposite sense from that of the shielding, and hence cannot be responsible for the anomaly. The latter has so far been demonstrated only with colloidal acids, since the contribution of the hydrogen ion to the total conductivity is so great. Colloidal particles in water normally show mobilities of the same order of magnitude as those of large monovalent ions in true solution.

The evidence presented by Marshall and Krinbill (1942) clearly showed that in the sodium hydroxide titration of electro dialyzed Wyoming bentonite (montmorillonite), Putnam clay (beidellite), Illinois Grundite (illite), and kaolinite, the correspondence of sodium activities (as calculated from quasithermodynamic measurements) with specific conductivities was very close (Figs. 2 and 3). Every variation in sodium activity was reflected in a similar change in specific conductivity in the clay. This held true for the following clay concentrations: Wyoming bentonite, 1 percent and 0.3 percent; Putnam clay, 7, 4 and 1 percent; illite, 10, 5, and 1 percent; and kaolinite, 10 percent. In the case of 2.8 percent Wyoming bentonite the curves were in close agreement as regards relative slope changes up to 90 percent of equivalence. From here to 120 percent of equivalence the conductance calculated for the Na activity as measured, rose more rapidly. Since this was the most highly concentrated clay system in terms of ions, we may consider that here lies the danger point. The sodium activities in this region ranged upwards of 0.01. Ten percent Putnam clay also showed divergences in this region although the 7 percent clay did not. If one of the chief factors involved is the lack of uniformity in charge distribution, the two types of measurement might be expected to diverge at different ionic strengths for different clays.

The presence of marked thixotropic properties made no apparent difference to the correspondence in the potentiometric and conductometric data. The 2.8-percent bentonite system began to show the discrepancy just beyond the first thixotropic zone; that is, in the region where the system again became fluid.

Several factors affect the ratio: Cation conductivity/total specific conductivity, and to some extent they are mutually compensating. The activity figure is a



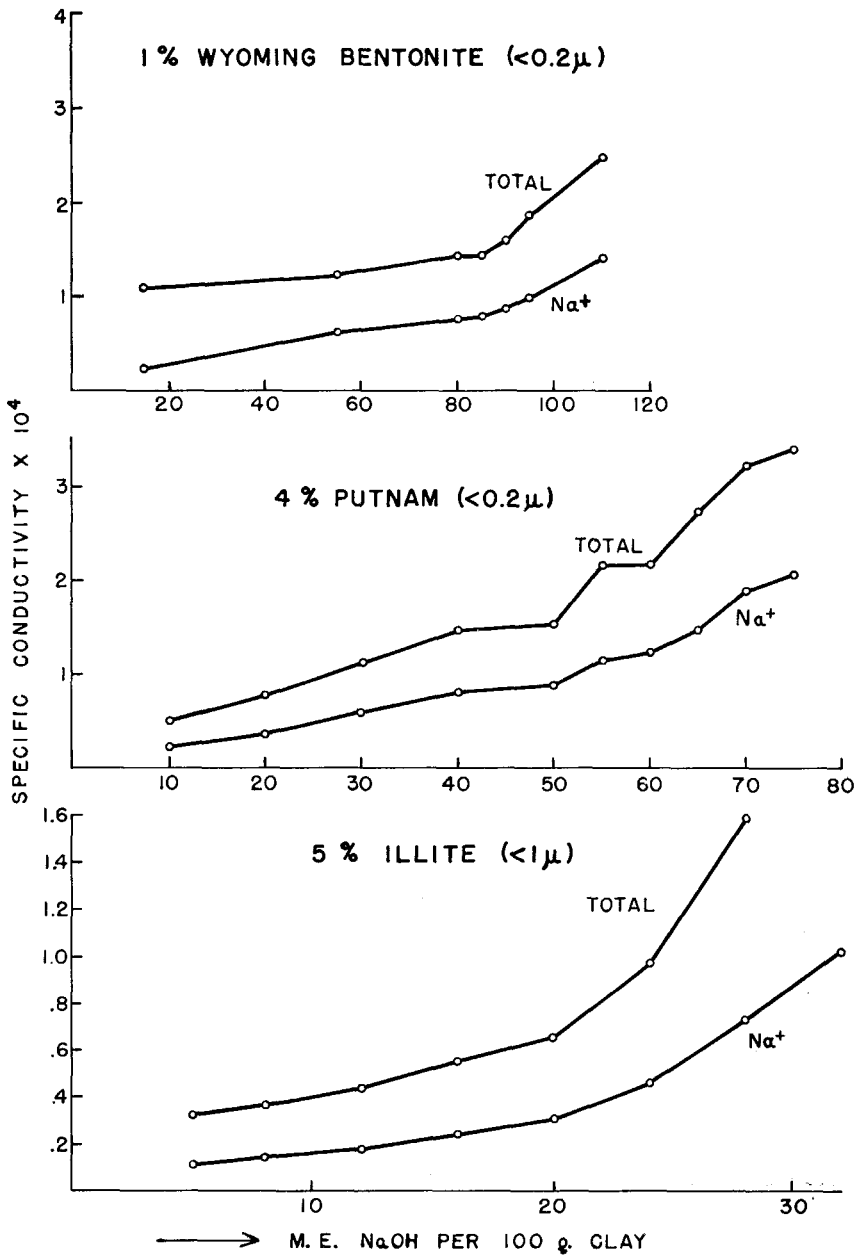


FIGURE 2.—Specific conductivities of clays of medium and low concentrations as compared with the calculated specific conductivities of the sodium ions measured potentiometrically.

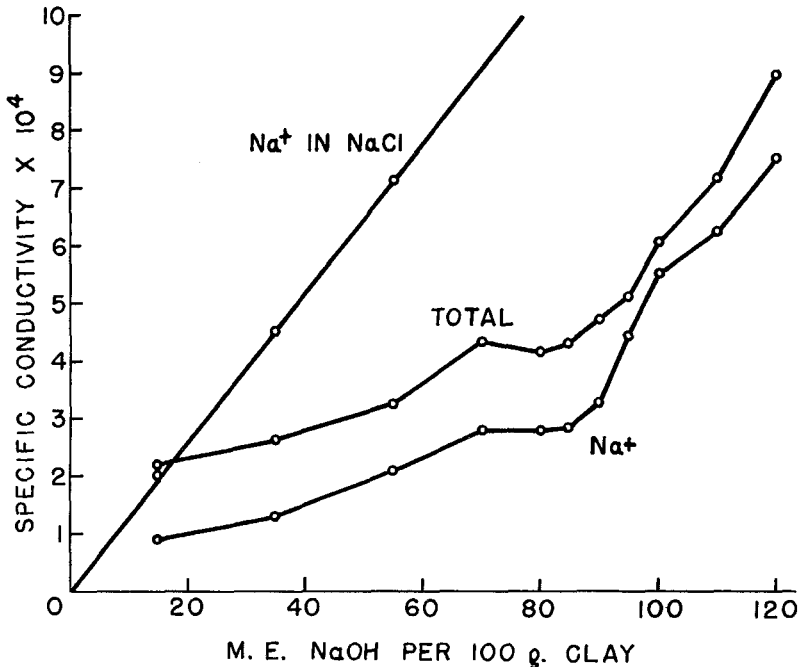


FIGURE 3.—Specific conductivity of a clay of high concentration (2.8 percent Wyoming bentonite,  $<0.2\mu$ ) as compared with the calculated specific conductivity of the sodium ions measured potentiometrically, and with the specific conductivity of the sodium in sodium chloride solutions.

geometrical average; yet in its conversion to a specific conductivity it is treated like an ordinary concentration of sodium ions. The range covered by this geometrical average will vary with dilution, being greatest for dilute systems where the ionic atmospheres are well separated. Increasing the concentration will cause more extensive interpenetration of atmospheres. The shielding effect will be greatest in dilute systems, thus lowering their specific conductivities. Variations in particle size and number with succeeding additions of base are also to be considered. These might cause variations in the ratio for a fixed concentration of clay and a variable amount of base. They would be of little importance in comparisons between different clay concentrations at the same stage of neutralization.

These ratios have been calculated for each point on each sodium hydroxide titration curve. Several examples are given in Figure 4. At high clay concentrations they vary slightly but smoothly over the titration curves except near equivalence, where a rapid rise occurs (2.8 percent bentonite and 10 percent Putnam). As the systems are diluted, the variation becomes much less. At the same time the values of the ratio diminish. A rough extrapolation to zero concentration indicates values around 0.40 for Wyoming bentonite, 0.36 for Putnam clay and 0.34 for illite.

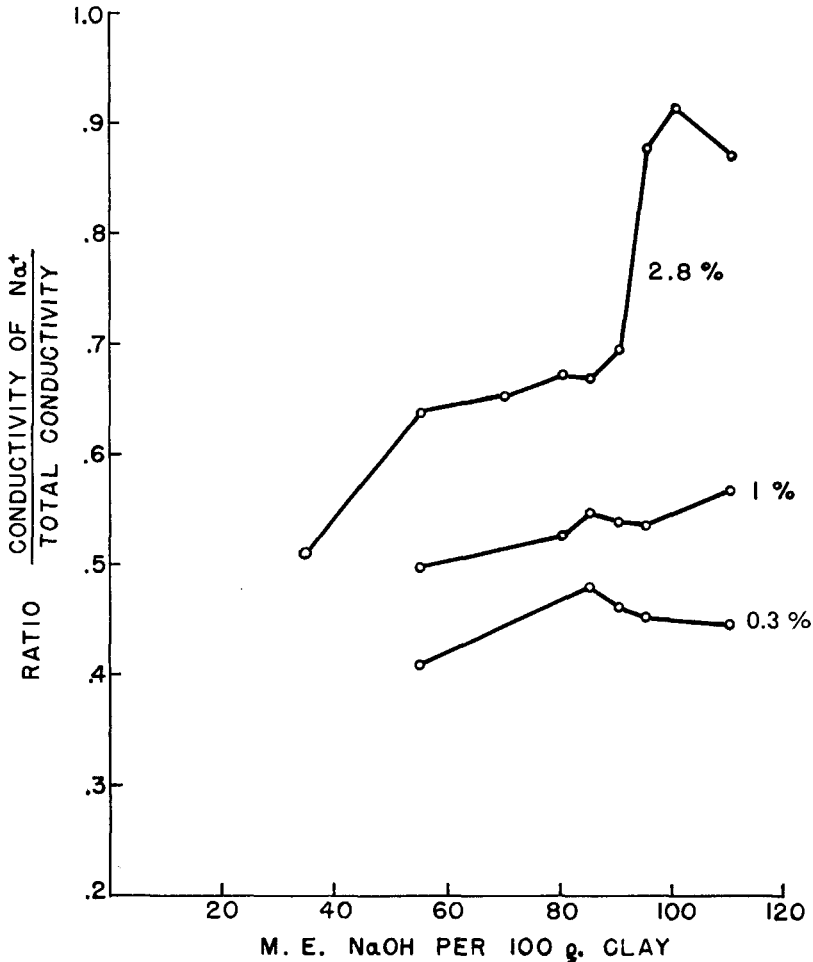


FIGURE 4.—The ratio, specific conductivity ascribed to  $\text{Na}^+$ /total specific conductivity of clay system, for various concentrations of Wyoming bentonite ( $<0.2\mu$ ) at various stages of neutralization.

The detailed figures for this ratio at different concentrations and degrees of saturation afford guidance also in the question, previously mentioned, as to what constitutes a "dilute" clay system. Smooth variations within the range 0.35 to 0.65 are clearly the rule. However, at high sodium concentrations, such as those given by 10 percent Putnam clay at 100 percent neutralization, or 2.8 percent bentonite at 95-110 percent neutralization there is a sudden jump to 0.8-0.9. It is of course not certain that this is due to a potential arising at the KCl bridge. However, as far as the more dilute systems are concerned the excellent concordance of the potentiometric and conductometric data seems to preclude

any appreciable salt-bridge error and to provide a means of defining the term "dilute."

The results may be interpreted in terms of the relative contributions of the cations and the colloidal anions to the total conductivity. At low concentrations of clay (0.04 percent), the maximum cataphoretic velocity of sodium Putnam clay particles, according to Beavers and Marshall (1951), is 5.6 microns per second per volt per centimeter. The absolute velocity of the sodium ion in dilute salt solutions is 4.5 microns per second per volt per centimeter. The ratio of the current carried by the sodium ion to the total is thus around 0.45. For illite and for Wyoming bentonite the figure was 0.52. The comparison of these figures with the extrapolated ratios (conductivity ascribed to  $\text{Na}^+$ /total conductivity), gives an idea of the relative importance of the inhomogeneity of the ion distribution at low concentrations as it affects jointly the mobility of the sodium ions and the discrepancy between the two kinds of averages. These, of course, will be functions of particle size and shape. The agreement is closest for Putnam clay which has the smallest platy particles; and the divergence is greatest for illite which has the largest, Wyoming bentonite being intermediate.

It will be evident that actual determinations of transport number in clay systems of varying concentration and ion status would provide material of great value in this difficult field, since cataphoresis experiments are practicable only at low clay concentrations. The ratios discussed above allow one to make the prediction that with increasing clay concentration the transport number of the sodium ions will rise, and that of the clay particles will correspondingly fall. Provided the clay concentration is not too high, the transport numbers should show only minor variation with degree of saturation with sodium. Certainly a combination of cataphoresis, transport number, specific conductivity, and activity determinations should lead to a more accurate evaluation of the electrical properties of cations in clay systems.

From the above discussion, it is evident that the interpretation of clay behavior in terms of ionic species is qualitatively identical for the quasithermodynamic and the nonthermodynamic approaches. Quantitatively also the two approaches are in close agreement, although it can be seen that the influence of second-order factors will affect them differently. The comparison of potentiometric with conductometric titration curves leads to the same conclusions as regards cations in relation to clay surfaces, and it may be expected that the addition of transport number determinations will further strengthen them.

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