

ELECTROCHEMICAL PROPERTIES OF CLAYS

BY LANNES E. DAVIS *

Introduction. The electrochemical properties of clay result from interactions between electrically charged particles, ordinary ions, and molecules of solvent. Flocculation and allied phenomena represent the effect of ions and solvent upon the particles. Cataphoresis and related effects are caused by interaction between particles and solvent, although ions may play an important part in producing the phenomena. The fabric of the clay and the electrical fields surrounding the particles influence the behavior of molecules of solvent and ordinary ions. This paper deals with theoretical aspects of the influence of particles upon ions.

The principal characteristics which determine the effect of particles upon ions are the multiple charge on the particles, the relatively large size and immobility of the particles, and the character of the pore space. The mobility and pore space are related to the consistency type of the clay, which may range from a fluid paste to a rigid block or sheet.

The fundamental theories, which we shall attempt to evaluate critically, have been developed for rigid membranes composed of collodion, zeolites, clay, and other materials. However, it is clear that the principles which are basic for these theories apply to materials in other consistency states. An attempt will be made to outline some aspects of a theory which can be extended to clay (or other colloidal materials) in various states.

The behavior of ions in a system containing relatively immobile charged entities is somewhat analogous to the behavior of electrons in a metal. Similarly, a phase of this type in contact with an ordinary solution of electrolytes resembles a metal electrode. In one case, we have particles which are mechanically immobilized and ions whose transference is affected in some manner by the electrical properties of the particles. In the other case, we have mechanically immobilized metal-lattice ions and electrons which do not transfer from one phase to another as free entities, because of quantum mechanical barriers.

One of the leading theories of electrode behavior is that proposed by Gurney (1932). According to his theory, ions make a transition between water dipoles and metal surfaces through a low quantum-mechanical potential barrier. It would be interesting to attempt an application of this theory to the transition of ions between a solution and a clay membrane, as Dole (1941) has applied it to the glass electrode. However, this paper will deal with the present line of development in the theory of membranes, which follows a different path. Many membranes are permeable to water and may, therefore, become aqueous phases. The interface between a membrane of this type and a solution of electrolytes is, thus, somewhat analogous to a liquid-liquid junction.

Terminology. Various authors, when dealing with membranes, have attached meanings to the common terms employed in electrochemistry which are at variance with generally accepted usage. Frequently, the implied definition can be determined only from the context and even then with some uncertainty. Some of the terms

used in this paper will be defined as precisely as possible to avoid confusion.

In a homogeneous system the "mobility" and transference numbers of various ionic species are invariants. Across an interphase boundary, these quantities may be variables. The terms used in the study of junctions, including membranes, should not be confused with critical constants tabulated in the literature.

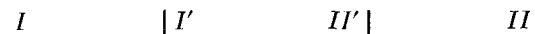
The ionic migration velocity, U_i , represents the hypothetical average resultant linear velocity of migration of the ions of the species, i , through a given plane oriented normal to the direction of transfer of electricity. The hypothetical transference number, t_i , represents the relative amount of electricity carried by the species, i , across a given plane. It is determined by the migration velocities and concentrations, c_i , of the ions at the given phase. The definition is

$$t_i = U_i c_i / \sum_i U_i c_i \quad (1)$$

The terms ionic mobility and sieve effect will not be used, because they have been employed loosely in the literature. The term mechanical sieve effect can be somewhat more precisely defined, however. Whenever any ion is larger than any portion of the pore space in a membrane, the ion will not be able to pass through the pore and is, thus, mechanically sieved. In some cases, the membrane may be entirely impervious to one or more species of ions. The term mechanical sieve effect refers to sieving, either partial or complete. It is, thus, primarily a qualitative concept, although presumably it could be given some degree of quantitative evaluation.

The Nernst Theory of Junction Potentials. The Nernst theory of junction potentials offers an avenue of approach to the membrane problem. It has generally been applied to liquid-liquid junctions and has frequently been restricted to transference junctions, i.e. junctions between two solutions of the same composition at different concentrations. However, the fundamental equation is so general that it can be applied to any junction, with appropriate modification in the interpretation of the terms.

Let us consider a three-phase system consisting of two solutions of electrolytes separated by an intervening phase, in this case a membrane. The system may be represented by the scheme:



The positions I and II lie in the solution phases, while I' and II' are in the peripheral laminae of the intervening phase. To fix our ideas, we shall assume throughout this paper that the membrane is a cation exchanger and that phases I and II consist of different concentrations of the same symmetrical electrolyte. Across any given plane between I and II , the transfer of electricity is governed by the equation

$$F y d E_f = \sum_i (t_i / z_i) d \ln a_i \quad (2)$$

This theory is a well-known modern expression of Nernst's theory. It is quasi-thermodynamic in character. The Faraday equivalent, $F y$, and the electrochemical va-

* Professor of Soils, Department of Soils, University of California, Davis, California.

lences, z_j , have known values. While overall transference numbers effective over a macroscopic path are measurable, the transference numbers, t_i , across a given plane are not measurable, although the concept is rigorously definable. To assign a hypothetical measure to t_i , certain assumptions must be made. E_J , the so-called junction potential, and the values of a_i , the ionic activities, are not generally measurable and require some care in definition. They are hypothetical quantities. Opinions differ as to the degree of meaning which can be attached to them. The problem lies entirely outside the scope of this paper. However, one may digress for a moment to suggest that a_i can be rather loosely designated as an inadequately determined function of ionic concentration and interaction with the environment. The individual ionic activity can be precisely defined for dilute solutions by the statistical method of Debye Hückel. Therefore, it stands as a symbol for an ionic property which conceivably determines the behavior of ions. It can be used as a tool, but only by means of assumptions which transform it, perhaps only approximately, to terms of well-defined character and measurable value. If such transformations are acceptable, E_J becomes adequately defined by equation (2), but is not necessarily measurable, unless we assume that we have a measure for t_i as well as a_i .

The junction potential is obtained by integration of equation (2) to give us

$$FyE_J = \int_I^{II} \sum_i (t_i/z_i) d \ln a_i \quad (3)$$

A membrane will behave as a perfect electrode if it completely impedes the migration of anions across any plane at which $d \ln a_i \neq 0$, since then $t_- = 0$, $t_+ = 1$, and (3) becomes

$$FyE_J = (RT/z_+) \ln(a_+^{II}/a_+^I) \quad (4)$$

For a symmetrical electrolyte we may perhaps assume, provisionally, that

$$a_+^I = a_-^I \text{ and } a_+^{II} = a_-^{II} \quad (5)$$

so that (4) becomes an equation with apparent thermodynamic significance,

$$FyE_J = (RT/z_+) \ln(a_-^{II}/a_-^I) \quad (6)$$

The assumption, equation (5), made in the derivation of equation (6) cannot be rigorously defended, although it is a plausible assumption. Equation (6) and allied equations cannot be established directly by any known experimental technic. As is well known, electrometric measurements are made in cells containing not less than two electrodes. When we are interested in establishing the behavior of one of the electrodes, assumptions must be made about the remaining electrodes. Thus, the alleged behavior of a given electrode is only apparent and not clearly established.

It is necessary to note carefully that if a membrane system has the properties described above, it will behave as a perfect electrode, but that the converse does not follow. A given membrane system may apparently obey equation (6) but we are not necessarily justified in assuming that it has any given set of properties which may be ascribed to it hypothetically in order to derive equation (6).

Many membranes do not behave in accordance with equation (6). In order to apply equation (3) to mem-

brane systems in general, we must set up a model. The various attempts to create a model have not been entirely satisfactory. Since equations (2) and (3) involve hypothetical entities, ad hoc assumptions are generally employed to interpret these equations in terms of measurable quantities. This situation is not novel in physical science. However, the partially ad hoc character of the methodology is not always recognized. Partial success of the formulation in predicting experimental results does not justify the conclusion that the assumptions are valid, particularly where they are not too plausible, *a priori*.

The Theory of Michaelis. One of the early theories was that of Michaelis. We shall present the theory as a solution of equation (3). Two assumptions are made: (a) The migration velocities, U_i , are constants; and (b) The ionic activities are equal to the ionic concentrations throughout the system. Both assumptions may well be questioned.

Equation (3) has been integrated by Henderson and by Planck for liquid-liquid junctions. When a single symmetrical electrolyte is present in all phases, both methods yield the same result,

$$FyE_J = RT \frac{U_+ - U_-}{U_+ + U_-} \ln c^I/c^II \quad (7)$$

where c^I and c^{II} are the electrolyte concentrations at I and II, respectively. It has been recognized generally that the derivations of Henderson and Planck represent a compromise with reality and are based upon several assumptions. This equation may be expropriated and applied to the membrane problem, although the justification is not too evident. When applied to membranes it represents Michaelis' theory of membrane potentials.

In any system for which U_- vanishes, we have a "perfect" electrode as defined by the Nernst theory,

$$FyE_J = RT \ln c^I/c^II \quad (8)$$

Equation (8) can be derived directly from (6) by assuming that the activity ratio is equal to the concentration ratio. It is also tempting to "correct" equation (7) by inserting activity coefficients and, thus, translating concentration values into activity values. However, it should be remembered that (7) was derived by assuming that the concentrations are equal to activities, so this device seems a bit shabby. It should be noted again that one may prepare a given electrode which, apparently, satisfies equation (6), but this fact does not validate the theory of Michaelis. In any event, a given electrode which apparently obeys equation (8) rather than (6) cannot be accepted as a "perfect" electrode in modern electrochemical practice.

The Theory of Teorell-Myers-Sievers. Perhaps the leading theory today is the M.S.T. theory independently expounded by Meyer and Sievers (1936 a, b, c), and by Teorell (1935), following ideas first presented by Willbrand. The treatment provided by Meyer and Sievers represents a genuine attempt to provide a straightforward derivation. Teorell merely assumed the final form of the equation. We shall consider the development presented by Meyer and Sievers. The discussion will be applied to a rigid, charged membrane without mechanical sieve effects. A single symmetrical electrolyte will be

considered. This model is plausible and is probably real for many membranes.

The first ad hoc assumption made by the authors is that U and U_- are equal to the values found in aqueous solution. This assumption is not very plausible. Furthermore, it is not necessary. We shall instead assume that the migration velocities are constants across the membrane, from I' to II' . This assumption is not implausible and provides an improvement in the model.

Meyer and Sievers base their theory upon an equation which they state has been derived from Nernst's theory of the diffusion potential. The equation is (using standard symbols)

$$FyE_J = RT \int_{I'}^{II'} \frac{t_+ - t_-}{t_+ + t_-} d \ln c \quad (9)$$

It is true that this equation can be derived from equation (3) by employing the identity $t_+ + t_- = 1$, assuming that $c = a_-$ and that $d \ln c_+ = d \ln c_- = d \ln c$. These may be approximately proper conditions for a transference (liquid-liquid) junction and possibly also for a membrane in the interval I' to II' . They are certainly not valid for the intervals I to I' and II to II' .

We shall bypass this difficulty for the moment and proceed to derive an intermediate equation, which represents a step omitted by the authors, but which is required for an orderly presentation. Introducing equation (1) into (9), we have

$$FyE_J = RT \int_{I'}^{II'} \frac{U_+c_+ - U_-c_-}{U_+c_+ + U_-c_-} d \ln c \quad (10)$$

It must be understood that this integral is intended to represent the sum of two external integrals which vanish where $d \ln c = 0$, and an internal integral within and extending across the membrane. Thus, while the limits refer to regions outside the membrane, c_+ and c_- refer to the two peripheral laminae of the membrane at I' and II' .

The unique character of the M.S.T. theory is the device by which c_+ and c_- are determined. Two Donnan equilibria are presumed to exist between the peripheral laminae of the membrane and the adjacent solution phases. It should be recognized that this situation cannot represent a final or stable state, but may well represent a metastable state or, possibly, a temporary steady state.

The thermodynamic equation for the Donnan equilibrium may be formally expressed as

$$(f_{\pm}^2 c^2)^I = (f_+ c_+ f_- c_-)^I \text{ and } (f_{\pm}^2 c^2)^{II} = (f_+ c_+ f_- c_-)^{II} \quad (11)$$

where f represents activity coefficients. Since f_+ and f_- are not measurable, an assumption is again made, namely that

$$(f_{\pm}^2)^I = (f_+ f_-)^I \text{ and } (f_{\pm}^2)^{II} = (f_+ f_-)^{II} \quad (12)$$

so that

$$(c^2)^I = (c_+ c_-)^I \text{ and } (c^2)^{II} = (c_+ c_-)^{II} \quad (13)$$

This crucial assumption has received little comment in the literature. For suspensions of clay in contact with dilute solutions, it is probably not even approximately valid, but one does not know its degree of validity with rigid membranes. Since some assumption is imperative,

one may perhaps utilize whatever is formally applicable. The theory becomes, however, of an *ad hoc* character, immediately we accept an assumption which we strongly suspect to be fundamentally invalid.

In any event, with the usual Donnan terminology, we may write

$$c_+ = c_- + A \quad (14)$$

where A is the number of unit charges on a negatively charged membrane.

Combining (14) with (13) and introducing the result into (10), we can integrate the resultant equation. After rearranging, we obtain the well-known formula,

$$FyE_J = RT \left[u \ln \frac{x^{II} + Au}{x^I + Au} + \frac{1}{2} \ln \frac{(x^I + A)(x^{II} - A)}{(x^I - A)(x^{II} + A)} \right] \quad (15)$$

where

$$u = \frac{U_+ - U_-}{U_+ + U_-} \text{ and } x = (4c^2 + A^2)^{1/2}$$

The authors point out that the first term in (15) represents the generalized Henderson diffusion potential, while the second term represents the difference between two Donnan potentials.

Equation (15) has the mathematical property that, as c^I and c^{II} approach zero, the first term also approaches zero, while the last term approaches $\ln c_2/c_1$. Thus, for low values of c^I and c^{II} , we approach the equation for a "perfect" electrode, i.e. equation (8). It may also be noted that equation (8) can be derived directly from equation (9) if $t_+ = 1$, $t_- = 0$. Also, we can derive equation (6) if c is replaced by a_- . Again, the fact that a given electrode provides a value of E_J consistent with equation (6) does not guarantee the validity of the theory.

Marshall's Clay Membranes. Marshall (1948) has prepared a number of types of clay membranes from various clay minerals as well as membranes composed of zeolites. Wyllie and Patnode (1950) have worked also with shale membranes. The degree of ionic selectivity and the reproducibility of results depends upon the character of the clay mineral and upon the treatment of the clay. The most satisfactory membranes were those dried at a temperature between 300° and 600°C. The reason for this is not known.

One very important fact discovered by Marshall was the partial specificity of clay minerals with respect to cations. For example montmorillonite produces excellent electrodes for use with potassium and ammonium ions, beidellite membranes work well with sodium, while Ca-bentonite membranes are superior to others for work with calcium. A hydrogen bentonite membrane heated at temperatures above 450°C is sensitive to univalent ions but not to bivalent ions. The reasons for this behavior are not understood at present.

We shall not discuss in detail the use of these membranes as electrodes. As stated above, they are partially specific but mostly so with respect to quality of behavior. Like most membranes of collodion and other materials, they exhibit little approach to complete specificity to the extent that Na^+ ion activities can be measured readily

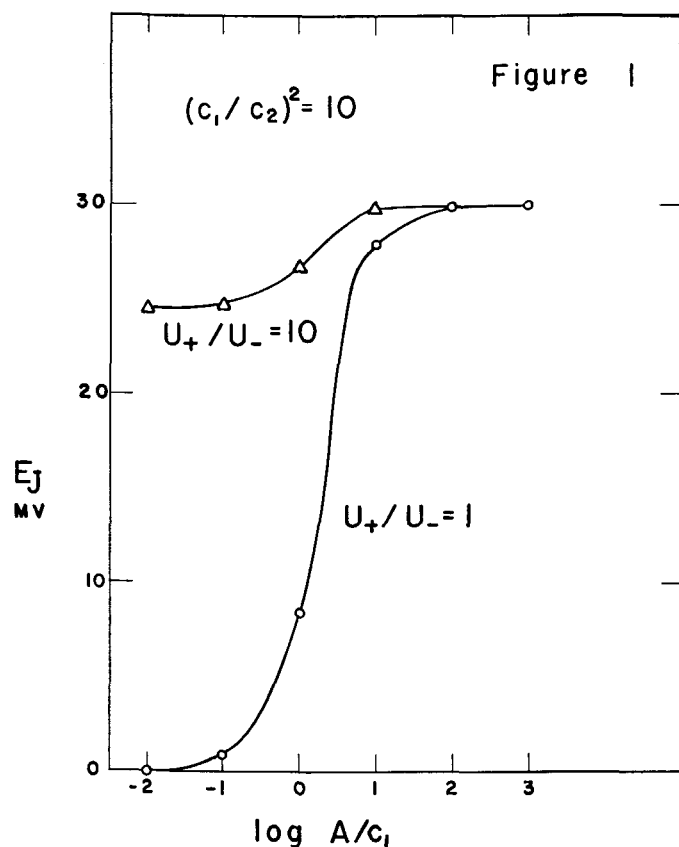


FIGURE 1. Theoretical curves illustrating M.S.T. equation. E_J is shown as a function of $\log A/c_1$ (where c_1 may be identified with c^I of text). Variable parameters are c_1/c_2 and U_+/U_- ; only one value of former is illustrated in this figure.

in a solution of Na and K salts, for example. However, Marshall has considered the problem of measurements in mixed systems. A hydrogen bentonite electrode heated to a temperature above 450°C can be used for the determination of the activity of a univalent ion in the presence of bivalent ions. For mixtures consisting of two univalent cations (or two bivalent cations), Marshall has proposed a method involving two membranes of different selectivity. Space will not permit consideration of this procedure.

Marshall has utilized the M.S.T. theory to interpret the behavior of his clay membranes. He has discussed the importance of the ratios U_+/U_- and A/c . As either increases, the behavior of an electronegative membrane approaches more closely to that of an ideal electrode. The theoretical curves shown in figure 1 indicate this behavior. For any given electrolyte, U_+/U_- would be increased by mechanical sieve action. The ionic selectivity is greater for a membrane with a large value of A , that is, with a large cation exchange capacity. The selectivity is also increased when c^I and c^{II} are small.

Sollner's Theory. Sollner (1950, 1950a) has worked only with collodion membranes. Negatively charged membranes are prepared by treating thin sheets with NaOH or KOH solutions. Apparently, oxidation of cellulose by the nitrite ions which are released in alkaline solution increases the permeability and the ion exchange capacity, that is, the surface-charge density on the pore walls.

Positively charged membranes are produced by impregnating collodion sheets with protamine. As Sollner has not worked with clays, we shall consider his interpretations rather than the practical use of his membranes.

Sollner has derived a theory of mosaic membranes containing both electro-positive and electro-negative regions. His theory of the behavior of such membranes involves an "all electrolyte electric circuit," the behavior of which has been successfully explored by means of a laboratory model.

Sollner has discussed bi-ionic potentials, for example, potentials in the system NaCl | KCl. He has also shown that negative osmosis exists in certain types of membranes as a result of counter electro-endosmosis.

Sollner has shown experimentally that the values of A , the charge on the membrane per unit volume of pore space, which can be calculated from the M.S.T. theory are much greater than those determined by the ion exchange capacity for collodion membranes. The calculation of values of A is based upon a measurement of E_J and assumed values of U_+ and U_- .

Sollner's theory is primarily qualitative rather than quantitative. To present his views in a proper perspective, three important conceivable mechanisms may be summarized, by which the transference of negative electricity across an electro-negative membrane is reduced.

1. The negative ions are mechanically sieved because they are too large for the pores. It is not necessary that all pores be too small if we wish to produce a finite value of E_J , but to realize equation (4) they should all be too small. It is doubtful that most recent types of membranes comply with this requirement.

2. Because of a very high value of A/c , the Donnan equilibrium yields a very low value of c_- . The transfer of negative electricity is reduced, not because of a barrier, but because of insufficient carriers. This is essentially the M.S.T. viewpoint.

3. The mobility of negative ions is greatly reduced by the electrical field because of the charges in the pore walls. This concept is illustrated by figure 2, in which a pore with negatively charged walls is shown. The negative field resulting from the charge on the pore wall is represented by a semi-circle. This representation, which is essentially Sollner's, requires some interpretation. It is closely related to the M.S.T. viewpoint. There will be more positive ions present in this system than negative ions, so that c_- may be small. However, there is another factor which has not been sufficiently explored. Does a structure of this type involve a retardation or acceleration upon positive and negative ions present in the field of the pore-wall charge? If so, the migration velocities averaged over a pore cross-section will be different from those in water.

Sollner assumes that negative potentials may block the movement of anions through a pore. His picture is primarily electro-mechanical. If a charged spot is at a narrow place in a pore, anions cannot pass. Structural factors determine the value of E_J ; the over-all value of A may not be a determining factor, a difficulty which is neglected by the Meyer-Sievers postulation. This difficulty probably is relatively great in collodion membranes of low exchange capacity and relatively less important in clay membranes of high exchange capacity.

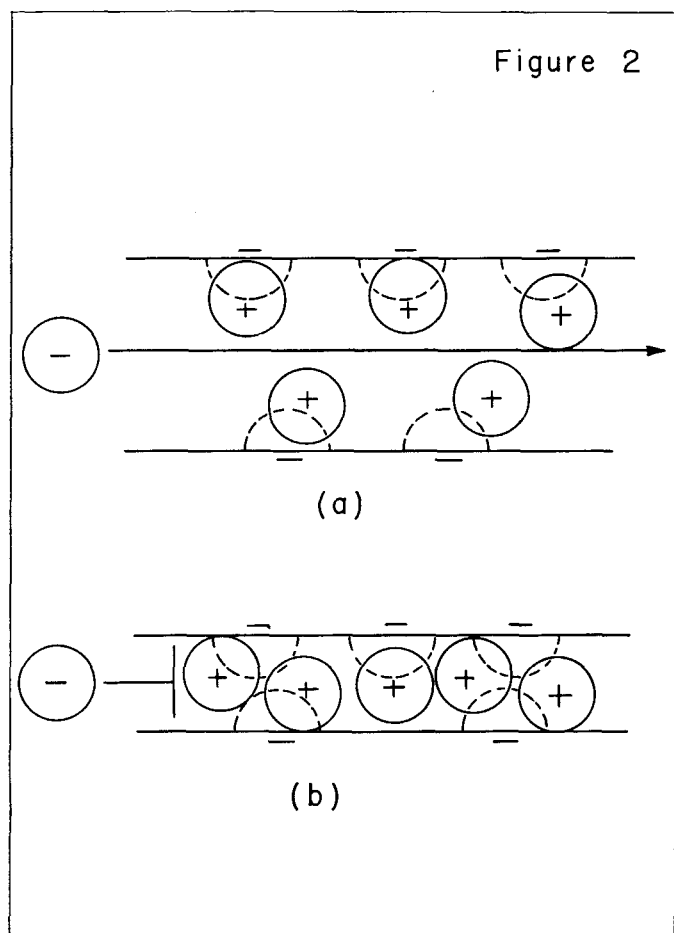


FIGURE 2. Permeability as a function of pore size. (a) A large pore exhibiting neither mechanical sieving nor complete electrical hindrance to migration of a small anion. Nevertheless, the cross-section free to anion migration is not as great as that available for cation migration (including replacement migration). A large anion would be mechanically sieved. (b) A small pore exhibiting no mechanical sieving. Cations can migrate by replacement; anions cannot.

Regardless of these considerations, one conceivable factor has been lost sight of by almost all workers except Sollner. As the electrolyte concentration on one side of a membrane increases, the peripheral negative potentials may be depressed. This probably is consistent with the usual concept that electrolytes tend to depress the "effective charge," that is, the field of the ion-swarm of a colloidal particle. If we assume that anions are impeded by these fields, the depression or elimination of them should facilitate the movement of electrolytes into the membrane. This effect might well be progressive. In time, the entire membrane might lose its selectivity.

Staverman's Theory. Staverman (1952) has recently applied the theory of non-equilibrium thermodynamics formulated by Onsager to membrane phenomena. Considering only the application to the electrochemistry of membranes, the theory involves the following concepts:

1. Thermodynamic methods yield results which are generally more nearly correct than those derived from a model.

2. On the other hand, a complete understanding of the behavior of a particular system requires an interpretation related to the molecular structure of the system.

3. Membrane systems are not generally at complete equilibrium.

4. Therefore, non-equilibrium thermodynamics is required to interpret the behavior of membranes.

Staverman has derived the following equation:

$$E_D = \sum t_i^r \Delta \mu_i \quad (16)$$

It is not clear why the Faraday equivalent, Fy , is omitted. E_D represents the membrane potential, while μ_i is the chemical potential ($\Delta \mu_i = RT \Delta \ln a_i$). The term t_i^r is defined as

$$t_i^r = t_i/z_i \quad (17)$$

The equation provides for the transference of uncharged molecules. For such molecules t_i and z_i are zero, but the ratio is a mathematical indeterminate, and may have a finite value. The significance of the transference of uncharged molecules may be seen when the phenomenon known as the streaming potential is considered. It is also important for the case of liquid-liquid junctions involving mixed solvents. In this case, the transfer of water of hydration cannot be neglected. Staverman makes the important point that the conditions within a membrane resemble those within a junction between mixed solvents. There is a large excess of one of the mobile ions, thus involving marked preferential transport of water by these ions. Furthermore, it is necessary to consider the probability that part of the apparent experimental value of E_J may be electrokinetic in origin.

Staverman makes another important suggestion: The excess ions in the membrane entrain solvent and the deficient ions will be impeded. He remarks that his expression for the membrane potential resembles Michaelis' formula much more than Meyer and Siever's. This comment is somewhat obscure. We shall see later that the distinction made is only apparent and not profound.

Conclusions. The M.S.T. theory has been widely accepted. It is conceptually plausible. A membrane differs from a simple liquid-liquid junction since there are immobile charges in the former. The movement of ions through membranes is so slow that a quasi-equilibrium may well exist across each surface.

Staverman apparently feels that his equation (18), which is actually a modified form of the Nernst equation (2), is inconsistent with the M.S.T. theory. In principle, however, the Nernst equation, when applied to a membrane system, is entirely consistent with the concept that there are two virtual equilibria across each face of the membrane.

Equation (2) may be expressed in the form

$$Fy dE_J = RT (t_+ d \ln a_+ - t_- d \ln a_-) \quad (18)$$

The fundamental equation for the Donnan equilibrium may be given in the form

$$d \ln a_+ a_- = 0 \quad (19)$$

so that

$$d \ln a_+ = - d \ln a_- \quad (20)$$

Inserting (20) into (18) we have

$$Fy dE_J = RT (t_+ + t_-) d \ln a_+ = RT d \ln a_+ \quad (21)$$

Now equation (18) may be integrated over the intervals $I-I'$, $I'-II'$, and $II'-II$. We may well provide a term for the transference of uncharged molecules, k . The resultant equation is

$$Fy E_J = RT \left[\ln \frac{a_+^{I'} a_+^{II'}}{a_+^I a_+^{II'}} + \int_{I'}^{II'} (t_+ d \ln a_+ - t_- d \ln a_- + t_k^r d \ln a_k) \right] \quad (22)$$

This equation may break down when the migration of ions is sufficiently rapid that virtual equilibrium does not exist, although a steady state may be realized which might be defined by a term analogous to the first term in this equation.

Equation (22), like Staverman's equation, may be correct, but it is still purely formal and can have no a priori application in the absence of a model. The present healthy confusion suggests that one more attempt to set up a model may be no more successful than earlier efforts.

It is conceivable that we should attempt to ascertain the actual characteristics and behavior of membranes by various experimental studies. This procedure may be preferable to our present methods. At present, we set up a model, prepare a system, and then measure a single experimental value, E_J (in itself only an apparent value).

Considerable parts of the work done by Sollner and recent studies by Jenny and others (Coleman 1951; Jenny 1950) point the way to a continued program. It is particularly pertinent to again suggest that the most fruitful work can be done with systems which do not behave as perfect electrodes. Furthermore, the function of clays as electrodes is of minor scientific importance. The actual properties of various states of consistency would seem to be of greater general interest.

We particularly require an understanding of the way in which ions are affected in their migration by the electrical fields surrounding the particles and the ions in narrow pores. Also, the viscous drag caused by water of hydration may be important as stated by Staverman. Although Sollner and Staverman have suggested that such effects are real and important, no quantitative formulation has been presented by these authors. Jenny and his group have made a genuine contribution to this phase of the problem. Unfortunately, emphasis has been placed upon other aspects of their work which are apparently controversial. Eriksson (1951) has recognized the relevancy of their findings to the problem of the electrochemistry of clays. He like others, however, is strongly committed to the M.S.T. theory.

In conclusion, the need of a fresh start is clearly indicated.* In particular, more ingenuity in devising techniques, more experimental work, and perhaps a partial moratorium upon model formation and the use of inadequate and implausible assumptions is needed.

* Since this paper was written an excellent new approach has been made by Scratchard (1953).

Summary. The properties of ion-selective membranes are considered to be a result of the interaction between charged clay particles and ions. Most theoretical treatments of such membranes have been developed in order to predict the value of the membrane potential.

It is apparent that all extant theories fall into two classes: (1) purely formal theories which cannot be evaluated experimentally because the terms have no operational significance, and (2) theories involving unverifiable assumptions.

The conclusion is reached tentatively that further experimental work, utilizing new methods of approach to the problem, is desirable.

DISCUSSION

E. A. Hauser:

In figure 2 you show a negatively charged capillary in which Na^+ ions would be able to pass through the force field while Cl^- ions would not. If the pores were smaller than the Na^+ ions, they would be adsorbed on the negatively charged surface. Will you elaborate on this point?

L. E. Davis:

Regardless of the relative size of the pore and the Na^+ ions, the Cl^- ions would not pass through, owing to the nature of the force field occasioned by the negatively charged surface. If the pores were smaller than the Na^+ ions neither the cation nor the anion would be able to pass through.

I. I. Cornet:

What experiments will further our electrochemical knowledge of clay? For example, is there some experimental technique for the determination of ion activities in a gel at equilibrium with a vapor; also, can we measure the transference number in gels?

L. E. Davis:

I know of no technique for the determination of ion activities of a volatile electrolyte such as acetic acid in a gel at equilibrium with a vapor. On the other hand, we can determine the activity of acetic acid in a clay suspension. If the vapor is truly in equilibrium with the clay, the activity of the acid must be that of the vapor phase, but that will not give the activity of the acetate ion or the H^+ ion. As regards the activities of ions in clay systems, the techniques now in use are questionable. They involve the use of the glass electrode, a salt bridge, and a calomel electrode. The work of Jenny and associates (1950) casts doubt on the usual interpretation. They have shown that when the concentration of KCl in the salt bridge is varied, the emf changes much more with a clay suspended in a solution of an electrolyte than it does when the solution is free from clay. This seems to indicate that something takes place at the salt bridge clay contact. Furthermore, the curve obtained by plotting emf against concentration of KCl in the salt bridge indicates that, were it possible to have a concentration greater than saturation, the emf would change still further. Accordingly, the technique now in use for determining ion activities is not entirely satisfactory.

We can be certain, I believe, of electrolyte activities where there are two electrodes and no liquid junction, that is, no salt bridge. At present we are attempting to determine the activity of an electrolyte, such as NaCl, in the presence of clay, in the hope of finding some property of Na^+ ions adsorbed on clay that can be measured by means of a membrane. The activity of NaCl can be measured with a membrane and an Ag-AgCl electrode. This is about as far as we can safely go at present.

Regarding the question of measurement of transference numbers, the answer is yes. This has been done by Jenny and others (1951) and the results are interesting. In my opinion we need more experiments in which activities of electrolytes are studied in relation to (a) electro-kinetic properties of materials, (b) transference numbers, and (c) conductivity. Different methods should be used, to ascertain whether or not the results are consistent.

E. A. Hauser:

In studying ion movement and similar matters in colloidal systems the concentration of the colloidal electrolyte used greatly influences the results. This point has not been given sufficient consideration in the publications with which I am familiar.

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