JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 70 MAY 3, 1948 NUMBER 4

[CONTRIBUTION OF COLLEGE OF AGRICULTURE, UNIVERSITY OF MISSOURI]

The Electrochemical Properties of Mineral Membranes. VI. Clay Membranes for the Determination of Calcium[1]

BY C. E. MARSHALL[2a] AND A. D. AYERS[2b]

Introduction

Three previous papers in this series[3] have dealt with the use of clay membranes in the potentiometric determination of potassium, ammonium, and sodium. In the course of this work it was found that most of the clay membranes prepared were sensitive also to divalent cations. An important and useful exception was provided by membranes prepared from hydrogen montmorillonite (electrodialyzed Wyoming bentonite) previously heated to 450–550°, which were sensitive to monovalent cations but not appreciably to divalent. These were used for the determination of potassium and ammonium. As regards calcium, some preliminary work had shown that quantitative results could be obtained at low concentrations using membranes prepared from Putnam clay (hydrogen beidellite), previously heated to 500–600°.[4] The present work is concerned with the variations in the properties of clay membranes which affect their suitability for the determination of calcium. We have studied two clays, Wyoming bentonite and Putnam subsoil clay, two exchange cations, hydrogen and calcium, and a range of temperatures of pretreatment from 300 to 600°.

Theoretical Considerations

In all our previous work considerable use has been made of the Teorell–Meyer and Sievers theory of porous, charged membranes. As the work has progressed it has become evident, firstly, that certain of its postulates are not fulfilled by clay membranes; secondly, that quantitative departures from its predictions are generally found. Necessary modifications of the theory for the essentially non-porous clay membranes will be dealt with in a later paper. However, the great importance of the charge A, which can be regarded as the thermodynamic activity of the ions associated with the membrane material itself, cannot be denied, and must be taken into account in any modification of the existing theory. The charge A, sometimes known as the selectivity constant, is responsible for the setting up of two Donnan potentials, one near each surface, which have the effect, in the case of a negatively charged membrane, of greatly reducing the anion activity in comparison with cation activity. Hence, the membrane acts as though the anions possess a greatly reduced or negligible mobility. In the limiting case the potential across it can then be calculated according to the Nernst equation, taking the cations only into consideration. In the practical development of membranes suitable for the determination of various cations, it is important in each case to establish the concentration limits over which accurate results can be obtained. The upper limit is chiefly determined by the magnitude of A. The lower limit varies in different cases; it is affected by the hydrolysis of the membrane itself as well as by hydrolysis of salts of weak bases and strong acids at high dilutions. In the case of potassium it was shown that using 490° hydrogen bentonite membranes accurate results could be obtained in the range 0.1–0.0001 molar.

With divalent cations two factors operate in reducing the charge A. Since the Donnan equi-

---

[1] Joint contribution from the Department of Soils, University of Missouri, and the U. S. Regional Salinity Laboratory, Bureau of Plant Industry, Soils and Agricultural Engineering, Agricultural Research Administration. Journal Series No. 1064 of the Missouri Agricultural Experiment Station.

[2] (a) Professor of Soils, University of Missouri. (b) Associate Chemist, U. S. Regional Salinity Laboratory.

[3] (a) C. E. Marshall and W. E. Bergman, THIS JOURNAL, **63**, 1911 (1941). (b) C. E. Marshall and W. E. Bergman, *J. Phys. Chem.*, **46**, 325 (1942). (c) C. E. Marshall and C. A. Krinbill, THIS JOURNAL, **64**, 1814 (1942).

[4] C. E. Marshall, *Soil Sci. Soc. Am. Proc.*, **7**, 182 (1942).

libria are evaluated in terms of molality, a membrane having a molal charge A in the monovalent case will automatically have a molal charge $A/2$ in the divalent case. Hence, the upper limit at which the Nernst equation is obeyed will correspond to a lower concentration of divalent than of monovalent cations. Secondly, the dissociation of divalent cations from charged surfaces is in general much less than that of monovalent (hydrogen excepted). The charge A can be regarded as the product of the cation exchange capacity and the fraction of cations active or dissociated. It will therefore be greatly lowered in cases where the cations are only slightly dissociated from the membrane surfaces. These factors are illustrated in Fig. 1. The left hand curve is drawn in the conventional manner from the Teorell–Meyer and Sievers equation for the case in which the anion and cation in solution have equal mobilities, $A = 1$; and the cation activities on the two sides of the membrane are in the fixed ratio $a_1/a_2 = 3.000$ throughout. The next curve is that experimentally found for 550° hydrogen beidellite membranes (Putnam clay), using sodium chloride solutions. Transferring to the divalent scale and allowing for the reduction in A to one-half its value gives the third curve. Finally, the curve farthest to the right is the experimental curve for calcium chloride solutions using the same membrane material. Whereas A for sodium chloride solutions is approximately 0.5, the value for calcium chloride is only 0.026. The practical consequence of this, as may be seen from the figure, is that calcium activities can only be determined with this membrane from 0.002 molar downwards. In order to select the most favorable materials, curves have been obtained for hydrogen and calcium bentonite (montmorillonite) and Putnam clay (beidellite) over a range of pretreatments from 300 to 620° (see below).

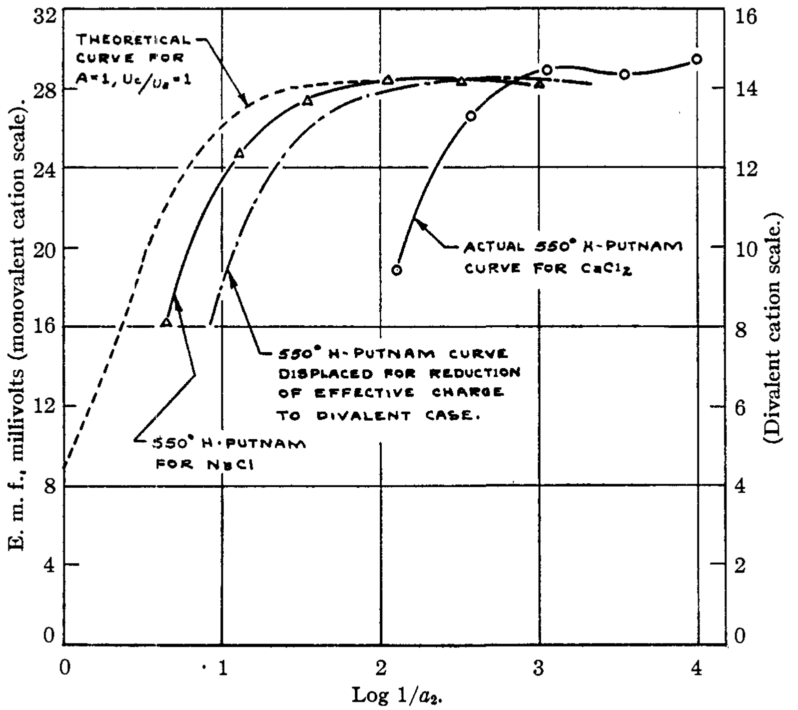

Fig. 1.

The relative behavior of porous membranes as regards different cations can be expressed in terms of mobility ratios. In this formulation the membrane is treated as the limiting case of a liquid junction in which the anions have zero mobility. By application of the Henderson or Planck equations, the potential across the membrane can then be expressed as a function of the activities of the two cations concerned, together with their cationic mobility ratio within the membrane. By measuring the potential when the membrane separates two different salt solutions of known cationic activities, the mobility ratio of the cations can be determined. The equations applicable to different cases have been discussed by Marshall.[5] Once the mobility ratios have been determined it then becomes possible to devise procedures for the analysis of mixtures of cations.

If clay membranes are treated as non-porous then a more rigorous alternative theory (to be discussed in a later paper), relates the potentials observed with different salts to the differential heats of adsorption of the cations concerned. This theory does not as yet facilitate the solution of analytical problems involving mixtures of cations. Hence, in this and the following paper dealing with magnesium, we shall continue to use mobility ratios.

The formulas used for the determination of mobility ratios in the three cases, monovalent–monovalent, divalent–divalent, and monovalent–divalent were derived from the Henderson equation for a liquid junction and are as follows:

Sodium salt on one side of the membrane, potassium salt on the other

$$E = \frac{RT}{F} \ln \frac{a^{\mathrm{I}}_{\mathrm{K}}}{a^{\mathrm{II}}_{\mathrm{Na}}} \frac{U_{\mathrm{K}}}{U_{\mathrm{Na}}} \tag{1}$$

Calcium salt on one side, magnesium salt on the other

$$E = \frac{RT}{2F} \ln \frac{a^{\mathrm{I}}_{\mathrm{Ca}}}{a^{\mathrm{II}}_{\mathrm{Mg}}} \frac{U_{\mathrm{Ca}}}{U_{\mathrm{Mg}}} \tag{2}$$

Potassium salt on one side, calcium salt on the other

---

(5) C. E. Marshall, *J. Phys. Chem.*, **48**, 67 (1944).

$$E = \frac{RT}{F}\left\{\frac{-a^{I}_{K} + \frac{U_{Ca}}{U_{K}}a^{II}_{Ca}}{-a^{I}_{K} + 2\frac{U_{Ca}}{U_{K}}a^{II}_{Ca}}\right\}\ln\frac{a^{I}_{K}}{2\frac{U_{Ca}}{U_{K}}a^{II}_{Ca}} \qquad (3a)$$

As it stands, this equation does not readily lend itself to the determination of U_{Ca}/U_{K} except by the use of successive approximations. However, if a^{I}_{K} is small compared with $U_{Ca}/U_{K} \times a^{II}_{Ca}$ then we have

$$E = \frac{RT}{F}\frac{1}{2}\ln\frac{a^{I}_{K}}{2\frac{U_{Ca}}{U_{K}}a^{II}_{Ca}} \qquad (3b)$$

The way in which mobility ratios so determined can be used may be illustrated by examples which have arisen in investigations of the titration curves of clay acids with bases. Thus in the monovalent–monovalent case we encounter systems comprising a standard potassium salt on one side of the membrane and a clay system containing both hydrogen and potassium ions on the other. Knowing U_{H}/U_{K}, a^{I}_{H} and a^{II}_{H} (from a glass electrode measurement) it is possible to calculate the unknown a^{II}_{K} by applying the equation

$$E = \frac{RT}{F}\ln\frac{a^{I}_{K}}{a^{II}_{K} + \frac{U_{H}}{U_{K}}a^{II}_{H}} \qquad (4)$$

Similarly in a calcium–hydroxide titration with a standard calcium solution on one side and a mixture of calcium and hydrogen ions on the other we have

$$E = \frac{RT}{F}\left\{\frac{a_{Ca} - a^{II}_{Ca} - \frac{U_{H}}{U_{Ca}}a^{II}_{H}}{2\,(a^{I}_{Ca} - a^{II}_{Ca}) - \frac{U_{H}}{U_{Ca}}a^{II}_{H}}\right\}\ln\frac{2a^{I}_{Ca}}{2^{II}_{Ca} + \frac{U_{H}}{U_{Ca}}a^{II}_{H}} \qquad (5)$$

Substitution of the known quantities E, a^{I}_{Ca} a^{II}_{H} and U_{H}/U_{Ca} does not lead immediately to a solution for a^{II}_{Ca}. This is arrived at by successive approximation, first putting the algebraic quantity before the logarithm equal to one-half and evaluating a^{II}_{Ca}; then using this value to get a better approximation to the quantity before the logarithm; finally using this to calculate an improved value of a^{II}_{Ca}. These three operations are generally sufficient.

Thus the characterization of membrane materials for analytical use involves both the determination of the range of activities over which the Nernst equation is obeyed and a series of mobility ratios. Good methods for the analysis of mixtures can only be developed in cases where the mobility ratio shows reasonable constancy over a sufficiently wide range of concentrations.

Experimental Methods

These were essentially the same as those described in earlier papers dealing with potassium[3a] and sodium.[3c] Since the membranes sensitive to calcium have relatively low resistances (<50,000 ohms) a galvanometer with a sensitivity of 0.025 microamp. per scale division could be used without amplifier in measuring to 0.1 millivolt. The cell measured was Hg, Hg_2Cl_2 Saturated KCl/Solution I/Membrane/Solution II/Saturated KCl Hg_2Cl_2 Hg, the calomel electrodes being of the special type previously described with upturned capillary tip containing saturated potassium chloride in a potassium agar gel. For accurate results fresh calomel electrodes were used whenever the calcium concentration in II was changed. This is important, since if an electrode of this type is transferred from one solution to another, liquid junction potentials which persist for some time can be set up between that part of the first solution which diffused into the capillary tip and the second solution employed. Corrections were applied for the asymmetry potential of the membranes (only those membranes were employed whose asymmetry potentials were less than 1 millivolt) and for the small differences between different calomel electrodes. All results were finally corrected to 25°.

Since the membranes themselves were of relatively low resistance in most cases, the concentrations of the two solutions had a measurable influence upon the total resistance of the cell. A considerable increase in total resistance was noticed in proceeding from $M/1000$ to $M/10{,}000$ solutions of calcium salts.

In membranes prepared from the same sheet of evaporated clay and subsequently treated similarly, individualities still persist, due probably to variation in film structure caused by differences in the rate of evaporation in different parts. They show themselves chiefly in the more concentrated solutions where the theoretical Nernst potential is not attained. Where different salts are employed on the two sides, the mobility ratios are affected and considerable departures from the average value are sometimes encountered. These differences in mobility ratio values are more marked for the monovalent–divalent cases than for monovalent–monovalent or divalent–divalent.

As in previous work, the membranes were first selected for uniformity of thickness and freedom from cracks. They were then mounted and were soaked twenty-four to forty-eight hours—sometimes up to five days—in a calcium chloride solution more concentrated than those employed in measurements. A selection was then made of those with asymmetry potentials below 1 millivolt. The results reported below are averages of from 6–12 membranes so chosen.

In characterizing membranes in their behavior toward calcium ions a series of calcium chloride solutions was required, so adjusted that the calcium ion activities were, for successive pairs, in the fixed ratio 3.000 to 1. The calculations from the activity coefficients of the salt involve two non-thermodynamic assumptions; (1) that in potassium chloride solutions the anion and cation contribute equally to the total activity; (2) that in potassium chloride and calcium chloride solutions of equal ionic strength the chloride ion activities are the same. The primary data used were those of Shedlovsky and MacInnes[6] on potassium chloride and those of McLeod and Gordon[7] on calcium chloride. At any given value of the ionic strength, the following relationship holds.

$$\overset{+}{\gamma}_{Ca^{++}} = \frac{(\gamma^{\pm}_{CaCl_2})}{(\gamma^{\pm}_{KCl})^2}$$

where $\overset{+}{\gamma}_{Ca^{++}}$ is the activity coefficient of the calcium ion alone, $\gamma^{\pm}_{CaCl_2}$ is the mean activity coefficient of the calcium chloride, and $\gamma^{\pm}_{KCl}$ is that of the potassium chloride. Thus the data are assembled from which a final plot of the activity of the calcium ion against the molality of the calcium chloride could be made. Several such curves were drawn to cover the whole range from 0.1 to 0.0001 molal in suitable steps. Table I presents the data as used for making up standard calcium chloride solutions.

---

[6] T. Shedlovsky and D. A. MacInnes, THIS JOURNAL, **59**, 503 (1937).

[7] H. G. McLeod and A. K. Gordon, *ibid.*, **68**, 58 (1946).

TABLE I

Calcium ion activity, $a_{Ca^{++}}$	Calcium chloride molality, m	G. $CaCl_2$ per 1000 g. H_2O
0.0001	0.000108	0.01198
.0003	.000350	.03884
.0009	.001150	.12763
.0027	.004250	.47167
.0081	.017300	1.91996
.0243	.077000	8.54546

The Effects of Heat Treatments upon Membrane Potentials.—For the four clays used, hydrogen and calcium bentonite (montmorillonite, fraction <200 mμ), and hydrogen and calcium Putnam clay (beidellite, fraction <200 mμ) the relationships are apparent from Figs. 2–5.

(a) **Hydrogen Bentonite (Fig. 2).**—Only membranes pretreated at temperatures below 450° gave reproducible results for calcium. This is in line with the fact previously discovered,[3a] that 490° hydrogen bentonite membranes were sensitive to monovalent cations, but not to divalent. Membranes pretreated at 300, 350 and 400° were closely alike and gave theoretical results for calcium ion activities below 0.0081.

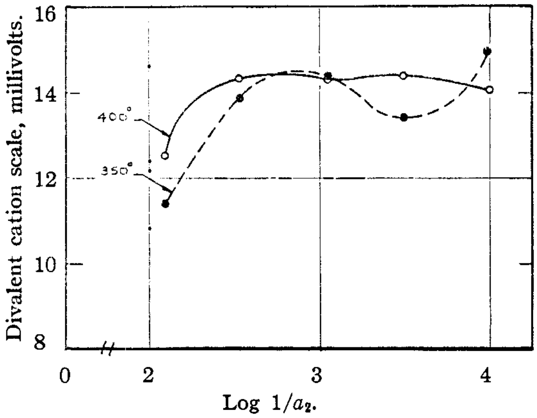

Fig. 2.—Hydrogen bentonite with $CaCl_2$.

(b) **Calcium Bentonite (Fig. 3).**—Between 300° and 600°, increase in the temperature of pretreatment afforded only slight improvement in the electrochemical properties. The 550–600° membranes gave potentials less than 1 millivolt below the theoretical value of 14.1 millivolts even for the 0.0243 and 0.0081 $a_{Ca^{++}}$ solutions. Thus calcium activities below 0.02 extending down to 0.0001 can readily be determined with these membranes.

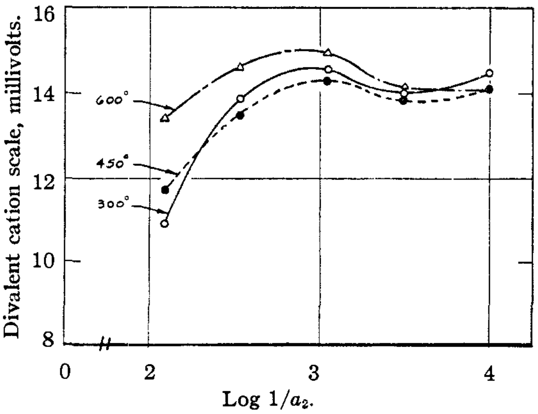

Fig. 3.—Calcium bentonite with $CaCl_2$.

(c) **Hydrogen Putnam Clay (Fig. 4).**—A steady improvement in electrochemical properties with increasing temperature of pretreatments may be seen. None are as good as the corresponding calcium bentonite membranes.

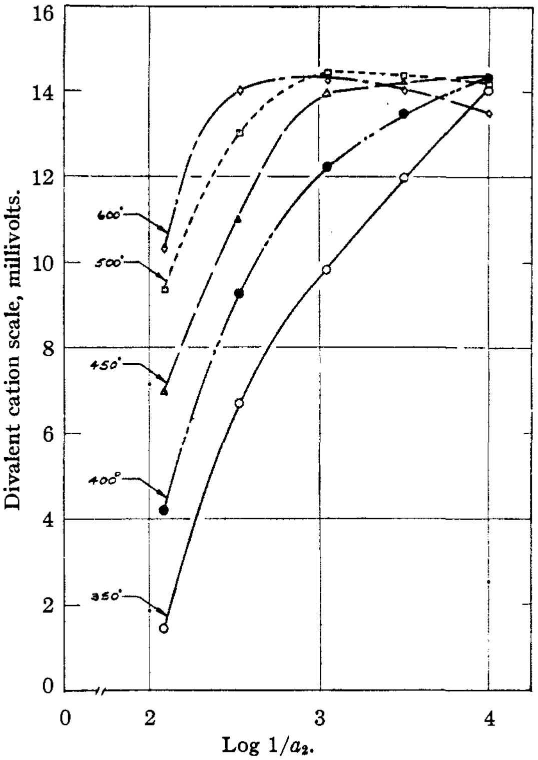

Fig. 4.—Hydrogen Putnam with $CaCl_2$.

(d) **Calcium Putnam Clay (Fig. 5).**—These membranes were consistently a little better than those from hydrogen Putnam clay and in the range 500–600° were very similar to one another, and to the corresponding calcium bentonite membranes. However, at the highest concentration used the latter are somewhat better.

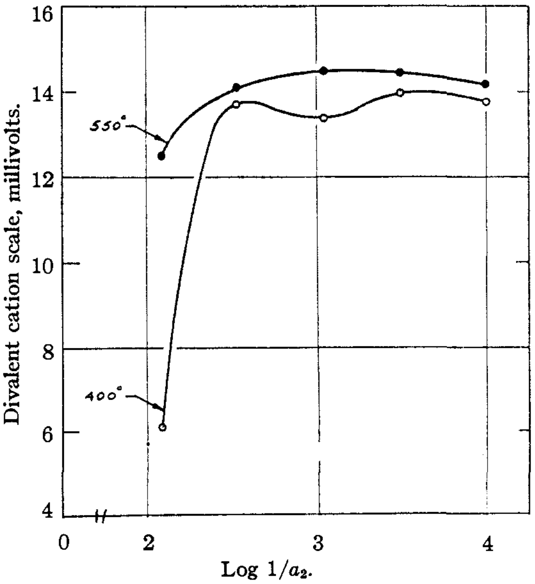

Fig. 5.—Calcium Putnam with $CaCl_2$.

The over-all accuracy of calcium ion determinations in the activity range 0.02–0.0001 using the best membranes is thus around 2–3%. Comparisons of calcium ion activities which are closely alike can be made somewhat more precisely than this, but even here deviations up to 2% are not uncommon.

Cationic Mobility Ratios in Relation to Pretreatment.—More time was needed to establish reproducible potentials with two different cations than where the same cation was present on both sides of the membrane. This was especially true for the monovalent/divalent ratios and in some instances constant values could only be obtained after six to twelve hours contact, with several renewals of the two solutions.

The range of concentrations which can be used in investigating monovalent/divalent mobility ratios is distinctly circumscribed by the fact that if equation 3b is to be used the activity of the monovalent ion must be small compared with the activity of the divalent ion multiplied by the mobility ratio divalent cation/monovalent cation.

As will be evident from the data, monovalent/divalent mobility ratios vary in most cases considerably with concentration. Varying temperatures of pretreatment affect this variation, but not consistently, and change in a somewhat erratic manner the magnitude of the ratio. Table II illustrates the experimental technique for two cases, one of wide variability with concentration and one showing reasonable constancy.

(1) **Calcium–Hydrogen Mobility Ratios.**—In Table III the minimum and maximum values obtained in experiments similar to those of Table II are assembled for clay membranes pretreated at various temperatures. In utilizing these data in the selection of membranes best suited for quantitative work with calcium and hydrogen it must be remembered that if U_{Ca}/U_H is very small, then a_H is multiplied by a large number (U_H/U_{Ca}) and variations in a_H may cause more change in the total potential than variations in a_{Ca}. Other conditions being favorable, the best membranes for this case are those for which U_{Ca}/U_H comes closest to unity.

TABLE II

Membrane material	$a_{Ca^{++}}$	a_{H^+}	Mean mobility ratio, U_{Ca}/U_H
615° Calcium	0.0081	0.000549	0.052
putnam	.0081	.000229	.099
	.0081	.000091	.138
	.0027	.000549	.313
	.0027	.000229	.085
	.0027	.000091	.172
615° Calcium	.0081	.000549	.457
bentonite	.0081	.000229	.545
	.0081	.000091	.466
	.0027	.000549	.674
	.0027	.000229	.615
	.0027	.000091	.496

Hydrogen bentonite membranes pretreated at temperatures between 350 and 420° afford reasonably constant values of U_{Ca}/U_H not far removed from unity. Above 450° these membranes, as previously noted, become insensitive to Ca^{++}.

Calcium bentonite membranes pretreated at 350 and 465° give somewhat lower values, but for 615° membranes the mobility ratio U_{Ca}/U_H varies less with concentration and rises to a value similar to those of the 350 and 415° hydrogen bentonite membranes discussed above.

Hydrogen Putnam membranes show considerable variation with concentration and U_{Ca}/U_H is low, although it rises somewhat with increasing temperature of pretreatment.

Calcium Putnam membranes also show unfavorable properties and the variation with concentration is very marked for those pretreated at 615°.

Thus in work involving mixtures of calcium and hydrogen, such as potentiometric titrations, the most favorable conditions are afforded by the 350–415° hydrogen bentonite and the 615° calcium bentonite membranes. The hydrogen ion activity is first measured using the glass electrode, and by applying equation 5 the calcium ion activity can be computed.

(2) **Calcium-Potassium Mobility Ratios.**—Table III summarizes the minimum and maximum values obtained with calcium chloride and potassium chloride solutions in experiments similar to those with hydrogen chloride. Two calcium activities, 0.0081 and 0.0027, were employed, and three potassium activities, 0.001, 0.00033 and 0.00011. The 360° hydrogen bentonite membranes gave the highest calcium/potassium mobility ratios of any tested, with a moderate degree of variability with concentration.

The 350° calcium bentonite membranes showed considerable variation in mobility ratios, some values being higher than unity and some lower. However, the 615° membranes were much more uniform and closely resembled the 360° hydrogen bentonite membranes in actual values. It is interesting to note that a close similarity exists between 350° hydrogen bentonite and 615° calcium bentonite membranes in their calcium/hydrogen mobility ratios.

The hydrogen Putnam membranes showed extreme variation with concentration at low temperatures of pretreatment, but became much more constant beyond 450° where U_{Ca}/U_K became greater than unity. For the lower temperatures values of U_{Ca}/U_K markedly less than unity were found. Around 450° a considerable change occurs in the electrochemical properties of the hydrogen Putnam membranes. It is much less evident in the calcium/hydrogen series discussed above.

The 465° calcium Putnam membranes showed some variability, but the 615° membranes were relatively constant in their Ca/K mobility ratios.

Thus in selecting membranes for determinations of calcium and potassium in mixtures the 615 calcium Putnam membranes are superior to the others. With some attention to concentration limits, the 360° hydrogen bentonite,

TABLE III

THE RANGE OF MOBILITY RATIOS FOR CALCIUM–HYDROGEN AND CALCIUM–POTASSIUM MEMBRANES PREHEATED TO VARIOUS TEMPERATURES

Membrane material	U_{Ca}/U_H, at temp. 350°	415°	465°	615°
H-bentonite	0.49–0.73	0.35–0.71	......	
Ca-bentonite	0.13–0.35	......	0.11–0.28	.46–0.67
H-Putnam	0.021–0.094	......	0.057–0.13	.46–0.17 (595°)
Ca-Putnam	....	......	0.039–0.085	.052–0.31
		U_{Ca}/U_K		
H-bentonite	2.9–5.7 (360°)	......	......	......
Ca-bentonite	0.43–1.81	......	......	2.8–5.0
H-Putnam	0.018–0.33	0.026–0.48	0.80–1.86	1.02–1.86 (595°)
Ca-Putnam	....	......	0.59–1.70	2.03–2.61

615° calcium bentonite and 595° hydrogen Putnam membranes are probably usable. For the potassium determinations alone, membranes insensitive to calcium, such as the 490° hydrogen bentonite membranes previously described, are required.

(3) **Calcium-Sodium Mobility Ratios.**—Only the 615° calcium bentonite and 615° calcium Putnam membranes were examined. As would be expected, the ratios U_{Ca}/U_{Na} were somewhat greater than the corresponding U_{Ca}/U_K values. They showed also more variability with concentration.

(4) **Calcium-Magnesium Mobility Ratios.**—A limited series was determined using high temperature membranes. Much greater constancy was found than with the monovalent-divalent series. These results will be discussed in the succeeding paper, which deals with the determination of magnesium.

Summary

Membranes prepared from hydrogen and calcium bentonite (montmorillonite) and hydrogen and calcium Putnam clay (beidellite), preheated to various temperatures, were examined as to their suitability for the determination of calcium. Hydrogen bentonite membranes heated to 300–415° are suitable; at 450° and higher these are insensitive to divalent cations, but sensitive to monovalent. Calcium bentonite membranes are suitable and are improved only slightly by pretreatment between 300° and 550°. Hydrogen Putnam clay membranes showed great improvement with increasing temperature of pretreatment, but even the 600° membranes were somewhat inferior to the 600° calcium bentonite membranes. The calcium Putnam membranes throughout were better than the hydrogen Putnam, but in the range 500–600° were still slightly inferior to the 500–600° calcium bentonite membranes.

Mobility ratios for calcium–hydrogen, and calcium–potassium were also determined. In many cases this ratio varied greatly with concentration. However, the 350–415° hydrogen bentonite and the 615° calcium bentonite membranes showed reasonable constancy for U_{Ca}/U_H and could be employed for the analysis of mixtures containing calcium and hydrogen ions. For calcium–potassium the 615° calcium Putnam membranes were the most favorable.

COLUMBIA, MISSOURI RECEIVED SEPTEMBER 29, 1947

[CONTRIBUTION FROM COLLEGE OF AGRICULTURE, UNIVERSITY OF MISSOURI]

The Electrochemical Properties of Mineral Membranes. VII. Clay Membranes for the Determination of Magnesium[1]

BY C. E. MARSHALL[2a] AND L. O. EIME[2b]

The theoretical and experimental considerations which have been discussed in the preceding paper of this series[3,4] apply in large measure to the determination of magnesium. The same membrane materials were under investigation and no change was needed in the experimental techniques.

The magnesium chloride solutions employed were arranged in a series according to the calculated magnesium ion activities, adjacent members being in the fixed ratio 3.00. The calculations employed for this purpose were precisely similar to those described for calcium. The basic data were taken from Landolt–Börnstein,[5] and because the activity coefficients of magnesium chloride solutions only extend down to 0.05 molal, a more extensive extrapolation to low concentrations was required than for calcium chloride. Table I gives the activities and concentrations employed. The latter were checked by gravimetric determination of the magnesium as pyrophosphate.

TABLE I

Magnesium ion activity, $a_{Mg^{++}}$	Magnesium chloride molality, m	Grams $MgCl_2$ per 1000 g. water
0.0001	0.000106	0.0101
.0003	.000330	.0314
.0009	.001152	.1098
0027	.00398	.379
.0081	.01490	1.419
.0243	.05600	5.340

The Effects of Heat Treatments upon Membrane Potentials.—Figures 1–4 illustrate the general situation for the four clays hydrogen bentonite, calcium bentonite (montmorillonite), hydrogen Putnam clay, and calcium Putnam clay (beidellite). One marked difference is apparent in all cases between these curves for magnesium and those previously given for calcium. In the case of magnesium the curves fall off more or less sharply after attaining the maximum value. This greatly restricts the range over which accurate determinations of magnesium ion activities can be made.

(a) Hydrogen Bentonite.—As in the case of calcium, the three curves for 300, 350 and 400° membranes lie very close together. They attain the theoretical e.m.f. at a slightly lower activity of magnesium than of calcium. Down to 0.0003 $a_{Mg^{++}}$ they give good values, but beyond it the

---

[1] This work was aided by a research grant made by the International Minerals & Chemical Corporation to the Department of Soils, for which the authors wish to express their appreciation.

[2a] Professor of Soils, University of Missouri.

[2b] Research assistant and graduate student in Soils and Chemistry, respectively.

[3] C. E. Marshall and A. D. Ayers, THIS JOURNAL, **70**, 1297 (1948).

[4] Journal series No. 1065 of the Agricultural Experiment Station, University of Missouri.

[5] Landolt–Börnstein, Physikalisch-Chemische Tabellen, 5 Auflage, 2 Ergänzungsband, 2 Teil, 1931.