The Electrochemical Properties of Mineral Membranes. I. The Estimation of Potassium Ion Activities*

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Introduction

The potentiometric determination of cationic activities in solutions containing the more electropositive metals has so far been limited to the higher concentrations. It has been recognized for some time that these limitations of metallic electrodes might be overcome by the use of suitable membranes. The glass electrode proved so successful in the determination of hydrogen ion activities that the use of similar membranes for the estimation of other ions seemed possible. Glasses of various compositions have been investigated by Horovitz[1] and Schiller,[2] but their behavior was complex and their study has not led to the development of practicable methods. The use of crystalline mineral membranes has been discussed by Tendeloo[3] and Anderson[4] again without tangible results.

The use of hydrated zeolitic membranes has been discussed recently by Marshall.[5] Using the background provided by the theory suggested independently by Meyer and Sievers[6] and by Teorell,[7] the conditions favorable to the quantitative use of cationic membrane electrodes were seen to be (a) a mechanical sieve action, or (b) a high negative charge per unit volume of the membrane. Chabazite and apophyllite were investigated from this point of view. The results were encouraging, and the present paper reports their further development.

The equation of Meyer and Sievers, and of Teorell, for the potential across a membrane separating two solutions of the symmetrical valence type is

$$E = \frac{RT}{nF}\left\{ U \ln \frac{\sqrt{\frac{4a_1^2}{A^2}+1}+U}{\sqrt{\frac{4a_2^2}{A^2}+1}+U} + \right.$$

$$\left. \frac{1}{2}\ln \frac{\left(\sqrt{\frac{4a_2^2}{A^2}+1}+1\right)\left(\sqrt{\frac{4a_1^2}{A^2}+1}-1\right)}{\left(\sqrt{\frac{4a_2^2}{A^2}+1}-1\right)\left(\sqrt{\frac{4a_1^2}{A^2}+1}+1\right)}\right\} \quad (1)$$

where

$$U = \frac{U_c - U_a}{U_c + U_a}$$

and n is the valency, a_1 and a_2 are the molal activities of the solutions. U_a and U_c are the mobilities of the anion and cation within the membrane, and A is the charge on the membrane expressed as an ionic activity. For a solution of potassium chloride having ions of almost equal mobility in water, the ratio U_c/U_a within the membrane may be taken as a measure of the sieve action. Each membrane may thus be characterized by two experimentally determined constants, A and U_c/U_a for potassium chloride.

Hitherto, the theory has been applied by using molar concentrations rather than activities. In view of the accuracy with which the activity coefficients of potassium chloride are known, this is no longer justifiable. However, if the ratios a_1/a_2 are chosen according to molar concentrations rather than activities, it is possible to make the necessary correction.
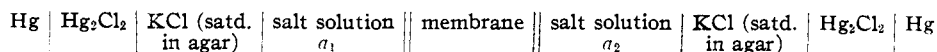
Experimental

Technique and Procedure.—The technique employed in obtaining the membrane potentials was similar to that used by Marshall.[5] In all cases the membranes were cemented on the ground ends of Pyrex glass tubing. Hard deKhotinsky cement was found to be most suitable for this purpose. The tubes were held in rubber stoppers placed in a small beaker. Saturated calomel electrodes having an agar bridge were used as reference electrodes. Control experiments indicated that the agar bridge did not function as a membrane itself, and that the liquid junction potentials between the agar bridges and the salt solutions used were well within experimental errors. The cells used may thus be represented diagrammatically as shown.

Any difference in potential between the two calomel electrodes used was measured, and the correction applied. All readings reported are in millivolts and corrected to 25°.

Before using any membrane it was soaked in an approximately molar solution of potassium chloride until zero asymmetry potential was attained. It was found that any membrane having an asymmetry potential was not

* Read before the Colloid Chemistry Division at the 101st meeting of the American Chemical Society in St. Louis on April 8, 1941.
(1) Horovitz, Z. physik. Chem., 115, 424 (1925).
(2) Schiller, Ann. Physik, [4] 74, 105 (1924).
(3) Tendeloo, J. Biol. Chem., 113, 333 (1936); 118, 253 (1937).
(4) Anderson, ibid., 115, 323 (1936).
(5) Marshall, J. Phys. Chem., 43, 1155 (1939).
(6) Meyer and Sievers, Helv. Chim. Acta, 19, 649, 665, 987 (1936).
(7) Teorell, Trans. Faraday Soc., 33, 1054 (1937).

| Hg | Hg$_2$Cl$_2$ | KCl (satd. in agar) | salt solution a_1 | | membrane | | salt solution a_2 | KCl (satd. in agar) | Hg$_2$Cl$_2$ | Hg |

satisfactory since the asymmetry potential sometimes showed sudden fluctuations.

All solutions of potassium chloride were made up according to molal activities using the activity coefficients determined by Shedlovsky and MacInnes.[8] The activity coefficients employed for other electrolytes were taken from the data compiled by Latimer[9] or by MacInnes.[10]
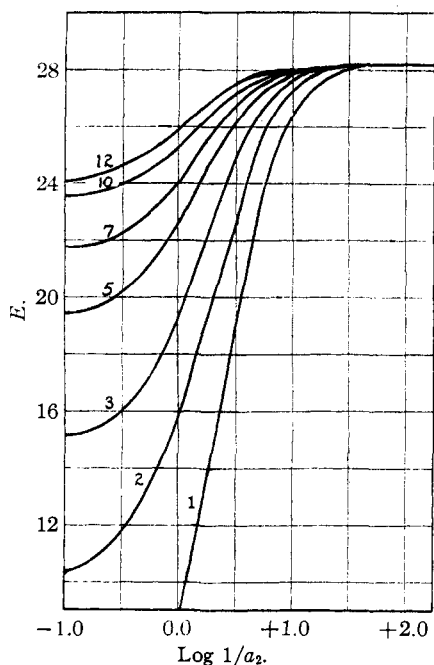

Fig. 1.—Theoretical curves obtained from the membrane potential equation for several values of U_c/U_a and for $A = 1$ when $a_1/a_2 = 3$. The numbers above each curve indicate the ratio of U_c/U_a.

Apophyllite Membranes.—The experiments with apophyllite membranes described by Marshall were extended in order to test more completely the equation proposed for membrane potentials. The activity ratio of potassium chloride was set at 3.000 instead of 10.00 as previously. The data obtained with some of these membranes are shown graphically in Fig. 2. The theoretical curve derived from equation (1) by setting $U_c/U_a = 1$ and $A = 1$ is also given in Fig. 2. The lateral displacement of this curve from the experimentally obtained curve is a measure of log A and gives A a value of 0.417.

The observed potentials decrease rapidly as the concentration of a_1 and a_2 increases. In dilute solutions when the concentration ratio is small the results become erratic. This same phenomenon was noted for some of the other membranes. However, by increasing the ratio of a_1 to a_2 steady values could be obtained for dilute solutions, and

(8) Shedlovsky and MacInnes, THIS JOURNAL, **59**, 503 (1937).

(9) Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 323.

(10) MacInnes, "Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1939, p. 167.

these values approximated to the theoretical values calculated from the Nernst equation for a concentration cell.

The data previously reported for apophyllite membranes were obtained from potential differences found with very dilute solutions of potassium chloride. As shown in Fig. 1, the theoretical curves obtained by means of equation (1) by plotting as ordinates the calculated potentials for particular values of U_c/U_a and for $A = 1$ against log $1/a_2$ are nearly straight lines parallel to the abscissa when a_2 is small. Hence, conclusions based upon determinations obtained with dilute solutions could lead to highly erroneous results if in error by only a few millivolts. One must bear in mind also that the bases of this equation are the Donnan membrane theory and the Henderson equation for liquid junction potentials, which at best are only valid for dilute solutions. Hence, application of the theory of Teorell and of Meyer and Sievers to a particular membrane material can give but qualitative information regarding U_c/U_a and A unless extreme reproducibility in dilute solutions can be obtained.
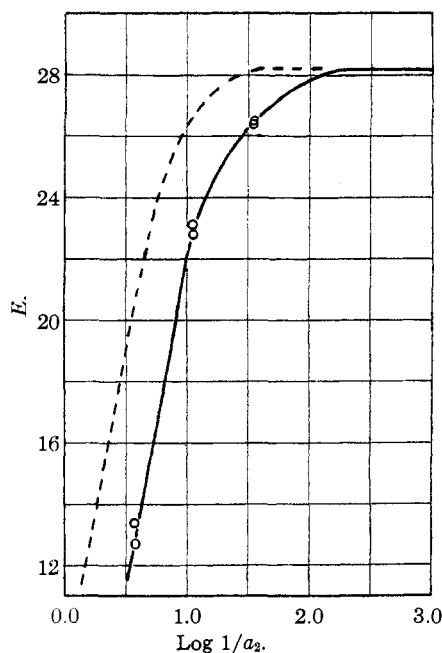

Fig. 2.—Experimental curve obtained for apophyllite membranes using potassium chloride solutions with an activity ratio $a_1/a_2 = 3$. The theoretical curve for $U_c/U_a = 1$ and for $A = 1$ is shown as a dotted line.

In general the results obtained with apophyllite were not highly reproducible and depended upon the previous history of the membrane. This is not surprising since the mineral undergoes a slow base exchange reaction. Many of the apophyllite membranes maintained a high, erratic asymmetry potential even though ground to a thickness of 0.05 mm. Others maintained a resistance too high to permit potentials to be measured accurately. In either case electrodialysis of potassium chloride through the mineral did not remedy the situation.

The more complete curve now obtained for apophyllite gives it no appreciable sieve action and a higher charge per unit volume than was previously reported.[5] In view of the manifest difficulties of obtaining reproducible results with this mineral other materials for membranes were considered.

Montmorillonite Membranes.—Attention was directed toward the artificially prepared membranes of the colloidal clays—the so-called "alsifilm" membranes described by Hauser and le Beau.[11] Since many of the clays have a high base exchange capacity, membranes prepared from them should fit the prerequisites set down for a cationic electrode; and colloidal bentonite (montmorillonite), which has one of the highest base exchange capacities of the clays, seemed to offer good possibilities. The authors are indebted to Dr. E. A. Hauser and Dr. D. S. le Beau for supplying samples of these membranes for the preliminary experiments.

The electrodialyzed bentonite membranes used in the experiments reported below were prepared from a 1% suspension of bentonite in which the effective particle size was less than 0.2 μ and which had a pH of 2.9. This suspension was concentrated to a thin, uniform gel by heating with gentle stirring on a water-bath. This gel was spread on a suitable surface (sheet copper or celluloid was found satisfactory) and dried with infrared radiation at 80°. Membranes having a thickness of 0.1 to 0.5 mm. were found to be satisfactory. Thicker membranes are difficult to prepare.

The potassium, sodium, and calcium bentonite membranes were prepared by the same process after having titrated the electrodialyzed bentonite suspension to a pH of 8 with the appropriate base. The pH was determined about eight hours after the titration to permit equilibrium to be reached.

The membranes so prepared were cut to size (10-mm. diameter) and dried in a furnace at the desired temperature. These membranes, cemented on to Pyrex glass tubing, were soaked in approximately molar potassium chloride until zero asymmetry potential was attained. Those dried below 250° reached equilibrium quickly, but were extremely fragile, and dispersed or cracked readily. Measurements were possible only on some 10% of those prepared. The membranes dried at 490° were mechanically stable and about 60% came to zero asymmetry potential within three days. Of these, nearly all were satisfactory for use. Careful checking of the results showed that these membranes could be used for about ten days.

The resistances of the potassium and calcium bentonite membranes were generally low enough so that an amplifier was not needed. The electrodialyzed bentonite membranes dried at 490° had a resistance of 1 to 10 megohms, and this resistance did not decrease appreciably with use. All membranes dried above 550° have a low resistance and give very low potentials for all ratios of a_1 to a_2, indicating no sieve action and disappearance of the charge.

The results obtained with montmorillonite membranes, using an activity ratio of potassium chloride of 3.00, are shown graphically in Figs. 2, 3, and 4. These results, especially with the membranes dried at 200° and higher, were very reproducible.

A careful comparison of the experimental with the theoretical curves indicates that for low concentrations of a_2 the membranes have a higher sieve action, U_c/U_a, than at high concentrations. This is especially apparent with the electrodialyzed bentonite membranes. In Fig. 5, for these
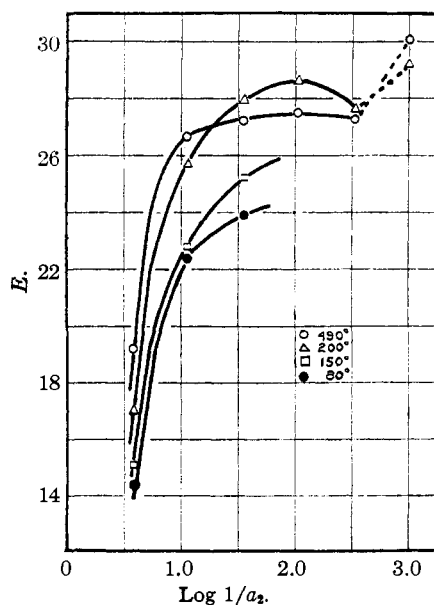

Fig. 3.—Experimental curves obtained with calcium bentonite membranes dried at various temperatures using potassium chloride solutions with an activity ratio $a_1/a_2 = 3$.

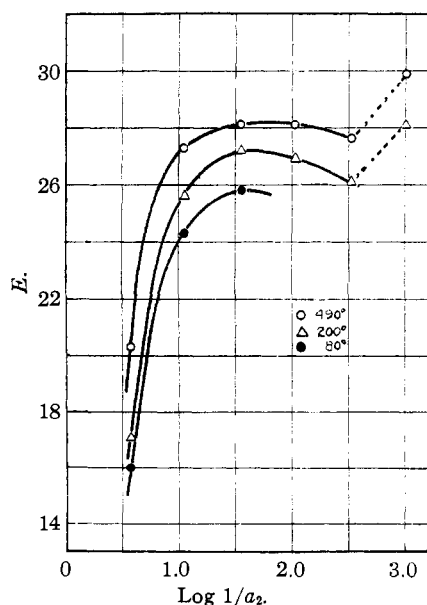(11) Hauser and le Beau, *J. Phys. Chem.*, **42**, 961 (1938).

Fig. 4.—Experimental curves obtained with potassium bentonite membranes dried at various temperatures using potassium chloride solutions with an activity ratio $a_1/a_2 = 3$.

membranes the theoretical curves for $U_c/U_a = 1$ and $U_c/U_a = 2$ are shown as dotted lines numbered 1 and 2, respectively. The slopes at the upper portions of the experimental curves correspond to the slopes of the theoretical curves having a ratio of $U_c/U_a = 2$ or greater.
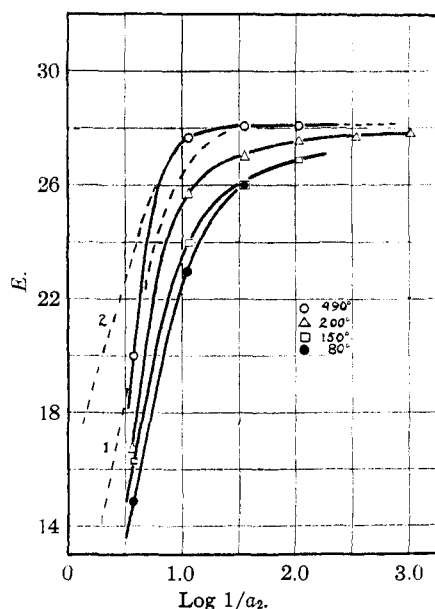

Fig. 5.—Experimental curves obtained with electrodialyzed bentonite membranes dried at various temperatures using potassium chloride solutions with an activity ratio $a_1/a_2 = 3$. The theoretical curves for $U_c/U_a = 1$ and $U_c/U_a = 2$ and for $A = 1$ are shown as dotted lines numbered 1 and 2, respectively.

If it is assumed that the theoretical curves hold even for large concentrations of a_1 and a_2, then it must be concluded that in concentrated salt solutions the charge on the membrane, A, is thermodynamically decreased, U_c/U_a becomes unity, and the sieve action is therefore zero. In dilute solutions the membranes show an appreciable sieve action.

Values for A obtained by measuring the lateral displacement of the experimental curves from the theoretical curves at a potential of 20 to 22 millivolts are summarized in Table I.

TABLE I

THE CHARGE ON THE MEMBRANE (EXPRESSED AS AN IONIC ACTIVITY) AS RELATED TO THE TEMPERATURE OF DRYING

Membrane	Dried at			
	80°	150°	200°	490°
Calcium bentonite	0.47	0.56	0.79	0.94
Hydrogen bentonite	.50	.63	.79	1.0
Potassium bentonite	.71	..	.79	1.0

Of these bentonite membranes, those of hydrogen bentonite dried at 490° seemed to be the most satisfactory, and further experiments were conducted with them in preference to potassium bentonite, which gave slightly lower results.

In view of the results obtained one can only hope to determine potassium ion activities in solutions of less than 0.1 molal activity. Otherwise the potentials would fall too far below those calculated from the Nernst equation. Thus it was decided to use 0.081 $a_\pm$ (0.1059 molal) potassium chloride as the reference solution, a_1, while the concentration of the salt a_2 was varied. The results with potassium chloride, sulfate, ferricyanide and ferrocyanide in a_2 are reported in Table II. In the third column of this table, the values calculated by means of the Nernst equation are given. The experimental results agree well with these calculated values over the entire concentration range employed.

TABLE II

MEMBRANE POTENTIALS WITH POTASSIUM SALT SOLUTIONS. EFFECT OF ANION UPON DETERMINATION OF POTASSIUM (ELECTRODIALYZED BENTONITE MEMBRANES DRIED AT 490°) (0.081 $a_\pm$ KCl AS REFERENCE SOLUTION)

Compn. of a_2, N	a_{K^+}	E. m. f. calcd.	E. m. f. obsd.
KCl 0.0312	0.027	28.2	28.1
.00998	.009	56.4	57.1
.00319	.003	84.7	84.5
.001035	.001	112.9	115.6
K$_2$SO$_4$ .027	.02237	33.1	35.7
.009	.008001	59.5	61.2
.003	.002790	86.5	87.5
.001	.000960	113.9	115.3
.0005	.0004855	131.4	133.9
.0001	.0000987	172.4	171.1
K$_3$Fe(CN)$_6$ .081	.05917	8.1	8.6
.027	.02192	33.6	34.0
.009	.007866	59.9	59.9
.003	.002766	86.7	86.1
.001	.000953	114.1	113.4
.0005	.0004835	131.6	131.2
.0001	.0000985	172.4	164.3
K$_4$Fe(CN)$_6$ .09290	.06531	5.5	7.8
.03097	.02440	30.8	32.4
.01032	.008803	57.0	57.0
.003441	.003124	83.6	84.2
.001147	.001082	110.9	110.1

These results indicate that the observed potential may be calculated by means of the Nernst equation

$$E = \frac{RT}{F} \ln \frac{a_1}{a_2} \qquad (2)$$

Further, all the data fit this equation best when the values of a_1 and a_2 represent those of the po-

tassium ion alone. For potassium chloride solutions the mobilities of cation and anion are nearly equal; and hence the assumption is made that the individual ion activities are equal to the mean activity of the salt. The value for individual potassium ion activities may be calculated according to the method described by Lewis and Randall.[12] In the absence of reliable data for the mean activity coefficients for a particular electrolyte the assumption is made that the potassium ion activity coefficient is the same as that in potassium chloride solutions at a corresponding ionic strength.

The validity of this method of treating the data may be shown by the results obtained by using solutions of potassium chloride containing either calcium chloride or magnesium sulfate. These experiments were performed after it was noted that both calcium chloride and magnesium sulfate solutions, when used alone with potassium chloride as the reference solution, gave rather anomalous results. Hence, it was decided to see what effect these divalent ions would have upon the membrane potential in the presence of potassium. These results are summarized in Table III. In Column 5 the value calculated by making the assumption that the potassium ion activity coefficient is the same as in potassium chloride solutions at the same ionic strength is given. The latter values agree remarkably well with the experimental values over the entire concentration range employed.

TABLE III

MEMBRANE POTENTIALS IN PRESENCE OF DIVALENT CATIONS (ELECTRODIALYZED BENTONITE MEMBRANES DRIED AT 490°) (0.081 $a_\pm$ KCl AS REFERENCE SOLUTION a_1)

Compn. KCl	a_2, N CaCl$_2$	$\sqrt{\text{Ionic strength}}$ $\mu^{1/2}$	a_{K^+} at $\mu^{1/2}$	E. m. f. calcd.	E. m. f. obsd.
0.02	0.02	0.2236	0.01633	41.1	39.7
.02	.01	.1871	.01674	40.5	39.7
.02	.001	.1466	.01726	39.7	40.1
.001	.01	.1265	.00088	116.2	110.5
.001	.002	.0342	.000964	113.8	107.8
	MgSO$_4$				
.02	.02	.3464	.01512	116.6	111.7
.001	.01	.1449	.000865	43.1	40.5

Since this method of treating the data applies for all the potassium salts used, it follows that the anion enters into the net cell reaction only in so far as it contributes to the ionic strength of the solution and affects the activity of the cation.

(12) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 379.

This is analogous to the determination of hydrogen ion activities with the glass electrode.

From the results thus far presented it may be concluded that potassium ion activities may be determined in neutral solutions of potassium salts. That other monovalent cations would interfere with the determination of potassium was apparent from data obtained with sodium chloride and with pure acid solutions. The results obtained with these solutions in a_2 using potassium chloride as the reference solution were not very reproducible, the acids being particularly erratic. They gave results which were low by about 30 millivolts as compared with the value calculated by using the measured activity of the hydrogen ion for the value of a_2. Sodium chloride solutions gave potentials about 35 millivolts higher than the value calculated by using activity of the sodium ion for a_2. These deviations are probably due to the differences in the mobilities of the potassium ion and the hydrogen and sodium ions. In addition the acids attack the membrane, giving rise to erratic results.

It remained to be determined to what extent pH of the solution affected determination of po-

TABLE IV

EFFECT OF pH AND LARGE ANION ON THE MEMBRANE POTENTIAL (ELECTRODIALYZED BENTONITE MEMBRANES DRIED AT 490°) (0.081 $a_\pm$ KCl AS REFERENCE SOLUTION a_1)

Soln. in a_2	pH (glass electrode)	a_{K^+} computed	E. m. f. calcd.	E. m. f. obsd.
	Potassium acid phthalate			
0.05 m	4.008	0.04080	17.6	19.6
.01	4.094	.00901	56.1	57.0
.001	4.216	.000965	112.2	110.4
	p-Toluenesulfonic acid half neutralized with KOH			
0.1 N	1.567	0.03845	5.4 $ca.$ −12	
.01	2.394	.00460	57.5 $ca.$ +43	
.001	3.317	.0004835	113.8	90.3
	Potassium salt of p-toluenesulfonic acid			
0.01 N	6.53	.00902	56.4	55.3
.001	6.60	.000967	113.7	110.9
	p-Nitrophenol half neutralized with KOH			
0.1 N	7.43	.03845	19.1	18.1
.01	7.40	.00460	73.7	70.8
.001	7.30	.0004835	131.6	126.3
	p-Nitrophenol neutralized with KOH			
0.01 N	11.18	.00902	56.4	59.1
.001	10.06	.000967	113.7	117.3
	Potassium hydroxide			
0.006685	...	.006431	65.1	67.8
.001337	...	.001321	105.8	108.6

tassium in the absence of other monovalent cations. Three different acids were used: acid phthalate, p-toluenesulfonic and p-nitrophenol. Salts of these acids also could be used to determine the effect of a large anion upon the membrane potential. Potassium hydroxide solutions were used to obtain the effect of the hydroxide ion. Use of the membranes in strongly alkaline solutions is restricted due to attack of the alkali on the cement. The results are summarized in Table IV. From these data it may be seen that the anomalous effect due to hydrogen disappears above a pH of 4. At pH of 4 and above the potentials follow the simple Nernst equation as given provided a_2 is replaced by the sum of the activity of the hydrogen and the potassium. This, of course, is only important when the potassium ion activity is low.

Discussion

The results obtained with electrodialyzed bentonite membranes dried at 490° indicate that potassium ion activities may be determined in absence of other monovalent cations with a precision within 5% at pH values above 4. A high degree of reproducibility is possible using commercial Wyoming bentonite from which all particles larger than 200 mμ in equivalent spherical diameter have been removed by supercentrifuging.

The method is at present being used for the study of potassium ion activities in negatively charged colloidal systems and the results will be reported in due course.

Preliminary experiments indicate that these membranes may serve as electrodes for the determination of other monovalent cations. The results with sodium appear promising. Search is being continued for membrane materials which will serve as electrodes for the determination of divalent cations.

Acknowledgment.—The authors are indebted to the Research Council of the University of Missouri for a grant-in-aid which has made this work possible.

Summary

1. The detailed electrochemical behavior toward potassium ions of apophyllite and montmorillonite membranes has been investigated.

2. Apophyllite membranes are difficult to prepare and were found to show a variable behavior with potassium.

3. Montmorillonite membranes dried at 490° gave reproducible results with solutions of several potassium salts; and at concentrations below 0.1 N, estimations of potassium ion activities can be made with a precision within 5%.

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Studies on High Molecular Weight Aliphatic Amines and their Salts. II. Solubilities of Primary Aliphatic Amine Hydrochlorides and Acetates in Ethanol and Benzene

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In connection with the investigation of the properties of high molecular weight aliphatic amine salts a series of solubility measurements has been made. Solubilities have been determined for the hydrochlorides of the series decylamine through octadecylamine in 95% ethanol and for the acetates of the series dodecylamine through octadecylamine in 95% ethanol and in anhydrous benzene. A number of interesting peculiarities in the behavior of these salts have become evident as a result of this work.

Experimental Part

The amine salts used were prepared from amines, the preparation of which has been previously described.[1] The hydrochlorides were obtained by treating an ethanol solution of the amine with concentrated hydrochloric acid. The resulting solution was evaporated to dryness under reduced pressure and the salt recrystallized from a mixture of ethanol and ether. The acetates were obtained by adding the calculated amount of glacial acetic acid to an ether solution of the amine. The acetates were recrystallized from a mixture of ethanol and ether until further crystallization failed to raise the melting point of the salt. Constants for the salts used are given in Table I.

The ethanol used was commercial 95% ethanol. The benzene was Baker C. P. thiophene-free grade and was dried over sodium wire.

(1) Ralston, Selby, Pool and Potts, *Ind. Eng. Chem.*, **32**, 1093 (1940).