very weak samples of radioactive protein, etc. The uncertainty in the computed limiting diffusion coefficient of ovalbumin due to both the uncertainty in the accepted molecular weight of ovalbumin and the experimental errors in sedimentation measurements is about 5%. However, extrapolation of ordinary diffusion data for ovalbumin leads to much the same result,[7] indicating that this computed limiting value cannot be too far off.

TABLE I

THE SELF-DIFFUSON COEFFICIENTS OF WATER AND OVALBUMIN IN AQUEOUS OVALBUMIN SOLUTIONS AT 10.0° WITH *p*H 4.76

Concn. of ovalbumin (% by wt. of dry protein)	$D_{H_2O} \times 10^5$, cm.²/sec.	$D_{\text{protein}} \times 10^7$ cm.²/sec.
0	1.675 ± 0.016	(5.80)[6]
10.6	1.38 ± .03	3.32 ± 0.10
19.0	1.13 ± .015	1.62 ± .07
24.4	0.979 ± .009	0.87 ± .05
24.5	0.978 ± .006	

The self-diffusion coefficients listed in Table I are compared with viscosity data[8] in Table II.

TABLE II

COMPARISON OF THE SELF-DIFFUSION COEFFICIENTS WITH VISCOSITY DATA OF AQUEOUS OVALBUMIN SOLUTIONS AT 10.0°

Concn. of ovalbumin, % by wt.	η/η_0	$D_p(\eta/\eta_0) \times 10^7$, cm.²/sec.	$D_{H_2O}(\eta/\eta_0) \times 10^5$, cm.²/sec.
0	1	(5.80)[6]	1.675
10.6	1.61	5.34	2.22
19.0	3.4	5.51	3.84
24.4	6.7	5.83	6.56

Because of the low specific activity of the radioactive ovalbumin, the short capillaries and the ease with which ovalbumin denatures at 10°, the experimental uncertainties in the above D_p values may be as high as 5%. It is hoped that these values can be much improved in the near future by using labeled proteins of higher specific activity, *e.g.*, radioactive iodo-proteins, etc. Values of the relative viscosities in Table II were computed from the data of Chick and Lubrzynska[8] by interpolation. In spite of the tentative nature of these values, Table II shows that the product $D_p(\eta/\eta_0)$ remains fairly constant when η/η_0 varies by a factor of 6.7, indicating that the self-diffusion coefficient of ovalbumin is approximately proportional to the fluidity of the solutions. This observation may also be taken as a suggestion that no appreciable amount of permanent aggregates of ovalbumin molecules exists even in fairly concentrated solutions, because if these aggregates do exist in considerable amount it is very unlikely that they will affect D_p and η/η_0 to exactly the same extent so that their product remains constant.

On the other hand, values in Tables I and II indicate that the relationship between the self-diffusion coefficient of water and the viscosity of ovalbumin solution is more complicated. A quantitative treatment of the concentration dependence of the self-diffusion coefficient of water in protein solutions is given in a separate communication.[9]

Acknowledgment.—The present work was supported by Contract(30-1)-1375 between the U. S. Atomic Energy Commission and Yale University.

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[7] J. T. Edsall, Chap. 7, "The Proteins" (Edited by H. Neurath and K. Bailey), Vol. 1, Part B, Academic Press, Inc., New York, N. Y., 1953.

[8] H. Chick and E. Lubrzynska, *Biochem. J.*, **8**, 59 (1914).

[9] J. H. Wang, THIS JOURNAL, **76**, 4755 (1954).

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, BOSTON UNIVERSITY]

Electrochemical Behavior of Cation Exchange Membranes[1,2] in Liquid Ammonia

BY MARTHA J. BERGIN[3] AND ARNO H. A. HEYN

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Cationic ion-exchange membrane electrodes are used successfully in liquid ammonia, alcohol and water solutions to measure junction potentials. These measurements may be then utilized in standard electrochemical equations to calculate cationic concentrations. In addition such membrane electrodes are shown to be valuable as a means of determining the ratios of activity coefficients of salts in the above mentioned media.

The electrochemical properties and uses of ion-exchange membranes depend on the fact that they form a special type of junction between two solutions. When two solutions containing different concentrations of the same electrolyte are in contact, a potential will be set up at the junction which is caused by the difference in speed of migration of the various ions. The potential may be expressed by the well-known equation

$$E = (2t_+ - 1)RT/F \ln a_1/a_2 \qquad (1)$$

or

$$E = \frac{t_+ - t_-}{t_+ + t_-} RT/F \ln a_1/a_2$$

in which $t_+ + t_- = 1$. E is, therefore, a function of the transference numbers of the anions and cations.

If the two solutions are separated by a cation-exchange membrane, the migration of the negative ions can be restricted. Membranes made of ion-exchange material act as ion sieves. An ideal membrane made of cation-exchange material would allow only cations to pass through, *i.e.*, $t_+ = 1$ and $t_- = 0$. Equation 1 than reduces to

$$E = RT/F \ln a_1/a_2 \qquad (2)$$

It has been demonstrated experimentally that an

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[1] From Ph.D. Thesis of Martha J. Bergin, May, 1952, presented in part at the 122nd A.C.S. Meeting, Atlantic City, N. J., Sept., 1952.

[2] Supported in part by a Grant in Aid of the Research Corporation, New York, N. Y.

[3] Sylvania Electric Products, Inc., Salem, Mass.

ideally selective membrane can actually be obtained making it thus possible to determine activities of a solution of a single electrolyte.[4] This investigation concerns the extension of the application of ion-exchange membranes to liquid ammonia solution, and, incidentally, to alcohol solutions. Liquid ammonia solutions of ammonium nitrate and ammonium chloride were investigated.

Ideally, the following cell system should be used

Reference Electrode	Ammonium nitrate C_I Liquid ammonia	Membrane	Ammonium nitrate C_2 Liquid ammonia	Reference Electrode

The expression for the potential of the total system would be

$$E = (2t_+ - 1)\ RT/F \ln \frac{\gamma\pm\ (C_2)}{\gamma\pm\ (C_1)} + C \qquad (3)$$

where $\gamma_\pm$ is the mean activity coefficient of ammonium nitrate in liquid ammonia and t_+ is the positive transference number across the membrane. Some initial experiments were made with cells in an all ammonia system, but such cells were abandoned because the membranes could not withstand the vacuum technique used for the handling of liquid ammonia. The cell system used in this investigation was designed so that the membrane was not endangered by evacuation:

Silver	Silver nitrate 0.001 M	Ammonium nitrate varying concn.	Membrane	Ammonium nitrate 0.001 M	Silver nitrate 0.001 M	Silver
	Liquid ammonia			Alcohol		
E_1	I		E_2	II		E_3

This arrangement introduces complications which require a more complete theoretical treatment. These complications are: (a) the use of mixed media, and (b) the use of mixed electrolytes.

Theory

Since the chemical potential of a substance does not depend directly on the nature of the solvent, the fundamental electrochemical equations which are known to be valid for aqueous solutions can be applied to any other solvent. Therefore, a general equation for the potential of the above cell may be derived.

The electrode potential E_1 may be expressed by

$$E_1 = RT/F \ln (a_{\mathrm{AgNO_3}})_{\mathrm{I}} \qquad (4)$$

where $(a_{\mathrm{AgNO_3}})_{\mathrm{I}}$ is the mean activity of silver nitrate in liquid ammonia. In an analogous manner E_3 may be represented by

$$E_3 = -RT/F \ln (a_{\mathrm{AgNO_3}})_{\mathrm{II}} \qquad (5)$$

where $(a_{\mathrm{AgNO_3}})_{\mathrm{II}}$ is the mean activity of silver nitrate in alcohol.

The potential at the membrane (E_2) depends on the activities of the two cations, Ag^+ and NH_4^+. The Henderson–Plank equation,[5] which has been used successfully in the calculations of liquid junction potentials for mixed electrolytes, may be applied to the above system. The derivation of this equation utilizes the concept that the junction consists of a continuous series of solutions produced by the mixing of the two solutions. This condition may be considered to be satisfied in the case of the membrane junction. For a cell system in which all of the ions are univalent, this equation reduces to

$$E_2 = RT/F \frac{(U_{\mathrm{I}} - V_{\mathrm{I}}) - (U_{\mathrm{II}} - V_{\mathrm{II}})}{(U_{\mathrm{I}} + V_{\mathrm{I}}) - (U_{\mathrm{II}} + V_{\mathrm{II}})} \ln \frac{(U_{\mathrm{I}} + V_{\mathrm{I}})}{(U_{\mathrm{II}} + V_{\mathrm{II}})} \qquad (6)$$

where U, the total contribution of positive ions to the transport of current, and V, the total contribution of negative ions, are defined as

$$\begin{aligned} U_{\mathrm{I}} &= a_{\mathrm{Ag^+}}{}^{+\mathrm{I}}\ u_{\mathrm{Ag^+}}{}^{+\mathrm{I}} + a_{\mathrm{NH_4}}{}^{+\mathrm{I}}\ u_{\mathrm{NH_4^+}}{}^{+\mathrm{I}} \\ V_{\mathrm{I}} &= a_{\mathrm{NO_3^-}}{}^{-\mathrm{I}}\ u_{\mathrm{NO_3^-}}{}^{-\mathrm{I}} \\ U_{\mathrm{II}} &= a_{\mathrm{Ag^+}}{}^{+\mathrm{II}}\ u_{\mathrm{Ag^+}}{}^{+\mathrm{II}} + a_{\mathrm{NH_4^+}}{}^{+\mathrm{II}}\ u_{\mathrm{NH_4^+}}{}^{+\mathrm{II}} \\ V_{\mathrm{II}} &= a_{\mathrm{NO_3^-}}{}^{-\mathrm{II}}\ u_{\mathrm{NO_3^-}}{}^{-\mathrm{II}} \end{aligned}$$

The ionic mobilities, u_+ and u_-, and the ionic activities, a_+ and a_-, for the mixture of electrolytes ($AgNO_3$ and NH_4NO_3) must be known in order to use equation 6 in calculating junction potentials. No such data are available for solutions—liquid ammonia or ethyl alcohol, or for electrolytes within the exchange resin. Since the concentrations of the solutions in which the measurements were made were sufficiently low, properties which have been found to hold in dilute solutions of uni-univalent salts in any medium may be used in the simplification of equation 6.

For these dilute solutions it may be assumed that the mobility of a specific ion is virtually independent of changes either in the concentration of that ion used or in the ionic strength. In addition, the data below show that the mobilities of Ag^+ and NH_4^+ in liquid ammonia and in ethyl alcohol are very nearly equal. The ratio of equivalent conductances of NH_4NO_3 and $AgNO_3$ in liquid ammonia (−33.5°) in the concentration range of 0.001 to 0.004 M is between 1.01 and 1.04.[6] In ethyl alcohol, the ratio of ionic conductances of NH_4^+ to Ag^+ at infinite dilution is 1.11,[7] and the ratio of equivalent conductances of NH_4NO_3 and $AgNO_3$ at 0.005 M is 1.05.[8] Although the absolute mobilities in the membrane phase are unknown, it is to be expected that the relation between mobilities of ions found in a conventional solution will also hold true in the membrane.

Since the ratio of the conductance of ammonium ion to silver ion is close to unity for the case in which the ammonium ion concentration is several times as great as that of the silver ion, the mobility of the ammonium ion alone can be substituted into equation 6.

It has been found in aqueous solutions that activity coefficients of uni-univalent salts in dilute solutions are very nearly equal to each other[9]; the same may be expected to be true in very dilute liquid ammonia solutions. This also has been found to be true in alcoholic solutions. For most measurements the concentration of ammonium nitrate was much greater than that of silver nitrate thereby jus-

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(5) D. A. MacInnes, "Principles of Electrochemistry," Reinhold Publ. Corp., New York, N. Y., 1939.

(6) Landolt-Börnstein, "Physikalisch Chemische Tabellen," 5th ed., Supplement 3, Vol. 3, Julius Springer, Berlin, 1936, 2064.

(7) Reference 6, p. 2064.

(8) Reference 6, p. 2077.

(9) G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1923, Chapter XXVIII.

tifying this assumption. If the same solvent were used on each side of the membrane, the effect of any difference in the activity coefficients of the two salts would be minimized because the ratio of these activity coefficients would be nearly the same for each solution. Even though different media were used on the two sides of the membrane, differences between the ratios of activity coefficients of the univalent salts in the two media cancel out because only differences in cell potentials (corresponding to different concentrations of ammonium nitrate in liquid ammonia) were measured. With these simplifications equation 6 can be expressed as

$$E_2 = \frac{u_+ - u_-}{u_+ + u_-} \ln \frac{\gamma_\pm{}^{\mathrm{I}}(C_{\mathrm{AgNO_3}} + C_{\mathrm{NH_4NO_3}})^{\mathrm{I}}}{\gamma_\pm{}^{\mathrm{II}}(C_{\mathrm{AgNO_3}} + C_{\mathrm{NH_4NO_3}})^{\mathrm{II}}} \quad (7)$$

Since the transference number, t_+, of the positive ion is $u_+/u_+ + u_-$ and the transference number, t_-, of the negative ion is $u_-/u_+ + u_-$, equation 7 may be rewritten as

$$E_2 = (2t_+ - 1)RT/F \ln \frac{\gamma_\pm{}^{\mathrm{I}}(C_{\mathrm{AgNO_3}} + C_{\mathrm{NH_4NO_3}})^{\mathrm{I}}}{\gamma_\pm{}^{\mathrm{II}}(C_{\mathrm{AgNO_3}} + C_{\mathrm{NH_4NO_3}})^{\mathrm{II}}} \quad (8)$$

The total potential of the cell is equal to the sum of all potentials

$$E_{\mathrm{total}} = E_1 + E_2 + E_3$$

$$E_{\mathrm{total}} = RT/F \ln \frac{(a_{\mathrm{AgNO_3}})^{\mathrm{I}}}{(a_{\mathrm{AgNO_3}})^{\mathrm{II}}} - (2t_+ - 1)\, RT/F \ln \frac{\gamma_\pm{}^{\mathrm{I}}(C_{\mathrm{AgNO_3}} + C_{\mathrm{NH_4NO_3}})^{\mathrm{I}}}{\gamma_\pm{}^{\mathrm{II}}(C_{\mathrm{AgNO_3}} + C_{\mathrm{NH_4NO_3}})^{\mathrm{II}}}$$

or

$$E_{\mathrm{total}} = RT/F \ln \frac{(a_{\mathrm{AgNO_3}})^{\mathrm{I}}}{(a_{\mathrm{AgNO_3}})^{\mathrm{II}}} - (2t_+ - 1)RT/F \ln \gamma_\pm{}^{\mathrm{II}}(C_{\mathrm{AgNO_3}} + C_{\mathrm{NH_4NO_3}})^{\mathrm{II}} + (2t_+ - 1)RT/F \ln \gamma_\pm{}^{\mathrm{I}}(C_{\mathrm{AgNO_3}} + C_{\mathrm{NH_4NO_3}})^{\mathrm{I}} \quad (9)$$

II = alcoholic solution, I = liquid ammonia solution

Since the ammonium nitrate concentration is varied in the liquid ammonia half of the cell, the ionic strength of the solution will vary, thereby affecting the activity of the silver nitrate $(a_{\mathrm{AgNO_3}})^{\mathrm{I}}$ in that solution. A calculation of this change over the concentration range investigated (0.002–0.016 M), using activity coefficients obtained from a modified Debye–Hückel[10] equation, indicates that the potential change over the entire range would not exceed 4 millivolts. This change is within the experimental error.

The equation for the potential of the cell may then be expressed by

$$E_{\mathrm{total}} = (2t_+ - 1)RT/F \ln \gamma_\pm{}^{\mathrm{I}}(C_{\mathrm{AgNO_3}} + C_{\mathrm{NH_4NO_3}})^{\mathrm{I}} + C \quad (10)$$

Thus, the change of potential which occurs as the concentration of NH_4NO_3 in the liquid ammonia is increased from A to B may be expressed by

$$E_{\mathrm{B}} - E_{\mathrm{A}} = \Delta E = (2t_+ - 1)RT/F \ln \frac{\gamma_\pm(C_{\mathrm{AgNO_3}} + C_{\mathrm{NH_4NO_3}})B}{\gamma_\pm(C_{\mathrm{AgNO_3}} + C_{\mathrm{NH_4NO_3}})A} \quad (11)$$

This equation represents the potential change accompanying a change of electrolyte activity. It predicts that a plot of the logarithm of the cationic concentration *versus* the potential will result in a straight line since it was found that in the dilute region under investigation activity coefficients change linearly with concentration. The slope of the straight line should be dependent upon $(2t_+ - 1)RT/F$.

Calculation of Activity Coefficient Ratios and Transference Numbers

If the proper numerical values are substituted into equation 11, the relationship is obtained

$$E = (2t_+ - 1)\,(0.0443)\left[\log \frac{(\gamma_\pm)B}{(\gamma_\pm)A} + \log C_{\mathrm{B}}/C_{\mathrm{A}}\right] \text{ at } -50^\circ \quad (12)$$

where C_{B} and C_{A} represent cationic concentrations and $\gamma_\pm$ is the mean activity coefficient of ammonium nitrate. The solutions to which the calculations have been applied had a molar ratio of ammonium nitrate to silver nitrate of at least 5:1. In this concentration region, the errors introduced by previous assumptions become negligible.

Both the transference number (t_+) and ratio of activity coefficients cannot be determined by the same series of experiments. However, if either is known, the other may be determined.

The behavior of ion-exchange membranes departs sufficiently from the expected behavior over a wide range of concentrations so that the data obtained cannot be used for calculating activity coefficients; however, they are sufficiently accurate to calculate ratios of activity coefficients. This is true even of the data obtained in aqueous solution.

Experimental

Cell Assembly for Measurements.—The cell consisted of a modified 500-ml. round-bottomed flask (Fig. 1) into which the ion-exchange membrane unit, the sample addition unit,[11] the reference electrode for the outer half cell, and a Y adapter were inserted. In one arm of this adapter was placed a thermometer and the other arm was attached to a cold finger type of condenser which was in turn connected to

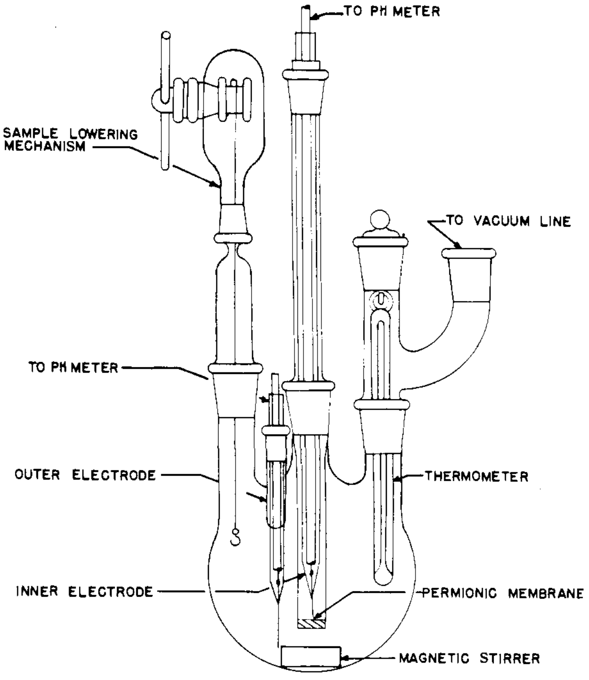

Fig. 1.—Cell assembly for measurements.

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[10] V. A. Pleskov and A. M. Monoszon, *J. Phys. Chem. U. S. S. R.*, **6**, 513 (1935) (Russian); also *Acta Physicochim. U. R. S. S.*, **1**, 713 (1935) (German).

[11] M. J. Bergin and A. H. A. Heyn, *Anal. Chem.*, **24**, 1383 (1952).

the vacuum line. The body of the round-bottomed flask was used as a container for the silver–silver nitrate reference electrode and the liquid ammonia solutions.

The Membrane Unit.—The membranes used in this work were prepared at Ionics, Inc., Cambridge, Massachusetts. The ion-exchange material, which was a phenol-sulfonic acid type resin, was formed directly in fritted glass discs of medium porosity sealed into 10 mm. glass tubing. By forming the ion-exchange membrane directly in the pores of the glass, the mechanical strength of the resulting membrane was greatly increased.

Dipping into the alcoholic reference solution (0.001 M with respect to both silver nitrate and ammonium nitrate) contained in the membrane-containing tube was the inner reference electrode. These components comprised the membrane unit. When this unit was not in use, it was stored in a large test-tube with the outside surface of the membrane dipping into alcohol.

General Procedure.—To obtain a series of measurements, the following general procedure was used. The desired amount of silver nitrate was weighed into the outer cell (the final concentration being 0.001 M), and a magnetic stirring bar was added. The outer reference electrode, the sample adding unit with the samples in the boats, and the Y tube containing the low temperature thermometer were inserted into the cell. A 24/40 plug replaced the membrane unit in the middle joint at this time. The cell was then evacuated. The calibrated flask was cooled to −50° by means of isopropyl alcohol and Dry Ice in a Dewar flask, and 330 ml. of ammonia was recondensed into the main cell. When all the ammonia had been condensed, the pressure in the system was allowed to increase to slightly above one atmosphere. At this point, the membrane unit, which had been pre-cooled in alcohol to −50°, was inserted, and the whole system was recooled to −50°. The potentiometer (Beckman Model G *p*H meter) was connected in series with the cell. Equilibrium was shown by a constant potential which was generally established within several minutes.

Experimental Results

Four cell systems were studied. The first may be represented schematically as

Silver	Silver nitrate 10^{-3} M	Ammonium nitrate varying concn.	Membrane	Ammonium nitrate 10^{-3} M	Silver nitrate 10^{-3} M	Silver
	Water			Water		

The concentration of ammonium nitrate was varied from 0.002 to 0.036 M and the results are presented graphically in Fig. 2.

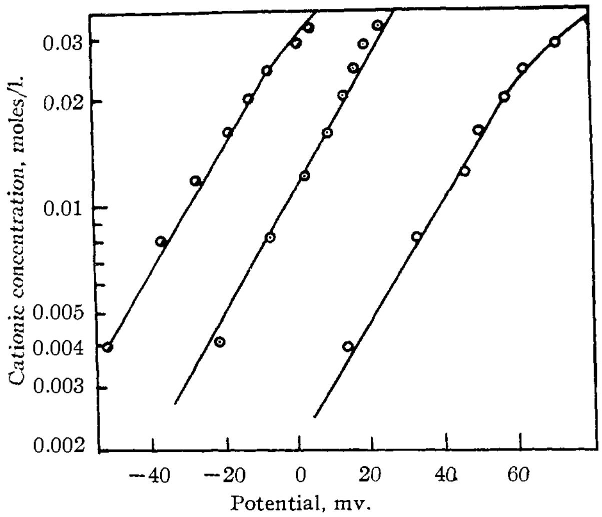

Fig. 2.—Variation of membrane potential with cationic concentration (various media): O, all alcohol; ◑, water–alcohol; ⊙, water.

In the second cell system an all-alcohol medium was used. The results are shown in Fig. 2.

The cell system using alcohol and liquid ammonia on the two sides of the membrane is shown above. The concentration range of 0.001 to 0.012 M with respect to ammonium nitrate was investigated at a temperature of −50°. The potentials obtained could be duplicated within ±1 millivolt not only for all consecutive series of measurements using the same membrane, but also for all series of measurements using different membranes. Figure 3 represents a specific set of two consecutive series of measurements using the same membrane. It is seen that the variation is well within the experimental error of the meter used.

Above a cationic concentration of 0.012 M, the experimental values deviate from linearity (Fig. 4). Measurements of the liquid junction potential (absence of the membrane) indicate that beyond this point this junction potential becomes significant. Also, the potential of the reference electrode may be changing due to the increase in the ionic strength.

Activity Coefficient Ratios.—It is apparent from equation 12 that either the transference number of the membrane or the activity coefficient of the salt can be obtained by this method. In the aqueous system, for the cation concentration range studied the ratio of activity coefficients is unity. The equation then becomes

$$E = (2t_+ - 1)\ RT/F \ln C_B/C_A \qquad (13)$$

Inserting the experimental values obtained into this equation a positive tranference number of the membrane is calculated as 0.94. The constancy of the slope indicates that this value remains constant over the range of concentrations studied.

As pointed out above, the usual methods of obtaining activity coefficient data are not applicable. However, the ratio of activity coefficients in this range may be obtained. The cationic concentration of 0.005 M was chosen as reference point since, at this point, the ratio of ammonium ions to silver ions is 5/1, and any contribution to the potential by the silver ion would be minimized. The transference number of the membrane in liquid ammonia was assumed to be same as that in water in the calculations. The ratios calculated in this manner are tabulated in Table I.

Table I

Activity Coefficient Ratios

Concn. ratio, M	As determined by membrane junction	As determined by Pleskov and Monoszon[10]	Calcd. by Debye and Huckel eq.
0.005/0.007	1.09	1.08	1.08
.005/0.009	1.16	1.17	1.13
.005/0.011	1.26	1.25	1.19
.005/0.013	1.35	1.32	1.23
.005/0.015	1.39	1.38	1.27

Discussion of Results

From the experimental data obtained, it is apparent that ion-exchange membranes may be utilized as electrodes in water, alcohol or liquid ammo-

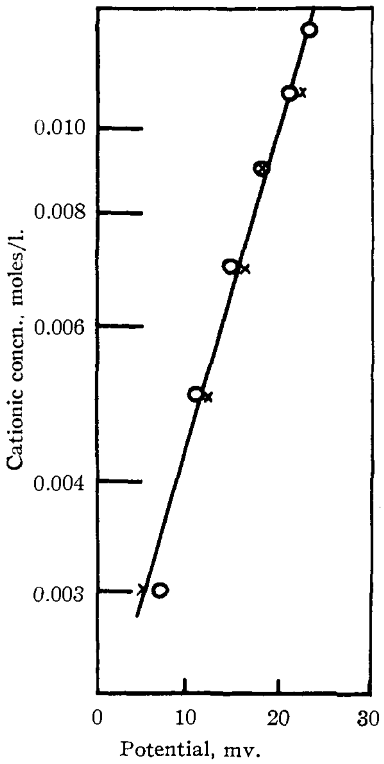

Fig. 3.—Variation of membrane potential with cationic concentration by liquid ammonia–alcohol cell.

nia solutions. At lower concentrations, the change in potential with concentration variation is found to be that predicted by equation 12.

In an all-water system, it is found that over the concentration range 0.003–0.03 *M* with respect to ammonium nitrate a straight line is obtained when *E* is plotted against logarithm of cationic concentration. From the slope of the plots, the positive transference number of 0.94 was determined.

Over a limited concentration range (0.003–0.025 *M*) the plots of the results for the alcohol–water system and the all–water system have slopes which are essentially the same. Therefore a change in the medium did not appear to change the transference number of the membrane. These data establish that a cell containing two media may be used and that electrode action exists at the membrane junction in non-aqueous medium.

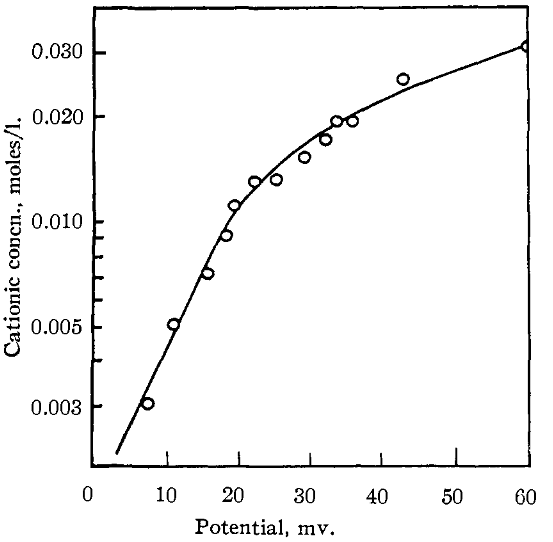

Fig. 4.—Variation of membrane potential with cationic concentration; liquid ammonia–alcohol cell.

In the liquid ammonia–alcohol system the predicted linear plot is also obtained, but over a somewhat narrower range, 0.002–0.017 *M*. Beyond this value the slope changes, possibly due to changes in liquid junction potentials or to changes in the potential of the outer reference electrode from increasing ionic strength, or both. It has not been attempted to distinguish between these two effects experimentally.

Although the values obtained may not be utilized to obtain activity coefficients, ratios of activity coefficients may be obtained. Table I indicates that the values obtained by this method are comparable to those obtained by other electrochemical methods and theoretical calculations.

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