BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2701—2708 (1973)

An Experimental Study of Gibbs-Donnan Membrane Equilibria Across Permselective Membranes Which Involve the Ions of Strong Inorganic Electrolytes*

Reita TAMAMUSHI

National Institute of Arthritis, Metabolism, and Digestive Diseases, National Institutes of Health, Bethesda, Md. 20014, U.S.A.

*The Institute of Physical and Chemical Research, Wako-shi, Saitama, Japan***

(Received March 29, 1973)

The Donnan membrane equilibria arising across permselective collodion matrix membranes were studied both by a static and a flow method in systems which contain only simple strong electrolytes at relatively high concentrations, up to 0.4 equiv/l. Experimental details of the flow method and its advantage in studying the ion activity behavior are presented. From the measurements of equilibrium concentrations and Donnan membrane potentials the ratios of ion activity coefficients were calculated for the following pairs of electrolytes in mixed solutions: sodium chloride–sodium nitrate, sodium sulfate–ammonium sulfate, potassium oxalate–ammonium sulfate, and potassium oxalate–ammonium oxalate. The experiments prove the feasibility of determining the ratios of ion activity coefficients in mixed solutions at concentrations where other methods lose their usefulness.

After the theory of the Gibbs-Donnan equilibrium was developed by Donnan in 1911[1]) extensive studies were carried out experimentally to test this theory.[2]) These studies, however, were for a long time restricted

---

* The experimental work reported in this paper was carried out in 1952—1953, while the author worked at the National Institute of Arthritis, Metabolism, and Digestive Diseases, supported by a travel grant under the Fulbright Act.

** Permanent address of the author.

1) F. G. Donnan, *Z. Elektrochem.*, **17**, 572 (1911).

2) For example: (a) F. G. Donnan and A. J. Allmand, *J. Chem. Soc.*, **105**, 1941 (1914); (b) E. Hückel, *Kolloid-Z.*, Erganzungsband zu Band XXXVI (Zsigmondy Festschrift), s. 204 (1925); (c) T. R. Bolam, "The Donnan Equilibria and Their Application to Chemical, Physiological and Technical Processes," G. Bell and Sons, London (1932).

to systems containing colloidal, semicolloidal or relatively large ions like the ferrocyanide ion as the nondiffusible species. Donnan stated quite early, in 1924,[3] that "an accurate experimental study of the equilibria produced by ionically semipermeable membranes may prove to be of value in the investigation of ionic activity coefficients" of strong inorganic electrolytes. For several decades, however, studies of this type remained impossible until "permselective" membranes of extreme ionic selectivity were developed by Sollner and collaborators[4–7] by means of which Gregor and Sollner in 1945[6,7] demonstrated the feasibility of studying membrane equilibria in systems with solutions containing only the ions of the simple strong inorganic electrolytes. Shortly thereafter Sollner[8] showed explicitly how to investigate the activity behavior of individual ions in mixed solutions by the use of permselective membranes. In later years the properties of the permselective collodion matrix membranes have been greatly improved,[9–11] and more precise measurements of membrane equilibria at higher concentrations thus became feasible. It hardly needs to be mentioned that one may use for such studies, more or less conveniently, any of the various types of permselective ion exchanger membranes which have been described by numerous investigators during the last twenty years[12,13] provided their ionic selectivity is sufficiently high. Recently the Donnan membrane equilibrium across commercial permselective membranes was used by Wallace[14] for the determination of dissociation (or stability) constants of some inorganic electrolytes in aqueous solutions.

The results to be presented below show that the method suggested by Sollner[8] is very promising when applied to the experimental determination of activity coefficients in mixed solutions at concentrations where current theories cannot be tested by other methods. This general approach to the study of membrane equilibria and membrane potentials has assumed increasing interest in recent years in view of the advent of the liquid ion exchanger membranes[15–22] and the observation reported by Shean and Sollner[17] that such membranes, if properly constituted, show virtually zero leakage of the nominally impermeable ion even in systems with electrolyte solutions up to several molar. This latter observation and the possibilities it opens up have prompted the author to publish the present paper at this time.

Theoretical

Though the Donnan equilibrium is discussed to some extent in many textbooks of physical chemistry, it is necessary to recapitulate here some of its essential features which must be clearly understood in the present context.

Let us consider a system, System I, of two solutions 1 and 2 which are separated by an ideally cation-permeable membrane, $|\leftarrow\!\oplus\!\rightarrow|$. For the sake of simplicity, solutions 1 and 2 are assumed to contain uni-univalent strong electrolytes A^+X^- and B^+X^-, respectively, at different concentrations c_1 and c_2. The two solutions are at the same temperature, but not necessarily at the same pressure. The initial state of the system is represented by the scheme:

$$\begin{array}{l|c|l} [A^+] = c_1 & & [B^+] = c_2 \\ & \leftarrow\!\oplus\!\rightarrow & \\ [X^-] = c_1 & & [X^-] = c_2 \\ \text{Solution 1} & & \text{Solution 2} \end{array} \qquad \begin{array}{l}\text{(System I,}\\ \text{initial state)}\end{array}$$

The ionic exchanges of permeable cations A^+ and B^+ across the membrane must proceed in such a way that the electrical neutrality is satisfied in the bulk of both solutions 1 and 2. The semi-permeable nature of the membrane results in an unequal ionic distribution and an electric potential difference between the two solutions at the equilibrium state:

$$\begin{array}{l|c|l} [A^+] = c_1 - x & & [A^+] = x \\ [B^+] = x & \leftarrow\!\oplus\!\rightarrow & [B^+] = c_2 - x \\ [X^-] = c_1 & & [X^-] = c_2 \\ \text{Solution 1} & & \text{Solution 2} \end{array} \qquad \begin{array}{l}\text{(System I,}\\ \text{equilibrium}\\ \text{state)}\end{array}$$

Membranes commonly available are more or less permeable to water, and the equilibrium regarding water between the two solution phases should be considered as well as the equilibrium with respect to the permeable ions. Thus the conditions for membrane

---

3) F. G. Donnan, *Chem. Rev.*, **1**, 73 (1924).

4) C. W. Carr and K. Sollner, *J. Gen. Physiol.*, **28**, 119 (1940); H. P. Gregor and K. Sollner, *J. Phys. Chem.*, **50**, 53, 470 (1946); **51**, 299 (1947).

5) (a) C. W. Carr, H. P. Gregor, and K. Sollner, *J. Gen. Physiol.*, **28**, 179 (1945); (b) H. P. Gregor and K. Sollner, *J. Phys. Chem.*, **50**, 88 (1946); (c) K. Sollner and H. P. Gregor, *J. Phys. Colloid Chem.*, **54**, 325, 330 (1950).

6) H. P. Gregor, Ph. D. Thesis., Minneapolis, 1945.

7) K. Sollner and H. P. Gregor, *J. Amer. Chem. Soc.*, **67**, 346 (1945).

8) K. Sollner, *ibid.*, **68**, 156 (1946).

9) R. Neihof, *J. Phys. Chem.*, **58**, 916 (1954).

10) M. H. Gottlieb, R. Neihof, and K. Sollner, *J. Phys. Chem.*, **61**, 154 (1957); M. Lewis and K. Sollner, *J. Electrochem. Soc.*, **106**, 347 (1959).

11) (a) K. Sollner, *J. Phys. Chem.*, **49**, 47, 171, 265 (1945); (b) *J. Electrochem. Soc.*, **97**, 139C (1950); (c) *Ann. N. Y. Acad. Sci.*, **57**, 177 (1953); (d) *J. Macromol. Sci. Chem.*, **A3**, 1 (1969).

12) F. Helfferich, "Ion Exchange," McGraw-Hill Book Co., New York (1962).

13) N. Lakschminarayanaiah, *Chem. Rev.*, **65**, 491 (1965); "Transport Phenomena in Membranes," Academic Press, New York (1969).

14) R. M. Wallace, *J. Phys. Chem.*, **70**, 3922 (1966); **71**, 1271 (1967).

15) C. Botrè and G. Scibona, *Ann. Chim.* (Rome), **52**, 1199 (1962).

16) K. Sollner and G. M. Shean, *J. Amer. Chem. Soc.*, **86**, 1901 (1964).

17) G. M. Shean and K. Sollner, *Ann. N. Y. Acad. Sci.*, **137**, 759 (1966).

18) O. D. Bonner and D. C. Lunner, *J. Phys. Chem.*, **70**, 1140 (1966).

19) K. Sollner, *Ann. N. Y. Acad. Sci.*, **148**, 154 (1968).

20) G. Eisenman, *Anal. Chem.*, **40**, 310 (1968).

21) F. Conti and G. Eisenman, *Biophys. J.*, **6**, 227 (1966); J. L. Walker, Jr. and G. Eisenman, *ibid.*, **6**, 513 (1966).

22) K. Sollner, "The Basic Electrochemistry of Liquid Membranes" in "Diffusion Processes, Proceedings of the Thomas Graham Memorial Symposium, Univ. of Strathclyde," ed. by J. N. Sherwood, A. V. Chadwick, W. M. Muir, and F. L. Swinton, Gordon and Breach, London, New York, and Paris (1971).

equilibrium of system I are given by a following set of equations:[23,24)]

for permeable cations A^+ and B^+,

$$\mu^{\circ(1)}_{A^+} + RT \ln a^{(1)}_{A^+} + F\phi^{(1)} = \mu^{\circ(2)}_{A^+} + RT \ln a^{(2)}_{A^+} + F\phi^{(2)} \quad (1a)$$

$$\mu^{\circ(1)}_{B^+} + RT \ln a^{(1)}_{B^+} + F\phi^{(1)} = \mu^{\circ(2)}_{B^+} + RT \ln a^{(2)}_{B^+} + F\phi^{(2)} \quad (1b)$$

for water,

$$\mu^{\circ(1)}_{H_2O} + RT \ln a^{(1)}_{H_2O} = \mu^{\circ(2)}_{H_2O} + RT \ln a^{(2)}_{H_2O} \quad (2)$$

The equalities between the chemical potentials between the two solutions do not hold for the anions X^-, that is

$$\mu^{\circ(1)}_{X^-} + RT \ln a^{(1)}_{X^-} - F\phi^{(1)} \neq \mu^{\circ(2)}_{X^-} + RT \ln a^{(2)}_{X^-} - F\phi^{(2)} \quad (3)$$

where $\mu_i{}^{\circ}$ and a_i are the standard chemical potential and the activity, respectively, of the species i in the solutions specified by superscripts (1) and (2), $\phi^{(1)}$ and $\phi^{(2)}$ are the electric potentials of solutions 1 and 2, and the other symbols have their usual meaning.

The Donnan membrane potential is determined by the condition that, at the equilibrium, the work associated with the transfer of permeable cations should be counterbalanced by the electrical energy due to the potential difference between the two solutions. From Eqs. (1a) and (1b) we obtain,

$$\begin{aligned} E = \phi^{(2)} - \phi^{(1)} &= \frac{RT}{F} \ln \frac{a^{(1)}_{A^+}}{a^{(2)}_{A^+}} + \frac{1}{F}(\mu^{\circ(1)}_{A^+} - \mu^{\circ(2)}_{A^+}) \\ &= \frac{RT}{F} \ln \frac{a^{(1)}_{B^+}}{a^{(2)}_{B^+}} + \frac{1}{F}(\mu^{\circ(1)}_{B^+} - \mu^{\circ(2)}_{B^+}) \quad (4) \end{aligned}$$

for the Donnan membrane potential E, and

$$\begin{aligned} &\frac{a^{(1)}_{A^+}}{a^{(2)}_{A^+}} \exp\left\{\frac{1}{RT}(\mu^{\circ(1)}_{A^+} - \mu^{\circ(2)}_{A^+})\right\} \\ &\qquad = \frac{a^{(1)}_{B^+}}{a^{(2)}_{B^+}} \exp\left\{\frac{1}{RT}(\mu^{\circ(1)}_{B^+} - \mu^{\circ(2)}_{B^+})\right\} \quad (5) \end{aligned}$$

for the activity ratios of the permeable cations at the equilibrium.

The equilibrium condition for water, Eq. (2), will generally reslut in a pressure difference between the two solutions, which is called the osmotic pressure difference. Under the presence of the osmotic pressure difference, the standard chemical potential of the permeable cation in solution 1 is not equal to that in solution 2, *i.e.* $\mu^{\circ(1)}_{A^+} \neq \mu^{\circ(2)}_{A^+}$ and $\mu^{\circ(1)}_{B^+} \neq \mu^{\circ(2)}_{B^+}$. Such a difference in the standard chemical potentials due to the osmotic pressure difference, however, has been proved both theoretically and experimentally to be very small, and can be neglected in many cases, provided that the solutions are not too concentrated.[25)] Experimentally, the osmotic pressure difference can be eliminated by adding a proper amount of impermeable neutral species to the solution of a lower concentration.[7)]

Under such conditions the following relations can be used in place of Eqs. (4) and (5) for the membrane equilibrium with a sufficiently high accuracy:
for the Donnan membrane potential,

$$E = \frac{RT}{F} \ln \frac{a^{(1)}_{A^+}}{a^{(2)}_{A^+}} = \frac{RT}{F} \ln \frac{a^{(1)}_{B^+}}{a^{(2)}_{B^+}} \quad (6)$$

and for the Donnan activity ratio,

$$\frac{a^{(1)}_{A^+}}{a^{(2)}_{A^+}} = \frac{a^{(1)}_{B^+}}{a^{(2)}_{B^+}} \text{ or } \frac{c^{(1)}_{A^+}}{c^{(2)}_{A^+}} \frac{\gamma^{(1)}_{A^+}}{\gamma^{(2)}_{A^+}} = \frac{c^{(1)}_{B^+}}{c^{(2)}_{B^+}} \frac{\gamma^{(1)}_{B^+}}{\gamma^{(2)}_{B^+}} \quad (7)$$

where c is the equilibrium concentration and γ the activity coefficient. In a particular case when the ratios of activity coefficients, $\gamma^{(1)}/\gamma^{(2)}$, are the same for A^+ and B^+ in the pairs of solutions 1 and 2, Eq. (7) and the condition of electrical neutrality give the simplified original formula of Donnan,[1,2c)]

$$\frac{c^{(1)}_{A^+}}{c^{(2)}_{A^+}} = \frac{c^{(1)}_{B^+}}{c^{(2)}_{B^+}} = \frac{c^{(1)}_{X^-}}{c^{(2)}_{X^-}} \quad (8)$$

which refers to analytical concentrations rather than activities.

All the equations mentioned above have been derived by assuming the ideal permselectivity of membranes against cations and anions. Actual membranes, however, are not strictly ideal in their ionic selectivity, and show some leakage of nominally impermeable ions although this leakage is extremely small in the case of good permselective membranes. Such a small leak will not affect the equilibrium conditions for permeable ions seriously, and Eqs. (6) and (7) can be satisfied with a reasonably high accuracy, provided that the exchange rate of nominally impermeable ions across the membrane is very much lower than that of permeable ions.

These theoretical considerations lead to a useful conclusion as follows:[8)]

(i) Measurements of equilibrium concentrations of permeable ions in the two solutions give the information on the ratios of their activity coefficients in mixed electrolyte solutions: *i.e.* from Eq. (7) we obtain,

$$\frac{\gamma^{(1)}_{A^+}}{\gamma^{(2)}_{A^+}} \frac{\gamma^{(2)}_{B^+}}{\gamma^{(1)}_{B^+}} = \frac{c^{(1)}_{B^+}}{c^{(2)}_{B^+}} \frac{c^{(2)}_{A^+}}{c^{(1)}_{A^+}} \quad (9)$$

The left-hand side of Eq. (9) is directly calculated from the analytical concentrations of permeable ions at the equilibrium without introducing any further assumptions, and therefore its accuracy is determined only by the accuracy of the concentration determination. If one of the two solutions, say solution 2, is sufficiently dilute so that ionic activity coefficients or their ratios are known by some theoretical means, the ratio of activity coefficients of the permeable cations in the other solution, solution 1, can be calculated.

(ii) Concomitant measurements of equilibrium concentrations and the Donnan membrane potential enable us to calculate the ratios of activity coefficients of permeable ions in solutions 1 and 2: *i.e.* from Eqs. (6) and (7) we obtain,

$$\frac{\gamma^{(1)}_{A^+}}{\gamma^{(2)}_{A^+}} = \frac{c^{(2)}_{A^+}}{c^{(1)}_{A^+}} \exp\left(\frac{EF}{RT}\right), \quad \frac{\gamma^{(1)}_{B^+}}{\gamma^{(2)}_{B^+}} = \frac{c^{(2)}_{B^+}}{c^{(1)}_{B^+}} \exp\left(\frac{EF}{RT}\right) \quad (10)$$

The activity coefficients of each permeable ion in one of the two solutions can be determined provided that the ionic activity coefficients in the other solution are available.

The Donnan membrane potential is usually measured

---

23) E. A. Guggenheim, "Thermodynamics," North-Holland Publishing Company, Amsterdam (1967), Chap. 1.42, 8.07, and 8.08.

24) R. Haase, "Thermodynamics of Irreversible Processes," Addison-Wesley Publishing Company, Reading, Mass. (1969), Chap. 1-20.

25) N. Kameyama, *Phil. Mag.*, **50**, 849 (1925). See also Ref. 2c, pp. 25—26 and Ref. 23, Chap. 8.08.

with a cell, saturated calomel electrode/saturated KCl bridge/solution 1/membrane/solution 2/saturated KCl bridge/saturated calomel electrode. The electromotive force of such a cell involves the liquid junction potentials at the junctions between the KCl bridges and the solutions. Therefore, the accuracy of the ionic activity coefficients determined by Eq. (10) is affected by the accuracy of correcting the measured electromotive force for the liquid junction potentials.

This method of determining ionic activity coefficients in mixed solutions is not exclusively restricted to such a simple system as mentioned above, but can be equally applied to membrane equilibria which may involve any desired combination of uni-univalent and uni-multivalent electrolytes, if the membranes are properly selected.

Experimental

In studying Donnan membrane equilibria with simple electrolytes it is important to use membranes with the following properties: (i) a very high degree of ionic selectivity towards cations over anions or *vice versa*, (ii) sufficiently high rates of exchange of permeable ions across the membrane so that the system can reach the equilibrium state within a reasonable period of time, and (iii) low water permeability. The requirement for membranes to fulfill the last two conditions is somewhat antagonistic. The ohmic resistance of membranes is an indication of the rates of ion exchange and water movement across the membranes; membranes of lower resistance which allow higher rates of ion exchange, tend to show higher water permeability.

By far the most suitable porous membranes for the experimental study of Donnan membrane equilibria with simple electrolytes are the permselective collodion matrix membranes developed by Sollner and collaborators, particularly the exclusively cation-permeable sulfonated polystyrene collodion membranes and the exclusively anion-permeable protamine collodion membranes,[26] which show excellent ionic selectivities.[4,5,9–11] Moreover their ion exchange capacity per cm² is very low, a decided advantage in many experimental situations. The information available on these permselective membranes with respect to their ionic selectivity, the rate of exchange of permeable ions across them, the water permeability, *etc.* makes it possible to select membranes with a suitable combination of the properties mentioned earlier.

Permselective sulfonated polystyrene collodion membranes were prepared by the dissolution method described by Neihof,[9] and permselective protamine collodion membranes by the adsorption method.[5] The membranes were test-tube-shaped (25×100 mm) and mounted on glass collars. They were tested for (a) their ohmic resistance in 0.1 M KCl, (b) their ionic selectivity, and (c) their water permeability. Membranes with resistances of several tens ohm cm² were considered to be most suitable. The membrane concentration potential of a concentration cell, such as 0.4 M KCl/membrane/0.2 M KCl, is a good measure of the ionic selectivity. We selected the membranes which showed the membrane concentration potential in agreement with the theoretical maximum value within 0.5 mV.

In studying Donnan membrane equilibria the most important experimental consideration is that the rate of exchange of permeable ions across the membrane should be very much faster than the rate of leakage of nominally impermeable ions. Typical results given in Table 1, which is reproduced from a paper by Sollner,[11c] clearly show that the leak of anions, particularly that of bivalent anions, is practically negligible with membranes of the type used here.

The water permeability of membranes was measured by a method similar to that used by Neihof.[27] The test-tube-shaped membrane was tied to a glass collar which was fitted with a rubber stopper carrying a micro-measuring-pipette. The membrane was filled with 30 ml of 0.1 M KCl and immersed in a beaker containing 60 ml of distilled water. The increase in the volume of the inside solution was read by the micro-measuring-pipette at given intervals. The average rate of water movement under these conditions amounted only to 0.03—0.04 ml per 100 cm² of membrane area per hour.

Protamine collodion membranes have properties similar but slightly inferior to those of sulfonated polystyrene collodion membranes.

TABLE 1. RATES OF CATION EXCHANGE AND ANION LEAK ACROSS TWO CATION-PERMEABLE SULFONATED POLYSTYRENE COLLODION MEMBRANES USED IN THE STUDY OF DONNAN MEMBRANE EQUILIBRIA[a]

Resistance of membrane in 0.1 M KCl	Original solutions		Cation exchange after 1 hr	Anion leak after 1 hr	Cation exchange after 4 hr	Anion leak after 4 hr
	Solution 1 (inside)	Solution 2 (outside)				
Ohm cm²	equiv/l	equiv/l	per cent of possible exchange	per cent of actual cation exchange	per cent of possible exchange	per cent of actual cation exchange
60	0.1 NH_4Cl	0.1 $LiNO_3$	35.0	not detectable	83.0	<0.5
90	0.1 NH_4Cl	0.1 $LiNO_3$	29.0	not detectable	68.5	<0.5
60	0.1 $(NH_4)_2C_2O_4$	0.1 Li_2SO_4	35.0	not detectable	79.5	<0.05
90	0.1 $(NH_4)_2C_2O_4$	0.1 Li_2SO_4	29.5	not detectable	73.0	<0.05

a) The data were reproduced from Table 5 in Ref. 11c.

---

[26] After completion of this work new anion-permeable membranes of better properties than old protamine collodion membranes were developed by Sollner and collaborators (see Ref. 10).

[27] Ref. 9. See also K. Sollner and I. Abrams, *J. Gen. Physiol.* **24**, 1 (1940).

The ion distribution between two solutions separated by a membrane at the equilibrium was determined by the following two methods, one being called "static", and the other, "flow" or "dynamic" method. The latter is expected to be more suitable than the former for the systems of greater concentration ratios of impermeable ions and for the study of the activity behavior.

In the static method, the inside of a test-tube-shaped membrane was filled with 30 ml of one electrolyte (solution 1), and the membrane was immersed in a larger test tube containing 60 ml of the other electrolyte (solution 2). The membrane was equilibrated with the solutions to be examined prior to each experiment. Both solutions were stirred by passing purified nitrogen or air through the solution. After the membrane equilibrium had been attained, the solutions were analyzed for every ion involved.

Before each experimental run, a preliminary kinetic study was made to determine the time required to establish the equilibrium. Figure 1 shows an example of the kinetic study with a cation-permeable sulfonated polystyrene collodion membrane for the systems of potassium oxalate–ammonium oxalate and potassium oxalate–ammonium sulfate. In all our present systems the equilibrium was reached well within 15 hr.

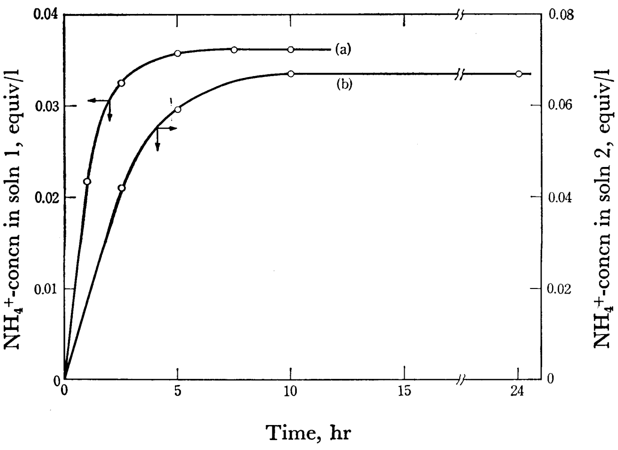

Fig. 1. Exchange of ammonium ions across a permselective cation-permeable sulfonated polystyrene collodion membrane in the course of approach to the membrane equilibrium by the static method. Initial state: (a), 0.200 M $K_2C_2O_4$ (soln 1) |←⊕→| 0.0100 M $(NH_4)_2C_2O_4$ (soln 2); (b), 0.100 M $(NH_4)_2SO_4$ (soln 1) |←⊕→| 0.100 M $K_2C_2O_4$ (soln 2). Volume of solution: soln 1/soln 2=30 ml/60 ml.

In studying the activity of ions by means of Donnan membrane equilibria, it is desirable to keep the composition of one of the two solutions practically unchanged during equilibration with the other solution. Theoretically this can be done by making the volume of the reference solution infinitely larger than that of the test solution.[8] The above-mentioned requirement is effectively satisfied by the *flow method*, that is, by running a large quantity of the reference solution (usually the more dilute solution) at a given constant rate by the outside of a test-tube-shaped membrane which contains the solution to be examined. By this method it is not necessary to determine analytically the equilibrium concentrations of ions in the reference solution; also, it makes it possible to use a very dilute reference solution and to study Donnan equilibria at large concentration ratios of impermeable ions. Furthermore, the flow method has the advantage that the approach to equilibrium can be checked by withdrawing a small amount of inside solution for analyses at given intervals; the change in the volume of the inside solution does not affect the equilibrium since the composition of the outside solution remains at the original, nominal level throughout.

In the present study, the initial volume of the inside solution (solution 1) was 25 ml, and about 60 l of the reference solution (solution 2) was run continuously by the outside of the membrane within about one week. The osmotic water movement across the membrane was compensated by adding a proper amount of impermeable neutral species, sucrose or glucose, to solution 2.[28] Both solutions were stirred by the gentle stream of purified nitrogen or air. A known quantity (1 ml) of the inside solution was pipetted out at given intervals, and analysed for the permeable ions in order to follow the kinetics of the ion exchange and to determine the equilibrium concentrations. The equilibrium was checked by running parallel the same experiments starting from both sides of the equilibrium with a common reference solution. Figure 2 shows a typical example of the kinetic approach to the equilibrium by the flow method, where the method was applied to the system containing potassium and ammonium oxalates. When the concentration ratio of impermeable ion was greater than 20, at least four days were required for the system to attain the equilibrium state.

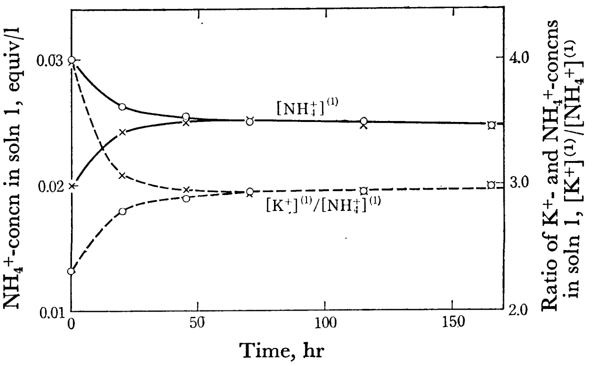

Fig. 2. Exchange of permeable ions, NH_4^+ and K^+, across permselective cation-permeable sulfonated polystyrene collodion membranes in the course of approach to the membrane equilibrium by the flow method. Initial state: solution 1, 0.0350 M $K_2C_2O_4$+0.0150 M $(NH_4)_2C_2O_4$ (-○-) and 0.0400 M $K_2C_2O_4$+0.0100 M $(NH_4)_2C_2O_4$ (-×-); common reference solution 2, 0.000750 M $K_2C_2O_4$+0.000250 M $(NH_4)_2C_2O_4$+0.120 M glucose. Solid lines represent the change in the NH_4^+-concentration in solution 1, and broken lines the change in the concentration ratio $[K^+]^{(1)}/[NH_4^+]^{(1)}$.

The membrane potential at the equilibrium was measured at 25.00±0.05 °C by constructing a conventional electrical cell with two saturated calomel electrodes.[5c] The contribution of liquid junction potentials was estimated by using Henderson's equation and ionic mobility data. The accuracy of the membrane potential thus obtained is considered to be ±0.5 mV in most cases.

---

28) The addition of impermeable neutral species to the less concentrated solution is a convenient and effective method of eliminating the osmotic water movement across the membrane. This method, however, has a drawback that the activity coefficients of the ions to be studied may or may not be influenced by the presence of some foreign materials. In the study of activity coefficients it will be better to use another method of compensating the effect of the osmotic water movement by blowing appropriately dried air at the proper rate through the more concentrated solution to keep its volume constant. Refer to R. Neihof and K. Sollner, *J. Phys. Chem.*, **61**, 159 (1957).

The concentrations of sodium and potassium ions were determined gravimetrically by the following method. A known volume of the sample solution was evaporated to dryness in order to remove ammonium salts present in the solution. Then the sodium or potassium salts were changed to the sulfate form by a conventional method using a proper amount of sulfuric acid. The sodium or potassium concentrations of the original solution were computed from the weight of the sulfate salts. Ammonium ions were determined by the micro-Kjeldahl method, chloride ions by the Volhard method, and oxalate ions were titrated with a standard potassium permanganate solution in acidic media. The accuracy of these analyses was better than ±0.5% except for concentrations below 0.05 equiv/l.

Results and Discussion

The results of seven typical experiments on Donnan membrane equilibria across permselective membranes, five obtained by the static method and two by the flow method, are given in the self-explanatory Tables 2, 3, and 4. Table 5 summarizes the ratios of activity coefficients of the permeable ions in mixed electrolyte solutions as calculated from the Donnan membrane equilibrium data (Tables 2—4) according to Eqs. (9) and (10).

From these results the following information is obtained with respect to the activity coefficients of the

TABLE 2. DONNAN MEMBRANE EQUILIBRIA ACROSS ANION-PERMEABLE PROTAMINE COLLODION MEMBRANE DETERMINED BY THE STATIC METHOD AT 25 °C
Volume of solution: solution 1/solution 2 = 30 ml/60 ml.

Exp.	Solute	Initial state Concentration (equiv/l) Soln 1	 Soln 2	Equilibrium state Concentration (equiv/l) Soln 1	 Soln 2	 Concentration ratio Soln 1/Soln 2
I	Cl^-	0.05000	—	0.0365 ±0.0002	0.00753 ±0.00005	4.85±0.06
	NO_3^-	—	0.01000	0.0137[a]	0.00287[a]	4.77
	Na^+	0.05000	0.01000	0.0502 ±0.0001	0.0104 ±0.0001	4.83±0.06
II	Cl^-	0.1000	—	0.0842 ±0.0003	0.00867 ±0.00005	9.71±0.10
	NO_3^-	—	0.01000	0.0147[a]	0.00153[a]	9.61
	Na^+	0.1000	0.01000	0.0989 ±0.0001	0.0102 ±0.0001	9.69±0.10

a) Calculated by difference.

TABLE 3. DONNAN MEMBRANE EQUILIBRIA ACROSS CATION-PERMEABLE SULFONATED POLYSTYRENE COLLODION MEMBRANE DETERMINED BY THE STATIC METHOD AT 25 °C
Volume of solution: solution 1/solution 2 = 30 ml/60 ml.

Exp.	Solute	Initial state Concentration (equiv/l) Soln 1	 Soln 2	Equilibrium state Concentration (equiv/l) Soln 1	 Soln 2	 Concentration ratio, (1)/(2)	 Membrane potential[c] (mV)	 Donnan activity ratio, (1)/(2)[d]
III	K^+	—	0.2000	0.135 ±0.001	0.134 ±0.001	1.01±0.01	−0.6±0.2	0.98 ±0.02
	NH_4^+	0.2000	—	0.0670 ±0.0003	0.0676 ±0.0003	0.99±0.01		
	$C_2O_4^{2-}$	—	0.2000	0.000 ±0.0005	0.202 ±0.001	1.00[b]		
	SO_4^{2-}	0.2000	—	0.202[a]	0.000			
IV	Na^+	0.4000	—	0.362 ±0.001	0.0187 ±0.0001	19.4±0.2	66.2±0.5	13.1 ±0.3
	NH_4^+	—	0.02000	0.0366 ±0.0002	0.00180 ±0.00002	20.3±0.2		
	SO_4^{2-}	0.4000	0.02000	0.399[a]	0.0205[a]	19.5		
V	K^+	0.4000	—	0.358 ±0.001	0.0185 ±0.0001	19.4±0.2	66.0±0.5	13.1 ±0.3
	NH_4^+	—	0.02000	0.0362 ±0.0002	0.00178 ±0.00002	20.3±0.2		
	$C_2O_4^{2-}$	0.4000	0.02000	0.394 ±0.001	0.0203 ±0.0001	19.4±0.2		

a) Calculated as the sum of the cation concentrations.
b) Concentration ratio of impermeable anions in solution 1 and in solution 2.
c) Sign refers to solution 2.
d) Calculated from the membrane potential by Eq. (6).

Table 4. Donnan membrane equilibria across cation-permeable sulfonated polystyrene collodion membrane determined by the flow method at 25 °C
In each case the equilibrium was determined by running two experiments A and B starting from the opposite sides of the equilibrium, two similar membranes and a common reference solution 2 being used.

Exp.	Solute	Initial state: Concentration (equiv/l) Soln 1 A	Soln 1 B	Soln 2	Equilibrium state: Concentration in solution 1 (equiv/l) A	B	Concentration ratio,[b] (1)/(2)	Membrane potential[c] (mV)	Donnan activity ratio,[d] (1)/(2)
VI	K^+	0.1500	0.1700	0.00800	0.153 ±0.001	0.156 ±0.001	19.3±0.2	64.4±0.5	12.5±0.3
	NH_4^+	0.0500	0.0300	0.00200	0.0397 ±0.0001	0.0404 ±0.0001	20.1±0.2		
	$C_2O_4^{2-}$	0.2000	0.2000	0.01000	0.193[a]	0.196[a]	19.5±0.2		
	sucrose	—	—	0.205	—	—	—		
VII	K^+	0.0800	0.0700	0.00150	0.0730 ±0.0005	0.0730 ±0.0005	48.7±0.7	88.6±0.5	31.4±0.5
	NH_4^+	0.0200	0.0300	0.000500	0.0245 ±0.0001	0.0245 ±0.0001	49.0±0.7		
	$C_2O_4^{2-}$	0.1000	0.1000	0.00200	0.0975[a]	0.0975[a]	48.8		
	glucose	—	—	0.120	—	—	—		

a) Calculated as the sum of the cation concentration.
b) Average of experiments A and B.
c) Sign refers to suoltion 2.
d) Calculated from the membrane potential by Eq. (6).

Table 5. Ratios of activity coefficients of the permeable ions in mixed electrolyte solutions calculated from the Donnan membrane equilibrium data at 25 °C

Exp.	Solute[a]	Composition of solutions: Concentration (equiv/l) Solution 1	Solution 2	Ratios of activity coefficients of permeable ions, i and j: $\gamma_i^{(1)}/\gamma_i^{(2)}$[b]	$\gamma_j^{(1)}/\gamma_j^{(2)}$[b]	$\{\gamma_i^{(1)}/\gamma_i^{(2)}\}/\{\gamma_j^{(1)}/\gamma_j^{(2)}\}$[c]
I	NaCl	0.0365	0.00753	—	—	1.01±0.02
	$NaNO_3$	0.0137	0.00287			(i=NO_3^-, j=Cl^-)
	c_t	0.0502	0.0104			
II	NaCl	0.0842	0.00867	—	—	1.01±0.02
	$NaNO_3$	0.0147	0.00153			(i=NO_3^-, j=Cl^-)
	c_t	0.0989	0.0102			
III	K_2SO_4	0.135	—	0.99±0.02	0.97±0.02	1.02±0.02
	$K_2C_2O_4$	—	0.134	(i=NH_4^+)	(j=K^+)	(i=NH_4^+, j=K^+)
	$(NH_4)_2SO_4$	0.0670	—			
	$(NH_4)_2C_2O_4$	—	0.0676			
	c_t	0.202	0.202			
IV	Na_2SO_4	0.362	0.0187	0.65±0.02	0.68±0.02	0.96±0.02
	$(NH_4)_2SO_4$	0.0366	0.00180	(i=NH_4^+)	(j=Na^+)	(i=NH_4^+, j=Na^+)
	c_t	0.399	0.0205			
V	$K_2C_2O_4$	0.358	0.0185	0.65±0.02	0.68±0.02	0.96±0.02
	$(NH_4)_2C_2O_4$	0.0362	0.00178	(i=NH_4^+)	(j=K^+)	(i=NH_4^+, j=K^+)
	c_t	0.394	0.0203			
VI	$K_2C_2O_4$	0.155	0.00800	0.62±0.02	0.65±0.02	0.96±0.02
	$(NH_4)_2C_2O_4$	0.0400	0.00200	(i=NH_4^+)	(j=K^+)	(i=NH_4^+, j=K^+)
	sucrose	none	0.205			
	c_t	0.195	0.0100			
VII	$K_2C_2O_4$	0.0730	0.00150	0.64±0.02	0.65±0.02	0.99±0.03
	$(NH_4)_2C_2O_4$	0.0245	0.000500	(i=NH_4^+)	(j=K^+)	(i=NH_4^+, j=K^+)
	glucose	none	0.120			
	c_t	0.0975	0.00200			

a) c_t: total concentration of nominally impermeable ions (the value being identical with the total electrolyte concentration).
b) Calculated by Eq. (10).
c) Calculated by Eq. (9).

permeable ions:

(i) In the sodium chloride–sodium nitrate systems with anion-permeable membranes (Experiments I and II), the constancy of the equilibrium concentration ratios as given by the original Donnan equation (8) is satisfied within the limit of experimental errors, which proves the almost identical behavior of the activity coefficients for chloride and nitrate ions in the solutions examined.

(ii) Experiment III shows that Eq. (8) is satisfied and the equilibrium concentration ratio is practically equal to the Donnan activity ratio in the ammonium sulfate–potassium oxalate system of the same anion concentration. This result shows that the activity coefficients of potassium and ammonium ions are not much affected by the change of anions from sulfate to oxalate.

(iii) In the potassium oxalate–ammonium oxalate system (Experiment VII), Eq. (8) is also satisfied with a reasonable accuracy, but the equilibrium concentration ratio is appreciably larger than the Donnan activity ratio. This means that the activity coefficients of potassium and ammonium ions in oxalate solutions decrease in a similar manner with increasing oxalate concentration from 0.002 to 0.1 equiv/l.

(iv) In Experiments IV—VI the constancy of the equilibrium concentration ratios is not fulfilled. The results given in Table 5 suggest that the activity coefficients of ammonium ion are slightly smaller than those of potassium and sodium ions in oxalate or sulfate solutions of concentrations higher than about 0.2 equiv/l.

The present study clearly demonstrates that the method proposed by Sollner[8) is quite feasible to the investigation of ionic activity coefficients in mixed electrolyte solutions on the basis of the Donnan membrane equilibrium. It was verified that the flow method has the following advantages over the static method when used in the study of the Donnan membrane equilibria: (i) a solution of a fixed composition can be used as the reference in a series of experiment, because the composition of the reference solution can be kept unchanged throughout the course to the equilibrium; and (ii) very dilute reference solutions can be employed in the determination of ionic activity coefficients in more concentrated solutions; this is of practical importance because with very dilute reference solutions the influence of any leakage of the membrane is minimized.

In principle, the Donnan membrane equilibrium is not restricted to the systems containing only strong electrolytes, but can equally be applied to any system involving partially dissociated electrolytes and neutral substances as well. With further developments of membranes of various types, porous or liquid, with ever increasing ionic selectivity and specificity, a large area will be opened up for the experimental study of ionic activity behavior in solutions of any desired composition and concentration. The studies along this line should be of interest not only in physical chemistry but also in colloid and biological chemistry.

This study was suggested by Dr. K. Sollner, Chief of the Section on Electrochemistry and Colloid Physics, National Institute of Arthritis, Metabolism, and Digestive Diseases, and carried out under his guidance. The author wishes to express his heartfelt thanks to Dr. Sollner for his valuable advice, critical discussions, and continual encouragement.