SEA WATER CONVERSION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

"Study of Permeability Characteristics of Membranes"

Quarterly Report No. 8

January 15, 1970

K. S. Spiegler, Principal Investigator
J. C. T. Kwak
D. A. Zelman
J. Leibovitz (part time)

Contract No. 952109
Jet Propulsion Laboratory
Pasadena, California

SEA WATER CONVERSION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

"Study of Permeability Characteristics of Membranes"

Quarterly Report No. 8

Covering Period August 9 - November 9, 1969

K. S. Spiegler, Principal Investigator
J. C. T. Kwak
D. A. Zelman
J. Leibovitz (part time)

Contract No. 952109
Jet Propulsion Laboratory
Pasadena, California

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, as sponsored by the National Aeronautics and Space Administration under Contract NAS 7-100.

"This report contains information prepared by the University of California, Sea Water Conversion Laboratory, Berkeley, under JPL subcontract. Its content is not necessarily endorsed by the Jet Propulsion Laboratory, California Institute of Technology, or the National Aeronautics and Space Administration".

TABLE OF CONTENTS

ABSTRACT, CONCLUSIONS AND RECOMMENDATIONS

The objective of this research effort is to construct an apparatus which will permit us to study the performance of separators and membranes from a minimum number of basic characterization measurements. To achieve this aim, instrumentation has been developed with which transport of salt, ions and water across membranes can be determined accurately and unambiguously with differences in concentration, electrical potential and pressure as driving forces, together with the measurement of membrane potential and streaming potential. Construction, assembly and testing of the apparatus was finished during the first contract year.

A series of transport experiments was completed to evaluate the measurement system and to obtain <u>approximate</u> transport properties for the membrane used. Accurate dialysis-osmosis experiments, and electromigration-electroosmosis experiments in a system with different concentrations of the solutions bounding the membrane, were performed in the second year.

The results, described in detail in the body of this report, show that we indeed achieved strict linearity of transport with time. Diffusional and electrical transport through the AMF* C-103 membrane seem to be additive but further verification is necessary. A strong dependence of salt diffusion and osmotic transport on the pre-treatment of the membrane was found. Previous direct-current passage and stretching of the membrane under pressure seem to alter the transport properties, even though the used pressure differences were low and the stretching appeared to be reversible. Where comparison of our results with data

---

*American Machinery and Foundary Co., Stamford, Connecticut reported in the literature is possible, agreement was found to be reasonable.

During the second contract year some important improvements in the measurement system were made, including a sealless gear-pump in the demineralizing system, and solid state relays in both feedback systems. The problem of small volume losses from each half-cell was solved satisfactorily. After incorporation of these improvements the performance of the system with respect to concentration and temperature constancy was found to satisfy the originally intended requirements.

The experience obtained from these experiments leads to the following recommendations:

1) Now that the apparatus is improved and satisfies the specifications originally aimed at, the systematic series of transport experiments now in progress should be continued, in order to reap the harvest of the effort invested in the development of the "concentration clamp" method.
2) In these experiments all membranes should be subjected to a standard pre-treatment procedure. This procedure should include several cycles of re-equilibration and several periods of direct-current passage. Pressure experiments should be performed after all other experiments have been completed.
3) Additivity of diffusional and electrical salt and water transport should be checked by performing electromigration-electroosmosis experiments first with the positive current in the direction of the salt transport by diffusion, and then with the positive current in a direction opposite to the salt transport by diffusion. The same should be done for pressure permeation.

I. INTRODUCTION

This is the eighth quarterly report of a research program designed to (a) construct one apparatus in which transport of salt, ions and water across membranes can be determined with differences in concentration, electric potential and pressure as driving forces, together with the measurement of membrane and streaming potential, and (b) perform a variety of transport measurements in it to determine the range in which linear relationships between fluxes and forces exist. This will permit us to study the performance of separators and membranes from a minimum number of basic characterization measurements. The experimental system has been described in the first annual report (November, 1968). Minor alterations in this system have been reported in the fifth (February, 1969), sixth (May, 1969) and seventh (August, 1969) quarterly reports. Since the project has been in progress for two years, this report also serves as an annual summary of the progress in the whole second year, November 9, 1968 - November 9, 1969, over and above describing the progress in the eighth quarter.

II. THEORETICAL CONSIDERATIONS

The following theoretical considerations and literature review formed part of a lecture presented to the symposium: "The Limits of Industrial Separations" of the Industrial and Engineering Chemistry Section of the American Chemical Society Meeting in New York, September 10, 1969, by Jan C. T. Kwak, D. Allen Zelman, J. Leibovitz and K. S. Spiegler.

List of Symbols

a	activity, mole cm^{-3}
c	concentration in the solution, mole cm^{-3}
$\bar{c}$	concentration in the membrane, mole cm^{-3}
f_{ij}	friction coefficient, defined by Eq. (7), joule sec $mole^{-1}$ cm^{-2}
i	electric current density, amp cm^{-2}
I	electric current, amp
J	molar flux, positive from left to right, mole cm^{-2} sec^{-1}
L_{EE}	conductance coefficient defined by Eq. (4c), joule sec cm^2 equ^{-2}
l_{ij}	conductance coefficient defined by Eq. (1), $mole^2$ cm^{-1} sec^{-1} $joule^{-1}$
L_{ij}	conductance coefficient defined by Eq. (3) or (4), $mole^2$ cm^{-2} sec^{-1} $joule^{-1}$
L_p	hydraulic permeability, cm^4 $joule^{-1}$ sec^{-1}
p	pressure, joule cm^{-3} (dekabar i.e. units of 10 bar or 9.87 atm)
R	gas constant, 8.3170 joule $(°K)^{-1}$ $mole^{-1}$
T	absolute temperature, °K
u	linear velocity, cm sec^{-1}
$\bar{v}_j$	partial molar volume of species j, cm^3 $mole^{-1}$
x	length coordinate, cm
z_j	valency number, positive for cations, negative for anions
Δ	difference, right minus left
E	electrical potential, volt (= joule $coul^{-1}$)
$\tilde{\mu}_j$	total chemical potential of species j, joule $mole^{-1}$
μ_j^o	standard chemical potential of species j, joule $mole^{-1}$
μ_j^c	concentration-dependent part of the chemical potential of species j, RT ln a_j, joule $mole^{-1}$
ω	solute permeability coefficient, mole cm $joule^{-1}$ sec^{-1}

π	osmotic pressure, joule cm^{-3}
σ	reflection coefficient
ξ_{ij}	reduced friction coefficient, $\xi_{ij} \equiv f_{ij}/c_j$, joule sec cm $mole^{-2}$
$\mathcal{F}$	Faraday's constant, 0.9650 coul equ^{-1}

Subscripts m, s and w stand for membrane, solute and water respectively.

The increasing use of membranes for separating solutes and solvents in industrial processes and medical practice has created a need for accurate and unambiguous measurements of the transport properties of membrane-solution systems. Obviously it would not be practical to perform a separate transport experiment for each possible combination of driving forces. Characterization procedures based on a minimum number of measurements are necessary for the description of the transport properties of membranes and separators and for performance predictions.

For an isothermal system consisting of two aqueous solutions of a solute, s, separated by a membrane, m, the following processes can take place when a concentration difference, Δc_s, a pressure difference, Δp, or (in case of an ionic solute) a current, I, is applied.

With a concentration difference as driving force , the transport of solute, through the membrane is called *solute diffusion* or *dialysis*, the transport of solvent, *osmosis*. If the solute is an electrolyte, the electric potential difference between the two solutions is the *membrane potential*. When pressure is applied to one solution, *hydraulic flow* takes place. The solution emerging on the low pressure side is often less concentrated than on the high pressure side. This phenomenon is called *hyperfiltration* or *reverse osmosis*. The electric potential difference, caused by the pressure difference, is called *streaming potential*. The ionic transport caused by an electric current passed through the membrane is called *electromigration* and the fraction of the current carried by ion j the *transport number* of j. The concomitant solvent transport across the membrane caused by the electric current is called *electroosmosis* and the number of moles of solvent transported per Faraday of current passed is the *water* *transport number*. Finally, the electric conductivity is defined by the derivative $di/d\Delta E$.

In the last analysis all these phenomena depend on the ease of migration of solute and solvent ions or molecules through the membrane; they are therefore related to each other. These relations follow directly from macroscopic theory, based on the thermodynamics of irreversible processes.

Measurements of one or more of the transport properties mentioned above for ionic or neutral membranes in contact with aqueous solutions of various single salts and salt mixtures, or with solutions of organic compounds (e.g. urea or glucose), have been reported in a large number of papers. Reviews of this work and of existing theories have been given by Helfferich(1), Friedlander and Rickles(2), Lakshminarayanaiah(3), Shaffer and Mintz(4), Johnson, Dresner and Kraus(5), Merten(6), and Meares(7). Staverman(8) first applied non-equilibrium thermodynamics to membrane transport processes. This theory assumes that the flux of a species *i*, J_i, is proportional to a linear combination of the driving forces acting on all species *j*. For a uniform temperature process:

$$J_i = \sum_j l_{ij} \, (-\text{grad } \tilde{\mu}_j) \tag{1}$$

The l_{ij} are conductance coefficients and $\tilde{\mu}_j$ the total chemical potential of j:

$$\tilde{\mu}_j = \mu_j^\circ + \bar{v}_j \, p + \mathcal{F} z_j \, E + RT \ln a_j \tag{2}$$

μ_j° is the chemical potential of *j* in the standard state, $\bar{v}_j$ is the partial molar volume and z_j the valency (positive for cations, negative for anions, zero for water) of species *j*. p, E and $\ln a_j$ are the pressure, electric potential and logarithm of the activity of *j* respectively, at a given point.

R is the gas constant, T the temperature and $\mathcal{F}$ Faraday's constant.

Equations of type (1) describe the transport properties of many systems at a given temperature and all transport parameters mentioned above can be expressed in terms of the conductance coefficients, l_{ij}. In a membrane system containing n mobile species there are n^2 possible conductance coefficients. Onsager's reciprocity relation states that $l_{ij} = l_{ji}$; hence only $\frac{n}{2}(n + 1)$ coefficients are independent. The utility of any set of transport coefficients for the prediction of flows under different forces depends on the independence of these coefficients on the forces. Classical linear laws e.g. ~~Kohlrausch's~~ law of ion migration in electrolyte solutions and d'Arcy's permeability law indicate that for many materials the conductance coefficients are often more or less independent of the applied electric field or pressure respectively. However, in aqueous solutions they are found to be dependent on concentration(9,10). When transport measurements can be performed at one point in which the gradient of the activity is known, or when suitable derivatives of transport properties with respect to concentration can be taken, this concentration dependence may easily be evaluated. However, in membrane systems we measure flows from one side of the membrane to the other, and equations (1) are necessarily integrated across the concentration profile in the membrane. This integration can be performed when steady-state conditions prevail. A new set of conductance coefficients L_{ij} is obtained:

$$J_i = \sum_j L_{ij} (-\Delta \tilde{\mu}_j); \quad L_{ij} = L_{ji} \tag{3}$$

where $\Delta \tilde{\mu}_j$ is the difference (right minus left)* in total chemical potential between the two solutions bounding the membrane**. Flows from left to right

---

*Some authors(13,14) use the opposite sign for Δ. We prefer to have the same sign for Δ and the gradient, $\Delta y = \int_{\text{left}}^{\text{right}} dy$.

**A "bounding" solution is a solution in contact and in equilibrium with a membrane surface.

are counted positive. Kirkwood(11) showed that reciprocity is maintained for the new coefficients L_{ij}. For solutions consisting of one solvent, w, and one ionic or neutral solute, s, equations (3) can be transformed to a set of equations containing conductance coefficients which are easily calculated from the experimental results of characterization measurements(12):

$$J_w = -L_{VV}\ (\Delta\mu_w^c + \bar{v}_w\Delta p) - L_{VS}\ (\Delta\mu_s^c + \bar{v}_s\Delta p) + L_{VE} \cdot i/\mathcal{F} \qquad (4a)$$

$$J_s = -L_{SV}\ (\Delta\mu_w^c + \bar{v}_w\Delta p) - L_{SS}\ (\Delta\mu_s^c + \bar{v}_s\Delta p) + L_{SE} \cdot i/\mathcal{F} \qquad (4b)$$

$$-\mathcal{F}\Delta E = +L_{EV}\ (\Delta\mu_w^c + \bar{v}_w\Delta p) + L_{ES}\ (\Delta\mu_s^c + \bar{v}_s\Delta p) + L_{EE} \cdot i/\mathcal{F} \qquad (4c)$$

In these equations $\mu_w^c = RT \ln a_w$ and $\mu_s^c = RT \ln a_s$. ΔE is the electrical potential difference measured between two anion-reversible electrodes at each side of the membrane, corrected for a small pressure dependence [for Ag/AgCl electrodes $\Delta E = \Delta E(\text{measured}) - (\bar{v}_{AgCl} - \bar{v}_{Ag})\ \Delta p$].

In experiments in which only solvent flow and total solute flow (rather than separate and independent ionic flows) are measured, the description of the flux-force relationships reduce to equations (4a) and (4b) with $i=0$. These equations have been transformed into the following form containing the osmotic pressure, π, by Kedem and Katchalsky(13,14):

$$J_V = L_p\ [-(\Delta p - \sigma\Delta\pi)] \qquad (5a)$$

$$J_s = \omega\ (-\Delta\pi) + (1 - \sigma)\ J_V\ c_{s,M} \qquad (5b)$$

where J_V is the total volume transported:

$$J_V = \bar{v}_w\ J_w + \bar{v}_s J_s \qquad (5c)$$

The solute term, $\bar{v}_s J_s$, being relatively small in most cases. $\Delta\pi$ is the osmotic pressure of the right side solution minus the osmotic pressure of the left side solution,

$$\Delta\pi = -\Delta\mu_w/\bar{v}_w \qquad (5d)$$

$c_{s,M}$ is defined by:

$$c_{s,M} \equiv \Delta\pi/\Delta\mu_s \tag{5e}$$

For very dilute solutions:

$$c_{s,M} = (c_s'' - c_s')/\ln (c_s''/c_s') \tag{5f}$$

where c' and c" denote the solution concentrations on the left and right side of the membrane respectively. L_p is the *hydraulic permeability*, ω the *solute permeability* and σ the *reflection coefficient*(8). L_p, ω and σ are of course related to the transport coefficients of equations (4). For dilute solutions these relations are(14):

$$\sigma \simeq 1 - \frac{L_{VS}\, c_W}{L_{VV}\, c_{s,M}} \tag{6a}$$

$$L_p \simeq L_{VV}\, \bar{v}_W^{\,2} \tag{6b}$$

$$\omega \simeq \frac{1}{c_{s,M}} \left[L_{SS} - \frac{L_{VS}\, L_{SV}}{L_{VV}} \right] \tag{6c}$$

Note that the conductance coefficients, $L_{vs} = L_{sv}$ and L_{ss}, are strongly dependent on the concentration profile in the membrane, which in turn depends on the bounding solution concentrations. L_p, σ and ω are claimed to be much less concentration-dependent(15).

Another step in the phenomenological description of the transport processes is the expression of the L-coefficients in terms of concentrations in the membrane, $\bar{c}$, and *friction coefficients* f_{ij}(16). This friction coefficient formalism is independent of the reference frame chosen for the fluxes(17). The coefficients f_{ij} appear in a system of equations based on an application of Stefan's basic model concept(18) to membrane solution systems:

$$-\frac{d\tilde{\mu}_i}{dx} = \sum_j f_{ij}\, (u_i - u_j) \tag{7}$$

Equation (7) is similar to the Stefan-Maxwell equations used extensively in the description of diffusion(17-20) and various kinds of liquid junction potentials(21). Onsager's reciprocity relations take the form(17):

$$c_i \, f_{ij} = c_j \, f_{ji},$$

a relation which can also be derived using a mechanistic approach(16). It is sometimes advantageous to use *reduced friction coefficients*(17,22):

$$\xi_{ij} \equiv \frac{f_{ij}}{c_j}$$

These reduced friction coefficients are normalized for the "interaction" of one mole of i and one mole of j, and are usually considerably less dependent on the concentration than the f_{ij}'s. When ξ_{ij} values are assumed to be independent of the concentration they can be used for rough estimates of transport properties in systems for which no data are available. If necessary a further refinement can be obtained by assuming a certain concentration dependence of the reduced friction coefficients based on a model or theory of the transport process(20).

It must be kept in mind that the physical interpretation of friction coefficients should be assessed cautiously. For instance the occurrence of negative friction coefficients in some systems shows that f_{ij}/c_j can not be considered to represent only the friction between one mole of i and one mole of j. In many cases however (e.g. in gases and dilute solutions) the friction model gives a description which is in accordance with molecular models of the transport process. For a complete characterization of the transport properties at uniform temperature of a membrane-solution system either of the sets of equations (3), (4), [or, for neutral solutes (5 a, b)] or (7) may be used.

When the bounding solutions consist of one non-electrolyte dissolved in water, three independent measurements are necessary (e.g. solute diffusion, osmosis and hydraulic flow). For a solution consisting of one electrolyte dissolved in water, six independent transport measurements are needed (e.g. solute diffusion, osmosis, hydraulic flow, electroosmosis, electromigration and conductance).

Several investigations have been reported in which a complete or almost complete set of measurements was performed. Lorimer, Boterenbrood and Hermans(12) measured electroosmosis, electromigration and membrane potential of a cation-exchange membrane in contact with KCl solutions and checked the validity of Onsager's reciprocity relation. Bennion and Rhee(23) measured osmosis, salt diffusion, transport number, hydraulic flow, hyperfiltration and electrical conductance through cellulose acetate membranes of different density in contact with NaCl solutions. Conductance coefficients similar to the coefficients of equation (4), and friction coefficients [equation (7)] were calculated for these systems. The authors found a strong increase of the friction coefficients with increasing membrane density, except for the $f_{Na,Cl}$ which is larger in the looser membranes. Except for $f_{w,m}$ all coefficients are dependent on the salt concentration. $f_{Cl,w}$, $f_{Cl,m}$, $f_{Na,w}$ and $f_{Na,m}$ increase very strongly with increasing salt concentration in the tight membrane, but only slowly in the loose membrane. However, in the tight membrane, $f_{Na,Cl}$ decreases with increasing salt concentration whereas it increases in the loose membrane.

Krämer and Sauer(24) investigated the system ethylene glycol-methanol in contact with a cellulose membrane and measured diffusion permeabilities of the components, hydraulic flow and ultrafiltration over the whole concentration range of the mixture, and were able to verify Onsager's reciprocity relation for this system within experimental error. Kaufmann and Leonard(25) measured net volume transfer under a concentration and a pressure gradient and solute transfer under a concentration gradient through a cellophane membrane. Glucose, sucrose and raffinose were used as solutes in water. In this investigation a correction was made for the mass-transfer resistance of the solution-membrane boundary layer. The corrected transport properties were converted to conductance and friction coefficients, resulting in complete description of this membrane-solution system. Lacey(26) measured transport number, electroosmotic water transport, salt diffusion, osmotic flow and electric conductance for a number of neutral membranes in contact with NaCl solutions. Both admittance and friction coefficients were calculated for these systems.

In the investigations described above diffusion or membrane potential measurements were combined with hydraulic flow and electromigration-electroosmosis measurements to obtain a set of phenomenological coefficients. An inherent problem in this kind of set-up is the difference in concentration profile inside the membrane existing in different measurements. Hydraulic flow or electroosmosis-electromigration measurements, for instance, are performed with equal concentrations at each side of the membrane (in electroosmosis experiments a correction for *back diffusion* is made or the experimental time is short enough not to cause appreciable concentration changes). On the other hand, in a solute-diffusion/osmosis experiment a concentration difference is maintained between the two sides of the membrane and a certain concentration profile exists inside the membrane that may be changed by bulk-flow(27,28,29). Because of the concentration dependence of the transport parameters, the set of coefficients calculated from such experiments, which combine data from measurements with and without a concentration difference between the two boundary solutions, contains inherent ambiguities.

To avoid this problem it has been suggested(16) that for dilute solutions five experiments, none of which would involve concentration differences other than for species present in tracer quantities, would be sufficient to characterize a system consisting of a high capacity membrane in contact with a solution of one salt. The experiments are "self-diffusion" (tracer diffusion) of co-ions and counter-ions, electrical conductivity, electroosmosis and co-ion or counter-ion transport number. These experiments are especially suited for description by the friction coefficient formalism. In order to be able to calculate a set of coefficients f_{ij} defined by equation (7) both the interaction of isotopes of one species during self diffusion and the co-ion/counter-ion interaction have to be neglected. Mackay and Meares$^{(31)}$ carried out such an investigation for a cation-exchange membrane in contact with a NaCl solution. Scattergood and Lightfoot$^{(32)}$ measured conductivity, electroosmotic water transport, hydraulic flow and counter-ion tracer diffusion ("self diffusion") for a cation-exchange membrane in the Na^+ and Ag^+ form, in contact with NaCl and $AgNO_3$ solutions respectively. These authors$^{(32)}$ used low external salt concentrations; the co-ion concentration in the membrane was negligible. They calculated four friction coefficients including the isotopic interaction coefficient.

It is interesting to compare these results of transport measurements in ionic membranes with those of Kaufmann and Leonard$^{(26)}$ for a neutral membrane in contact with a solution of carbohydrates. Scattergood and Lightfoot showed that for a cation-exchange membrane in contact with a dilute $AgNO_3$ or NaCl solution the coefficient $f_{+,w}$ may be smaller than $f_{+,m}$.* Similar conclusions can be drawn from the work of George$^{(33)}$ and George and Schlaikjer$^{(34)}$ using cation and anion-exchange membranes in contact with dilute salt solutions. [These authors measured conductivity, electroosmotic transport and used a rough estimate for the self diffusion coefficient of the counter-ion]. On the other hand, the results of Kaufmann

---

*The subscripts in the f_{ij} have the following meaning: +=cation, w=water, m=membrane, s=solute.

and Leonard for a neutral membrane in contact with carbohydrate membranes show that for all three sugars used as solute f_{sw} is much <u>larger</u> than f_{sm}. Also f_{sw} and f_{sm} increase strongly with increasing size of the solute molecules, while f_{wm} remains relatively constant. These results are in accordance with expectations from the structure of ion-exchange membranes, which suggests that the counter-ions are located close to the matrix and interact strongly with it (16,28), whereas this is not the case for the transport of the uncharged carbohydrate molecules in loose, neutral membranes. In these cases the experimental trends indicate useful correlations between the simple friction model and elementary notions of ionic and molecular transport through membranes.

In a recent series of papers, Meares and co-workers have measured transport numbers(35), conductance and electroosmosis(36) and self diffusion(37) using a tracer method and maintaining constant and equal concentration at each side of the membrane. A cation-exchange membrane, in contact with NaBr, CsBr and $SrBr_2$ solutions or mixed solutions of these salts, was used. Some of their results at low salt concentrations were seriously affected by concentration polarization at the membrane-solution interface, especially when salt mixtures were used. Their results again indicate the importance of coupling terms in the description of membrane transport processes and the potential usefulness of the friction model for such a description.

A problem associated with the measurement of transport properties of membranes is the mass transfer resistance of the membrane-solution boundary layers. In almost all investigations reported a provision was made for some kind of solution agitation, but quantitative information concerning the effect of stirring on the transport measurements is scarce. Of course this influence will be more important for thin or highly permeable membranes; even for the more compact ion-exchange membranes however, the boundary layer resistance can not always be neglected. Kaufmann and Leonard(25) corrected their carbohydrate diffusion measurements through cellophane for the boundary layer mass-transfer resistance by extrapolating the observed dialysis coefficients to infinite stirring speed. At the highest stirring speed this extrapolation still accounted for approximately 5% of the measured diffusional resistance. Litt and Smith(38) used a rotating disk membrane cell for the measurement of transport through thin, neutral membranes. The mass transfer resistance of the diffusion layer can be calculated from first principles for this geometry with an estimated accuracy of 1%. Scattergood and Lightfoot(32) replaced the membrane by a Ag/AgCl electrode and calculated the boundary layer correction for diffusion through an ion-exchange membrane from the experimental current-voltage curves measured with this electrode at different stirring speeds. About 15% of the observed diffusional resistance was attributed to the membrane-solution boundary layer. It should be noted however, that diffusion layers at membrane-solution interfaces do not exhibit the same properties as at metal-solution interfaces, although simplified transport theories indicate complete analogy(39).

The difficulties in obtaining a complete characterization of the transport properties of a membrane-solution system necessary for the prediction of the performance of a membrane under different conditions may be summarized as follows:

All transport coefficients are expected to be dependent on the solute concentration. Therefore uncertainties are introduced when concentration differences are allowed to build up or decrease during a measurement; only approximate values of admittance or friction coefficients are obtained in that case. The "concentration-clamp" method developed in this research was designed to solve this problem.

Even when the bounding solutions are held constant, transport coefficients may vary with the nature of the applied force, however, hence an experimental approach is necessary to evaluate the influence of this effect.

It is necessary to have similar hydrodynamic conditions in the solutions in all experiments in order to avoid influencing some properties by the boundary layer resistance and others not.

When tracer diffusion methods are employed the difficulties with concentration-dependent transport properties can be avoided because a concentration difference between the two sides of the membrane is not necessary to perform an experiment. However, in this case additional transport parameters are introduced necessitating approximations in the calculation of a set of friction or admittance coefficients. Moreover, the final results cannot easily be applied to practical separation processes in which a concentration difference between the two sides of the membrane exists, requiring a knowledge of the concentration dependence of transport coefficients. In some systems the variation of friction coefficients(23,26,40) or reduced friction coefficients(41,42,43) with concentration has been measured. If such data are not available, definite assumptions about the variation (or constancy) of the reduced friction coefficients with the concentration have to be made.

III THE "CONCENTRATION CLAMP" SYSTEM OF TRANSPORT MEASUREMENT

In view of the problems mentioned in the last paragraphs an experimental set-up was developed which permits us to perform different transport measurements on membrane-electrolyte solution systems with the same membrane, and with minimal change of the concentration profile during the course of an

---

*The authors thank Professor R. Caplan of Harvard Medical School for coining this name for their method.

experiment. All membrane transport parameters are obtained while the membrane is bounded by the same salt solutions (different left and right), under the same hydrodynamic conditions. In this way, sets of experiments can be performed for a series of concentration differences between the bounding solutions and the usefulness of linear flux equations containing transport parameters, which are average values over a certain concentration profile, can be evaluated.

The Concentration Feedback Mechanism. In the system built, the salt concentrations of the two solutions bounding the membrane are kept constant while salt and water transport is taking place. This was achieved by introducing concentration-feedback mechanisms in the enriched and depleted cell compartments. The system diagram is shown in Figure 1. Small conductivity probes (cell constant about 6) are introduced into the two half-cells separated by the tested membrane. The resistance of each probe is compared to a reference resistance, and the difference is monitored continuously by means of a 1605-AH grounded impedance comparator (General Radio Co., West Concord, Mass). Large capacitors are inserted between one of the conductance probes and the respective comparator to block the DC loop via ground between the two half cells. One oscillator only is used to energize the measuring bridges of both comparators, in order to reduce an AC loop current through the membrane.

The output voltage of each impedance comparator is amplified and when the monitored resistance difference (between the reference resistance and the conductance probe) reaches a preset value, a feedback mechanism is actuated by means of a relay system. At the depleted side of the membrane the relay actuates an automatic microburet (American Instrument Company, Silver Springs, Md.) which injects concentrated salt solution into the cell compartment, until the resistance of the conductivity probe again falls

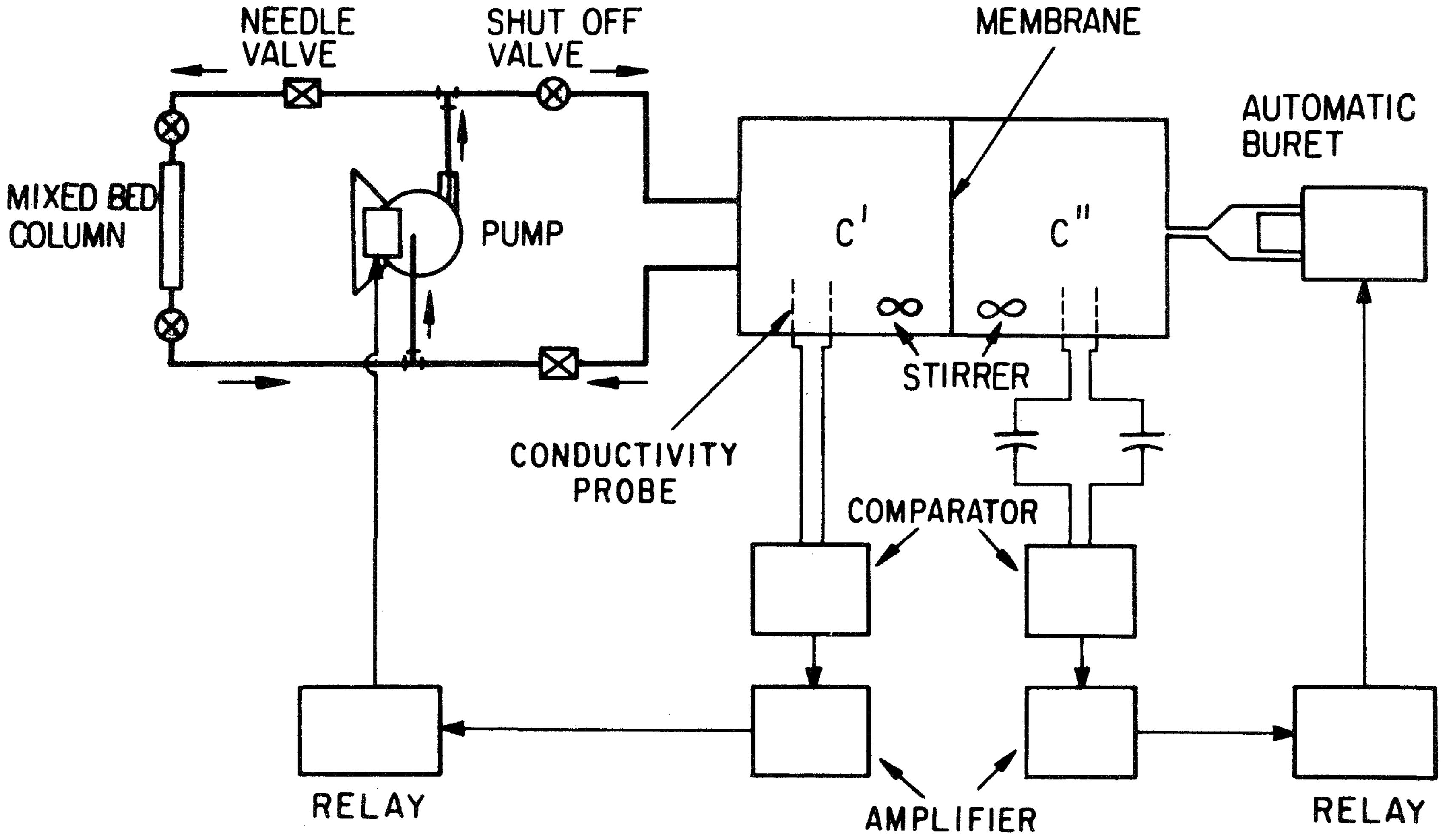


FIGURE I. SCHEMATIC REPRESENTATION OF THE CONCENTRATION FEEDBACK MECHANISM below the value of the reference resistance*. At the enriched side the relay actuates a small, magnetically coupled gear pump made of stainless steel (Catalogue No. 7004-8, Cole Parmer Co., Chicago, Ill.). This pump replaces the plastic centrifugal pump (Cole Parmer No. 7004-1) used in earlier experiments. It has "Teflon" gears in a body made of 316-stainless steel. The internal volume is very low (a few cc) and even at high flow rates there is virtually no heat transferred to the liquid. The pump is driven by a universal motor and can be operated at very low flow rates. It circulates a small part of the cell solution through a mixed-bed ion-exchange column to remove salt from the solution and stops when the column has taken up enough salt to decrease the solution conductivity to its initial value. Thus the amounts of salt and water transported are not calculated from changes in solution concentration, but rather from the amount of salt added by the buret or removed by the column, together with the volume changes in the two compartments measured in capillaries connected to each half-cell. In order to verify the mass balance, the salt transport and water transport rates are measured at both sides of the membrane. Normally the system is able to keep the half-cell concentrations constant within 0.03% over long periods. The maintenance of constant concentration depends on the temperature stability, the rate of solution agitation in-

---

*The amount of concentrated solution, injected into the cell by the automatic buret each time the concentration falls below the preset value, has to be very small to minimize a concentration overshoot. This was achieved by inserting a mechanical recycling contact, which closes only 3% of the cycle time (2 seconds), between the relay and the variable transformer used to slow down the buret motor. Thus the buret motor can be operated at a sufficiently high voltage for smooth operation while a low injection rate is maintained.

side the half-cells, solution concentration, and the concentration of the solution in the microburet. The present apparatus has several demineralizing columns in parallel. In this way different experiments can be performed successively by switching the cell-solution circulation from one column to the other using shut-off valves made of 316 stainless steel (RS-4, Whitey Research Tool Company, Emeryville, Calif.). By regulating the two stainless steel metering needle valves, Fig. 1, (4L, Nupro Company, Cleveland, Ohio) only a small amount of solution is taken up from the cell, although a fairly rapid circulation rate through the ion-exchange column is maintained. This arrangement ensures that at any time the solution in the resin column is very dilute, even in those regions where the resin is already exhausted.

The Membrane Transport Measurements Cell. The transport cell (Figure 2), used for all measurements, is a cylindrical two-compartment cell. It consists of interchangeable cylinders and end parts, clamped together by two supporting steel plates and steel rods. "Buna N" rubber gaskets are used as seals between the various parts. All parts were machined of "Lexan" (General Electric Co., Plastics Div., Pittsfield, Mass.), a transparent polycarbonate plastic. The cylinders have outer and inner diameters of 4.5 and 2.0 inches respectively. The end parts are 1.25 inches thick. The volume of each half-cell is approximately 200 cm^3. A Ag/AgCl working electrode for electroosmosis-electromigration experiments, Ag/AgCl potential-measuring electrode, volume measurement pipet, conductance probe, thermistor for temperature measurements and the inlet and outlet for the concentration feedback mechanism are fitted into each half-cell by means of "Swagelok" (Crawford Fitting Company, Cleveland, Ohio) connectors. Magnetic "Spin-

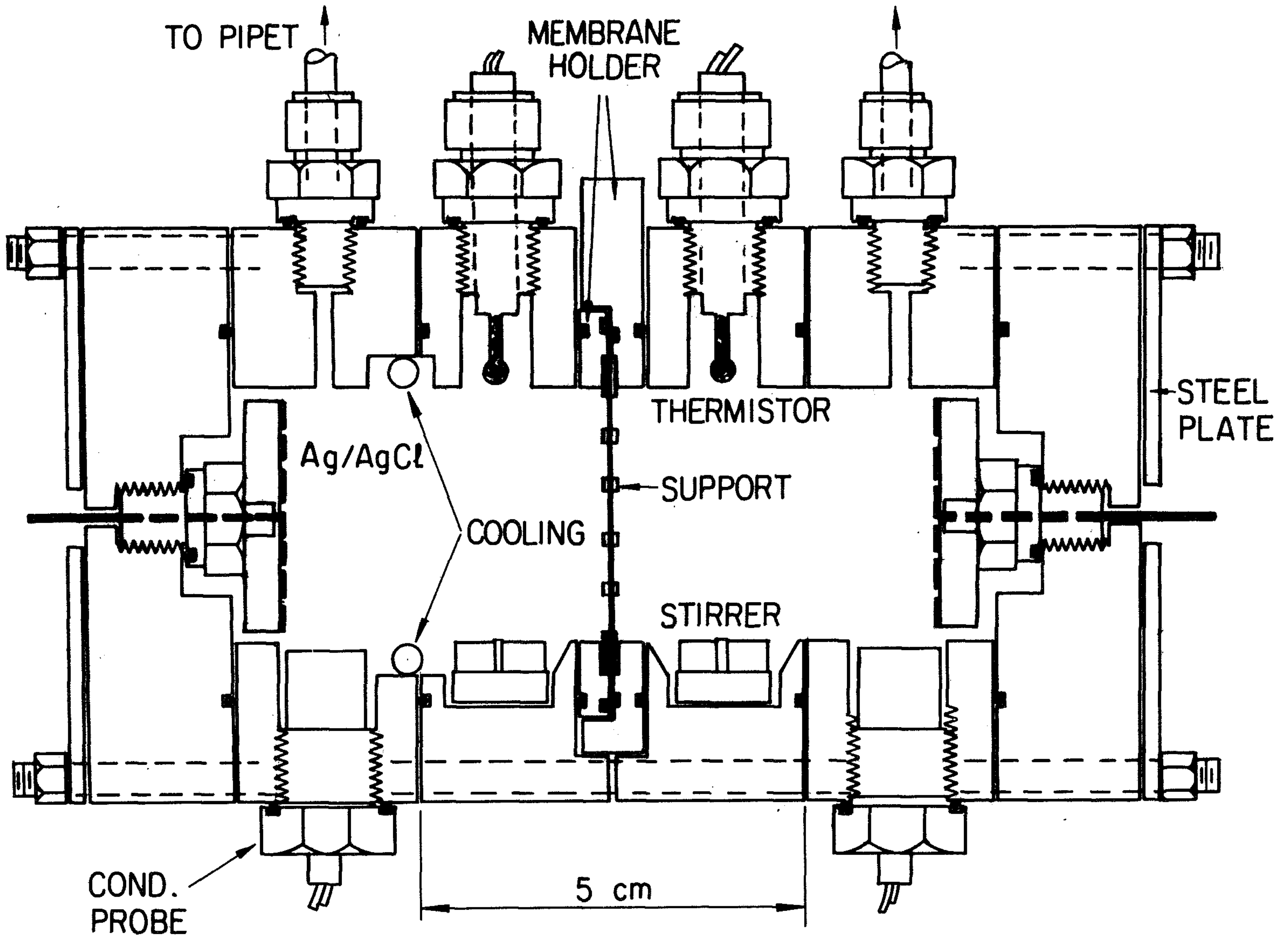


FIGURE 2. CELL FOR MEASUREMENT OF MEMBRANE TRANSPORT PROPERTIES

Fin" stirrers, 3/4 inch diameter (Bel Art, Pequannock, N. J.), are located close to the membrane and are rotated at the same (adjustable) speed. The membrane is sealed in the membrane holder by an O-ring at each side. Two 0.16 cm thick perforated membrane supports made of glassfiber-reinforced plastic are inserted in the membrane holder. In the experiments reported here, each support had 130 holes of 2.78 mm diameter, reducing the membrane area to 7.88 cm^2 (but different supports can be used if necessary). The transport cell and the circulation system for the demineralizing column have been pressure-tested up to 5 atm. All experiments can be performed in the same cell, permitting a long run of different transport measurements to be performed on one membrane sample without disassembling the cell.

The apparatus is located in a room with coarse temperature regulation (20 ± 1°C). The cell is located in an air thermostat which is maintained at at 25°C within 0.1°C. Cooling coils inside each half-cell are connected to a constant-temperature circulation bath. In each half-cell the temperature is measured by means of a glass embedded thermistor (Cat. No. 47 A13 Victory Engineering Company, Springfield, N. J.). Solution temperatures are kept constant to ± 0.01°C over the experimental periods. The temperatures in the two half-cells agree within measurement accuracy.

IV EXPERIMENTAL PROCEDURE

The procedure described in this section is essentially the same in dialysis-osmosis, electromigration-electroosmosis or hyperfiltration experiments. In each of these experiments the transport of salt and water through the membrane causes concentration changes of the cell solutions;

these changes are compensated by the feedback systems.

The transport cell, described in the previous section, is assembled and filled with deaerated and distilled water. The autoburet, filled with a deaerated 3M NaCl solution, and the demineralizing system are connected to the cell. The demineralizing system has four columns in parallel which can be used one at a time. The columns are filled with cation exchange resin (H^+ form) and anion exchange resin (OH^- form) (Amberlite IR-120 and Amberlite IRA-410 respectively, C. P. Mallinckrodt Chemical Works, New York), in the volume ratio of two parts anion-exchange resin to one part cation-exchange resin. The anion-exchange resin was purified by very slow elution with a 0.5M NaOH solution (40 liter of NaOH solution for 500 g resin during one week) followed by rinsing with deionized water. To test the elution procedure used after each experiment, a 0.1M NaCl solution containing 3 mmoles NaCl was passed through 8 ml of mixed-bed resin and then eluted again with 100 ml 0.5M $NaNO_3$ solution. The amount of chloride present in the eluant was determined by argentometric titration and agreed within analytical error (0.2%) with the amount of NaCl originally passed through the column.

At the start, the cell is filled with deaerated and distilled water only, and initial volume changes are allowed to reach a steady, low rate. Calibrated capillaries (0.2 ml total volume) are connected to each half-cell to register volume losses caused by leakage, water absorption of the "Lexan" plastic, slowly dissolving air bubbles and other error sources. These losses can be as high as 10 to 20 x 10^{-3} cm^3/hr from each half-cell during the first hours. After several days, this rate decreases to less than 10^{-3} cm^3/hr on the autoburet side and about 2 x 10^{-3} cm^3/hr at the side of the demineralizing system. When this constant, low leak rate is reached, solid NaCl is added to each half-cell until the solution concentrations are close to the desired values. This is checked by measuring the resistance of the conductivity cells inserted in each half-cell. Then additional small amounts of deaerated 3M NaCl solution or deaerated distilled water are added to reach the desired concentration within 0.2%. The final correction is made by operating the feedback mechanism.

This rather elaborate starting procedure is necessary in order to be able to measure the "leak" rate for each half-cell in the absence of osmotic flow. In order to ensure the attainment of steady state the system can now be left for long periods under the desired concentration gradient, which is maintained by the feedback mechanism. During this time the largest of the four demineralizing columns, designated as "clean up column", is used. When steady state is reached, a switch-over is made to a smaller column, and from that moment on the transport properties are measured.

Volume changes during an experiment can be measured by either of two methods. The first is to attach long capillaries to each half-cell and register the displacement of the liquid meniscus. Disadvantages of this method are the low capacity of capillaries of reasonable length and diameter and, in our case, the necessity of opening the constant temperature box every time a measurement has to be made. (It should be possible, however, to modify our apparatus for cathetometric observation of the meniscus from the outside of the constant-temperature box). The second method is to collect the overflow of one cell compartment in a calibrated graduated cylinder and weigh the total amount of solution collected during an experiment. At the same time a capillary connected to the other half-cell dips into a weighing bottle filled with a pre-weighed quantity of solution and sucks this solution into the half-cell. With this method the total volume transported during an experiment can be determined very accurately; while the experiment is in progress, the rate of volume transport can be followed (with moderate accuracy) only for the volume-accepting cell, where the solution is collected in a calibrated cylinder. In general, the first method is believed to be more accurate in experiments with low volume transport, the second in experiments with moderate and high volume transport. The second method was used in most experiments reported here, because the volume transport was appreciable.

Before and after each experiment, solution samples are taken to check the correct operation of the feedback system and the resistance measurements. To start the measurements after the system has reached steady state, the "clean up column" is closed and one of the other three columns is opened. Temperature, resistance of the conductivity cells and the volume reading of the autoburet are recorded, together with either the position of the meniscus in the capillaries or the weight of the empty graduated cylinder and the filled weighing bottle (depending on which method is used for the measurement of volume transport). During an experiment the same readings are made at regular time intervals, except the weights of the graduated cylinder and the weighing bottle which are determined only at the beginning and the end of each experiment. When enough salt and water have been transported the experiment is terminated; solution temperatures, conductances and autoburet volume are measured, the demineralizing column is isolated, the graduated cylinder and the weighing bottle, which now contains less solution than before the experiment are weighed. In the next section the method for obtaining the actual salt and volume transport from these data is presented.

Between different experiments the feedback system keeps operating, using the "clean up column". In this way three experiments in a row can be performed without disassembling any part of the system. When all columns have been used they are disconnected and their salt content is eluted with a deaerated 0.5M $NaNO_3$ solution. (When the $NaNO_3$ solution is not deaerated bubbles form in the column during the elution process). The amount of chloride in the eluant of each column is determined by titration. After certain corrections described in the next section are applied, the amount of salt transported through the membrane can be calculated from the data of each half-cell separately, permitting an internal check on the reliability of each experiment by mass balance.

V. Calculation of Volume and Salt Transport

V.A. Notation and Symbols

c	concentration, mole cm^{-3}
I	total electrical current, amp
n_{Bu}	moles of salt injected by autoburet, mole
n_c	salt correction for concentration change of solution, mole
n_{col}	salt uptake of demineralizing column, mole
n_e	salt correction for change of volume of electrode, mole
n_t	salt transport in time t, mole* (see footnote at end of table)
n_V	salt correction for change of volume of solution, mole
t	time, sec.

$\bar{v}$	partial molar volume, cm^3 $mole^{-1}$
V_{Bu}	volume ejected by autoburet, cm^3
V''_{Bu}	volume change of solution due to injection of V_{Bu}, cm^3
V_e	volume change of electrode caused by current passage, cm^3
V_{hc}	volume of half-cell, cm^3
V_L	volume loss from half-cell (leakage), cm^3
$\dot{V}_L$	rate of volume loss, cm^3 sec^{-1}
V_{meas}	total apparent volume change measured in capillary or by weighing, cm^3
V_t	volume transport* in time t, cm^3
ρ	density, g cm^{-3}
ρ_{Bu}	density of autoburet solution, g cm^{-3}
$\mathcal{F}$	Faraday's constant, coulomb $mole^{-1}$

Superscripts ' and " refer to salt-accepting and salt-donating half-cells respectively.

*Transport into a half-cell is taken positive, out of a half-cell negative.

V.B. Calculation of the Volume Transport

The total apparent volume change of the solution in a half-cell (V_{meas}), is calculated from the position change of the liquid meniscus in the capillary, or from the weight change of the solution in the weighing bottle (decreased volume side) and the amount of solution collected in the graduated cylinder (increased volume side). V_{meas} is the difference between initial and final volume, and can be positive or negative. For each half-cell certain corrections have to be applied to V_{meas} to obtain the volume transported through the membrane during the experiment. Different corrections are necessary for the autoburet (salt-depleted) side and the demineralizing (salt-enriched) side.

V.B.1. Volume Transport Calculation for the Salt-donor Half-cell

To calculate the volume transported through the membrane, V''_t, from the data for the half-cell containing the salt-donating solution, the following three corrections have to be made.

a) During the experiment the autoburet injects a volume V_{Bu} of a solution, with NaCl concentration c_{Bu}, into the half-cell. This concentrated salt solution expands when it is diluted to the lower salt concentration of the solution in the half-cell. This dilution process takes place at constant cell solution concentration because of the simultaneous salt and water transport through the membrane. Conservation of mass yields:

$$\rho_{Bu}\ V_{Bu} = \rho''\ V''_{Bu}$$

where V''_{Bu} is the volume increase of the cell solution after injection of V_{Bu}. Hence:

$$V''_{Bu} = \rho_{Bu}\ V_{Bu}\ /\ \rho'' \qquad (1)$$

V''_{Bu} has to be subtracted from V''_{meas}.

b) In an experiment in which an electric current is passed between the two Ag/AgCl electrodes the volume of each electrode changes because of the electrode reaction:

$$\text{AgCl (solid)} + e^- \underset{\text{anodic}}{\overset{\text{cathodic}}{\rightleftharpoons}} \text{Ag (solid)} + \text{Cl}^- \text{(solution)}$$

The volume change of the electrode, V_e, caused by this reaction is given by:

$$V''_e = \pm(\bar{v}_{AgCl} - \bar{v}_{Ag}) .I.t.\mathfrak{F}^{-1} \qquad (2)$$

where + stands for the anodic reaction and - for the cathodic reaction. V''_e has to be subtracted from $V''_{meas.}$ In most cases the anodic reaction will take place at the electrode in the salt-donor half-cell, but this is not always so (e.g. when the decrease in salt concentration caused by the electrode reaction and Na^+ transport through the membrane is smaller than the increase in salt concentration caused by diffusion from the other half-cell).

c) The apparent leakage* from the half-cell, V''_L, measured prior to an experiment has to be added to V''_{meas}:

$$V''_L = \dot{V}''_L.t \qquad (3)$$

where $\dot{V}''_L$ is the leak rate in cm^3/sec and t the time of the experiment.

Taking these factors into account the corrected volume transport through the membrane, as calculated from the data for the salt-donor half-cell, then becomes:

---

* The term "leak" is used for the observed reduction of total solution volume; this is not necessarily due to real leaks. Water absorption by the plastic has the same effect.

$$V''_t = V''_{meas} - \rho_{Bu} \cdot V_{Bu} / \rho'' - (\pm(\bar{v}_{AgCl} - \bar{v}_{Ag}).I.t.\mathfrak{F}^{-1}) + \dot{V}''_L.t \qquad (4)$$

V.B.2. Volume Transport Calculation for the Salt-acceptor Half-cell.

The following corrections have to be made to V'_{meas} of the salt-accepting (demineralizing system) half-cell.

a) The demineralizing process in the mixed-bed ion exchange column is caused by the reactions:

$$\begin{gathered} R^+\text{-}OH^- + Cl^- \longrightarrow R^+\text{-}Cl^- + OH^- \\ R^-\text{-}H^+ + Na^+ \longrightarrow R^-\text{-}Na^+ + H^+ \\ H^+ + OH^- \longrightarrow H_2O \end{gathered} \qquad (5)$$

where R stands for the ion exchange resin. Because of the experimental set-up (Fig. 1) the resin is in contact with a NaCl solution of very low concentration; during the period necessary to demineralize 0.05 ml of cell solution the water inside the demineralizing system (more than 20 ml) is circulated through the column several times. It may be assumed that under these circumstances the volume change of the whole system, caused by the demineralizing process is small compared to the volume transport through the membrane.

b) As in the case of the salt-accepting half-cell, the correction for the volume change of the electrode in an experiment with an electric current has to be subtracted from V'_{meas}:

$$V'_e = \pm(v_{AgCl} - v_{Ag}) .I.t.\mathcal{F}^{-1} \qquad (2)$$

Again + stands for the anodic reaction and - for the cathodic reaction.

c) The leak rate $\dot{V}'_L$ (normally around 2 µl/hr) has to be added to V'_{meas}:

$$V'_L = \dot{V}'_L.t \qquad (3)$$

Taking these three factors into account, the expression for the volume transport through the membrane, as calculated from the data for the salt-enriched half cell becomes:

$$V'_t = V'_{meas} - (\pm(v_{AgCl} - v_{Ag}).I.t.\mathcal{F}^{-1}) + \dot{V}'_L.t \qquad (6)$$

The following total mass balance should hold within experimental error:

$$V'_t = - \rho'' V''_t / \rho' \qquad (7)$$

In most experiments the deviations from this relation were less than 50 microliter. This deviation is not dependent on the total volume transport during an experiment and is believed to be caused by experimental errors.

V.C. Calculation of the Salt Transport

The concentration feedback mechanism keeps the salt concentrations in each half-cell constant within narrow limits. Thus the main factors in calculating the salt transport are the quantity of salt injected by the autoburet for the salt-donor half-cell, and the salt uptake by the demineralizing column for the salt-acceptor half-cell. The expressions for the corrections necessary to obtain the actual salt transport from these numbers are the same for the two half-cells.

The amount of salt (in moles) injected by the autoburet is given by:

$$n_{Bu} = c_{Bu} V_{Bu} \qquad (8)$$

c_{Bu} is determined analytically with about 0.1% accuracy. The autoburet was calibrated with water. V_{Bu}, as read from the digital dial, was found to be accurate to ±0.1% in our experiments. The NaCl uptake by the column, n_{col} is determined analytically by eluting the column with 0.5M $NaNO_3$ and determining the chloride content in the eluant. The repeatability of this process is ±0.2%.

The following corrections have to be applied to n_{Bu} and n_{col} to obtain n_t'' and n_t', the salt transport calculated from the salt-donating and accepting half-cells respectively.

a) Although the concentration feedback system keeps the concentrations of the solutions accurately constant, small deviations (normally less than ±0.03%) do occur. The temperature constancy is ±0.01°C, approximately equivalent to a change in solution conductance of ±0.02%. Another factor is the overshoot of the feedback system, which is normally 0.01% to either side, although larger overshoots sometimes occur. Even these small differences between initial and final concentrations, or between any two times of measurement, do constitute a small correction factor in the salt transport. This correction, n_c, has to be subtracted from n_{Bu} or n_{col}:

$$n_c = V_{hc} (c_f - c_i) \qquad (9)$$

where V_{hc} is the total volume of the half-cell; c_f and c_i are the final and initial concentrations respectively. Since the total salt transport, n_t, is normally of the order of 2-5 mmole and $V_{hc} \cong 200$ ml, in a 0.5M solution n_c can be as much as 2% of n_t. Although V_{hc} is only known approximately, due to the various connections, tubing and capillaries,even an error of 20 ml in V_{hc} would change the salt transport by only 0.2% at maximum. n_c has to be subtracted from n_{Bu} or n_{col}. The method for calculating the solution concentrations from the temperature and resistance readings is given in Section V.D.

b) The volumes of the solutions in the two half-cells change during an experiment because of the salt and water transport. This volume change causes a correction in the salt transport, n_v. The registered volume change in the capillaries or weighing bottles, V_{meas} is not the actual change in volume of the solution. A correction to V_{meas} has to be made for the volume change of the electrodes when an electric current is passed:

$$n_V = c_{solution}[V_{meas} - (\pm (\bar{v}_{AgCl} - \bar{v}_{Ag}).I.t.\mathfrak{F}^{-1})] \qquad (10)$$

n_V includes the salt "lost" from each half-cell by virtue of the small volume leakage term. In dialysis-osmosis, and especially in hyperfiltration experiments n_V is a sizeable correction factor. For a 0.5M solution, as used for the high-concentration solution, it may be as much as 40% of n_t. Since V_{meas} and c' or c" are known accurately, the possible error in n_V is less than 0.5%.

Taking these factors into account, the equations for the salt transport become:

at the salt-depleted (autoburet) side

$$-n''_t = V_{Bu}c_{Bu} - V''_{hc}\,(c''_f - c''_i) - c''[V''_{meas} - (\pm(\bar{v}_{AgCl} - \bar{v}_{Ag}).I.t.\mathfrak{F}^{-1})] \qquad (11)$$

and at the salt-enriched (demineralizing system) side

$$n'_t = n_{col} - V'_{hc}\,(c'_f - c'_i) - c'[V'_{meas} - (\pm(\bar{v}_{AgCl} - \bar{v}_{Ag}).I.t.\mathfrak{F}^{-1})] \qquad (12)$$

As for the volume change, the last terms of the right hand side of equations (11) and (12) are positive for an anodic reaction and negative for a cathodic reaction. In each experiment n'_t should be equal to $-n''_t$ within experimental error.

Equations (4), (6), (11) and (12) enable us to calculate the salt and volume transport through the membrane for each half-cell separately. They hold for all transport experiments. Normally one of the two half-cells gives a more accurate result than the other, dependent on the amount transported, the solution concentrations and the various experimental errors. Even so, the system always enables us to make an internal check on the reliability of the results.

V.D. The Measurement of Minor Concentration Changes During an Experiment

Before and after each experiment a sample of each solution is taken to determine the NaCl concentration. At the same times, and at regular intervals during the experiment, the electrical resistance and temperature of the two solutions are measured.

The estimated error of the chloride titration is less than 0.2%. This is not accurate enough to detect the small variations in concentration, usually less than 0.05%, of the cell solutions between two measurement times. Therefore the resistance measurements are used to calculate the correction for these concentration differences (Section V.C., a). Since only concentration changes appear in this correction factor all changes are measured relative to the initial concentration which is determined by titration. Temperature and concentration vary during an experiment and both variations influence the measured resistance of the solution. To calculate the concentration of the solution relative to the initial concentration, first the measured electrical resistance of the conductivity cell is corrected for the temperature variation. In this way all resistances are reduced to a standard temperature

(25.00°C for experiments at, or close to, this temperature). Then the changes in resistance, at 25°C, are converted into concentration changes using literature data for the concentration-conductance relationship. Differences in temperature of as little as 0.002°C can be detected, using a thermistor (70,000 Ohm, at 25°C, 4.4% resistance change per °C) and a d.c. resistance bridge. The resistance of the conductance cell is measured relative to a fixed standard resistance, with a repeatability of ±0.005%. For each temperature T, the resistance of the conductance cell, R_T, and the resistance of the thermistor at this temperature, r_T are recorded. The resistance of the conductance cell at 25°C is calculated from:

$$R_{25} = R_T \ [1 + \frac{1}{R_T} \cdot \left(\frac{\partial R}{\partial T}\right)_c \cdot \frac{\partial T}{\partial r} (r_T - r_{25})] \qquad (A.1)$$

where R_{25} and r_{25} are the resistance of the conductance cell and of the thermistor at 25°C respectively. $\partial T/\partial r$ and r_{25} of each thermistor are determined by calibration against a standard thermometer. $\frac{1}{R_T} \cdot \left(\frac{\partial R_T}{\partial T}\right)_c$ between 18 and 25°C is 0.0206 $°C^{-1}$ for a 0.5M NaCl solution and 0.0214$°C^{-1}$ for a 0.1M NaCl solution. For a 0.5M NaCl solution R_{25} is around 120 Ohm. The temperature control mechanisms reduce the difference between R_T and R_{25} generally to less than 0.02%.

Once this temperature correction is made the concentration differences are obtained from R_{25} and literature data for the specific conductance, κ. The specific conductance, κ_f, of the final solution with unknown concentration c_f, is calculated from the measured resistance of the final solution, at 25°C, R_f, the resistance of the initial solution, R_i and the known specific conductance of this solution, κ_i by:

$$\kappa_f = R_i\kappa_i \;/\; R_f \tag{A.2}$$

Finally the concentration of the final solution, c_f, is obtained from κ_f, using conductance tables.

This procedure is followed for each measurement point of an experiment. At the end of the experiment a concentration sample is taken also. Titration of the initial and final samples should yield results in agreement with the calculation from resistance measurements.

VI. RESULTS

The instrument that has been developed is being used for characterization measurements of membranes in contact with different salt solutions. Some preliminary experiments were described in the first annual report, and the results of the first complete set of measurements will be presented in one of the following quarterly reports. In the following the results of some standard test procedures for the first membrane used in our investigations are described, and the preliminary transport experiments are summarized.

VI.A. Membrane Characterization

The first membrane tested was the AMF C-103 (American Machine and Foundry Co., Springdale, Conn.) cation-exchange membrane. This is a polyethylene-styrene graft copolymer, with sulfonate as active group. Samples with batch number GJ-3 were used. Thickness, wet weight, ion-exchange capacity and water content determinations were done, following standard test procedures (U. S. Office of Saline Water, Research and Development Report No. 77).

The following procedures were used:

1) Equilibration with H^+. (Procedure 202.1). The samples are shaken with 1 N HCl solutions during 48 hours; the HCl is changed several times. Then the samples are shaken with three changes of deionized water.

2) Thickness, H^+ form, (procedure 401.1). Thickness of the sample was measured using a micrometer with a 1/4" dia. anvil. The membrane sample was quickly blotted with filter paper and the thickness was measured at at least 8 locations of the sample. Color differences between different samples corresponded with differences in thickness, the darker samples being up to 10% thinner. Only the lighter colored samples were used in the following tests and will be used for the experiments. The uniformity in the thickness of these samples is ± 1.5%.

3) Wet weight, H^+ form (procedure 412.1). The membrane sample is taken out of the water, quickly blotted with filter paper and put into a stoppered weighing bottle. The measurement is repeated at least four times for each sample. The area of each sample is measured with a steel ruler. Repeated measurements for one sample had a standard deviation of 0.4%, the standard deviation between the 5 samples used was 0.5%. Results are expressed as weight per cm^2.

4) Ion-exchange capacity, conversion to Na^+ form (procedure 502.1). The samples in the H^+ form are blotted with filter paper and placed in a dry 250 ml Erlenmeyer flask. 200 ml of a standardized solution of 0.1 N

NaOH in 5% NaCl is added and the Erlenmeyer is closed with a rubber stopper. After six hours shaking,30 ml aliquots are taken out, 30 ml standardized 0.1 N HCl is added to each one and the excess HCl is titrated with 0.1 N NaOH, using phenolphtalein as indicator. Results are expressed in meq. per gram wet H^+ form and meq. per cm^2 wet H^+ form.

5) Thickness, Na^+ form. The same procedure as for the H^+ form is used.

6) Wet weight, Na^+ form. Same as H^+ form, repeatabilities are similar.

7) Water content, Na^+ form (procedure 412.1). The wet weight of two membrane samples in the Na^+ form were determined. The membranes were placed in a vacuum oven and dried under vacuum, using an oil pump, at 50°C. Weighing and drying of the membranes was repeated until a constant weight was obtained. This only took a few hours. Results are expressed as percent water of wet weight (Na^+ form). The water contents for the two samples were 19.0 and 19.2 weight percent respectively.

The results of these determinations are given below.

TABLE I.

Equilibrium Membrane Properties

Membrane: AMF C-103, batch number GJ-3

	H^+ Form	Na^+ Form
Thickness (mm)	0.178 ± 0.003	0.175 ± 0.003
Wet Weight (g/cm^2)	0.01815 ± 0.00010	0.01784 ± 0.00015
Water Content (%)		19.1 ± 0.1
Capacity	1.18 ± 0.01 meq/gram wet H^+ Form or 0.0214 ± 0.0002 meq/cm^2 wet H^+Form	

These results are in reasonable agreement with the measurements of Kawabe, Jacobson, Miller and Gregor(44).

VI.B Preliminary Volume and Salt Flow Experiments

Extensive "leak" testing experiments have been carried out in the first months covered by this report. Because of the low flow rates expected for the ion-exchange membranes under pressure and/or osmotic forces, only very low volume losses can be allowed. The term "leak" covers diverse losses, as discussed in Section IV.

In most osmosis-dialysis or hyperfiltration experiments, flow rates between 10 and 100 μl/hr are expected for the membrane area of approximately 7.8 cm^2 exposed. This means that if the leak rate is lower than 1 μl/hr*, and constant in time within 10%, an error in the flow rate determination of less than 1% is introduced in the least favorable case.

Preliminary electroosmosis-electromigration experiments were described in the Annual Report (November, 1969). It was found that for the AMF C-103 cation-exchange membrane (American Machine and Foundry Company, Springdale, Conn.), bounded by 0.2 M and 0.05M NaCl solutions, the transport number of Na^+ is between 0.98 and 1.00. The water transport number was found to be about 7.0 moles of H_2O per Faraday transported. These preliminary results are in good agreement with literature values(32). Low-flow osmosis and hyperfiltration experiments were performed in order to determine the constancy of the leak rate in time and to check the possibility of correcting the observed volume flows for the leak rate as measured in advance.

In a typical experiment, with c' = 0.1M NaCl and c" = 0.08M** NaCl the

---

[*] 1 μl = 10^{-3} milliliter

[**] Primes and double primes denote properties on left and right side respectively. Positive flow is from left to right.

following results for the volume flow (measured at the low-pressure side) were obtained:

$p'' - p' \equiv \Delta p = 0$ atm. $\quad J_V = -5.21 \pm 0.05$ µl/hr
$\Delta p = -0.48$ atm. $\quad J_V = -1.2 \pm 0.10$ µl/hr
$\Delta p = -0.98$ atm. $\quad J_V = +3.0 \pm 0.20$ µl/hr
$\Delta p = -1.49$ atm. $\quad J_V = +6.94 \pm 0.20$ µl/hr

From these figures we can calculate the hydraulic permeability of the AMF C-103 membrane in contact with these NaCl solutions. The result, $L_p = (2.8 \pm 0.3) \times 10^{-6}$ cm^4 Joule^{-1} sec^{-1} is in reasonable agreement with previous experience(32).

A number of preliminary dialysis-osmosis experiments (i.e. transport experiments without imposition of a hydraulic pressure head) have also been carried out. The diffusional permeability, K_s, defined by $K_s \equiv J_s/(c'' - c')$ was found to be strongly dependent on the history of the membrane. It decreased after a d.c. current had been passed through the freshly equilibrated membrane but soon reached a reasonably constant value. After a hydraulic pressure difference had been applied across the membrane the diffusional permeability again decreased sharply. For these reasons standard pre-treatments should be given to membranes used in transport experiments.

Some more recent results with membranes subjected to more extensive pretreatment are presented in the next section. A complete set of measurements will be reported in forthcoming progress reports.

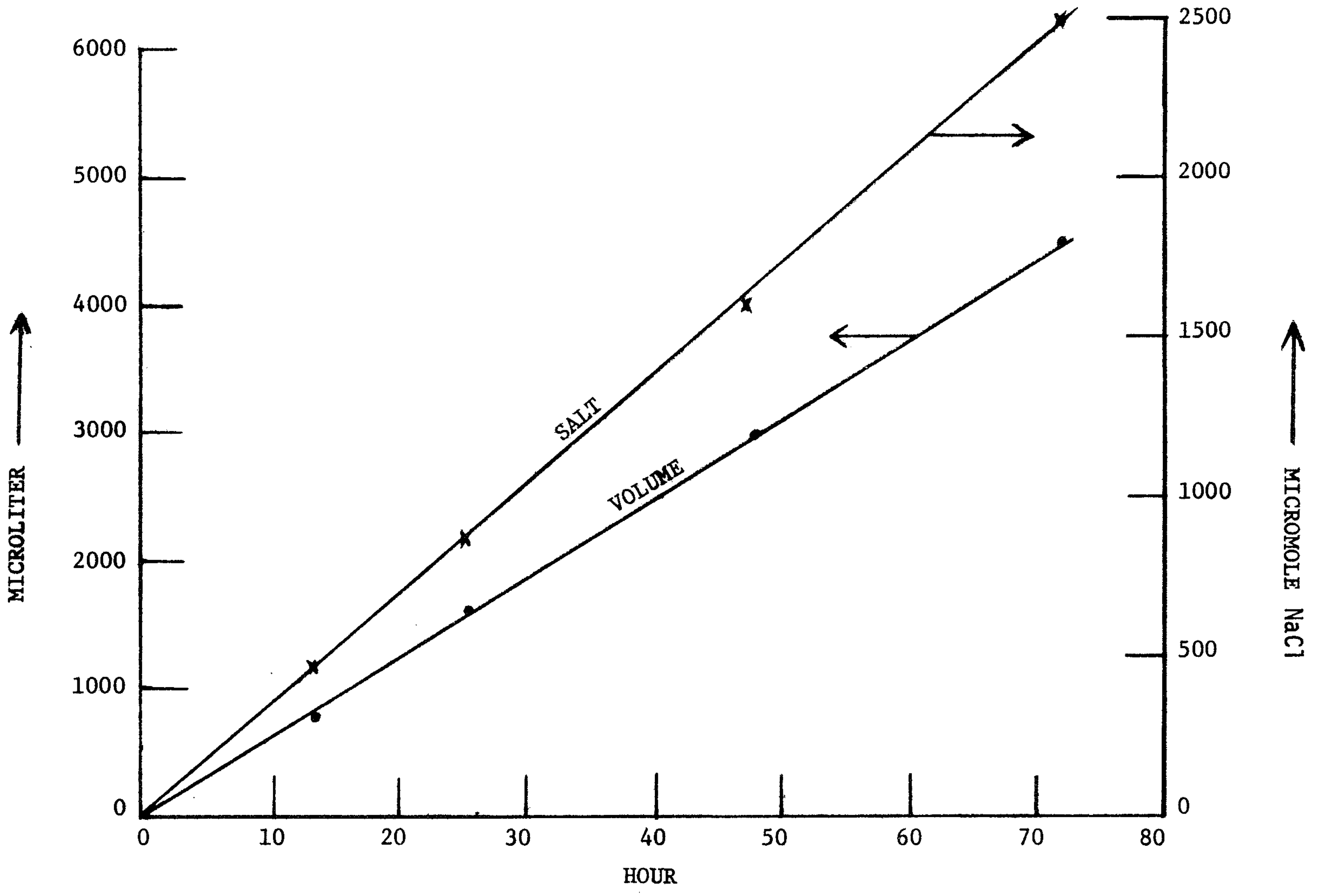
VI.C. Dialysis-osmosis and electromigration-electroosmosis experiments

Results for the salt flow and volume flow in a dialysis-osmosis experiment and for the apparent total salt flow and the volume flow in an electromigration-electroosmosis experiment are presented in Figures

3 and 4. These experiments are part of the series of measurements performed in the 0.5M NaCl/AMF C-103/0.1M NaCl system. The figures describe the salt and volume flow calculated from the data measured on the high concentration (0.5 M NaCl) side. The microburet added salt to this half-cell in both experiments; in the electrical experiments the Ag/AgCl electrode in this half-cell was the anode. The membrane area (7.88 cm^2) is the area exposed to the solution by the holes in the plastic supports.

In the dialysis-osmosis experiment the salt flux was found to be: $J_s = +(1.23 \pm 0.06) \times 10^{-9}$ mole cm^{-2} sec^{-1}, and the volume flux $J_v = -(2.27 \pm 0.05) \times 10^{-6}$ cm sec^{-1}. Flow from left (high concentration side) to right (low concentration side) is counted positive. Volume flow as calculated from the two compartments agrees to ± 1.5%. A larger deviation for the salt flow was found: elution of the demineralizing column at the low-concentration side gave a value for the salt flow 10% lower than the rate calculated from the high-concentration side. Since these last data are obtained from a series of individual measurements rather than from one measurement, the data for the salt-donating side are used here for the calculation of the salt flow and the single value obtained from the salt-accepting side is used as an "order of magnitude" check. For the volume flow, the average of the two rates calculated for each half-cell is used. In this experiment concentrations were constant to ± 0.01% at both sides. The temperature variation was less than ± 0.01°C.

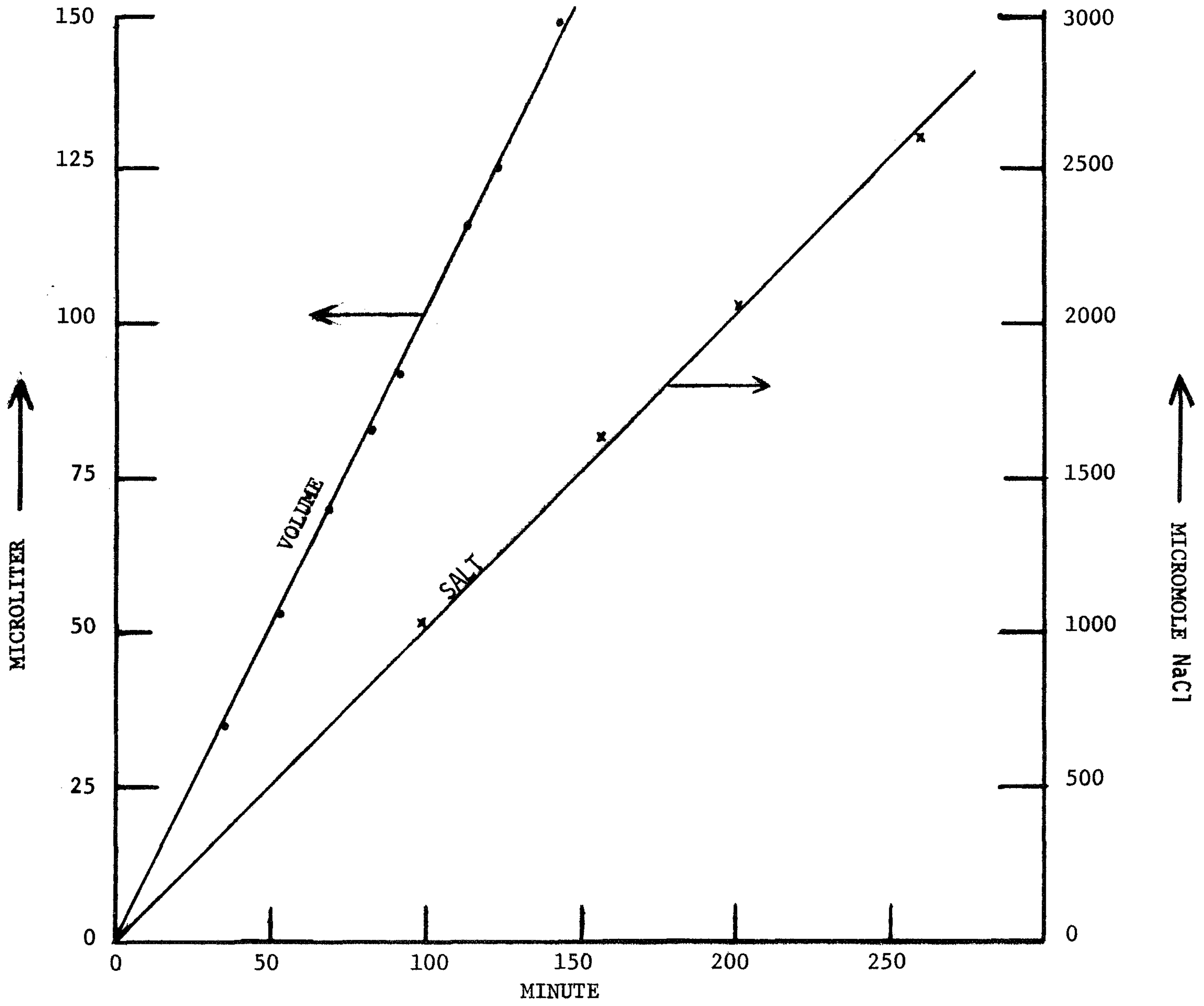
In the electromigration-electroosmosis experiment a current density of 2.000 ± 0.001 mA cm^{-2} was maintained. Electromigration and diffusion



DIALYSIS ⟷ OSMOSIS

Active Membrane Area 7.88 cm^2, 0.5 vs. 0.1 N NaCl, 25°C. AMF C-103 Membrane

FIGURE 3



ELECTROMIGRATION —— ELECTROOSMOSIS

Active Membrane Area 7.88 cm^2, 0.5 vs. 0.1 N NaCl, i = 2 ma cm^{-2}, 25°C. AMF C-103 Membrane

FIGURE 4

caused salt flow in the same direction, viz. from left to right. A total apparent salt flux $J_s = +(21.5 \pm 0.6) \times 10^{-9}$ mole cm^{-2} sec^{-1}, and a volume flux (corrected for the change in volume of the electrode) $J_v = +(2.26 \pm 0.05) \times 10^{-6}$ cm sec^{-1} were found. The current density of 2.000 mA cm^{-2} corresponds to 20.73×10^{-9} Faraday cm^{-2} sec^{-1}. If we assume the diffusional flow of salt in the dialysis-osmosis and in the electromigration-electroosmosis experiment to be exactly the same, we can calculate the transport number of the positive ion:

$$t_{Na+} = \frac{(21.5 \pm 0.6) - (1.2 \pm 0.1)}{20.7}, \text{ or } t_{Na+} = 0.98 \pm 0.04.$$

It is believed that the actual accuracy is better than the maximum error indicated. Subsequent experiments showed a repeatability of this value of ± 1%. The validity of the assumption that the salt flows measured in the two experiments are additive should be verified experimentally . This could be done by performing two electromigration experiments, one with the positive current in the direction of the diffusional salt flow and one with the positive current in the opposite direction. Our apparatus will enable us to perform these experiments and an attempt in this direction will be made during the forthcoming contract period.

References

1. F. Helfferich, "Ion Exchange", McGraw Hill Book Company, Inc., New York, Chapter 8 (1962).
2. H.Z. Friedlander, R.N. Rickles, Analytical Chemistry 37, 27A (1965).
3. N. Lakshminarayanaiah, Chem. Rev. 65, 491 (1965).
4. L.H. Shaffer, M.S. Mintz, in "Principles of Desalination", K.S. Spiegler, editor, Academic Press, New York, Chapter 6 (1966).
5. J.S. Johnson, Jr., L. Dresner, K.A. Kraus, in "Principles of Desalination", K.S. Spiegler, editor, Academic Press, New York, Chapter 8 (1966).
6. U. Merten in "Desalination by Reverse Osmosis", U. Merten, editor, The M.I.T. Press, Cambridge, Mass., Chapter 2 (1966).
7. P. Meares in "Diffusion in Polymers", J. Crank and G.S. Park, editors, Academic Press, London, Chapter 10 (1968).
8. A.J. Staverman, Trans. Farad. Soc. 48, 176 (1952).
9. D.G. Miller, J. Phys. Chem. 70, 2639 (1966).
10. P.J. Dunlop, L.J. Gosting, J. Phys. Chem. 63, 86 (1959).
11. J.G. Kirkwood in "Ion Transport Across Membranes", Academic Press, New York, 119 (1954).
12. J.W. Lorimer, E.W. Boterenbrood, J.J. Hermans, Disc. Farad. Soc. 64, 1135 (1956).
13. A. Katchalsky and P.F. Curran, "Non Equilibrium Thermodynamics in Biophysics", Harvard University Press, Cambridge, Mass., (1967).
14. O. Kedem and A. Katchalsky, Biochimica and Biophysica Acta 27, 229 (1958).
15. K.S. Spiegler, O. Kedem, Desalination 1, 311 (1966).
16. K.S. Spiegler, Trans. Farad. Soc. 54, 1408 (1958).
17. L. Onsager, Ann. N.Y. Acad. Sci. 46, 251 (1946).
18. J. Stefan, Wien, Sitzungsber. 63, 63 (1871).
19. J. C. Maxwell, Papers 1, 377 (1860) as quoted by C. Truesdell, J. Chem. Phys. 30, 2336 (1962).
20. J. Newman, D. Bennion, C. W. Tobias, Ber. Bunsenges. 69, 608 (1965).
21. W.H. Smyrl, J. Newman, J. Phys. Chem. 72, 4660 (1968).

22. I.W. Richardson, A. Katchalsky, to be published.

23. D.N. Bennion, B.W. Rhee, Univ. of Calif., Los Angeles, College of Engineering, Report No. 67-55 (Oct., 1967).

24. H. Krämer, F. Sauer, Ber. Bunsenges. 71, 855 (1967).

25. T.G. Kaufmann, E.F. Leonard, A.I.Ch.E. Journal 14, 110 (1968).

26. R.E. Lacey, Final Report to the Office of Saline Water, Contract No. 14-01-0001-464, Project 1607, Report 13, March, 1968.

27. R. Schlögl, Z. Physik. Chem. (Frankfurt) 3, 73 (1955).

28. J.S. Mackie, P. Meares, Proc. Roy. Soc. (London) A232, 498 (1955).

29. F. Helfferich, "Ion Exchange", McGraw Hill Book Company, Inc., New York, 353 (1962).

30. R. Caramazza, W. Dorst, A.J.C. Hoeve, A.J. Staverman, Trans. Farad. Soc. 59, 2415 (1963).

31. D. Mackay, P. Meares, Trans. Farad. Soc. 55, 1221 (1959).

32. E.M. Scattergood, E.N. Lightfoot, Trans. Farad. Soc. 64, 1135 (1968).

33. J.H.B. George, U.S. Office of Saline Water, Research and Development Report No. 159, Grant No. 14-01-0001-372, Dec., 1965.

34. J.H.B. George, C.R. Schlaikjer, U.S. Office of Saline Water, Research and Development Report No. 203, Grant No. 14-01-0001-372, Sept., 1966.

35. P. Meares, A.H. Sutton, J. Coll. Sci. 28, 118 (1968).

36. W.J. McHardy, P. Meares, A.H. Sutton, J.F. Thain, J. Coll. Sci. 29, 116 (1969).

37. W.J. McHardy, P. Meares, J.F. Thain, J. Electrochem. Soc., 116, 920 (1969).

38. M. Litt, W.G. Smith, Science 160, 201 (1968).

39. K.S. Spiegler and coll., U.S. Office of Saline Water, Research and Development Report No. 353, Grant No. 14-01-0001-652, Aug., 1968.

40. P. Meares, D.G. Dawson, A.H. Sutton, J.F. Thain, Ber. Bunsenges. 71, 765 (1967).

41. R.W. Laity, J. Chem. Phys. 30, 382 (1959).

42. E.P. Honig, J.A.A. Ketelaar, Trans. Farad. Soc. 62, 190 (1966).

43. J.A.A. Ketelaar, J.C.T. Kwak, Trans. Farad. Soc. 65, 139 (1969).

44. H. Kawabe, H. Jacobson, I.F. Miller, H.P. Gregor, J. Coll. Sci. 21, 79 (1966)