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SEA WATER CONVERSION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

"Study of Permeability Characteristics of Membranes"

Quarterly Report No. 11

October 15, 1970

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R. M. Messalem
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Contract No. 952109
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ABSTRACT, CONCLUSIONS AND RECOMMENDATIONS

This report deals primarily with the permeability characteristics of the AMF C-103[*] cation-exchange membrane. The results are based on the transport measurements achieved with the "Concentration-Clamp" method, developed especially for precise measurements of water and electrolyte transport through membranes under the influence of electric, osmotic and pressure forces or any combination thereof.

The evaluation of our transport measurements as reported in the tenth quarterly report (January, 1970) is described in this report, rather than new experimental data.

A refined set of transport equations has been derived in terms of J_w and J_s, water and salt flux respectively, rather than the previous and time-honored use of volume flux, J_V, which turns out to be a non-conservative flux, because of the non-negligible variation of the partial molar volumes of water and electrolyte with the concentration.

Water and salt permeabilities were calculated, as well as respective transport numbers. In order to compare with previous researches by others (in which some, but not all transport phenomena were measured), we present our results also in terms of "practical" transport coefficients, namely the reflection coefficient, σ, the hydraulic permeability, L_p, and the solute permeability, ω. It was found that where fragmentary literature data do exist, there is fair agreement with those measured by us with the "Concentration-Clamp" method. The results, described in detail in the body of this report show that some transport coefficients are concentration-

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[*] American Machine and Foundry Co., Springdale, Connecticut

dependent and that hydrostatic pressure seems to alter the transport properties of the membrane; mechanical side effects of the pressure may compact the membrane, even though the used pressure differences were low.

Some improvements in the experimental system, including a new membrane holder (to reduce traces of cross-compartment leakage) and two new micro-metering valves in the demineralization loop (for increased flow control sensitivity) were introduced during the current reporting period. They will be described in the next quarterly report.

Summarizing the results of the past experiments, we recommend the following: (a) perform transport experiments at uniform concentration and (b) design precise membrane conductivity measurements.

Re (a): It is of particular theoretical and practical interest to measure transport coefficients in a membrane-solution system with no concentration gradients whatsoever throughout the performance of the experiments. For once, transport coefficients can be determined without making any assumptions on how to "average" them over the existing concentration gradient; second, the "concentration-clamp" method is ideally suited for uniform-concentration conditions. Therefore, electroosmosis-electromigration experiments with no concentration gradient across the AMF C-103 membrane which we used previously, were started. A series of experiments, covering the range of 0.05 N - 0.5 N NaCl in solution concentration and the range of 0.5 - 2.0 ma/cm^2 in current density was already begun.

Re (b): To transform the data into more fundamental parameters, e.g. friction factors, which should make predictions over wide ranges of forces and fluxes possible, it is necessary to measure the membrane conductance with great precision. We are now considering the application of the technique developed by Guillou and Buvet in Paris in recent years* for this purpose, and hope the apparatus developed may be of use for a wide range of electrolytes at different concentrations.

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*"Membranes à Permeabilité Selective", Editions du C.N.R.S. (1969), Paris, p. 131; article by M. Guillou, D. Guillou, R. Buvet.

List of Symbols

a_k	Chemical activity of species k, mole cm^{-3}
A	Effective surface area of membrane, cm^2
c_s, c_w	Concentration of salt and water respectively, mole cm^{-3}
ΔE	Total E.M.F. measured between Ag/AgCl reversible electrodes, volt
$\mathscr{F}$	Faraday's constant, $9.6491 \cdot 10^4$ amp sec eq^{-1}
i	Current density, amp cm^{-2}
I	Electric current, amp
J_s, J_w	Flux of salt and water, mole sec^{-1} cm^{-2} (positive from left to right)
J_V	Volume flux, ℓ sec^{-1} cm^{-2}
L_p	Hydraulic permeability, ℓ sec^{-1} cm^{-2} atm^{-1} [Eq. (19)]
M_s, M_w	Molecular weight of salt and water respectively, g $mole^{-1}$
n_s, n_w	Moles of salt and water, respectively
p	Hydrostatic pressure, atm
Pm_s, Pm_w	Permeability coefficient of salt and water respectively, cm sec^{-1}
R	Gas constant, 8.314 watt sec deg^{-1} $mole^{-1}$
t	time, sec
$\bar{t}_+$, $\bar{t}_-$	Transport number of cation and anion respectively, in the membrane
T	Temperature, °C
V	Volume, cm^3
$\bar{V}_j$	Partial molar volume of species j, cm^3 $mole^{-1}$
$\dot{V}_L$	Rate of solution loss of a half-cell, cm^3 sec^{-1}

Δ	Denotes difference, right minus left
δ	Denotes difference, final state minus initial state
$\tilde{\mu}$	Electrochemical potential, cm^3 atm $mole^{-1}$
μ^c	Chemical potential, cm^3 atm mole
π	Osmotic pressure, atm
ρ	Solution density, g cm^{-3}
σ	Reflection coefficient
ω	Solute permeability coefficient, mole cm^{-2} atm^{-1} sec^{-1}
ψ	Electrical potential, volt

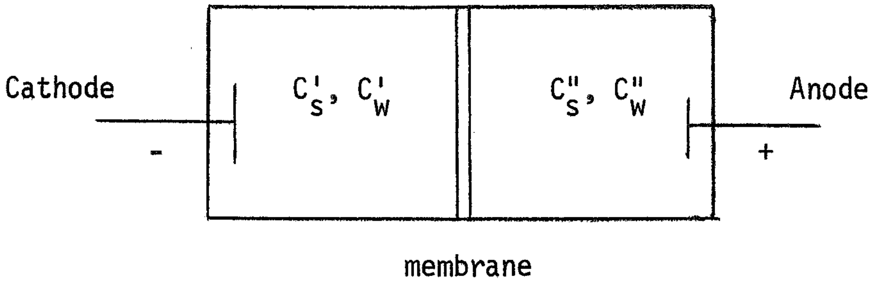
Superscripts

'	Single prime denotes "property of the demineralizing column half cell"
"	Double prime denotes "property of the auto-buret side"
c	Denotes "measured under a positive concentration difference", $C''_s > C'_s$
c-p	Denotes "measured under a positive concentration difference and a negative hydrostatic pressure difference"
c-p-i	Denotes "measured under a positive concentration difference, a negative pressure difference and a negative current density"
-i	Denotes "due to negative current density alone"
-p	Denotes "due to negative hydrostatic pressure difference alone", $\Delta P < 0$
-c-i	Denotes "measured under a negative concentration difference and a negative current density"

Subscripts

Bu	Buret
Col	Demineralizing column
el	Electrode
f	Final State
L	Leak
m	Membrane
o	Initial state
s	Salt
sol	Solution
w	Water

Column side $\equiv$ left side Buret Side $\equiv$ right side



J_s, J_w = Flux of salt and water respectively, positive from left to right

$n_{w,m}$ = Inflow of water through the membrane, in mole; in many experiments, the anode (positive electrode) is in the buret compartment. When a cation-exchange membrane is used, there is an electroosmotic outflow of water, i.e. J_w is negative.

FIGURE 1. Some Notations and Definitions

I. Introduction

This is the eleventh 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 and the extended eighth quarterly report (January, 1970) which serves as the second annual report. The tenth quarterly report (July, 1970) described the measuring systems (voltage, pressure, electric current) and included a complete series of transport measurements.

This report deals with the calculation of water and salt transport and the permeability characteristics of the membrane, namely, the salt and water permeabilities and the various transport numbers determined in our system.

II. Calculation of Water and Salt transport:

In our eighth quarterly report (January, 1970) we described our transport measurement results in terms of salt and volume fluxes. Because the partial molar volumes of salt and water depend upon salt concentration, volume is not a strictly conserved quantity. Therefore, when discussing transport measurements, we shall describe them here and in the future in terms of molar water flux, J_w and molar salt fulx, J_s, rather than volume flux, J_V.

II. 1. Mass-Balance for the Salt-Donor Half-Cell (Buret Side)

The water gain (in mole) for the buret-side, $\delta n''_w$, equals the inflow of water through the membrane, $n_{w,m}$, (see Figure 1, page x), the "loss" term[*], $n''_{w,L}$, and the buret contribution of water when salt is added to this half-cell, $n_{w,Bu}$:

$$\delta n''_w = -n_{w,m} - n_{w,L} + n_{w,Bu} \tag{1}$$

$$\delta n''_w = -J_w \cdot A \cdot t - \dot{V}''_L \cdot t \cdot c''_w{}^{**} + c_{w,Bu} \cdot \delta V_{Bu} \tag{2}$$

where:

δV_{Bu} = the buret reading of the volume change, in cm^3; it is a positive increment.

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[*] The term "loss" is used for the observed reduction of total solution volume; this is not necessarily due to real leaks. Water absorption by the plastic has a similar effect, assuming no salt is lost.

[**] The relation between the concentration of water and salt in any volume of solution is through the solution density, ρ, which equals:

$$\rho = c_w M_w + c_s M_s \tag{2a}$$

Hence:

$$c_w = \frac{\rho - c_s M_s}{M_w} \tag{2b}$$

On the other hand,

$$\delta n''_w = c''_w \cdot \delta V''_{sol} + V''_{sol,o} \cdot \delta c''_w \qquad (3)$$

the second term on the right side of eq. (3) is due to changes in concentration of water during the time, t, between the recording of two sequential sets of experimental data. It is a small correction factor due to the fact that the experimental set-up keeps the concentrations constant within 0.02% or less, but since $V''_{sol,o} \simeq 200$ ml, this term should be taken into account.

The <u>salt</u> gain of the solution, $\delta n''_s$, equals the salt added by the buret, $n_{s,Bu}$, plus the salt which enters the solution, $n_{s,m}$, as a result of flow through the membrane and the electrochemical reaction at the anode:

$$\text{Ag (solid)} + \text{Cl}^- \text{ (solution)} \underset{\text{cathodic}}{\overset{\text{anodic}}{\rightleftharpoons}} \text{AgCl (solid)} + e^- \qquad (4)$$

For each Faraday passed, t_+ mole of Na^+ leave and $(1 - t_+)$ mole of Cl^- enter through the membrane, (t_+, t_- are the transport numbers of the ions in the membrane); 1 mole of Cl^- leaves the solution to become part of the electrode. Hence, the result of the electrical transport is the loss by the solution of t_+ mole NaCl. In other words, the molar loss of salt, $J_s \cdot A$, of the solution in the buret compartment equals the molar outflow of sodium ions, $J_+ \cdot A$. Therefore:

$$\delta n''_s = -n_{s,m} + n_{s,Bu} \qquad (5)$$

$$\delta n''_s = -J_s \cdot A \cdot t + c_{s,Bu} \cdot \delta V_{Bu} \qquad (6)$$

$$\delta n''_s = c''_s (\delta V''_{sol}) + (\delta c''_s) \cdot V''_{sol,o} \qquad (7)$$

$c_{s,Bu}$ is determined analytically with about 0.1% accuracy. The autoburet was calibrated with water. δV_{Bu}, as read from the digital dial, was found to be accurate to ± 0.1% in our experiments.

The volume change in the compartment, $\delta V''_{meas}$, measured in the capillary or calculated from the recorded weight change of the weighing bottle, $\delta w''_{meas}$, equals the gain of water and salt in the solution, $\delta V''_{sol}$, and the electrode volume change, δV_{el}; therefore:

$$\delta V''_{meas} = \delta V''_{sol} + \delta V''_{el} \tag{8}$$

$$\delta V''_{meas} = \delta n''_w \cdot \bar{V}''_w + \delta n''_s \cdot \bar{V}''_s + \frac{t \cdot I}{\mathfrak{F}} (\bar{V}_{AgCl} - \bar{V}_{Ag}) \tag{9}$$

$$\delta V''_{sol} = \delta V''_{meas} - \frac{t \cdot I}{\mathfrak{F}} (\bar{V}_{AgCl} - \bar{V}_{Ag}) \tag{10}$$

We have five unknowns, namely: $\delta n''_w$, $\delta n''_s$, $\delta V''_{sol}$, J_w and J_s, and five equations: (2), (3), (6), (7) and (10). By substituting $\delta n''_w$ from eq. (2) into eq. (3) and the equivalent of $\delta V''_{sol}$ from eq. (10) into eq. (3), the water flux, J_w, is solved as follows:

$$J_w = \frac{1}{A \cdot t} \left\{ + \delta V_{Bu} \cdot c_{w,Bu} - \dot{V}''_L \cdot t \cdot c''_w - c''_w \left[\delta V''_{meas} - \frac{t \cdot I}{\mathfrak{F}} (\bar{V}_{AgCl} - \bar{V}_{Ag}) \right] - \delta c''_w \cdot V''_{sol,o} \right\} \tag{11}$$

The salt flux, J_s, is solved by the same way; by substituting $\delta n''_s$ from eq. (6) into eq. (7) and the right side terms of eq. (10) for $\delta V''_{sol}$ into eq. (7), we get the following equation:

$$J_s = \frac{1}{A \cdot t} \left\{ \delta V_{Bu} \cdot c_{s,Bu} - c''_s \left[\delta V''_{meas} - \frac{t \cdot I}{\mathfrak{F}} (\bar{V}_{AgCl} - \bar{V}_{Ag}) \right] - \delta c''_s \cdot V''_{sol,o} \right\} \tag{12}$$

Both the salt and water fluxes can be calculated from measurements on the buret-side or the column-side. Usually, they are calculated for both sets of data as an internal check on the results.

II. 2. Mass-Balance for the Salt-Receiving Half-Cell (Column Side)

Following reasoning of Section II. 1, we derive here too, equations for the water gain, salt gain and for the volume change of the salt-receiving compartment.

The water gain (in mole) for the column-side, $\delta n'_w$, equals the inflow of water through the membrane, $n_{w,m}$, minus the "loss" term, $n'_{w,L}$, plus the equivalent of water released by the ion-exchange column, $n_{w,col}$, during the following reaction:

$$R_1\text{-}H^+ + R_2\text{-}OH^- + Na^+ + Cl^- \longrightarrow R_1\text{-}Na + R_2\text{-}Cl + H_2O \tag{13}$$

where R_1, R_2 respectively represent the negative and positive active groups fixed in the mixed-bed ion-exchange column. The NaCl uptake by the column, $n_{s,col}$, is equal to the equivalent of water released by the column, $n_{w,col}$. $n_{s,col}$ is determined by eluting the column with 0.5N $NaNO_3$ and determining the chloride content in the eluate. The repeatability of this process is ± 0.2%.

Therefore:

$$\delta n'_w = n_{w,m} - n'_{w,L} + n_{w,\ col} \tag{14}$$

Following the reasoning of Section II. 1, this equation can be rewritten as follows:

$$\delta n'_w = J_w \cdot t \cdot A - \dot{V}_L \cdot t \cdot c'_w + n_{w,col} = c'_w \cdot \delta V'_{sol} + \delta c'_w \cdot V'_{sol,o} \tag{15}$$

The salt gain (in mole) of the solution equals the salt uptake by the column, $n_{s,col}$, plus the salt which enters the solution as a result flow through the membrane and the electrochemical reaction at the cathode, eq. (4). In fact, the molar gain of salt of the solution in the column compartment equals the molar inflow of sodium ions, as explained in Section II. 1. Therefore:

$$\delta n'_s = n_{s,m} - n_{s,col} \tag{16}$$

$$\delta n'_s = -J_s \cdot A \cdot t - n_{s,col} = \left(\delta V'_{sol}\right) \cdot c'_s + \left(\delta c'_s\right) \cdot V'_{sol,o} \tag{17}$$

The volume change, $\delta V'_{meas}$, measured in the capillary equals the volume change of the solution, $\delta V'_{sol}$, plus the volume change of the electrode (the cathode), due to the reversed electrochemical reaction, eq. (4):

$$\delta V'_{meas} = \delta V'_{sol} + \delta V'_{el} \tag{18}$$

$$\delta V'_{meas} = \delta V'_{sol} + \frac{t \cdot I}{\mathfrak{F}} \left(\bar{V}_{Ag} - \bar{V}_{AgCl}\right) \tag{19}$$

The water flux, J_w, and salt flux, J_s, are calculated from equations (15) and (17) respectively, by substituting $\delta V'_{sol}$ from equation (19):

$$J_w = \frac{1}{A \cdot t} \left\{ c'_w \left[\delta V'_{meas} - \frac{t \cdot I}{\mathfrak{F}} \left(\bar{V}_{AgCl} - \bar{V}_{Ag}\right)\right] + \delta c'_w \cdot V'_{sol,o} + \dot{V}'_L \cdot c'_w \cdot t - n_{w,col} \right\} \tag{20}$$

$$J_s = \frac{1}{A \cdot t} \left\{ -c'_s \left[\delta V'_{meas} - \frac{t \cdot I}{\mathfrak{F}} \left(\bar{V}_{AgCl} - \bar{V}_{Ag}\right)\right] - \delta c'_s \cdot V'_{sol,o} - n_{s,col} \right\} \tag{21}$$

The solution concentrations are calculated from the temperature and resistance readings, following the method reported in the eighth quarterly report (January, 1970).

III. Permeability Characteristics of the membrane:

The same membrane segment was used throughout all our reported transport measurements; it is a cation-exchange membrane AMF C-103 (American Machine and Foundry Co., Springdale, Connecticut), a polyethylene-styrene graft polymer, with sulfonate as the active group. The equilibrium properties of the membrane, such as ion exchange capacity, water content, thickness, were determined by standard test procedures, as described in the O.S.W. R & D Report No. 77[1], and the results were reported in the eighth quarterly report (November, 1969). We report here the measured fluxes from the dialysis, electromigration-electroosmosis and pressure permeation experiments described in the tenth quarterly report (July, 1970); they are classified in Table (1).

III. 1. Water and Salt Permeabilities

Permeability coefficients may be calculated from our dialysis ↔ osmosis experiments. These coefficients are defined as positive parameters:[4]

$$Pm_w = |J_w|/|\Delta c_s| \quad \text{"(Osmotic) Water Permeability"} \qquad (22)$$

$$Pm_s = |J_s|/|\Delta c_s| \quad \text{"Dialysis Coefficient"} \qquad (23)$$

Pm_w and Pm_s are not material constants, but are inversely proportional to the membrane thickness. It should be noted that they are somewhat dependent on the solution concentrations on both sides of the membrane.

The "osmotic water permeability", Pm_w as calculated from our data (see Table 1) was:

$$Pm_w = (3.25 \pm 0.03) \times 10^{-4} \text{ cm sec}^{-1}$$

TABLE 1

THE MEASURED FLUXES*

	Previous Notation
I. Dialysis ↔ osmosis:	
$\Delta c_s = 0.5 - 0.1$ N NaCl	
$(J_w)_{\substack{i=0\\ \Delta p=0}} = (+130 \pm 1) \times 10^{-9}\ \text{mole sec}^{-1}\ \text{cm}^{-2}$	$J_w^{\ c}$
$(J_s)_{\substack{i=0\\ \Delta p=0}} = (-1.2. \pm 0.01) \times 10^{-9}\ \text{mole sec}^{-1}\ \text{cm}^{-2}$	$J_s^{\ c}$
II. Electroosmosis ↔ Electromigration:	
(a) $\Delta c_s = 0.5 - 0.1$ N NaCl; $i = -2\text{ma/cm}^2$	
$(J_w)_{\Delta p=0} = (-311 \pm 2) \times 10^{-9}\ \text{mole sec}^{-1}\ \text{cm}^{-2}$	$J_w^{\ -c-i}$
$(J_s)_{\Delta p=0} = (-18.4 \pm 0.1) \times 10^{-9}\ \text{mole sec}^{-1}\ \text{cm}^{-2}$	$J_s^{\ -c-i}$
(b) $\Delta c_s = 0.1 - 0.5$ N NaCl; $i = -2\ \text{ma/cm}^2$	
$(J_w)_{\Delta p=0} = (-147 \pm 1) \times 10^{-9}\ \text{mole sec}^{-1}\ \text{cm}^{-2}$	
$(J_s)_{\Delta p=0} = (-20.9 \pm 0.3) \times 10^{-9}\ \text{mole sec}^{-1}\ \text{cm}^{-2}$	$J_s^{\ c-i}$
III. Pressure-Permeation:	
(a) $\Delta c_s = 0.5 - 0.1$ N NaCl; $\Delta p = 1.5$ atm	
$(J_w)_{i=0} = (+101 \pm 0.6) \times 10^{-9}\ \text{mole sec}^{-1}\ \text{cm}^{-2}$	$J_w^{\ c-p}$
$(J_s)_{i=0} = (-0.442 \pm 0.008) \times 10^{-9}\ \text{mole sec}^{-1}\ \text{cm}^{-2}$	$J_s^{\ c-p}$
(b) $\Delta c_s = 0.08 - 0.1$ N NaCl	
$\Delta p = 0.000$ atm; $J_V = (-1.48 \pm 0.03) \times 10^{-10}\ \text{l sec}^{-1}\ \text{cm}^{-2}$	$J_V^{\ -c}$
$\Delta p = -\ 0.985$ atm; $J_V = (+1.41 \pm 0.03) \times 10^{-10}\ \text{l sec}^{-1}\ \text{cm}^{-2}$	$J_V^{\ -c-p_1}$
$\Delta p = -\ 1.490$ atm; $J_V = (+2.80 \pm 0.06) \times 10^{-10}\ \text{l sec}^{-1}\ \text{cm}^{-2}$	$J_V^{\ -c-p_2}$

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*All fluxes were measured across AMF C-103 cation selective membrane, at 25.00 ± 0.01°C.

TABLE 1 (Continued)

THE MEASURED FLUXES[*]

IV. "Combined" experiment:

		Previous Notation
Δc_s	= 0.5 - 0.1 N NaCl; Δp = 1.5 atm; i = -2 ma/cm^2	
J_w	= $(-98.1 \pm 0.9) \times 10^{-9}$ mole sec^{-1} cm^{-2}	J_w^{c-p-i}
J_s	= $(-20.5 \pm 0.2) \times 10^{-9}$ mole sec^{-1} cm^{-2}	J_s^{c-p-i}

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[*] All fluxes were measured across AMF C-103 cation selective membrane, at 25.00 ± 0.01°C.

The "dialysis coefficient", Pm_s, measured in our experiments, for the same concentration difference, $\Delta c_s = 0.5 - 0.1$ N NaCl, was (see Table 1):

$$Pm_s = (3.02 \pm 0.03) \times 10^{-6} \text{ cm sec}^{-1}$$

It is worthwhile to compare these values to data from the literature. It should be noted that the water and salt permeabilities through membrane systems are expected to be related to equilibrium properties of the membranes, such as water content, charge density and dielectric constant of the material[17]. It is unlikely to find a unique relationship between these equilibrium parameters and the permeabilities. Because of the lack of accuracy in the experiments reported in the literature and also because only fragmentary data are available, no such relationship is evident yet. Previous transport measurements made by other authors were always performed with a concentration change of the solutions while our "concentration-clamp" technique makes it possible to maintain constant concentrations on both sides of the membrane. So, we shall look for a trend in the reported values rather than a unique relationship between one of the equilibrium parameters, namely the water content of the membrane and the water and salt permeabilities, as reported in Table 2.

In these published values (Table 2) both the "dialysis coefficient", Pm_s, and the"osmotic water permeability", Pm_w, increase with increasing water content but is is probable that future measurements will show that water content is not the only parameter determining permeabilities and that other equilibrium properties of the membrane also influence the permeabilities.

TABLE 2

VARIATIONS OF Pm_w, Pm_s WITH WATER CONTENT

Cation-exchange membrane	Pm_w x 10^4 cm sec^{-1}	Pm_s x 10^6 cm sec^{-1}	Water Content %	Reference
Polystyrene Sulfonate[a]	1.04	1.3	17	(2)
AMF C-103	3.25	3.02	20	our work
Ion-X-Negative[b]	6.2	120	53	(4)
Zeo-Karb 315[c]	22	200	80	(3)

a. High-density Polystyrene Sulfonate membrane (supplied by Central Laboratorium TNO, Delft).

b. Cation-selective cellophane membrane (Polymer Research Corporation of America).

c. Sulfonated resin of the phenol-formaldehyde type (Permutit Co., Ltd. London).

Interestingly enough, the water permeabilities in biological membranes are of the same order of magnitude[5]: 2.1×10^{-4} cm sec^{-1} for arbacia eggs; 1.8×10^{-4} cm sec^{-1} for nittela; 6.3×10^{-4} cm sec^{-1} for rabbit lencocytes; and 6.3×10^{-4} cm sec^{-1} for onion skin, although all these biological membranes are much thinner.

III. 2. The "Practical" Coefficients:

Since the permeability coefficients, Pm_w, Pm_s (Section III. 1.) are not material constants but rather are concentration dependent, one may desire to define alternate membrane parameters which are less dependent on the salt concentrations. A group of three coefficients which often satisfy this requirement are the "reflection coefficient", σ[6], the solute permeability, ω, and the hydraulic permeability L_p. With this choice of coefficients the following equations, valid for non-ionic membranes, can be derived [9, 14] for the volume flux J_V*, and the salt flux, J_s, with some approximations:

$$J_V = L_p(\Delta p - \sigma\Delta\pi) \tag{24}$$

$$J_s = \omega\Delta\pi + (1 - \sigma)\, J_V \bar{c}_s \tag{25}$$

---

*Note that the volume flux is the sum of water and salt flux:

$$J_V = J_w \cdot \bar{V}_w + J_s \cdot \bar{V}_s \tag{26}$$

$\bar{c}_s$ in eq. (25) is an average salt concentration; for large volume flow and high concentration gradient, the changing concentration profile inside the membrane has to be taken into account, instead of the average $\bar{c}_s$ and eq. (24), (25) have to be transformed into the <u>local</u> flux equations [15, 16, 17].

The <u>hydraulic permeability</u>, L_p, was calculated from the measured fluxes brought about by (1) osmotic force only and (2) by a hydrostatic pressure and osmotic forces:

when $\Delta p=0$, $$(J_V)_{\Delta p=0} = -L_p \sigma \Delta\pi \tag{27}$$

$$J_V = L_p(\Delta p - \sigma\Delta\pi) \tag{28}$$

Substracting eq. (28) from eq. (27), we obtain an equation for L_p which does not contain σ:

$$L_p = [J_V - (J_V)_{\Delta p=0}] \cdot \Delta p^{-1} \tag{29}$$

The numerical L_p values for two different pressures were as follows (see Table 1):

(L_{p_1}) for $\Delta p = 0.985$ atm equals: $2.89 \times 10^{-10} / 0.985 = 2.93 \times 10^{-10}$ l $\sec^{-1}\text{cm}^{-2}\text{atm}^{-1}$

(L_{p_2}) for $\Delta p = 1.49$ atm equals: $4.28 \times 10^{-10} / 1.49 = 2.89 \times 10^{-10}$ l $\sec^{-1}\text{cm}^{-2}\text{atm}^{-1}$

It is seen that there is fair agreement between the two values. Moreover, this value is in good agreement with L_p measured by Lakshminarayanaiah[7]. He used an AMF C-103 membrane, deionized water, a stainless steel mesh membrane support with a piece of filter paper between the membrane and the support and Δp in the range of 2 - 4 atm. The reported value for L_p was:

2.2×10^{-10} l sec^{-1} cm^{-2} atm^{-1}. Scattergood and Lightfoot[8] measured L_p for AMF C-103 membrane with $\Delta p = 3.1$ atm, 0.1 N NaCl solution concentration and a filter paper membrane support; their value for L_p was: 5×10^{-10} l sec^{-1} cm^{-2} atm^{-1}, i.e. of the same order as ours, but about sixty percent higher, These differences may be due to variations in membrane manufacture and possibly to the different nature of the support. σ is Staverman's "reflection" coefficient, an adequate measure of membrane selectivity. In an entirely unselective membrane, in which a concentration gradient does not cause volume flow at all, $\sigma = 0$. In an ideally semipermeable membrane, $\sigma = 1$; thus σ is a measure of the degree of semipermeability of the membrane, i.e. its ability to pass solvent in preference to solute. It is important to realize that the value of σ depends on the properties of both the membrane and the solute.

The reflection coefficient, σ, for the AMF C-103 membrane was calculated from our measurements, using eq. (27) and found to be: $\sigma = 0.41$ for $\Delta c_s = 0.5 - 0.1$ N NaCl and 0.59 for $\Delta c_s = 0.08 - 0.1$ N NaCl. No values for comparison were found in the literature. The increase of σ as c_s decreases is expected because Donnan exclusion lowers the salt concentration in the membrane with the decrease in the concentration of the bounding solutions; therefore the salt permeability decreases with a corresponding increase in the reflection coefficient, σ. (Helfferich[18], Kedem and Hoffer[19]).

The third coefficient involved is ω, the solute permeability at zero volume flow; it is defined as[9]:

$$\omega = (J_s/\Delta\pi)_{J_V = 0} \tag{30}$$

ω is not quite identical to Pm_s, defined in eq. (23)*. We used eq. (25) rather than eq. (30) to calculate ω, since we have no measurements at zero volume flow. It should be kept in mind that ω is concentration dependent[17]. Hence the values obtained in an experiment with a finite concentration difference across the membrane yield a broad average of ω. The average volume flow, J_V, was calculated from eq. (26) using our measured value of J_w and J_s (Table 1). Since the partial molar volume of salt, $\bar{V}_s$, is concentration dependent, an arithmetic mean was used in the calculation. The result, for the concentration difference, Δc_s = 0.5 - 0.1 M NaCl, was $\omega = 8.6 \times 10^{-10}$ mole sec^{-1} cm^{-2} atm^{-1}. It is of some interest to refer to Table 2, Ref. [9], (page 123) where a few comparable values for biological membranes are reported; for example, when the solute is acetamide and the membrane is toad skin, $\omega = 0.0041 \times 10^{-15}$ mole dyne^{-1} sec^{-1}, σ is 0.89 and the hydraulic permeability, L_p, is 0.4×10^{-11} cm^3 dyne^{-1} sec^{-1}, (work done by Andersen and Ussing,[10]). Such measurements may be useful in obtaining a better understanding of membrane properties. For example, Solomon[11], has utilized measurements of σ to estimate the size of equivalent aqueous channels in the membrane.

III. 3. Water and Salt transport numbers:

The water transport number, L_{WE}, was calculated from the following:

$$L_{WE} \equiv \mathcal{F}\left[J_w - (J_w)_{i=0} \right] \cdot i^{-1} \tag{31}$$

where J_w is the water flux under the influence of both current and concentration gradient (combined osmosis and electroosmosis) while $(J_w)_{i=0}$ is the

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*For ideal solutions, $\Delta\pi = RT\Delta c_s$, hence $\omega = P_s/(RT)$

water flux under the same concentration gradient, but without current (osmosis). When the osmotic and electroosmotic fluxes are in the same direction, $L_{WE} = 8.73$ (see Table 1). Lakshiminarayanaiah and Subrahmanyan[12] reported a value of $L_{WE} = 7.0$ on AMF C-103 membrane, under uniform concentration conditions, at $c_s = 0.01$ M NaCl and $i = 1.58$ ma cm^{-2}. Scattergood and Lightfoot[8] measured L_{WE} for AMF C-103 membrane using uniform concentration conditions, 0.1 M NaCl and obtained $L_{WE} = 7.58$. The larger values obtained here are due to the difference in membrane samples or may indicate a change in the properties of the membrane, due to deformation by pressure. A further comparison could have been carried, primarily from the measurement of the streaming potential, as reported in the previous tenth quarterly report (July, 1970). Unfortunately, the streaming potential is extremely non-linear in the hydrostatic pressure ranges used in our experiments. A further series of streaming potential measurements is strongly suggested.

The absolute <u>cation transport number</u>, L_{SE}, was calculated from the measured fluxes, using either one of the equations (see Table 1):

$$(L_{SE})_1 = (J_s^{c-i} - J_s^{c}) \cdot \mathcal{F} \cdot i^{-1} \qquad = 0.950 \pm 0.01$$

$$(L_{SE})_2 = (J_s^{-c-i} + J_s^{c}) \cdot \mathcal{F} \cdot i^{-1} \qquad = 0.946 \pm 0.01$$

$$(L_{SE})_3 = (J_s^{c-p-i} - J_s^{c-p}) \cdot \mathcal{F} \cdot i^{-1} \qquad = 1.04 \pm 0.05$$

The value calculated from the pressure-permeation experiments is larger than unity, a result which is physically unreasonable, since salt transport numbers should not exceed unity. It seems to support our previous conclusion that pressure may compact the membrane, and furthermore, may increase the cation-selectivity of the membrane.

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