

# FAILURE OF THE NERNST-EINSTEIN EQUATION TO CORRELATE ELECTRICAL RESISTANCES AND RATES OF IONIC SELF-EXCHANGE ACROSS CERTAIN FIXED CHARGE MEMBRANES

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**ABSTRACT** The electrical resistances and rates of self-exchange of univalent critical ions across several types of collodion matrix membranes of high ionic selectivity were studied over a wide range of conditions. The relationship which was observed between these quantities with membranes of a certain type, namely those activated with poly-2-vinyl-*N*-methyl pyridinium bromide, cannot be explained on the basis of current concepts of the movement of ions across ion exchange membranes. Rates of self-exchange across these membranes were several times greater than those calculated from the electrical resistances of the membranes on the basis of an expression derived by the use of the Nernst-Einstein equation. The magnitude of the discrepancy was greatest at low concentrations of the ambient electrolyte solution and was independent of the species of both critical and noncritical ions. The data obtained with other types of collodion matrix membranes were, at least approximately, in agreement with the predictions based on the Nernst-Einstein equation. Self-exchange rates across the anion permeable protamine collodion membranes, and across the cation permeable polystyrene sulfonic acid collodion membranes, were about 20% less than those calculated from the electrical resistances. The direction and magnitude of these differences, also observed by other investigators, are qualitatively understood as an electroosmotic effect. With cation permeable membranes prepared by the oxidation of preformed collodion membranes, almost exact agreement was obtained between measured and calculated self-exchange rates; the cause of the apparent absence of an electroosmotic effect with these membranes is unknown.

## INTRODUCTION

A close relationship, defined by the Nernst-Einstein equation, between the rates of diffusion of ions and the rates of their electromigration (1), implicitly or explicitly, forms the basis of most theoretical approaches to transport processes across mem-

branes both in physiological and physicochemical systems (2-6). It therefore seemed of considerable interest when, in the course of systematic studies on the electrochemistry of ion exchange membranes, we found that the rates of self-exchange<sup>1</sup> of anions across certain anion permeable fixed charge membranes are several times greater than would be predicted from the electrical resistances of the membranes on the basis of current concepts. The presentation of these observations is the purpose of this paper. A meaningful discussion of molecular mechanisms which might underlie this effect, and of its possible implications in electrophysiology must await additional experimental data.

The Nernst-Einstein equation for univalent ions may be written as

$$D = \frac{RT}{F^2} \lambda, \quad (1)$$

where  $D$  is the diffusion coefficient of an ion,  $\lambda$  its equivalent conductance, and  $R$ ,  $T$ , and  $F$  are the gas constant, absolute temperature, and the Faraday constant. The validity of this expression is confirmed by numerous experimental data on diffusion coefficients and equivalent conductances of ions in free solution (1). The more limited data on these quantities within ion exchange materials have been found to be essentially in accord with Equation 1 (7-9). Provided that certain experimental conditions are fulfilled, a straightforward application of Equation 1 to the (univalent) counterions of the fixed charge groups of a membrane of high ionic selectivity leads to the following relationship between the electrical resistance  $\rho$ , and the rate of self-exchange of the critical ions  $\varphi$ , across any given area of a membrane:

$$\varphi = \frac{RT}{F^2 \rho}; \quad (2)$$

at 25°C,

$$\varphi = \frac{958}{\rho} \quad (2 a)$$

where  $\varphi$  is expressed in microequivalents ( $\mu\text{eq}$ ) per hr and  $\rho$  as ohms. The experimental conditions which must be fulfilled for the strict applicability of these equations, the assumptions inherent in them, and their detailed derivation are reviewed

<sup>1</sup> Several terms which are used in this paper are defined here for the convenience of readers who may not be acquainted with the literature on ion exchange membranes. An *ion selective membrane* is preferentially, in limiting cases exclusively, permeable to *critical ions*, the ionic species which constitute the counterions to the fixed charge groups of the membrane. A membrane of this type ideally is completely impermeable to *noncritical ions*, ions of the same sign of charge as the fixed charge groups. The radioisotopically measurable, one-for-one exchange of critical ions across an ion selective membrane which separates solutions of the same single electrolyte at the same concentrations is, in this paper, referred to as *self-exchange of critical ions*.

in Appendix I. The few published data on the electrical resistances and the rates of self-exchange of critical ions across both cation selective (10, 11) and anion selective (12) fixed charge membranes are essentially in agreement with Equation 2.

In this paper we report systematic measurements of the electrical resistances and of the rates of self-exchange of critical ions across membranes of the type which exhibit the divergent behavior, namely collodion matrix membranes activated with poly-2-vinyl-*N*-methyl pyridinium bromide (PVMP) (13).<sup>2</sup> Analogous systematic measurements, made under the same conditions, with several other types of collodion matrix membranes yielded results which were essentially in accord with Equation 2 *a*. These membranes included anion permeable membranes of another type, prepared with the protein protamine as activating polyelectrolyte (14), and two types of cation permeable membranes, some activated with polystyrene sulfonic acid (PSSA) (15) and some obtained by oxidation of preformed collodion membranes (16).

The parameters covered in our study were: the absolute ionic permeability of the membranes of the various types; the species of the critical and noncritical ions; and the concentration of the ambient solution.<sup>2</sup>

## EXPERIMENTAL

### Materials

**Membranes.** The details of the preparation and the properties of the various types of membranes used have been described previously. The PVMP and protamine membranes were prepared by the adsorption of the appropriate polyelectrolyte on preformed highly porous collodion membranes, and subsequent drying of these membranes (13, 14). The polystyrene sulfonic acid (PSSA) membranes were cast from collodion solutions containing this polyelectrolyte (15). The oxidized collodion membranes were made by the controlled oxidation of preformed collodion membranes (16). These membranes have the shape of test tubes, are about 24 mm in diameter, 95 mm long, and 30–40  $\mu$  thick; for mechanical support, glass rings approximately 30 mm long were inserted at the top of the membranes. The functional membrane area is about 50 cm.<sup>2</sup>

The membranes were selected on the basis of their electrical resistance in 0.1 N KCl, ( $\rho^*$ ) as a general measure of the magnitude of their ionic permeability, and on the basis of the potential in concentration cells:

Saturated calomel electrode	0.10 N KCl	membrane	0.010 N KCl	Saturated calomel electrode
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<sup>2</sup> Results similar to those found with the PVMP membranes were also observed in a few experiments with collodion matrix membranes activated with two other quaternary ammonium polyelectrolytes: polyvinyl benzyl trimethyl ammonium chloride (Dow Chemical Co., Midland, Mich.) and polymethyl diethyl methacroxy ethyl ammonium methosulfate (Daktose B) (E. I. du Pont de Nemours and Co., Wilmington, Del.). When PVMP membranes are commented on in a general context in this paper, the comments also apply to these other quaternary ammonium polyelectrolyte-collodion matrix membranes. We thank the above-mentioned companies for samples of the two polyelectrolytes.

as a measure of their selectivity for critical over noncritical ions. These potentials were, in all instances, greater than  $\pm 54.3$  mv (corrected for the asymmetry of the potentials at the two liquid junctions). Membranes with the higher standard resistances closely approached the theoretical maximum potential,  $\pm 55.1$  mv (at  $25^{\circ}\text{C}$ ).

**Radioisotopes.** The radio tracers  $^{40}\text{K}$ ,  $^{22}\text{Na}$ ,  $^{134}\text{Cs}$ ,  $^{36}\text{Cl}$ , and  $^{131}\text{I}$  were obtained from Oak Ridge National Laboratories, Oak Ridge, Tenn.;  $^{35}\text{S}$ -labeled KCNS, and  $1\text{-}^{14}\text{C}$ -labeled sodium acetate were purchased from Tracerlab Corp., Boston, Mass. The potassium isotope was supplied as the solid carbonate, which was dissolved and neutralized with an appropriate acid; the solution was boiled to free it from  $\text{CO}_2$ . The radioactive sodium, cesium, and chloride were received in weak HCl solutions, which were neutralized with the appropriate hydroxides. The iodide came in basic  $\text{Na}_2\text{SO}_3$  solution, which was neutralized with HI to pH 6, and subsequently aerated to remove the  $\text{SO}_2$ . The potassium thiocyanate and the sodium acetate were supplied as the solid salts; the former was dissolved and used without further treatment, the latter was converted into potassium acetate by passing it through a column of Dowex 50 in the potassium form.

Approximately  $100\text{ }\mu\text{C}$  quantities of the radioactive materials were added to 50 ml of the appropriate solutions of electrolyte. The concentrations of these solutions were adjusted to within 0.1% of the desired concentrations, as determined conductometrically.

### Methods

Prior to the measurements of the electrical resistances and of the rates of self-exchange, the membranes were immersed for several days in a solution of the appropriate composition.

All measurements were made at  $25.0 \pm 0.1^{\circ}\text{C}$ . Ordinarily, the resistance was measured both before and after the measurement of the rate of self-exchange; no significant differences were observed.

**Measurement of the Electrical Resistance.** The cell for the measurement of the electrical resistances of the test tube-shaped membranes has been previously described in detail (16), and is shown schematically in Fig. 1 *a*. The test tube-shaped electrodes were made

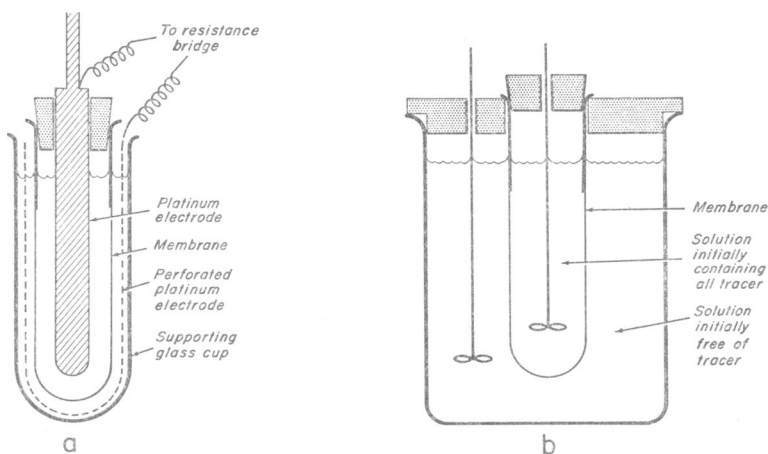


FIGURE 1 Schematic drawings of the cells used to measure (a) the electrical resistances of membranes, and (b) the rates of self-exchange of critical ions across membranes.

of sheet platinum; the outer electrode was perforated to approximately equalize the electrode areas. The functional membrane area and the electrodes were completely covered by the solutions. A Kohlrausch bridge was used with frequencies of 60–10,000 cycle/sec. To obtain sharp minima, it was necessary to put capacitors of varying sizes in parallel with one arm of the bridge.

The resistance of the membrane is the difference between the resistances of the cell without the membrane and that with the membrane in place. For the measurement in the absence of the membrane, the inner electrode was fitted with a glass ring with the same dimensions as that supporting the membrane, so that the obstruction of the current by the ring was the same in both cases. The resistance of the layer of solution displaced by the membrane was not corrected for, being negligible at concentrations of 0.01 N and higher (16).

The membrane resistances were independent of frequency in the region 60–200 cycle/sec. There was in most instances a decrease in resistance in the region 200–10,000 cycle/sec which, at 10,000 cycle/sec, with some membranes was as small as 10% and with others as large as 30%. The magnitude of the decrease of resistance with frequency appeared to be specific for each individual membrane. There were no significant differences among the various types of membranes, and the decrease in resistance did not vary in a regular manner with either standard membrane resistance or with solution composition. The resistances measured in the low frequency region were taken as relevant in the present context. The reproducibility of these measurements was about  $\pm 1\%$ .

Electrical resistances are reported on a  $\text{cm}^2$  basis, assuming that each membrane had a functional area of  $50 \text{ cm}^2$ ; the directly measured resistance of the membrane multiplied by 50 gives the resistance of the membrane,  $\rho$ , in  $\text{ohm-cm}^2$ . The numerical comparison of the unit area resistance of a membrane with the unit area rate of self-exchange is not affected by any inaccuracy in the assumption of a functional area of exactly  $50 \text{ cm}^2$  for our membranes.

*Determination of Radioactivity.* Radioactivity was determined by standard techniques:  $^{36}\text{Cl}$ ,  $^{35}\text{S}$ , and  $^{14}\text{C}$  were counted, after drying on filter paper, using a thin window Geiger-Mueller tube;  $^{24}\text{Na}$ ,  $^{42}\text{K}$ ,  $^{134}\text{Cs}$ , and  $^{131}\text{I}$  were determined in most cases in solution with a well-type scintillation counter, but in some cases with a Geiger-Mueller tube. All samples were counted for at least 4,000 counts at a counting rate of about 500 cpm on the Geiger-Mueller tube and 1500 cpm on the scintillation counter. Background on the Geiger Mueller-tube was about 20 cpm, on the scintillation counter about 125 cpm.

When it was necessary to dilute a sample for counting, nonradioactive solution of the same chemical composition was used as diluent.

*Measurement of the Rates of Self-Exchange.* The simple arrangement used for the measurement of self-exchange rates is shown schematically in Fig. 1 *b*. The solution volumes were 33.0 ml and 350 ml, respectively, in the inner and outer compartments. The levels of both solutions reached above the lower rim of the glass ring supporting the membrane. Both solutions were stirred mechanically.

The rate of self-exchange was calculated from the rate of movement of radioactive critical ions from the inner compartment to the outer compartment, with only the inner compartment containing radiotracer ions at the start of the experiment. The rate of appearance of radiotracer in the outer solution was determined with three 2.00 ml aliquots withdrawn at appropriate intervals. The reduction of the volume of the outer solution was neglected, since during the course of the experiment it was only slightly greater than 1%. At the end of the experiment, the quantity of radiotracer in the inner solution was determined.

In most instances, the rate of movement of radiotracer across the membranes could be accurately determined after only an insignificant fraction of the initial radiotracer content

of the inner solution had crossed the membrane into the outer solution. When this was the case, the rate of appearance of radiotracer in the outer solution did not change measurably during the course of the experiment. In these instances, the rate of self-exchange of critical ions across the membrane was calculated by multiplying the total quantity of critical ions in the inner solution by the fraction of radiotracer content of this solution which crossed the membrane per unit time. As with the membrane resistance data, the measured rates of self-exchange will be expressed on a  $\text{cm}^2$  basis, and for convenience in units of  $\mu\text{eq}$  per hr per  $\text{cm}^2$ :

$$\phi = \frac{10^6}{50} \frac{n_s^{*''} c_s V'}{(n_s^{*'} + n_s^{*''}) t} \quad (3)$$

Here  $t$  is the period of time, in hr, necessary for the quantity of radiotracer  $n_s^{*''}$  to enter the outer solution;  $n_s^{*'}$  is the experimentally determined quantity of radiotracer in the inner solution;  $c_s$  is the concentration of critical ions in the two solutions in eq per liter; and  $V'$  is the volume of the inner solution, in liters.

In a few instances, namely with systems combining membranes of high permeability with dilute solutions, accurate self-exchange rates were best obtained by continuing the experiments until a significant fraction, up to 25%, of the radioactive material had moved across the membrane. Under these conditions, the decreasing difference between the concentrations of radiotracer material in the inner and in the outer solutions leads to a decrease in the rate at which radiotracer crosses the membrane as the experiment progresses. When this effect is significant, Equation 3 is not applicable. A more general expression, for degrading systems, which includes the ion exchange capacity of the membrane as a parameter is derived in Appendix II. There it is shown that this latter factor is of no significance in the present work and that an approximate expression:

$$\phi = -\frac{10^6}{50} \times 2.3 \frac{c_s}{t} \frac{V' V''}{(V' + V'')} \log \left[ 1 - \frac{n_s^{*''}}{(n_s^{*'} + n_s^{*''})} \frac{(V' + V'')}{V''} \right] \quad (4)$$

is applicable. Here,  $V''$  is the volume of solution in the outer compartment in liters; the other symbols have the same meanings as before. The time course of the appearance of radiotracer in the outer solution was found to agree with Equation 4.

Preliminary experiments under conditions in which the effects of unstirred layers of solution at the membrane-solution interfaces are maximal, i.e. in 0.01 N solution and with the membranes of the highest permeabilities (see Results), showed that the rates of exchange were dependent on the rates of rotation of the stirrers up to about 500 rpm. Accordingly, stirring rates well above this were used throughout.

Exploratory experiments also established that steady-state rates of exchange were obtained within 5 min with membranes having the lowest resistances, and within 30 min with those having the highest resistances. Accordingly, prior to the measurement of the rate of self-exchange, an exchange of radiotracer ions for nonradiotracer ions across the membrane was allowed to proceed for about 15 min with the lowest resistance membranes, and for about an hour with the other membranes. Thereafter, the self-exchange measurement proper was initiated by replacing the outer solution by fresh radiotracer-free solution (which had been stored at 25.0°C).

The accuracy of the measurements of the rate of self-exchange is estimated to be better than  $\pm 2\%$ .

## EXPERIMENTAL RESULTS

The measured rates of self-exchange,  $\varphi_{\text{exp.}}$ , of chloride ions in  $\mu\text{eq hr}^{-1} \text{cm}^{-2}$ , across several PVMP membranes, with potassium chloride and magnesium chloride solutions of various concentrations, are shown in Fig. 2 as solid circles connected by solid lines. The rates calculated, using Equation 2 *a*, from the unit area electrical resistances of the membranes,  $\rho$ , in the same solution are shown in this fig. as open circles connected by broken lines. (The points indicated by squares are values which have been corrected for unstirred layers of solutions and the less than ideal ionic selectivities of the membranes, in those cases in which as discussed below, these corrections are significant.) Corresponding data for another PVMP membrane, with chloride, acetate, and thiocyanate as critical ions, are given in Table I *A*. Analogous data for the other type of anion permeable membrane studied, the protamine collodion membrane, are presented in the same manner in Fig. 3 and in Table I *B*.

The measured rates of self-exchange and those calculated from the electrical resistances, for cation permeable membranes in KCl and  $\text{K}_2\text{SO}_4$  solutions, are shown in Figs. 4 and 5 for PSSA and oxidized collodion membranes, respectively. Table II presents data with sodium and cesium ions as critical ions.

At this point we must evaluate the influence of diffusion layers and of the deviations of the membranes from ideal ionic selectivity, on the experimental results and on the correlation between  $\varphi_{\text{exp.}}$  and  $\varphi_{\text{calc.}}$ .

The exchange of ions across a membrane which separates two stirred solutions involves not only the diffusion of the ions across the membrane proper, but also the diffusion of the ions across layers of solution at each membrane-solution interface, which remain unstirred.

An estimate of the magnitude of diffusion layer effects can be made on the basis of an expression derived by Peterson and Gregor (17), which in a modified form, reads:

$$\frac{1}{\varphi} = \frac{1}{\varphi^*} + \frac{2\delta}{3600 \times 10^3 D c} \quad (5)$$

Here,  $\varphi$  and  $c$  are, as previously defined, the measured rate of self-exchange ( $\mu\text{eq hr}^{-1} \text{cm}^{-2}$ ) and concentration of the ion in the solution (eq/liter);  $\varphi^*$  is the "true" rate of self-exchange ( $\mu\text{eq hr}^{-1} \text{cm}^{-2}$ ), i.e. the rate which would be measured if the solution were well stirred up to the membrane;  $\delta$  (cm) is the thickness of the diffusion layer, and  $D$  ( $\text{cm}^2 \text{sec}^{-1}$ ) is the diffusion coefficient of the ion in solution. A commonly accepted value for  $\delta$  is  $30 \times 10^{-4} \text{ cm}$  (18), and the diffusion coefficients for  $\text{Cl}^-$  and  $\text{K}^+$  in solution are about  $2.0 \times 10^{-5} \text{ cm}^2 \text{sec}^{-1}$  (19). The second term on the right-hand side of Equation 5 represents the reciprocal of the rate at which the ions are capable of diffusion across the unstirred layers of solution.

In the most dilute solution used in the present work,  $c = 0.01 \text{ N}$ , the reciprocal

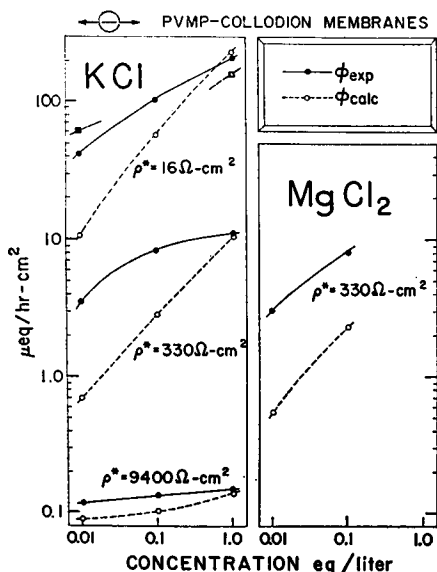


FIGURE 2 Experimental rates of self-exchange,  $\phi_{exp}$ , and the corresponding rates of self-exchange calculated from electrical resistances,  $\phi_{calc}$ , for PVMP collodion membranes. (See text for meaning of squares:  $\blacksquare$ ,  $\square$ .)

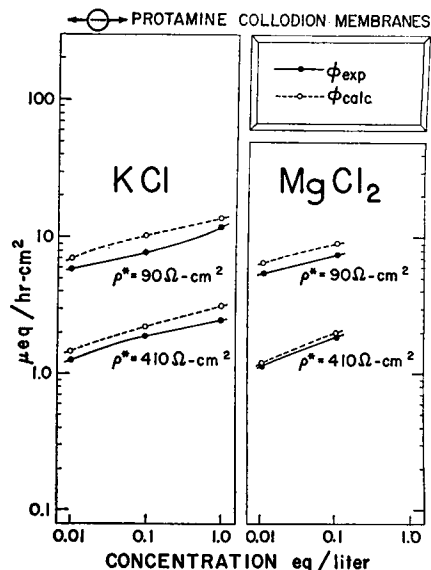


FIGURE 3 Experimental rates of self-exchange,  $\phi_{exp}$ , and the corresponding rates of self-exchange calculated from electrical resistances,  $\phi_{calc}$ , for protamine collodion membranes.

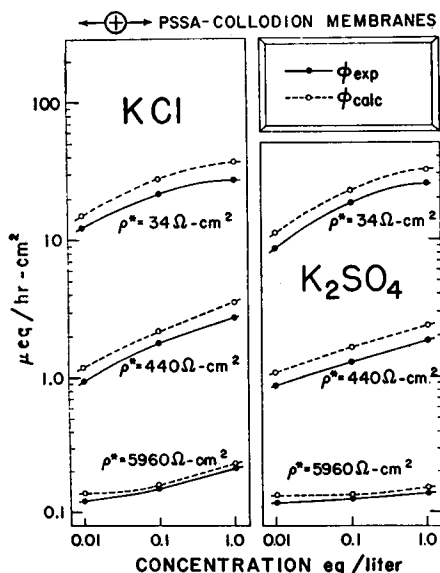


FIGURE 4 Experimental rates of self-exchange,  $\phi_{exp}$ , and the corresponding rates of self-exchange calculated from electrical resistances,  $\phi_{calc}$ , for PSSA collodion membranes.

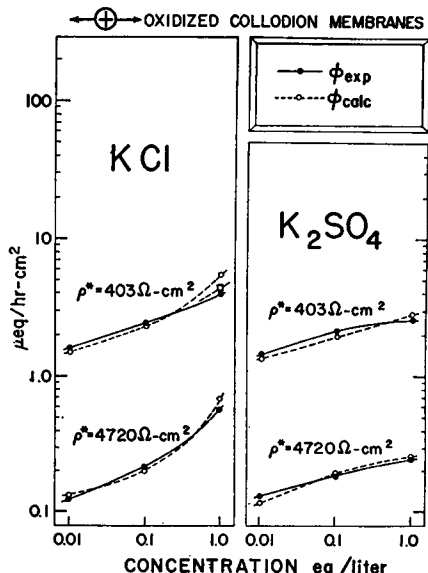


FIGURE 5 Experimental rates of self-exchange,  $\phi_{exp}$ , and the corresponding rates of self-exchange calculated from electrical resistances,  $\phi_{calc}$ , for oxidized collodion membranes. (See text for meaning of square,  $\square$ .)



TABLE I  
ELECTRICAL RESISTANCES AND CALCULATED AND EXPERIMENTAL  
RATES OF SELF-EXCHANGE ACROSS PVMP AND PROTAMINE COLLODION  
MEMBRANES WITH VARIOUS CRITICAL IONS

Standard resistance of membrane $\rho^*$	Solution	Elec- trical resist- ance $\rho$	Rate of self- exchange cal- culated from resistance $\varphi_{\text{calc.}}$	Experimen- tal rates of self-exchange $\varphi_{\text{exp.}}$	$\varphi_{\text{exp.}}/\varphi_{\text{calc.}}$
A. PVMP membrane					
		<i>ohm-cm<sup>2</sup></i>	$\mu\text{eq hr}^{-1}\text{ cm}^{-2}$	$\mu\text{eq hr}^{-1}\text{ cm}^{-2}$	
160 ohm-cm <sup>2</sup>	0.10 N KCl	160	5.99	17.5	2.9
	0.01 N KCl	675	1.42	8.75	6.1
	0.10 N KAc†	330	2.91	9.63	3.3
	0.01 N KAc	1220	0.785	5.10	6.5
	0.10 N KCNS	225	4.26	8.75	2.1
	0.01 N KCNS	1200	0.798	4.53	5.7
B. Protamine membranes					
		<i>ohm-cm<sup>2</sup></i>	$\mu\text{eq hr}^{-1}\text{ cm}^{-2}$	$\mu\text{eq hr}^{-1}\text{ cm}^{-2}$	
90 ohm-cm <sup>2</sup>	0.10 N KAc	295	3.25	2.75	0.85
	0.01 N KAc	650	1.47	1.18	0.80
	0.10 N KCNS	225	4.26	3.37	0.79
	0.01 N KCNS	315	3.04	2.50	0.82
410 ohm-cm <sup>2</sup>	0.10 N KAc	1150	0.834	0.692	0.83
	0.01 N KAc	3150	0.304	0.245	0.80
	0.10 N KCNS	715	1.34	1.14	0.85
	0.01 N KCNS	1310	0.75	0.61	0.83

† Ac = acetate.

of the second term on the right-hand side of Equation 5 is  $120 \mu\text{eq hr}^{-1} \text{ cm}^{-2}$ . Thus, if the experimental rates of self-exchange in 0.01 N solutions are much smaller than about  $120 \mu\text{eq hr}^{-1} \text{ cm}^{-2}$ , the error due to unstirred diffusion layers is negligible. Referring to the systems with 0.01 N solutions in Figs. 2-5 and in Tables I and II, it is evident that unstirred solution layers play a significant role only with the PVMP, protamine and PSSA membranes having the highest permeabilities ( $\rho^* = 16, 90$ , and  $34 \text{ ohm-cm}^2$ ). With these membranes the experimental self-exchange rates were respectively 40, 6, and  $12 \mu\text{eq hr}^{-1} \text{ cm}^{-2}$ ; the "true" rates of self-exchange, calculated using Equation 5, are respectively 60, 6.3, and  $13.3 \mu\text{eq hr}^{-1} \text{ cm}^{-2}$ . With 0.10 N solutions, in which the quantity  $3600 \times 10^3 Dc/2\delta = 1200 \mu\text{eq hr}^{-1} \text{ cm}^{-2}$ ,

the effects of unstirred solution layers are significant only with the PVMP membrane  $\rho^* = 16 \text{ ohm-cm}^2$ , where the measured self-exchange rate was  $105 \mu\text{eq hr}^{-1} \text{cm}^{-2}$ . In this case, the "true" rate of self-exchange, as calculated from Equation 5, is  $115 \mu\text{eq hr}^{-1} \text{cm}^{-2}$ . In 1.0 N solutions, the effects of unstirred layers are essentially negligible in all the systems reported here.

Deviation of the membranes from ideal ionic selectivity entails a contribution by the noncritical, nominally nonpermeating ions, to the conductances of the mem-

TABLE II  
ELECTRICAL RESISTANCES AND CALCULATED AND EXPERIMENTAL  
RATES OF SELF-EXCHANGE ACROSS PSSA AND OXIDIZED COLLODION  
MEMBRANES WITH VARIOUS CRITICAL IONS

Standard resistance of membrane $\rho^*$	Solution	Electrical resistance $\rho$	Rate of self-exchange calculated from resistance $\varphi_{\text{calc.}}$	Experimental rates of self-exchange $\varphi_{\text{exp.}}$	$\varphi_{\text{exp.}}/\varphi_{\text{calc.}}$
A. PSSA membranes					
		$\text{ohm-cm}^2$	$\mu\text{eq hr}^{-1} \text{cm}^{-2}$	$\mu\text{eq hr}^{-1} \text{cm}^{-2}$	
235 ohm-cm <sup>2</sup>	0.10 N NaCl	275	3.48	2.55	0.73
	0.01 N NaCl	475	2.02	1.51	0.75
	0.10 N CsCl	520	1.84	1.34	0.73
2800 ohm-cm <sup>2</sup>	0.10 N NaCl	3180	0.301	0.242	0.80
	0.01 N NaCl	5710	0.168	0.145	0.86
B. Oxidized collodion membrane					
		$\text{ohm-cm}^2$	$\mu\text{eq hr}^{-1} \text{cm}^{-2}$	$\mu\text{eq hr}^{-1} \text{cm}^{-2}$	
2520 ohm-cm <sup>2</sup>	0.10 N NaCl	2900	0.330	0.338	1.02
	0.01 N NaCl	6610	0.145	0.145	1.00

branes. To the extent that such deviations occur, rates of self-exchange of critical ions calculated from electrical resistances will be erroneously high. The contribution of noncritical ions to the electrical conductance can be estimated from either rates of leakage of noncritical ions or from concentration potentials, measured under comparable conditions. Previously reported measurements with membranes similar to those used here (13-16, 20), indicate that the permeabilities to noncritical ions of all membranes referred to in Figs. 2-5 and Tables I and II, are less than 1% of that to critical ions in all the instances except for the systems with univalent noncritical ions in 1.0 N solution. With 1.0 N solutions having univalent noncritical

ions, the estimated contributions of the noncritical ions to the conductances are more substantial, being about 30, 5, 2.5, and 30%, respectively for the PVMP, protamine, PSSA, and oxidized collodion membranes of lowest standard resistance shown in Figs. 2-5. In the cases of the PVMP and PSSA membranes with  $\rho^* = 330$  and 440 ohm-cm<sup>2</sup> respectively, the contribution of the noncritical ions to the conductances in 1.0 N solution is estimated to be about 2.5%; for the highest standard resistance membranes of each of the four types, this contribution is estimated to be about 5%.

In the three instances in which the corrections for diffusion layer effects and non-ideality of the membrane were particularly large, i.e.  $\varphi_{\text{exp.}}$  with the PVMP membrane  $\rho^* = 16$  ohm-cm<sup>2</sup> at  $c = 0.01$  N, and for  $\varphi_{\text{calc.}}$  in 1.0 N KCl for the same membrane and for the oxidized collodion membrane  $\rho^* = 403$  ohm-cm<sup>2</sup>, the estimated corrected rates of self-exchange are indicated in Figs. 2 and 5 by solid and open squares, respectively. It is apparent that with the PVMP membranes, the corrections are in the direction opposite to that which would be required to account for the large discrepancies between  $\varphi_{\text{calc.}}$  and  $\varphi_{\text{exp.}}$  observed with these membranes.

## DISCUSSION

Figs. 2-5 and Tables I and II show that reasonably satisfactory agreement between calculated and experimental self-exchange rates was obtained with the protamine, PSSA, and oxidized collodion membranes. In contrast to this, under most conditions the experimental rates of self-exchange of critical ions across PVMP membranes are much higher than those predicted from their electrical resistances. Specifically:

(a) The rates of self-exchange of critical ions across the *PVMP membranes*, over a wide range of conditions, are up to *five times higher* than those calculated from the electrical resistances. The discrepancies between  $\varphi_{\text{exp.}}$  and  $\varphi_{\text{calc.}}$  are greatest at low solution concentrations. They are essentially independent of the species of the critical and noncritical ions.

(b) The rates of self-exchange of critical ions across the *protamine membranes and the PSSA membranes* are *about 20% lower* than the rates calculated from the electrical resistances. This difference does not vary significantly with the solution concentration, the species of critical and noncritical ions, and the magnitude of the permeability of the membrane for critical ions.

(c) The rates of self-exchange across *oxidized collodion membranes* agree very closely with those calculated from the electrical resistances with all critical and noncritical ions, at all solution concentrations, and over the whole range of membrane permeabilities.

The observation that the rates of self-exchange across the *PSSA and protamine membranes* are about 15-25% smaller than those calculated from the electrical resistances, is in agreement with the findings of other workers who studied ion exchange resins (7-9) and ion exchange resin-type membranes (10-12). These investigators attribute this effect to electroosmosis, the bulk movement of solvent

in an applied electric field, which accompanies the unidirectional movement of the counterions of the fixed charges. According to this concept, the rate of movement of the counterions, when the electrical resistance is measured, is equal to their rate of movement relative to the water in the pores of the membrane *plus* the rate at which this pore water moves electroosmotically. The rate of movement of the counterions in the electric field is therefore greater than predicted from the Nernst-Einstein equation which refers to the movement of the counterions relative to the water only. An expression derived by Despic and Hills (8), on the basis of this concept, can be used to estimate the magnitude to be anticipated for the effect of electroosmosis:

$$\frac{\Delta\lambda}{\lambda} = \frac{m_1 M_E}{1000} \quad (6)$$

In this expression,  $\Delta\lambda/\lambda$  is the fractional increase in conductance of the counterions due to electroosmosis;  $m_1$  is the molar concentration of the counterions in the pore water in moles per liter; and  $M_E$  the volume of water in  $\text{cm}^3$ , transferred electroosmotically per farad.

Data on electroosmotic flow rates are available for PSSA membranes similar to those used in this study; with PSSA membranes of  $\rho^* = 420, 140$ , and  $25 \text{ ohm-cm}^2$ , the electroosmotic rates were respectively 57, 63, and  $207 \text{ cm}^3$  per faraday.<sup>3</sup> The counterion concentrations in these membranes are estimated to be respectively, 1.2, 1.6, and  $2.0 \text{ M}$  (15). Thus, electroosmotic increases in conductance of 7, 10, and 40% are predicted from Equation 6 for PSSA membranes similar to those used in the present work. The protamine membranes used have counterion concentrations and electroosmotic permeabilities similar to the PSSA membranes (20, 21), and the effect of electroosmosis on the conductance of these membranes may therefore be expected to be approximately as large as with the PSSA membranes. Thus the observed discrepancies between  $\varphi_{\text{calc.}}$  and  $\varphi_{\text{exp.}}$  for the PSSA and protamine membranes are of a magnitude which can be attributed to electroosmotic effects.

The closeness of the agreement of  $\varphi_{\text{calc.}}$  with  $\varphi_{\text{exp.}}$  in the case of the *oxidized collodion membranes* is rather unexpected. There is no obvious reason for the apparent absence of the effects of electroosmosis on  $\varphi_{\text{calc.}}$  with these membranes. A meaningful discussion of this problem would require experimental data on the ion exchange capacities of these membranes, and on electroosmosis across them. Such data presently are not available.

The degree of agreement between observed and calculated rates of self-exchange with the protamine, PSSA, and oxidized collodion membranes indicates that the movement of critical ions across these membranes is in satisfactory agreement with current concepts. It also provides convincing evidence that the anomalous results

<sup>3</sup> Wagner, J., and K. Sollner. Paper in preparation.

observed with the PVMP membranes do not stem from some unrecognized inadequacy in the experimental methods. Thus, the PVMP type membranes seemingly do not fulfill one or more of the assumptions made in the derivation of Equation 2 in Appendix I.

It seems most unlikely that the nonfulfillment of the conditions of an idealized pore geometry and of a uniform charge distribution could be responsible for complications with the PVMP membranes, without having a significant effect with the other three types of collodion matrix membranes. There is nothing in our knowledge of PVMP membranes to give any a priori reason to doubt the other explicit assumptions made in deriving Equation 2, i.e. that the movements of ions within the PVMP membranes by diffusion and in an electric field occur by essentially the same mechanism, and that the transition of critical ions across the membrane-solution interfaces is extremely rapid compared to their rate of movement across the body of the membrane.

The absence of ion pair formation between the fixed ionogenic groups and their counterions is another, implicit assumption in the derivation of Equation 2. However, since the formation of such ion pairs per se would be expected to affect the diffusion and the conductance of the ions to the same extent, additional, ad hoc, assumptions would have to be made to explain the observed behavior of the PVMP membranes on the basis of ion pair formation. The absence of differences among the various anions speaks against ion pair formation as a possible cause of the observed behavior of these membranes.

Since the methods of preparation of the PVMP and protamine membranes are the same, the conclusion can hardly be avoided that the peculiarity of the PVMP membranes is connected in some manner with the chemical difference between these two activating polyelectrolytes. The ionogenic groups of the polypeptide protamine are essentially the strongly basic guanidinium groups, while the ionogenic groups of PVMP, and of the other polyelectrolytes mentioned in footnote 2 are of the quaternary ammonium type. However, quaternary ammonium type ionogenic groups per se do not always give rise to anomalies of the type found with the PVMP membranes, since Andelman and Gregor (12), have found that Equation 2 adequately describes the relationship between the rate of self-exchange and electrical resistance across an ion exchange resin type membrane which had quaternary ammonium ionogenic groups. It therefore appears that the peculiar behavior of the PVMP-type collodion matrix membrane stems neither solely from the chemical nature of the fixed charge groups nor solely from some specific property of the membrane matrix, but from a combination of these factors.

The observation that the chemical nature of the critical ions does not affect the extent of the anomalous behavior, though unexpected and undoubtedly significant, does not provide, for the present, any insight into the cause of the anomalous properties of the PVMP-type membranes.

In any attempt to clarify the observations reported in this paper, it is of primary importance to determine the site of the processes which give rise to the peculiar behavior of the PVMP-type membranes, that is, whether these processes occur within the bulk of the membrane or at the membrane-solution interfaces. Measurements in which the influence of processes occurring at the membrane-solution interfaces have been eliminated will be reported on in a future paper.<sup>3</sup>

The literature, as far as we know, does not contain any reference to analogous discrepancies between the rates of diffusional and electrical movement of ions in any comparable physicochemical system. It is entirely possible that the disparate behavior of the PVMP-type membranes has its origins in molecular processes which have not been previously recognized as affecting the movement of ions across membranes. The only instances of large deviations from the predictions of the Nernst-Einstein equation, in the same direction as found with the PVMP-type membranes, occur in systems of an entirely different nature, certain fused salts and ionic crystals in which the diffusion of lattice vacancies is believed to be the underlying mechanism (22).<sup>4</sup> In terms of recently developed concepts in the irreversible thermodynamics of membrane processes, the anomaly observed with the PVMP membranes might be classified as a case of "negative isotope interaction" (23). We hope to carry out in the near future an experimental study of this aspect of the behavior of these membranes.

Before the molecular causes of the anomalous behavior of the PVMP-type membranes can be meaningfully speculated upon, additional descriptive information must be gathered on such factors as the influence of temperature, the nature of the substituent groups of the polyelectrolyte, the chemical nature of the membrane matrix, etc. Work in this direction is in progress.

## APPENDIX I

The theoretical relationship between the rates of self-exchange of critical ions across a membrane and the electrical resistance of the latter, on the basis of the Nernst-Einstein equation is derived here for the case of univalent critical ions and membranes of ideal ionic selectivity.<sup>5</sup> As is commonly done in dealing with complex structures, this relationship will be de-

<sup>4</sup> With some silicate glasses, deviations from the Nernst-Einstein equation have been observed which are in the direction opposite to that found with the PVMP-type membranes. These effects have been ascribed to lattice vacancies; it has been postulated that the kinetic jumps of diffusing ions are not completely random in direction, but occur preferentially in a direction which is "correlated" with the direction of their preceding jumps (24).

<sup>5</sup> The restriction of this derivation to membranes of ideal ionic selectivity does not imply a restriction to membranes which are completely free of nonexchange electrolyte, i.e. cations and anions present in the membrane in equivalent amounts as a result of equilibration with the ambient solution. In real membranes, in which geometry and electrochemical properties of a pore vary along its length, the ionic selectivity of the pore as a whole would be determined by that portion of the pore which has the highest degree of ionic selectivity. To a large extent this selectivity would be independent of the quantity of nonexchange electrolyte in other regions of the pore. The presence of nonexchange electrolyte in a membrane does not affect our considerations, since the critical ions of the nonexchange electrolyte would contribute to both the conductance and the diffusion of this ionic species across the membrane in the same manner as those critical ions which are counterions of the fixed charges.

rived for an idealized system. The membrane is assumed to be structurally uniform, to have parallel pores which are perpendicular to the surface of the membrane, and to have a uniform distribution of fixed charge groups.

The basic assumption in the subsequent treatment is that the movement of ions across the *body of the membrane* is the rate determining step both in diffusion and in electromigration. Implicit in this is the assumption that the transition of ions between the solution layer adjacent to the membrane and the surface of the membrane, and vice versa, occurs at a rate which is very high compared to the rate at which ions move across the body of the membrane. Factors which might negate this assumption could be, for example, changes in the state of solvation of the ions, or the formation of specific complexes by the ions on their transition between the solution and membrane. A corollary of the above assumption is that equilibrium is maintained at all times in the distribution of ions between the surfaces of the membrane and the immediately adjacent layers of the solutions.

It is also assumed that a uniform composition of the solutions is maintained up to the surface of the membranes, i.e. that the effects of unstirred diffusion layers are absent in the case of the self-exchange measurements (see Experimental Results), and that concentration polarization is avoided in the measurement of the electrical resistances.

In order to apply the Nernst-Einstein equation, it is necessary to express the rate of self-exchange and the electrical resistance in terms of the diffusion coefficient, and the equivalent conductance, respectively, of critical ions with the membranes. The following symbols will be used:

- $A$  cross-sectional area of the membrane in  $\text{cm}^2$
- $c$  concentration of critical ions in equivalents/liter
- $D$  diffusion coefficient of the critical ion in  $\text{cm}^2 \text{sec}^{-1}$
- $l$  thickness of the membrane in  $\text{cm}$
- $n$  quantity of critical ions in equivalents
- $t$  time in  $\text{sec}$
- $t$  time in  $\text{hr}$
- $x$  distance measured across the membrane, with  $x = 0$  at the labeled solution/membrane interface and  $x = l$  at the ether membrane/solution interface
- $\lambda$  the equivalent conductance of the critical ions
- $\rho$  the resistance of the membrane in ohms
- $\rho_{\text{sp.}}$  the specific resistance of the membrane in  $\text{ohm-cm.}$
- $\Phi$  rate of self-exchange of ions in  $\text{eq sec}^{-1}$
- $\varphi$  rate of self-exchange of ions in  $\mu\text{eq hr}^{-1}$

The subscript,  $s$ , refers to a quantity in the solution phase.

The subscript,  $m$ , refers to a quantity within the pores of the membrane.

The superscript,  $'$ , denotes either the labeled solution, or the membrane at the membrane/labeled solution interface.

The superscript,  $''$ , denotes either the unlabeled solution, or the membrane at the membrane/unlabeled solution interface.

The superscript,  $*$ , refers to the radiotracer species of critical ions.

To obtain the *electrical resistance of the membrane in terms of the equivalent conductance of the critical ion species within the membrane*, the relationship between the specific resistance of a membrane and the equivalent conductance of the ions in it is first written in a manner analogous to that used in describing electrical resistance in free solution:

$$\rho_{\text{sp.}} = \frac{1000}{\lambda_m c_m} \quad (\text{A.1})$$

The actual resistance,  $\rho$ , of a membrane of area  $A$  and thickness  $l$  is related to its specific resistance by:

$$\rho = \rho_{sp} \cdot \frac{l}{A}. \quad (\text{A.2})$$

Therefore

$$\lambda_m = \frac{1000l}{\rho c_m A}. \quad (\text{A.3})$$

The most convenient means of expressing *the rate of self-exchange of critical ions in terms of the diffusion coefficient of this species of ions within the membrane* is to treat the situation in which all critical ions in the solution on one side of the membrane are radiotracer ions, and all critical ions in the solution on the other side are nonradioactive species. Under these conditions, all of the exchange sites at the membrane/solution' interface are occupied by radioactive critical ions, and all exchange sites at the membrane/solution'' interface by nonradioactive critical ions, i.e.

$$c_m^{\star'} = c_m \quad \text{and} \quad c_m^{\star''} = 0.$$

The measured rate of exchange of radiotracer for nonradiotracer ions, after steady-state conditions have been established, is equal to the total rate of self-exchange of critical ions across the membrane. It is assumed that this rate of exchange can be measured without a significant depletion of radiotracer in the initially labeled solution and without a significant buildup in radiotracer in the solution which is initially tracer-free.

The rate of self-exchange, in the steady state,  $\Phi$ , is equal to the number of radiotracer ions leaving solution' and appearing in solution'' per unit time:

$$\Phi = \frac{-dn_s^{\star'}}{dt} = \frac{dn_s^{\star''}}{dt}. \quad (\text{A.4})$$

Under steady-state conditions, the rate at which radiotracer ions move across each cross-section of the membrane is also equal to  $\Phi$ . Therefore, applying Fick's first law to the diffusion of radiotracer ions within the membrane:

$$\Phi = \frac{D_m^{\star} A}{1000} \frac{dc_m^{\star}}{dx}. \quad (\text{A.5})$$

The factor 1000 is required because  $c$  is expressed in the dimensions of moles per liter instead of in moles/cm<sup>3</sup>, as necessitated by the dimensions of the other quantities in Equation A.5. Since we have assumed a steady-state situation, the concentration gradient of the tracer ions across the membrane is constant. Therefore,

$$\frac{dc_m^{\star}}{dx} = \frac{c_m^{\star'} - c_m^{\star''}}{l}. \quad (\text{A.6})$$

Since  $c_m^{\star'} = c_m$  and  $c_m^{\star''} = 0$ ,

$$\frac{dc_m^{\star}}{dx} = \frac{c_m}{l}. \quad (\text{A.7})$$



Combining Equations A.5 and A.7, it follows that:

$$D_m^* = \frac{1000\Phi l}{Ac_m}. \quad (\text{A.8})$$

Since the properties of tracer and nontracer species are identical,  $D_m^* = D_m$  and:

$$D_m = \frac{1000\Phi l}{Ac_m}. \quad (\text{A.9})$$

By comparing Equation A.3 with A.9, it can be seen that *the relationship between the experimental quantities of interest,  $\Phi$  and  $1/\rho$ , is the same as that between  $D_m$  and  $\lambda_m$* . Combining these equations, the relationship:

$$\frac{\Phi}{D_m} = \frac{1}{\rho\lambda_m} \quad (\text{A.10})$$

is obtained.

Since the Nernst-Einstein equation is assumed to apply to the critical ions within the membrane:

$$D_m = \frac{RT}{F^2} \lambda_m. \quad (\text{A.11})$$

Combination of Equation A.10 with Equation A.11 gives the relationship between the rate of self-exchange and the electrical resistance:

$$\Phi = \frac{RT}{F^2\rho}. \quad (\text{A.12})$$

Thus the relationship between the two quantities is independent of all parameters of the membrane, i.e. the area, thickness, ion exchange capacity, and of all parameters referring to the mobilities of the ions.

At  $T = 298^\circ\text{K}$ , and with  $R = 8.31 \text{ joules } ^\circ\text{K}^{-1} \text{ mole}^{-1}$ , and  $F = 96,500 \text{ coul mole}^{-1}$ :

$$\Phi = \frac{2.66}{\rho} \times 10^{-7} \text{ equivalents per second}, \quad (\text{A.13})$$

or in the more convenient units used in the body of the paper:

$$\varphi = \frac{958}{\rho} \text{ microequivalents per hr.} \quad (\text{A.13 a})$$

## APPENDIX II

This appendix treats the computation of the rate of self-exchange from the experimental data in those instances in which the decreasing difference between the concentrations of radiotracer in the inner and in the outer solutions leads to a decrease in the rate at which radiotracer crosses the membrane. Otherwise, the same general assumptions will be made as in Appendix I: the membrane is structurally uniform with parallel pores which are perpendicular to the surface of the membrane; the distribution of fixed charge groups in the

pores is uniform; distribution equilibrium of radiotracer ions between the membrane surfaces and the adjacent solutions is established instantaneously; no concentration gradients exist within the solutions; the initial quasi-steady-state concentration gradients across the membrane have been established. The symbols used are the same as defined in Appendix I.

Since the properties of the radioactive and nonradioactive critical ions are taken as identical, the following equilibria exist at the two membrane/solution interfaces:

$$\frac{c_m^{\star'}}{c_m} = \frac{c_s^{\star'}}{c_s} \quad \text{and} \quad \frac{c_m^{\star''}}{c_m} = \frac{c_s^{\star''}}{c_s}. \quad (\text{A.14})$$

In the quasi-steady state, the concentration gradient of the radiotracer within the membrane is linear at all times. Applying Fick's first law we obtain:

$$\frac{dn_s^{\star''}}{dt} = \frac{AD_m(c_m^{\star'} - c_m^{\star''})}{1000l}. \quad (\text{A.15})$$

Substituting the values of  $c_m^{\star'}$  and  $c_m^{\star''}$  from Equation A.14 into A.15 gives:

$$\frac{dn_s^{\star''}}{dt} = \frac{AD_m c_m}{1000l c_s} [c_s^{\star'} - c_s^{\star''}]. \quad (\text{A.16})$$

According to Equation A.9 of Appendix I, the rate of self-exchange in terms of the parameters of the membrane is:

$$\Phi = \frac{AD_m c_m}{1000l}. \quad (\text{A.9})$$

Therefore Equation A.16 can be written as:

$$\frac{dn_s^{\star''}}{dt} = \frac{\Phi}{c_s} [c_s^{\star'} - c_s^{\star''}]. \quad (\text{A.17})$$

Since  $c_s^{\star'} = n_s^{\star'}/V'$  and  $c_s^{\star''} = n_s^{\star''}/V''$ , Equation A.17 can be written:

$$\frac{dn_s^{\star''}}{dt} = \frac{\Phi}{c_s} \left[ \frac{n_s^{\star'}}{V'} - \frac{n_s^{\star''}}{V''} \right]. \quad (\text{A.18})$$

The quantity  $n_s^{\star'}$  can be expressed in terms of  $n_s^{\star''}$  and of the total quantity of radiotracer in the system,  $N$ . The latter is constant and is equal to the quantity of radiotracer in the two solutions plus that in the membrane, i.e.

$$N = n_s^{\star'} + n_s^{\star''} + \frac{V_m(c_m^{\star'} + c_m^{\star''})}{2}, \quad (\text{A.19})$$

where  $V_m$  is the volume of the pore system of the membrane. Using Equation A.14, the quantity of radiotracer within the pores of the membrane can be written in terms of the concentrations of radiotracer in the two solutions:

$$\frac{V_m(c_m^{\star'} + c_m^{\star''})}{2} = \frac{V_m c_m (c_s^{\star'} + c_s^{\star''})}{2c_s} \quad (\text{A.20})$$

and in terms of absolute quantities of ions, as:

$$\frac{V_m c_m (c_s^{\star'} + c_s^{\star''})}{2c_s} = \frac{V_m c_m}{2c_s} \left[ \frac{n_s^{\star'}}{V'} + \frac{n_s^{\star''}}{V''} \right]. \quad (\text{A.21})$$

Accordingly, the total quantity of radiotracer in the system, as expressed in Equation A.19 is:

$$N = n_s^{\star'} + n_s^{\star''} + \frac{V_m c_m}{2c_s} \left[ \frac{n_s^{\star'}}{V'} + \frac{n_s^{\star''}}{V''} \right]. \quad (\text{A.22})$$

Denoting, for convenience, the term  $V_m c_m / 2c_s$  as  $B$ , Equation A.22 can readily be solved for  $n_s^{\star'}$ :

$$n_s^{\star'} = \frac{N - n_s^{\star''} \left( 1 + \frac{B}{V''} \right)}{\left( 1 + \frac{B}{V'} \right)}. \quad (\text{A.23})$$

By substituting the expression for  $n_s^{\star'}$  from Equation A.23 into Equation A.18, the expression:

$$\frac{dn_s^{\star''}}{dt} = \frac{\Phi}{c_s} \left[ \frac{N - n_s^{\star''} \left( 1 + \frac{B}{V''} \right)}{V' \left( 1 + \frac{B}{V'} \right)} - \frac{n_s^{\star''}}{V''} \right] \quad (\text{A.24})$$

is obtained. This expression can be rearranged so that the variables are grouped, i.e.

$$\Phi \frac{dt}{c_s} = \frac{dn_s^{\star''}}{\frac{N}{V' + B} - n_s^{\star''} \left[ \frac{V'' + B}{V''(V' + B)} + \frac{1}{V''} \right]}. \quad (\text{A.25})$$

Integration of Equation A.25 gives  $n_s^{\star'}$  as a function of time:

$$\frac{\Phi t}{c_s} = - \frac{1}{\frac{V'' + B}{V''(V' + B)} + \frac{1}{V''}} \ln \left[ \frac{N}{V' + B} - n_s^{\star''} \left( \frac{V'' + B}{V''(V' + B)} + \frac{1}{V''} \right) \right] + I, \quad (\text{A.26})$$

where  $I$  is the integrating constant.

At the start of the self-exchange measurement,  $t = 0$  and  $n_s^{\star''} = 0$ . Accordingly:

$$I = \frac{1}{\frac{V'' + B}{V''(V' + B)} + \frac{1}{V''}} \ln \left[ \frac{N}{V' + B} \right]. \quad (\text{A.27})$$

Substitution of this expression for  $I$  into Equation A.26 gives:

$$\frac{\Phi t}{c_s} = - \frac{1}{\frac{V'' + B}{V''(V' + B)} + \frac{1}{V''}} \ln \left[ \frac{\frac{N}{V' + B} - n_s^{\star''} \left( \frac{V'' + B}{V''(V' + B)} + \frac{1}{V''} \right)}{\frac{N}{V' + B}} \right]. \quad (\text{A.28})$$

A more convenient form of this equation is obtained as a result of some algebraic manipulation:

$$\Phi = -\frac{2.3c_s V''(V' + B)}{t(V'' + V' + 2B)} \log \left[ 1 - \frac{n_s^{*''}}{N} \left( \frac{V'' + V' + 2B}{V''} \right) \right]. \quad (\text{A.29})$$

Equation A.29 is the general expression for calculating the rate of self-exchange  $\Phi$ , from the fraction of the total quantity of radiotracer critical ions  $n_s^{*''}/N$ , which has crossed a fixed charge membrane in the time  $t$ .

If the ion exchange capacity of the membrane is neglected, that is setting  $B = 0$  and  $N = n_s^{*'} + n_s^{*''}$ , Equation A.29 gives:

$$\Phi = \frac{-2.3c_s V''V'}{t(V'' + V')} \log \left[ 1 - \frac{n_s^{*''}}{(n_s^{*'} + n_s^{*''})} \left( \frac{V'' + V'}{V''} \right) \right] \quad (\text{A.30})$$

in units of equivalents  $\text{sec}^{-1}$ . (For a membrane with an area of  $50 \text{ cm}^2$ , the self-exchange rate  $\phi$ , expressed in units of  $\mu\text{eq hr}^{-1} \text{ cm}^{-2}$ , is given in the text as Equation 4.) The error which arises by neglecting the ion exchange capacity of the membrane can be ascertained by calculating the self-exchange rate for a given set of conditions by both Equations A.29 and A.30. The value of  $N$  in Equation A.29 for a given system is obtained, using Equation A.22, from the experimental magnitudes  $n_s^{*'}$ ,  $n_s^{*''}$ , and the exchange capacity of the membrane. For that case in the present work in which the error due to the use of Equation A.30 would be the largest, i.e. with the most dilute solution ( $0.010 \text{ N}$ ), with the membrane with the highest exchange capacity (about  $50 \mu\text{mole}$ ), and with a 25% exchange of the radiotracer originally present in the inner solution, this error is calculated to be less than 1%.

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