

# THE RATES OF INTEREXCHANGE OF IONS ACROSS FIXED CHARGE MEMBRANES IN BI-IONIC SYSTEMS

MELVIN H. GOTTLIEB

*From the Laboratory of Physical Biology, National Institute of Arthritis and Metabolic Diseases, National Institutes of Health, Bethesda, Maryland 20014*

**ABSTRACT** This paper examines the applicability of the Nernst-Planck approach in treating the relationship between the initial rates at which critical ions interexchange across permselective membranes in bi-ionic systems and the rates of self-exchange of these ions across the same membranes. Data are presented for five species of univalent cations with two types of cation permeable membranes, a polystyrene sulfonic acid-collodion matrix membrane, and an oxidized collodion membrane; five species of univalent anions were studied with a protamine-collodion matrix anion permeable membrane. Except with systems involving  $H^+$  ion, the experimentally found relationships between the rates of interexchange and the rates of self-exchange were in agreement, in most cases within  $\pm 5\%$ , with the values calculated from an expression in which interaction between the critical ions in the membrane is not taken into account. In systems with  $H^+$  ion, the experimental rates of interexchange were from 27% to 40% less than calculated values.

## INTRODUCTION

Systems in which permselective<sup>1</sup> fixed charge membranes separate solutions of two electrolytes at the same concentration, which have different critical ions are termed *bi-ionic* membrane systems (2). For a membrane that is only permeable to cations,  $|\leftarrow\oplus\rightarrow|$ , a bi-ionic system may be illustrated by (a):



Because of the relative simplicity of bi-ionic systems, the electrical potential differ-

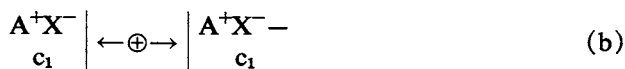
<sup>1</sup> The terminology of Sollner (1) will be used in this paper. *Permselective* membranes are fixed charge membranes which have a high degree of selectivity for those species of ions, termed *critical ions*, whose sign is the same as that of the counter-ions to the fixed charge groups of the membrane. In the limiting, ideal case, such membranes are completely impermeable to the *noncritical ions*, i.e., ions of the same sign as the fixed charge groups.

ence between the solutions, the *bi-ionic potential*, has been the subject of a number of studies (2-8). This potential difference has been shown to result from the ion-exchange specificity of the membrane with respect to the two species of critical ions, and from differences in the mobilities of these ions in the membrane.

Bi-ionic systems spontaneously degrade as a result of the nonequilibrium distribution of the critical ions between the two solutions. With the system illustrated in (a), for example, equivalent quantities of  $A^+$  and  $B^+$  interexchange across the membrane until the ratio of their concentrations (more properly of their activities) is the same in the two solutions (9). The rates of this interexchange of ions in bi-ionic systems have received little attention. The purpose of the present paper is to examine the adequacy of the classical Nernst-Planck approach, which is used to treat electrolyte diffusion in free solution (10), in relating the rates of interexchange of critical ions across membranes in bi-ionic systems to other functional properties of the membranes.

Apparently the only previous work on this topic is that of Helfferich and Ocker (11) whose comprehensive theoretical treatment took into account the effects of interaction between the two species of interexchanging critical ions within the membrane. These authors obtained an expression relating the rate of interexchange to a number of independently measurable quantities, including the concentration of fixed charge groups, the diffusion coefficients of the critical ions within the membrane, and the dependence of the diffusion coefficients and activity coefficients of these ions on the relative amounts of the two species of critical ions present in the membrane. Good agreement was reported between calculated and experimental rates in the systems studied, the interexchange of  $Na^+$  for each of three other cationic species across an ion-exchange resin type membrane.

It was considered desirable to include several types of membranes in the present study and to examine each membrane with a number of species of critical ions. Accordingly, an approach was adopted which, although less rigorous than that used by Helfferich and Ocker, requires fewer experimental quantities in the examination of the applicability of the Nernst-Planck treatment to the interexchange of ions in bi-ionic systems. In this approach the only experimentally determined quantities are the rates of interexchange of the critical ions across a membrane in a bi-ionic system such as illustrated previously in (a), and the rates of self-exchange of the two species of critical ions across the same membrane; these latter rates are measurable with radioisotopes in the systems (b) and (c):



and



where the solution concentrations, the species of noncritical ions, and the temperature are the same as in the bi-ionic system (a). As will be shown in the next section, a simple relationship between these quantities is predicted by the Nernst-Planck approach when interaction between the critical ions within the membrane can be neglected and certain other idealized conditions prevail. This predicted relationship is:

$$J^{AB} = \frac{J^{AA} J^{BB}}{J^{AA} - J^{BB}} \ln \frac{J^{AA}}{J^{BB}}, \quad (1)$$

where  $J^{AB}$  is the rate of interexchange of ion A for ion B across a membrane in a bi-ionic system, and  $J^{AA}$  and  $J^{BB}$  are the rates of self-exchange of ion A and of ion B across the same membrane. This expression can be also obtained as a limiting case of the equation used by Helfferich and Ocker (11).

Five species of univalent cations with two types of cation permeable collodion membranes, a polystyrene sulfonic acid (PSSA)-collodion matrix membrane (12) and an oxidized collodion membrane (13), and five species of univalent anions with a protamine-collodion matrix anion permeable membrane (14) are included in this study.

#### RELATIONSHIP BETWEEN RATES OF SELF-EXCHANGE AND RATES OF INTEREXCHANGE OF IONS IN AN IDEALIZED SYSTEM

Our considerations are limited to the initial steady-state rates of exchange of ions. These rates are assumed to be exclusively controlled by the rates of ionic movement within the body of the membrane. It is therefore assumed that equilibrium is rapidly established in the distribution of ions between the surface of the membrane and the immediately adjacent layer of solution, and that there are no complications due to unstirred diffusion layers (15).

As mentioned, it will be assumed that interaction between the interexchanging critical ions within the membrane can be neglected. Accordingly, the mobilities and activity coefficients of these ions are assumed to be independent of the relative quantities of the two species of critical ions in their vicinity. It will also be assumed that no movement of water between the solutions accompanies the interexchange of critical ions.

The membrane will be assumed to be completely impermeable to noncritical ions and to be free of nonexchange electrolyte. Its ionogenic groups are assumed to be completely dissociated and uniformly distributed through the membrane. As is usually done, the pores are considered to be of uniform cross section and to run only in the direction perpendicular to the plane of the membrane.

The derivation of the theoretical relationship between the rates of self-exchange and rates of interexchange will be given for the case of univalent cations; the same

relationship will obviously also apply to the exchange of univalent anions. It is also applicable to the interexchange of ionic species of the same valence higher than one. For the interexchange of critical ions which do not have the same valences refer to the paper of Helfferich and Ocker (11).

The following symbols will be used:

- A*        The area of the membrane.
  - c*        The concentration of counterions in the pores of the membrane, superscript denoting the species of counterions.
  - c*        The concentration of fixed charge groups in the pores of the membrane.
  - $dE/dx$    The electrical potential gradient at any point within the membrane.
  - f*        The activity coefficient of an ion in the membrane, a superscript indicating the species.
  - F*        The faraday.
  - J*        The rate of movement of ions across the membrane, the superscript indicating the species of ions involved. For example,  $J^A$  refers to the movement of ions of species A,  $J^{AA}$  refers to the isotopically measurable rate of self-exchange of A ions across the membrane, and  $J^{AB}$  refers to the rate of interexchange of A and B ions.
  - l*        The thickness of the membrane.
  - R*        The gas constant.
  - T*        The absolute temperature.
  - u*        The mobility of an ion within the pores of the membrane, a superscript indicating the species of ions.
  - x*        Distance within the membrane, with  $x = 0$  at the membrane/solution containing  $A+X^-$  interface, and  $x = l$  at the membrane/solution containing  $B+X^-$  interface.
  - \*
- An asterisk is used to indicate a radioactive species of ion.

Under the conditions in which the rates of interexchange of ions are considered, essentially all of the counterions of the fixed charge groups at each membrane surface are of the single critical ion species present in the adjacent solution. Therefore:

$$c_{x=0}^A = c, \quad c_{x=l}^A = 0 \quad (A1)$$

and

$$c_{x=0}^B = 0, \quad c_{x=l}^B = c.$$

Following the Nernst-Planck approach (10) at every point within the membrane, ions of each species move at a rate determined by their mobility, the gradient in their concentration, and the electrical potential gradient. For example, for species A:

$$J^A = -Au^A \left( RTc^A \frac{d \ln f^A c^A}{dx} + Fc^A \frac{dE}{dx} \right). \quad (A2)$$

Since interaction between the two species of critical ions within the membrane is neglected, and the concentration of counterions is assumed uniform throughout the membrane, the activity coefficients of the ions are constant, i.e.:

$$\frac{d \ln f^A}{dx} = 0. \quad (\text{A3})$$

Therefore, equation A2 can be written:

$$J^A = -Au^A \left( RT \frac{dc^A}{dx} + Fc^A \frac{dE}{dx} \right). \quad (\text{A4})$$

Similarly, the rate of movement of B ions within the membrane at any point is given by:

$$J^B = -Au^B \left( RT \frac{dc^B}{dx} + Fc^B \frac{dE}{dx} \right). \quad (\text{A4a})$$

Since electroneutrality must be maintained, the number of A ions diffusing per unit time across a given area must be equal to the number of B ions diffusing per unit time across that area in the opposite direction. Thus:

$$J^A = -J^B = J^{AB}. \quad (\text{A5})$$

Equating  $J^A$  and  $-J^B$  in equations A4 and A4a we obtain:

$$-u^A RT \frac{dc^A}{dx} - Fc^A u^A \frac{dE}{dx} = u^B RT \frac{dc^B}{dx} + Fc^B u^B \frac{dE}{dx}. \quad (\text{A6})$$

Since the membrane is assumed to be free of nonexchange electrolyte, the sum of the concentrations of the two species of interexchanging ions at each point within the membrane is equal to the concentration of fixed charge groups. Accordingly,

$$c^A + c^B = c \quad (\text{A7})$$

at every point within the membrane, and therefore:

$$\frac{dc^A}{dx} = -\frac{dc^B}{dx} \quad (\text{A8})$$

at every point within the membrane.

Substituting equation A8 into equation A6 we arrive at the expression:

$$-u^A RT \frac{dc^A}{dx} - Fc^A u^A \frac{dE}{dx} = -u^B RT \frac{dc^A}{dx} + Fc^B u^B \frac{dE}{dx}. \quad (\text{A9})$$

Equation A9 can be readily rearranged to solve for  $dE/dx$ , the electrical potential gradient within the membrane:<sup>2</sup>

$$\frac{dE}{dx} = -\frac{RT}{F} \frac{(u^A - u^B)}{(c^A u^A + c^B u^B)} \frac{dc^A}{dx}. \quad (\text{A9a})$$

The expression for the rate of interexchange of ions across the membrane is then obtained by substituting the expression for  $dE/dx$  from equation A9a into equation A4:

$$J^{AB} = -u^A A \left[ RT \frac{dc^A}{dx} - RT c^A \frac{dc^A}{dx} \frac{(u^A - u^B)}{(u^A c^A + u^B c^B)} \right]. \quad (\text{A10})$$

By use of equation A7 and some rearrangement of terms, the more convenient expression:

$$J^{AB} = \frac{RT u^A u^B A c}{u^B c + (u^A - u^B) c^A} \frac{dc^A}{dx} \quad (\text{A11})$$

is obtained. In the steady state,  $J^{AB}$  is constant for all points within the membrane. Therefore equation A11 can be integrated in the following manner:

$$J^{AB} \int_{x=0}^{x=l} dx = -RT u^A u^B A c \int_{x=0}^{x=l} \frac{dc^A}{u^B c + (u^A - u^B) c^A}. \quad (\text{A12})$$

This gives

$$[J^{AB} x]_{x=0}^{x=l} = \frac{RT u^A u^B A c}{(u^B - u^A)} [\ln [u^B c + (u^A - u^B) c^A]]_{x=0}^{x=l}. \quad (\text{A13})$$

Substitution of the boundary conditions indicated in equation A1 into equation A13 leads to an expression for the rate of interexchange in terms of the mobilities of the respective critical ions and the total concentration of critical ions:

$$J^{AB} = \frac{RT c A u^A u^B}{l(u^A - u^B)} \ln \frac{u^A}{u^B}. \quad (\text{A14})$$

The parameters  $c$ ,  $A$ ,  $l$ ,  $u^A$ , and  $u^B$  of equation A14 will now be expressed in terms of the *rates of self-exchange* of the two species of critical ions. This can be most readily done by treating the self-exchange of ions as a case of interexchange of a

<sup>2</sup> The integral of this potential gradient across the membrane is not equal to the *bi-ionic potential*. The bi-ionic potential includes the phase boundary potentials at the two membrane-solution interfaces, in addition to the intramembrane diffusion potential referred to in equation A9a. It is a corollary of the treatment presented here that these phase boundary potentials do not play a role in determining the rates at which ions interexchange across the membrane.

critical ion A, for another species of critical ion which has the same mobility as A, its radioisotope A\*. Equation A14 gives:

$$J^{AA^*} = \frac{RTcAu^A u^{A^*}}{l(u^A - u^{A^*})} \ln \frac{u^A}{u^{A^*}}. \quad (\text{A15})$$

Since  $u^A = u^{A^*}$ ,

$$\frac{\ln (u^A/u^{A^*})}{u^A - u^{A^*}} = \frac{(u^A/u^{A^*}) - 1}{u^A - u^{A^*}} = \frac{1}{u^{A^*}}, \quad (\text{A16})$$

and

$$J^{AA^*} = J^{AA} = \frac{RTcAu^A}{l}. \quad (\text{A17})$$

Similarly, the rate of self-exchange of critical ions of species B is given by:

$$J^{BB} = \frac{RTcBu^B}{l}. \quad (\text{A18})$$

Combining equations A17 and A18 with equation A14 gives the expression indicated by equation 1 for the rate of interexchange of ion A for ion B in terms of the two self-exchange rates:

$$J^{AB} = \frac{J^{AA} J^{BB}}{J^{AA} - J^{BB}} \ln \frac{J^{AA}}{J^{BB}}. \quad (\text{A19})$$

## EXPERIMENTAL

The choices of the particular membranes to be used in this study, and the concentration of the solutions, were made on the basis of attempting to simultaneously fulfill two of the assumptions made in the previous section, i.e. the complete impermeability of the membrane to noncritical ions, and the complete absence of effects due to unstirred Nernst layers. These conditions can be essentially achieved by using permselective collodion matrix membranes (12-14) selected to have electrical resistances (as measured in 0.1 N KCl) of the order of 100-500 ohms-cm<sup>2</sup>, in combination with solutions with concentrations of 0.10 N. The selectivities of such membranes for critical ions over noncritical ions in 0.10 N solutions are at least several hundred to one (12-14); the reduction in the rates of ion movement across such membranes by diffusion layers would be expected to be less than 1 % in 0.10 N solution, as discussed in a previous paper (16).

The noncritical ion species was Cl<sup>-</sup> in the experiments with the cation permeable membranes and K<sup>+</sup> in the experiments with the anion permeable membrane.

All measurements were made at 25.0 ± 0.1°C.

## MATERIALS

### *Membranes*

The details of the preparation and the properties of the various types of membranes used have been described (12–14). The cation permeable membranes were prepared by: (a) casting from a collodion solution containing polystyrenesulfonic acid (PSSA) (12) and (b) by the controlled oxidation of a preformed collodion membrane (13). The anion permeable membrane was prepared by the adsorption of protamine on preformed, highly porous collodion membranes (14). These membranes were test tube shaped, about 24 mm in diameter, 95 mm long, and 30  $\mu$  thick; when mounted on supporting glass rings their effective areas were about 50 cm<sup>2</sup>.<sup>3</sup> The membranes were characterized by previously described methods (12–14) (a) for their standard electrical resistance (that measured in 0.10 N KCl), and (b) for the potentials in concentration cells (0.20 N KCl | membrane | 0.10 N KCl) as an indication of their ionic selectivity. These potentials, corrected for asymmetry of the liquid junction potentials, were in all instances higher than 15.5 mv, the theoretical maximum potentials being 16.1 mv. The standard resistance of the PSSA membrane used was 350 ohm-cm<sup>2</sup>, that of the oxidized collodion membrane 400 ohm-cm<sup>2</sup>, and that of the protamine collodion membrane 120 ohm-cm<sup>2</sup>.

### *Radioisotopes*

The sources of supply and the treatment of the various radioactive materials were as indicated in a previous paper (16).

## METHODS

### *Rates of Interexchange of Critical Ions*

The *initial* rate of interexchange of ions in a bi-ionic system can best be obtained from measurements made during initial exchange periods in which the system has undergone little degradation. The degradation of bi-ionic exchange systems, unlike that of self-exchange systems, leads to the presence of two species of critical ions in each of the solutions separated by the membrane. Since ion-exchange membranes in general exhibit a specificity in the uptake of critical ions from a mixture, a knowledge of the specificity coefficient and of its possible variation with the relative quantities of the two critical ion species present in the solutions would be necessary to take the influence of degradation of the system into account. Rates of interexchange of ions were therefore obtained from measurements made with less than 3% of the ions present in the smaller (see below) of the two solution compartments having crossed the membranes. Under these conditions, the relationship between the quantities of ions having exchanged across the membrane and time was linear in all instances.

For the most part, radiotracers were used to provide a convenient analytical method for the determination of a small quantity of one of the critical ion species in the presence of a high concentration of the other species. In the single case in which no radiotracer was available for either of the interexchanging ions, the case of H<sup>+</sup>-Li<sup>+</sup> exchange across the PSSA membrane, H<sup>+</sup> was determined by titration with KOH.

The procedure for measuring the rates of interexchange was as follows. The test tube—

<sup>3</sup> It is not necessary for the present purposes to know the exact areas of the membranes since our concern is with the relationship between various rates of ion movement across the same membrane.



shaped membrane was first filled with 30 ml of a nonradioactive, "inner" solution of the same composition as that to be used in the experiment. It was then mounted in a 400 ml beaker which contained 350 ml of solution of the appropriate "outer" solution. After about an hour, the inner solution was replaced by a solution labeled with about 100  $\mu\text{c}$  of a radioisotope of the critical ion species; the outer solution was also replaced by fresh solution. The system was allowed to stand for another  $\frac{1}{2}$  hr, both solutions being stirred. After replacing the inner and outer solutions once more, the experiment proper was started. An aliquot of 1.00 ml of the outer solution was immediately withdrawn, at  $t = 0$ . At appropriate intervals additional aliquots were taken. The inner solution was sampled at the end of the experiment. The rate of interexchange of the critical ions was calculated by multiplying the fraction of the radioactivity of the inner solution crossing the membrane per unit time by the total quantity of electrolyte in that solution. The experimental error in the measurement of the rate of interexchange of ions across the membrane is estimated at  $\pm 2\%$ .

### *Rates of Self-Exchange*

In most cases, the rates of self-exchange of critical ions across the membranes were determined, as described previously in detail (16), in a manner analogous to that used to determine the rates of interexchange of critical ions in the bi-ionic systems.

Since radioactively labeled species are not available in the case of  $\text{Li}^+$  and  $\text{NO}_2^-$  ions, and the use of tritium as a tracer for  $\text{H}^+$  ion is not feasible because of exchange reactions with water, the rates of self-exchange of these ions could not be experimentally determined by the direct, radioisotope method. Instead we used the indirect method of calculating the rates of self-exchange of these ions from the electrical resistances of the membranes, measured under the same conditions as would prevail in a direct self-exchange measurement. With a critical ion of species  $y$ , for example, the Nernst-Einstein equation predicts the following relationship between the rate of self-exchange of  $y$  ions across the membrane,  $J_{\text{calc.}}^{yy}$ , and the measured electrical resistance of the membrane,  $\rho^y$ , (at  $25^\circ$ ) (16):

$$J_{\text{calc.}}^{yy} = \frac{958}{\rho^y}. \quad (2)$$

It has been observed that, although measured rates of self-exchange across oxidized collodion membranes are in quantitative agreement with the predictions of equation 2, only approximate agreement is shown by PSSA and protamine collodion membranes. However, with these membranes, the relative deviations from the calculated rates of self-exchange were essentially the same for all critical ions examined (16). The rates of self-exchange of  $\text{H}^+$ ,  $\text{Li}^+$ , and  $\text{NO}_2^-$  ions were calculated by assuming that the relative deviations from equation 2 which would be exhibited by these ions would be the same as those of ions whose rates of self-exchange were measured directly. The expression:

$$J^{yy} = \frac{\rho^z}{\rho^y} J^{zz}, \quad (3)$$

was used, where  $J^{yy}$  is the rate of self-exchange of the ion for which a radioisotopic method is not available,  $\rho^y$ , as before, is the measured electrical resistance of the membrane with this ion as critical ion;  $J^{zz}$  and  $\rho^z$  are the measured rate of self-exchange and electrical resistance for the case of a critical ion for which a radiotracer is available. With the cation permeable

membranes,  $K^+$  was used as this reference critical ion, and with the anion permeable membrane,  $Cl^-$ .

The stabilities of the various membranes over the course of the series of experiments were checked with electrical resistance measurements in 0.10 N KCl; no significant changes were observed.

*Radioactivity Measurement*

Radioactivity was determined by standard Geiger-Mueller or scintillation counting techniques as described previously (16).

*Bi-Ionic Potentials*

Bi-ionic potentials were measured with saturated KCl-calomel electrodes, the general procedure following that described in detail by Dray and Sollner (2).

RESULTS AND DISCUSSION

Tables I, II, and III present the experimental data obtained respectively with the PSSA collodion membrane, with the oxidized collodion membrane, and with the protamine collodion membrane. The first column of each table indicates the species of critical ion present in the "inner" compartment in the interexchange experiment, ion A, the species whose rate of movement across the membrane was actually monitored. The second column indicates the species of critical ion in the "outer" solution, ion B. The third column reports the bi-ionic potentials, in millivolts, the sign of the potential indicating the charge of the inner solution. The fourth and

TABLE I  
RATES OF SELF-EXCHANGE AND RATES OF INTEREXCHANGE OF  
CRITICAL IONS ACROSS A PSSA COLLODION MEMBRANE

Critical ion species A	Critical ion species B	Bi-ionic potential	$J_{AA}$	$J_{BB}$	$J_{AB}^{exp}$	$J_{AB}^{calc}$
		mv	$\mu eq\ hr^{-1}\ cm^{-2}$	$\mu eq\ hr^{-1}\ cm^{-2}$	$\mu eq\ hr^{-1}\ cm^{-2}$	$\mu eq\ hr^{-1}\ cm^{-2}$
$K^+$	$Cs^+$	+5.2	2.40	1.34	1.86	1.76
$K^+$	$Na^+$	-21.4	2.40	2.28	2.36	2.32
$K^+$	$Li^+$	-46.6	2.40	1.17†	1.58	1.62
$K^+$	$H^+$	+41.5	2.40	21.0‡	4.40	6.08
$Na^+$	$Cs^+$	+15.2	2.28	1.34	1.80	1.72
$Na^+$	$Li^+$	-21.3	2.28	1.17†	1.70	1.62
$Na^+$	$H^+$	+60.1	2.28	21.0‡	3.76	5.42
$Cs^+$	$Li^+$	-49.5	1.34	1.17†	1.32	1.28
$H^+$	$Li^+$	-79.3	21.0‡	1.17†	2.12	3.56

† Rate of self-exchange calculated from electrical resistance of membrane in 0.1 N LiCl.

‡ Rate of self-exchange calculated from electrical resistance of membrane in 0.1 N HCl.

fifth columns report, respectively, the rates of self-exchange of ions A and B across the membrane,  $J^{AA}$  and  $J^{BB}$ , in units of microequivalents per hour per  $\text{cm}^2$ , assuming an area of  $50 \text{ cm}^2$  for each membrane. The sixth column reports the measured rates of interexchange of ion A for ion B,  $J_{\text{exp}}^{AB}$ , in the same units as the self-exchange

TABLE II  
RATES OF SELF-EXCHANGE AND RATES OF INTEREXCHANGE OF  
CRITICAL IONS ACROSS AN OXIDIZED COLLODION MEMBRANE

Critical ion species A	Critical ion species B	Bi-ionic potential	$J^{AA}$	$J^{BB}$	$J_{\text{exp}}^{AB}$	$J_{\text{calc}}^{AB}$
		<i>mv</i>	$\mu\text{eq hr}^{-1} \text{ cm}^{-2}$	$\mu\text{eq hr}^{-1} \text{ cm}^{-2}$	$\mu\text{eq hr}^{-1} \text{ cm}^{-2}$	$\mu\text{eq hr}^{-1} \text{ cm}^{-2}$
K <sup>+</sup>	Na <sup>+</sup>	-29.1	2.38	1.90	1.96	2.14
K <sup>+</sup>	Li <sup>+</sup>	-51.8	2.38	0.82†	1.24	1.32
K <sup>+</sup>	Cs <sup>+</sup>	+5.5	2.38	1.00	1.60	1.52
Na <sup>+</sup>	Li <sup>+</sup>	-20.6	1.90	0.82†	1.24	1.22
Na <sup>+</sup>	Cs <sup>+</sup>	+32.6	1.90	1.00	1.44	1.36

† Rates of self-exchange calculated from electrical resistance of membrane in 0.1 N LiCl.

TABLE III  
RATES OF SELF-EXCHANGE AND RATES OF INTEREXCHANGE OF  
CRITICAL IONS ACROSS A PROTAMINE COLLODION MEMBRANE

Critical ion species A	Critical ion species B	Bi-ionic potential	$J^{AA}$	$J^{BB}$	$J_{\text{exp}}^{AB}$	$J_{\text{calc}}^{AB}$
		<i>mv</i>	$\mu\text{eq hr}^{-1} \text{ cm}^{-2}$	$\mu\text{eq hr}^{-1} \text{ cm}^{-2}$	$\mu\text{eq hr}^{-1} \text{ cm}^{-2}$	$\mu\text{eq hr}^{-1} \text{ cm}^{-2}$
Cl <sup>-</sup>	CH <sub>3</sub> COO <sup>-</sup>	+42.0	6.80	1.38	2.90	2.78
Cl <sup>-</sup>	CNS <sup>-</sup>	-24.5	6.80	3.04	4.20	4.36
Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	-14.7	6.80	4.66†	5.20	5.64
Cl <sup>-</sup>	I <sup>-</sup>	-10.3	6.80	2.86	4.20	4.28
CH <sub>3</sub> COO <sup>-</sup>	CNS <sup>-</sup>	-60.2	1.38	3.04	2.16	2.14
CH <sub>3</sub> COO <sup>-</sup>	I <sup>-</sup>	-51.5	1.38	2.86	2.00	1.96
CNS <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	+9.0	3.04	4.66†	4.00	3.74
CNS <sup>-</sup>	I <sup>-</sup>	+10.1	3.04	2.86	2.88	2.98
I <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	-3.0	2.86	4.66†	3.76	3.58

† Rates of self-exchange calculated from electrical resistance of membrane in 0.1 N KNO<sub>3</sub>.

rates; the seventh column indicates, in the same units,  $J_{\text{calc}}^{AB}$ , the rates of interexchange calculated from  $J^{AA}$  and  $J^{BB}$ , using equation 1.

Examination of Tables I-III indicates that, except for cases involving H<sup>+</sup> ion movement across the PSSA membrane, the agreement between measured rates of interexchange of ions and those calculated from the rates of self-exchange using equation 1 is reasonably good. The discrepancies between these quantities range

from 2 to 10%, in most instances being less than  $\pm 5\%$ ; they are but slightly greater than the cumulative sum of the estimated 2% error in each of the three measurements involved. These discrepancies have no apparent trend in direction, nor dependence on the type of membrane, nor species of critical ion. As may be seen from these tables, the systems in which the close agreement between experimental and calculated rates of interexchange of ions was observed include a wide range both of bi-ionic potentials, and of the ratios of the rates of self-exchange of the critical ions involved.

The data of Table I show that in the three cases involving the exchange of  $H^+$  across the PSSA membrane, the experimentally found rates of interexchange are from 27–40% lower than predicted from the self-exchange rates. These large discrepancies may stem in part from a large error in the numerical value of the rate of self-exchange of  $H^+$  ions, which, as indicated, was determined indirectly from the electrical resistance of the membrane. However, an error of this type could not completely explain the discrepancies found in cases involving  $H^+$  ion. A different value for the rate of self-exchange of  $H^+$  ions across the membrane would be required in the case of each of the three alkali metal cations to bring the rates of interexchange calculated from equation 1 into agreement with the experimental values, the required values for the rate of self-exchange of  $H^+$  ions being 9.2, 7.0, and  $4.4 \mu\text{eq hr}^{-1} \text{cm}^{-2}$  for the interexchange of  $H^+$  with  $K^+$ ,  $Na^+$  and  $Li^+$  ions, respectively. The discrepancies between experimental and calculated rates of interexchange of ions in the cases involving  $H^+$  are most probably due to a particularly large interaction between  $H^+$  and the other cations in the membrane. Accordingly, the more comprehensive experimental and theoretical methods described by Helfferich and Ocker (11) would appear to be required with systems involving  $H^+$  ions. It is also possible that the interexchange of  $H^+$  ions for the other cations involves a significant net flow of water across the membrane. An approach similar to that of Mackay and Meares (17) would be required to take into account the effect of such flow on the rate of the interexchange of ions.

In summary, the results of this study indicate that, except for cases involving  $H^+$  ion, the relationships between the rates of interexchange and the rates of self-exchange of critical ions are essentially as predicted from an expression derived on the basis of a Nernst-Planck approach which does not take into account interaction between the critical ions in the membrane.

The author expresses his appreciation to Dr. Karl Sollner for suggesting this investigation and for his helpful comments during both the experimental investigation and the preparation of the manuscript.

The experimental work reported here was done in the years 1953–1956 when the author was associated with the National Heart Institute, Bethesda, Maryland.

*Received for publication 23 May 1968.*

## REFERENCES

1. SOLLNER, K. 1950. *J. Electrochem. Soc.* **97**:139C.
2. SOLLNER, K. 1949. *J. Phys. Colloid Chem.* **53**:1211, 1226; DRAY, S., and K. SOLLNER. 1955. *Biochim. Biophys. Acta.* **18**:341.
3. MICHAELIS, L. 1933. *Kolloid-Z.* **62**:2.
4. STAVERMAN, A. J. 1952. *Trans. Faraday Soc.* **48**:176.
5. SCATCHARD, G. 1953. *J. Am. Chem. Soc.* **75**:2883.
6. WYLLIE, M. R. J. 1954. *J. Phys. Chem.* **58**:67; WYLLIE, M. R. J., and S. L. KANAAN. 1954. *J. Phys. Chem.* **58**:73.
7. HELFFERICH, F. 1956. *Discussions Faraday Soc.* **21**:83.
8. ANDELMAN, J. B., and H. P. GREGOR. 1966. *Electrochim. Acta.* **11**:869.
9. SOLLNER, K., and H. P. GREGOR. 1945. *J. Am. Chem. Soc.* **67**:346.
10. MOELWYN-HUGHES, E. A. 1957. *Physical Chemistry*. Pergammon Press, Inc., New York. 835.
11. HELFFERICH, F., and H. D. OCKER. 1957. *Z. Physik. Chem. (Frankfurt)*. **10**:213.
12. NEIHOF, R. 1954. *J. Phys. Chem.* **58**:916.
13. GREGOR, H. P., and K. SOLLNER. 1946. *J. Phys. Chem.* **50**:53.
14. GREGOR, H. P., and K. SOLLNER. 1946. *J. Phys. Chem.* **50**:88.
15. PETERSON, M. A., and H. P. GREGOR. 1959. *J. Electrochem. Soc.* **106**:1051.
16. GOTTLIEB, M. H., and K. SOLLNER. 1968. *Biophys. J.* **8**:515.
17. MACKAY, D., and P. MEARES. 1960. *Kolloid-Z.* **171**:139.