

Electrolyte Permeability and Electromotive Action of Mosaic Membranes Composed of Porous and Liquid Parts of High Ionic Selectivity for Ions of Opposite Signs

Karl Sollner and Gerald M. Shean

Laboratory of Chemical Physics, National Institute of Arthritis, Metabolism and Digestive Diseases, National Institutes of Health, Bethesda, Maryland 20205

Summary. A theory is presented of the electromotive and ion permeability properties of membranes which consist of a mosaic of highly ion selective *porous* membrane areas of ion exchanger nature and of areas of highly ion selective *liquid* ion exchanger membranes, the two types of areas being exclusively permeable to ions of opposite sign. It is demonstrated that, with properly chosen membranes, the preferential permeability of such porous-liquid mosaic membranes for ions of one sign of charge will be the opposite of that apparently indicated by their electromotive action.

The theory is based on the fact that the movement of ions across the porous membranes occurs in the dissociated state and in most instances is quantitatively linked to the resistance according to the Nernst-Einstein equation. The penetration of ions across liquid ion exchanger membranes, however, takes place essentially in a nondissociated state, and, as determined by self-exchange studies with radioactive tracers and stirred membranes, occurs at rates far in excess of those across porous membranes of the same resistance.

For the theoretical treatment the simplest case, two-membrane macro-model concentration cells, is discussed in detail. Qualitatively, it is evident that the ratio of the permeability of anions and cations across such porous-liquid mosaic membranes ordinarily will be strongly in favor of the ions which penetrate across its liquid parts; contrariwise, the electromotive actions of the mosaic membranes ordinarily are dominated by its porous parts.

Electric currents flow through all mosaic membranes; the strength of the current in a model cell may be calculated from the concentration potentials arising separately across the two membranes, and the resistances of the membranes and of the two solutions. From the strength of the current, the sign and the magnitude of the concentration potential arising

in the model cell may be computed; in many instances it should closely approach the concentration potential across the porous membrane.

For the tests of this theory with two-membrane macro-mosaic models, the electrolyte of choice for experimental reasons was RbSCN, tagged with $^{86}\text{Rb}^+$ and S^{14}CN^- . The porous membranes were polystyrene sulfonic acid collodion matrix membranes; the liquid membranes consisted of 0.02 M trioctyl propyl ammonium thiocyanate in 1-decanol. The ratios of the permeabilities across the model mosaic membranes determined by conventional rate of self-exchange measurements showed, as expected, that the permeability of the SCN^- ions is larger, up to 3600 times larger, than that of the Rb^+ ions. The potentials arising in these models agreed within the limits of experimental error with those predicted by theory, closely approaching that arising at the cation selective porous membranes.

In the electrochemistry of membranes it is commonly assumed that the sign of the potential of the more dilute solution in concentration cells is determined by the sign of the charge of the species of ions with the greater propensity to migrate across the membrane. This, however, is not necessarily true. Exceptions to this rule can be readily predicted on the basis of the extant information on the basic electrochemistry of membranes, as will be demonstrated here for a rather extreme case.

The theoretical consideration of the electromotive action and of the ion permeability of certain mosaic membranes composed of porous solid and of liquid parts of high ionic selectivity for ions of opposite sign leads to the prediction of an at-first-sight rather strange effect, namely, that the preferential permeability of such membranes for ions of one sign of charge

may be opposite to that apparently indicated by their electromotive action. This idea was outlined very briefly a few years ago [28]. In view of the probable bioelectric significance of this effect, it seems, however, appropriate to discuss it in some detail and to describe a series of experiments which confirm the theoretical predictions quantitatively. Moreover, the work reported here also seems to be significant because it indicates that membranes and membrane systems of still greater complexity too are now amenable to a rigorous physicochemical study.

Review of the Literature

The importance of *mosaic membranes* as a topic of physicochemical biology was first clearly recognized in 1928 by Rudolf Höber (1873–1953), one of the “fathers” of this field [12, 13], and his collaborator F. Hoffmann [14]. These investigators focused their attention on the electrolyte permeability of mosaic membranes of porous character which consist of an array of negative, highly cation selective, and positive, highly anion selective, micro areas. They came to the conclusion that such mosaic membranes must be essentially impermeable to electrolytes since, so they argued, the exclusively anion selective parts are impermeable to the electrolyte as a whole because cations could not diffuse through them, and, for an analogous reason, the preferentially cation permeable parts of the mosaic too are impermeable to the electrolyte [14]. At the time, a critical experimental test of this conception of the electrolyte permeability of charge mosaic membranes was not possible: membranes, particularly anion selective membranes, of the necessary degree of selectivity were not available. It is noteworthy that Höber and Hoffmann did not consider the possibility of an interaction of the two types of micromembranes nor mention their electromotive behavior.

Sollner [25], in 1930, utilized the known fact of the inherently heteroporous, mosaic structure of ordinary porous membranes — such as dialysis membranes — to explain “anomalous osmosis.”

The term anomalous osmosis is used to denote all those osmotic phenomena arising with solutions of electrolytes, which, with respect to magnitude or direction, seem to be contrary to the common experience with nonelectrolytes. With the nonelectrolytes, the direction of the flow of liquid across porous membranes which separate a solution from pure solvent (or a more dilute solution) is toward the side of the more concentrated solution and occurs at a rate roughly proportional to the concentration difference. With electrolyte solutions, the rate of movement of

liquid across the membrane depends in an involved manner on both the absolute concentration, the concentration difference of the two solutions, and the nature of the membrane. When an abnormally copious flow of liquid is directed towards the more concentrated solution, one speaks of “anomalous positive osmosis.” In the relatively rare instances when a flow of liquid occurs toward the side of the pure solvent (or the more dilute solution), one speaks of “negative anomalous osmosis,” or “negative osmosis,” a term suggested by Thomas Graham in 1854 [7].

Anomalous osmosis, observed early in the 19th century, was suspected as early as 1854 by Graham [7] to be of electroosmotic origin, a view which was adopted by virtually all later investigators. Observational information, mainly furnished by biologists, among whom Jacques Loeb [16] was foremost, became, in time, fairly voluminous; the molecular mechanism of anomalous osmosis, however, remained unexplained.

The literature on anomalous osmosis was extensively reviewed by Sollner [25], who demonstrated that the various attempts to explain the electroosmotic mechanism of anomalous osmosis were not compatible with well-established principles of electrochemistry. Sollner pointed out that ordinary porous membranes may be considered as “pore-width” mosaic membranes and that pores of different width yield electromotive forces of different magnitude in concentration, as well as in all other cells. Consequently, the different pores interact electrically with each other, and numerous microcurrents flow through the membrane, causing electroosmosis, i.e., “anomalous osmosis.” Furthermore, it was stressed that every inhomogeneity in a membrane, whatever its cause, which results in local differences in emf's must, of necessity, lead to electrical interaction and the flow of local electrical currents; all such membranes in principle must be considered electrochemically as mosaic membranes.

The pore-width mosaic concept was soon tested in macro-models in which two membranes of different average porosities acted upon each other, producing significant electroosmosis in the predicted direction, i.e., anomalous osmosis [9, 29]. Models of the same type with greatly improved membranes later confirmed these results [3]. In addition, analogous models were constructed to demonstrate that substantial anomalous osmoses also arise at “charge mosaic” macro-membranes in which two dialyzing-type membranes of opposite charge act upon each other [4, 28].

At this point it seems appropriate to make a few remarks concerning the experimental, especially the

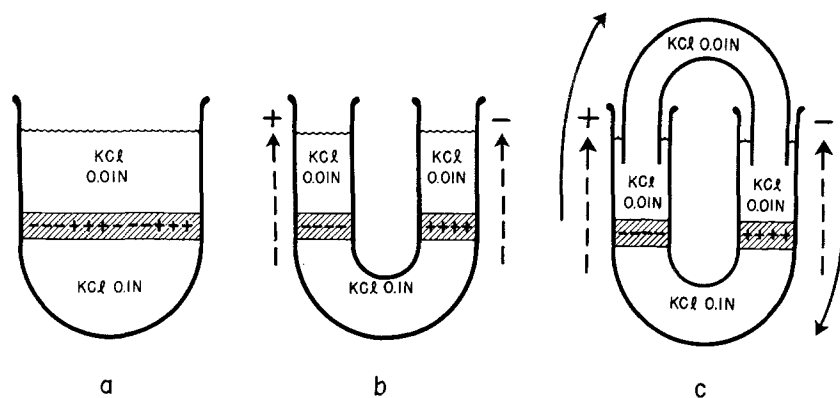


Fig. 1. Pictorial development of the theory of electrolyte permeability of mosaic membranes that are composed of ideally anion-selective and ideally cation-selective parts. *a.* Mosaic membrane with adjacent cation-selective and anion-selective parts. *b.* Spatial and electrical separation of the cation-selective and anion-selective parts of the membranes. *c.* The spatially separated cation-selective and anion-selective parts connected electrically by a bridge of solution in an all-electrolytic circuit

electrochemical, study of mosaic membranes by means of macro-models. A direct straightforward experimental study of the microprocesses occurring at true "micro-mosaic" membranes would be experimentally very difficult, if not outright impossible. An indirect way must, therefore, be taken to explore the basic physical chemistry of mosaic membranes, namely, by the construction of appropriate macro-model systems, in spite of certain shortcomings of this approach.

It is obvious that all transport effects arising from the interaction of the different macro-parts of macro-model systems must, for the following reasons, be much slower than with true micro-mosaic membranes. The electromotive forces arising at the different parts of micro-mosaic membranes are of the same magnitude as those originating at the macro-membrane of the corresponding macro-models. The distances, however, and, therefore, the resistances of the solutions through which the currents flow in the solutions of micro-mosaic membrane cells are, by several orders of magnitude, smaller than in the macro-models.

We return now to the question of the electrolyte permeability of mosaic membranes composed of highly anion and highly cation selective parts which was raised by Höber and Hoffmann [14]. The solution of this problem was suggested in 1932 by Sollner [26] who realized the essential electrochemical similarity of the cells discussed by Höber and Hoffmann and the electrochemical situation prevailing in the just-discussed cells in which anomalous osmosis arises. In both instances the membranes are mosaic structures consisting of areas yielding different emf's. Therefore, in both instances, these areas must interact electrically with each other. In the case of the narrow-pored "charge-mosaic" membranes discussed by Höber and Hoffmann, the open question was how the flow of local currents across such membranes may influence their electrolyte permeability.

Since the electrochemistry of porous "charge-mosaic" membranes consisting of anion and of cation selective parts of extreme ionic selectivity is the basis of the consideration of the problem to be treated in this paper, it is necessary to recapitulate here the arguments used in the treatment of the porous charge mosaic membranes.

The assumption, now realizable to a very high degree, is made that the membranes, or micro-areas of the membranes, are of virtually ideal anionic or cationic selectivity. The influence of an osmotic movement of water, which is minimal with the fairly dense membranes considered here, is neglected as in principle inconsequential for the problems dealt with here. Furthermore, to simplify the presentation, only cells with strong uni-univalent electrolytes will be considered explicitly.

From the onset it was clear that such charge mosaic membranes, as shown in Fig. 1 *a*, when interposed between solutions of different concentrations, must be readily permeable to electrolytes, anions moving through the anion permeable parts of the membrane and cations through the cation permeable areas. Since macroscopic electroneutrality must be maintained, cations and anions can move across the membrane only in electrically equivalent quantities. This process continues until the two solutions separated by the membrane are of equal concentration. In other words, in such charge mosaic systems, local micro-currents must flow [26], both sources of current driving the positive current in a clockwise direction.

For the theoretical treatment, we assume that the anion and the cation selective areas of the membrane in Fig. 1 *a* are combined into two macro-membranes that are mounted in a U-tube, as shown in Fig. 1 *b*. Here the two membrane concentration potentials are established, but no transport of electrolyte occurs across either membrane. The essentials of the situation shown in Fig. 1 *a*, however, are reestablished when the two solutions in Fig. 1 *b* are reconnected through

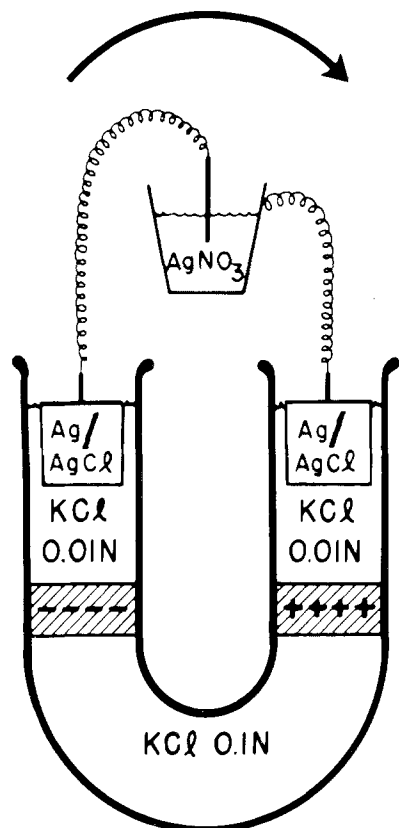


Fig. 2. Mosaic membrane model with auxiliary electrodes and a silver coulombmeter through which the current flows (schematic)

a conducting bridge, as shown in Fig. 1c. Now equivalent quantities of cations and anions can diffuse into the less-concentrated solution, and a corresponding current flows clockwise in this all-electrolytic ring system, as indicated in Fig. 1c by the curved arrows. The strength of the current, I , is given by Ohm's law, $I = E/R$, where E is the sum of the two membrane concentration potentials which drive the positive current in a clockwise direction, and R the total resistance of the system. The potential difference between any two points in the system of Fig. 1c is defined at any given moment by Ohm's law.

A decisive test of the outlined theory on the correlation of the quantity of electrolyte that in a given time permeates across the membrane of a mosaic cell and of the quantity of current flowing during the same period can be carried out in different ways, most easily in the way schematically indicated in Fig. 2, using a silver coulombmeter in appropriately constructed macro-models [20]. Another slightly more involved experimental approach is to monitor continuously, by means of two probe electrodes, the electromotive force operating during the experimental period across an invariant, high resistance, part of an appropriately constructed macro-model. From these data

the quantity of electricity moved may be computed and compared to the quantity of electrolyte transferred during the same interval [21].

When this theory of charge mosaic membranes was proposed in 1932, an experimental test was not possible, since membranes which combine reasonably low resistances with the high ionic selectivities required were not in existence. Such tests, however, became possible after both highly cation and anion selective membranes, "permselective membranes," had been elaborated [2, 5, 8, 19, 30]. In numerous experiments with various suitably constructed macro-models [20, 21], the quantities of electrolyte moving into the more dilute solution agreed within $\pm 2\%$ with the number of faradays that flowed during the same period; in other words, the conception developed in Figs. 1a-c and 2 was fully confirmed.

When the outlined theory of mosaic membranes was developed, the question of the potential difference between the two solutions was not discussed explicitly. It appeared obvious that it was determined by the electrical parameters of the various parts of the cell according to Ohm's law [26]. The tacit assumption was that membrane conductance and the propensity of the permeable ions to diffuse across the membrane are correlated to each other in an essentially similar manner, to that by which the ionic mobilities and diffusivities of ions in solution are interrelated according to the classical Nernst [22] theory of electrolyte solutions. Accordingly, it seemed clear that the sign of the potential of the more dilute solution would be determined by that species of ions in a given cell (with a uni-univalent electrolyte) that diffuses across that part of the charge mosaic which has the lower resistance. There was no particular reason to pursue this point further. Moreover, at that time there was no way to directly determine accurately and unequivocally, by analytical methods, the true intrinsic ion permeability of a membrane. This is now routinely accomplished by the measurement of the rates of exchange of appropriate isotopic radioactive tracers.

In the modern electrochemistry of membranes the close relationship between the intrinsic rate of diffusion of ions and the rates of their electromigration, according to the Nernst-Einstein equations, forms the basis of most theoretical approaches to ion transport processes across membranes [11, 15, 23]. A very detailed explicit treatment of the theoretical relationship of the rates of self-exchange of the permeable species of ions across membranes of high ionic selectivity and the electrical resistance of the latter was presented by Gottlieb and Sollner [6]. Thus, it should be sufficient to recapitulate briefly only those aspects of the matter which are of primary importance in our subsequent discussions.

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, λ its equivalent conductance, and R , T , and F are the gas constant, absolute temperature, and the faraday constant.

Provided that certain experimental conditions are fulfilled, a straightforward application of Eq. 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 ρ and the rate of self-exchange of the critical ions ϕ across any given area of a membrane:

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

at 25 °C

$$\phi = \frac{958}{\rho} \quad (2b)$$

where ϕ is expressed in microequivalents (μeq) per hr and ρ as ohms. The experimental conditions which must be fulfilled for the strict applicability of these equations were reviewed by Gottlieb and Sollner [6].

The electrical resistances and rates of self-exchange of univalent ions across several types of collodion matrix membranes were reported by these authors [6]. With cation selective oxidized collodion membranes, the data obtained were within 2% in agreement with Eq. 2b; with cation selective polystyrene sulfonic acid collodion membranes, the type used in the work reported below, the experimental rates of exchange were up to 25% less than calculated, and with the anion selective protamine collodion membrane the deviation was about 20% in the same direction. Conventional theory explains those deviations as a result of electroosmosis.¹

When *liquid ion exchanger membranes*, which combine high degrees of ionic selectivity with high permeabilities either for cations or for anions, became available, it became attractive to study also mosaic membrane cells involving such liquid membranes. This was the more interesting since it was immediately evident that such cells must show functional properties far different from those of the above-described cells with porous mosaic membranes.

¹ With anion selective poly-2-vinyl-*N*-methyl pyridinium bromide membranes, the experimental rates of exchange were up to six times larger than calculated from the membrane resistance by Eq. (2a). The cause of this large discrepancy is unknown.

The first observations on the electromotive behavior of membranes of liquid ion exchange nature and a rather clear insight into the mechanism of their electromotive action had been presented in 1909 by F. Haber and Klemensiewicz [10]. Their membranes, mostly consisting of nitrobenzene and nitrotoluene, yielded in concentration cells potentials which approached fairly closely the theoretically possible maximum, indicating a very high degree of cationic selectivity. The cause of the electromotive efficacy of these membranes was assumed to be the presence of a small quantity of some unknown acidic impurity. The improvement of the Haber-Klemensiewicz type of membranes remained for many years an essentially unsolved puzzling problem. The rather involved further developments in this field were reviewed repeatedly, recently by one of us [27].

The modern era of the electrochemistry of liquid membranes is a direct result of the elaboration of fairly high molecular weight organic acidic and basic compounds which are suitable as the functional components in liquid anion and cation exchangers. Since 1958, such compounds have become commercially available in increasing numbers.²

Liquid ion exchangers are solutions in water-insoluble organic solvents of substances consisting of an ionogenic group which is attached to an organic molecule of proper size and configuration to make these compounds, mostly with molecular weight from about 300 to 600, very sparingly soluble in aqueous electrolyte solutions.

The uptake by liquid exchangers of ions from adjacent solutions shows regularities strikingly similar to those observed with solid ion exchangers. Strong acid and strong base liquid exchangers readily exchange ions with neutral solutions; their degree of saturation with counterions is practically independent of the pH in a wide range around the neutral point. Weak base and weak acid liquid exchangers do not react significantly with neutral solutions of strong electrolytes. They do so only when in their salt forms, in contact with at least slightly acid or slightly basic solutions, respectively.

The molecules which carry the ionogenic groups tightly bound to their counterions in an undissociated

² It is of interest to recall that K.H. Meyer, who, after T. Teorell's first brief announcement [32] of the concept of the theory of porous, fixed charge ion-exchange membranes, developed this theory independently in considerable detail [18], stated specifically in 1935 that substances which could act as liquid analogs of porous ion exchangers and ion exchange membranes cannot exist, and explained in some detail the reasons for his opinion [17]. This apodictic negative statement by Meyer, one of the then leading organic chemists, undoubtedly discouraged for a lengthy period the search for materials suitable as essentially water insoluble functional compounds for liquid ion exchangers.

state, conventionally designated as RX, diffuse freely within the liquid exchanger phases, in some instances probably in part in the form of micelles. The dielectric constants of the solvents used in liquid exchangers are low, from 2 to 3 with hydrocarbon solvents and up to about 35 with nitrobenzene.

The electric resistivities of the liquid exchangers are very high, a definite proof that a very high degree of association exists between the functional groups of the liquid exchanger and their counterions. In other words, the counterions taken up from an aqueous solution by ion exchange form, in the organic phase, essentially undissociated salts with the ion exchanger compound. In moving from the aqueous phase into the organic exchanger phase and vice versa, the exchanging ions undergo a fundamental change in state, from hydrated to essentially unhydrated forms, and the inverse. Strong inorganic electrolytes as such are not dissolved to a detectable degree in most liquid exchangers; this means that there is no significant invasion of the exchanger phase by "non-exchange" electrolyte, contrary to the situation prevailing ordinarily with solid ion exchangers (though with dense high resistance porous permselective membranes the invasion by "nonexchange" electrolyte is minimal in many instances). The water content of most liquid exchangers is minimal. The liquid ion exchangers, due to their very nature as essentially undissociated electrolyte solutions, show specific resistances, many to several orders of magnitude higher than aqueous solutions of the same concentrations.

The first investigators to use one of the then-recently-developed liquid ion exchanger compounds in membranes were Botrè and Scibona in 1962 [1]. However, the slopes of their potential vs. concentration curves obtained with concentration cells deviated widely from that predicted by the Nernst equation as applied to membranes of high ionic selectivity. The first liquid ion exchanger membranes with which the thermodynamically possible maximum values were regularly reached, at least within a few tenths of a millivolt over wide concentration ranges, were described by Sollner and Shean in 1964 [31], and soon several other investigators confirmed and expanded their results. A systematic presentation of the basic physical chemistry of liquid membranes with numerous references was given in 1970 [27].

Since the transport of the exchangeable ions across such liquid ion exchanger membranes occurs in a virtually exclusively undissociated state, there is no primary meaningful correlation between their resistances and the rates of ion exchange across them. With stirred membranes, the rates of trans-membrane exchange of ions are determined by the rates of diffu-

sion across the diffusion layers at the two phase boundaries, as they would be across very thin unstirred membranes, while the resistance of the membrane is not affected by stirring. The rates of exchange of the permeating ions across liquid membranes are much larger with stirred membranes, by several orders of magnitude larger than those which might be calculated by a naive application of the Nernst-Einstein equation, Eq. 2a and b. This latter fact must be strongly emphasized because it is a major part of the theory of porous-liquid mosaic membranes presented in the subsequent section.

Theory

We turn now to a discussion of the electromotive properties, and of the ion permeability, of mosaic membranes which are composed of porous areas of extreme ionic selectivity for ions of one sign, and of parts consisting of a liquid ion exchanger which are virtually exclusively permeable to ions of the opposite sign.

The true permeabilities of membranes, for the ions of the electrolyte in solution, A^+L^- , are determined from the measurement of the rate of the trans-membrane exchange of the appropriate tracer ions $*A^+$ and $*L^-$ in concentration cells. In some of our experiments, the tracers were placed into the more concentrated solution, and in the others, into the more dilute ones. The potential difference between the two solutions is determined in the conventional manner by means of KCl bridges and calomel electrodes.

As in the case of the previously discussed cells with mosaic membranes composed exclusively of porous areas, only the least involved porous-liquid mosaic model cells will be treated here, i.e., concentration cells with uni-univalent strong electrolytes. The extension of our considerations to cells with uni-bivalent electrolytes and similar slightly more involved situations is rather obvious and would tend unnecessarily to complicate our presentation.

The conceptionally simplest systems of this type are cells in which the resistance, R_1 , of the, say, cationic selective porous membranes of $x\Omega$ is equal to the resistance, R_2 , of the anion selective liquid membrane. The essential features of such a hypothetical cell may be represented in Scheme 1.

The basic electrochemical situation in the porous-liquid model cell shown in this scheme is analogous to that prevailing in the cell with two porous membranes which is shown in Fig. 2c; a (positive) current

Scheme 1.

$0.01 N A^+ L^-$	
Cation-selective porous membrane	Anion-selective liquid ion exchanger membrane
$R_1 = x\Omega$	$R_2 = x\Omega$
Rate of self-exchange = $y \mu\text{eq h}^{-1}$	Rate of self-exchange $> > > y \mu\text{eq h}^{-1}$
$0.1 N^* A^+ * L^-$	

Scheme 2.

$0.1 N A^+ L^-$	
Cation-selective porous membrane	Anion-selective liquid ion exchanger membrane
$R_1 = x\Omega$	$R_2 > > > R_1$
Rate of self-exchange = $y \mu\text{eq h}^{-1}$	Rate of self-exchange $> > y \mu\text{eq h}^{-1}$
$0.1 N^* A^+ * L^-$	

flows clockwise, transported by cations through the porous membrane area and by anions through the liquid area. The strength of the current flowing in a clockwise direction is determined by the emf's of the cell, the sum of the two concentration potentials, E_1 and E_2 , across the porous and liquid membranes, of about 55 mV each, and the resistance of the circuit, $2 x\Omega$ plus the relatively very small resistances of the two solutions. The quantity of electrolyte that moves in a given time from the more concentrated to the more dilute solution, as in the porous-porous models, must be identical with the number of faradays of electricity that flow in the same period.

The *potential difference* between any two points of the circuit in the cell of Scheme 1 is defined by Ohm's law. According to the stated assumptions, the cell is electrically symmetrical; consequently, the potential difference between the two solutions must be zero.

However, with respect to the *rates of exchange* of cations and of anion exchange between the two solutions, there is a vast difference between the porous-liquid model of Scheme 1 and the porous-porous model of Fig. 1c. According to our assumptions, the rate of anion exchange across the stirred liquid ion exchanger membrane, as determined by radioactive tracers, would be many orders of magnitude greater than that of the cations across the porous area.

It would be rather difficult to assemble a model which would fulfill reasonably closely the assumptions on which the cell of Scheme 1 is based and still facilitate the necessary analytical work, since the rate of exchange of cations across porous membranes with resistance equal to those of the extremely high resistance anion selective liquid membranes would be prohibitively slow; the results also might be blurred by a small leak of cations across the liquid membrane. More important, such an experimental model would not bring out in full clarity the main objective of this study, namely, to demonstrate that the preferential permeability of such porous-liquid mosaic membranes for ions of one sign of charge will be the

opposite of that apparently indicated by their electromotive action.

We, therefore, have focused our attention on the much more instructive and fairly readily realizable type of cell shown in Scheme 2.

In this scheme, the resistance of the liquid anion exchanger membrane, R_2 , is very much higher than that of the porous cation exchanger membrane, R_1 ; in our experiments reported below, it is higher by a factor of about 100. Nevertheless, according to our assumptions, the *rate of exchange* of anions across the stirred liquid membrane is still very much larger than that of the cations across the porous membrane.

We now turn to the consideration of the *potential difference*, E_3 , which arises between the two aqueous solutions of Scheme 2.

From the electrochemical point of view, the model depicted in this scheme is strictly analogous to the cells of Fig. 1c and 2. It too represents two sources of current, the concentration potentials, E_1 and E_2 , which in the closed circuit are connected in series to each other by the two aqueous solutions; as in the circuits of Fig. 1c and 2, both emf's drive the (positive) current in a clockwise direction.

The internal resistance of the porous membrane is very much smaller than that of the liquid membrane. The resistances of the two aqueous solutions are small compared to that of the porous membrane, R_1 , and very much smaller than that of the liquid membrane, R_2 , in which resides the overwhelming fraction of the resistance of the whole circuit. Under the stated assumptions, the porous membrane is a virtually non-polarizable low resistance source of current which is connected through two low resistance leads (the two solutions) to the high resistance part of the circuit (the liquid membrane). The potential drop within the solutions, according to our assumptions, is negligibly small.

Qualitatively it is obvious that the *potential difference between the two solutions in the mosaic model of Scheme 2*, E_3 , must closely approach the corresponding concentration potential across the porous

membrane, E_1 .³ The corresponding theoretical value, E_4 , can be computed on the basis of Ohm's law.

The current I that flows in the model system is given by the expression:

$$I = \frac{E_1 + E_2}{R_1 + R_2} \quad (3)$$

in which E_1 and E_2 are the concentration potentials that arise at the two membranes in conventional, single-membrane concentration cells with the same two solutions. In Eq. (3), the resistances of the two aqueous solutions in the model of Scheme 2 are considered as negligibly small compared to the resistance of the liquid membrane, R_2 , an assumption that in our cells does not introduce a significant error.

From the strength of the current calculated by Eq. (3), I , the theoretical potential difference between the two solutions E_4 , may be computed by Eq. (4):

$$E_4 = E_1 - R_1 I. \quad (4)$$

In a perfect, ideal system, the experimental and calculated values, E_3 and E_4 , of the potential difference between the two solutions would coincide.

Experimental

The just-presented theory of porous-liquid ion exchanger mosaic membranes was outlined very briefly in 1976 by K. Sollner [28], when it was also remarked that it had been validated experimentally. At that time, it had still been our plan to delay the publication of a systematic paper until we could report experiments on models not only with anion selective liquid membranes used in the work presented below, but also on cells which were intended to make use of liquid cation exchangers that combine equally high ionic selectivity with a similarly low solubility in aqueous solutions. Since changed circumstances will prevent us from fulfilling our original plan, we present here the results of a series of experiments in which only liquid anion exchanger membranes were used, as these experiments are more than adequate to demonstrate that the theoretical predictions are quantitatively verified by the experiment.

The apparatus used in these experiments is shown in Fig. 3a. It consists of a cylindrical vessel which is divided into equal halves by a dividing wall, indicated in the figure by loosely spaced large

³ Readers not accustomed to think in abstract terms about galvanic circuits will readily visualize the essence of the situation by considering a closely analogous, more familiar case. Assume a large 12-volt, low resistance car battery connected in series through heavy copper leads to a 12-volt, very high resistance miniature battery in a closed circuit, both batteries driving the current in the same direction. The current flowing in this circuit obviously will be very weak and, accordingly, the voltage drop in the two high conductance leads will be minimal. The question discussed in the text is in essence: what is the potential difference between the two copper leads which corresponds to E_3 ? Everyday experience shows that this potential difference is that prevailing at the terminals of the large battery on closed circuit which under the assumed conditions very closely approaches its emf on open circuit.

dots, which separates the two magnetically stirred aqueous solution compartments. The dividing wall is higher on the left side than at the right side of the apparatus in Fig. 3a.

The left side of the dividing wall is provided with a circular opening of about 22 mm diameter, over which the porous membrane, indicated by more densely spaced small dots, is cemented with RTV 102 Silicone Rubber (General Electric). On the right-hand side, the upper part of the dividing wall is encased by a glass cylinder with open ends, which reaches from the top of the apparatus down to its middle. In the assembled apparatus the liquid membrane of 30 ml volume, with a thickness of about 20 mm, floats on the two aqueous solutions. It straddles the dividing wall, reaching about 10 mm below the top of the latter into the two solution compartments; it is also stirred magnetically. In the region of the liquid membrane, the inside of the glass cylinder and the dividing wall are "siliconed" to make these areas hydrophobic in order to prevent a creeping of the aqueous solution between the two solution compartments.

The situation that prevails during the experiment across the porous membrane on the left-hand side of the assembled model of Fig. 3a is immediately evident. The situation involving the liquid membrane that prevails on the right-hand side of the assembled model may be not so easily visualized; however, it becomes immediately evident by reference to Fig. 3b, which shows the cross-section perpendicular to the middle of the dividing wall of the right-hand side half of the apparatus.

The porous highly cation-selective membranes used in this apparatus were sulfonated polystyrene (SPS) collodion matrix membranes, prepared by the method described in detail by Neihof [19], which facilitates the production of membranes of virtually any desired unit area resistance, from 10 to at least $10^5 \Omega \text{ cm}^2$ when equilibrated with 0.1 N KCl solution. For our model studies, we used about 50 μ thick membranes with resistances of more than $9000 \Omega \text{ cm}^2$ in 0.1 N KCl, which, in 0.2|0.1 N KCl cells, gave concentration potentials which approached the theoretically possible maximum potential within 0.5 mV or better. When equilibrated with rubidium solutions, in the rubidium form, as used in our model experiments, the unit area resistances of these membranes were somewhat higher and the concentration potentials arising across them slightly lower than in the corresponding KCl cells.

The effective areas of the porous membranes used in the various experiments were slightly smaller than the circular opening in the dividing wall shown in Fig. 3a, varying from about 3.0 to 3.5 cm^2 according to the membrane area inadvertently covered with the silicon cement. The variation in the membrane areas, however, is of no consequence whatsoever since the resistances of the membranes were always measured in the mounted state (see below).

The electrolyte had to be chosen on the basis of several practical considerations: (i) it should be a strong electrolyte, with ions high in the Hoffmeister series, particularly the anion, so that a maximum degree of saturation of the liquid ion exchanger compound with the anion would be achieved, essentially independent of its concentration in the two adjacent solutions; (ii) the determination of the radioactivities of the anion and the cation should be feasible in the same solution without mutual interference; and (iii) both ions of the electrolyte chosen should be available with adequately high specific radioactivity.

An electrolyte fulfilling these requirements is RbSCN, containing ^{86}Rb and ^{14}C . The ions of this electrolyte are high in the Hoffmeister series, and, more important, their radiation energy levels are far enough apart to permit analyses of both isotopes in the same sample.

As $^{86}\text{RbS}^{14}\text{CN}$ was not commercially available, we had recourse to the conventional technique of doping our experimental solutions with very small quantities of appropriate salts of very high specific activity, in our case $^{86}\text{RbCl}$ and KS^{14}CN or NaS^{14}CN

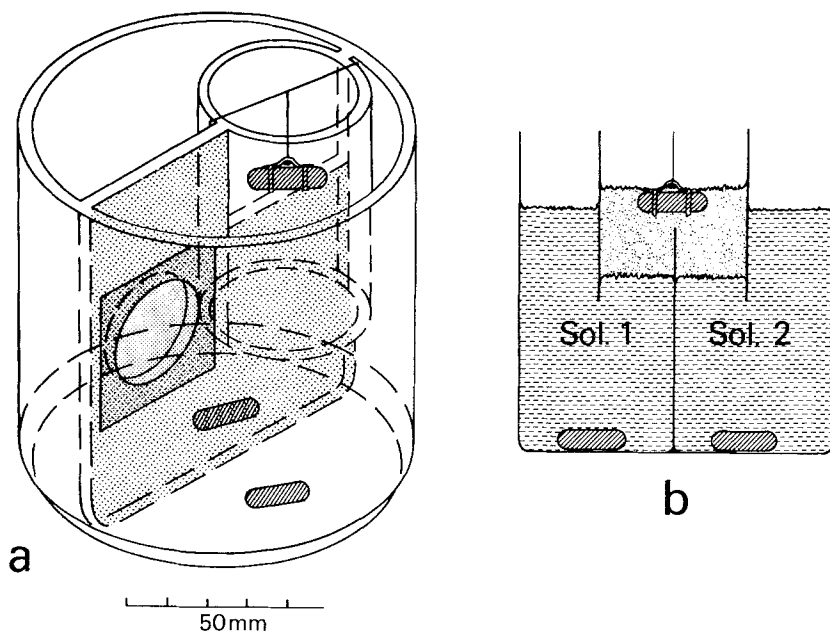


Fig. 3. Two-membrane macro-mosaic model cell. *a.* The cell with porous membrane (indicated by densely spaced small dots) mounted on left-hand side of dividing wall indicated by loosely spaced larger dots. *b.* Cross-section through right-hand side of the model in working condition, with liquid floating on the two solutions

Table 1. The electrical and permeability properties of model mosaic membranes composed of highly cation selective porous and highly anion selective liquid component parts

1	2 3 4 5				6 7 8 9 10 11 12							
	Component membranes separately ^a				Assembled mosaic model cell							
Cell	Porous cation selective mem. ^b		Liquid anion selective mem. ^c		Calcul. current <i>I</i> (μ A)	Mosaic potential		Maximum possible exchange of SC^*N^- and Rb^{*+} (%)	Ionic selectivity of mosaic model		Ratio of exchange rates $\frac{S^{14}CN^-}{^{86}Rb^+}$	
	Conc. E_1 (mv) ^d	Resist. R_1 (Ω)	Conc. E_2 (mv) ^d	Resist. R_2 (Ω)		Exper. E_3 (mv) ^d	Calcul. E_4 (mv) ^d		Initial rate of exchange of $S^{14}CN^-$ (%/hr)	Initial rate of exchange of $^{86}Rb^+$ (%/hr)		
0.001 N Rb*SC*N 0.1 N RbSCN	+107.5	7,330	-108.2	323,000	0.653	+ 98.1	+102.7	99	8.1	0.0022	3,680	
0.01 N Rb*SC*N 0.1 N RbSCN	+ 48.8	3,260	- 48.8	300,000	0.322	+ 48.8	+ 47.8	91	1.0	0.0034	294	
0.01 N Rb*SC*N 0.001 N RbSCN	+ 55.0	6,420	- 54.8	265,000	0.405	+ 50.5	+ 52.4	9.1	0.5	0.0012	417	
0.05 N Rb*SC*N 0.1 N RbSCN	+ 14.0	9,580	- 17.4	275,000	0.110	+ 10.2	+ 12.9	66.7	0.74	0.0018	411	
0.1 N Rb*SC*N 0.01 N RbSCN	+ 52.7	3,000	- 52.2	335,000	0.310	+ 52.3	+ 51.8	9.1	0.24	0.0024	100	
0.1 N Rb*SC*N 0.001 N RbSCN	+108.0	4,950	-110.8	325,000	0.663	+103.2	+104.7	0.99	0.061	0.0035	17	

^a As measured initially.

^b Sulfonated polystyrene (SPS) collodion matrix membranes.

^c 0.02 M trioctyl propyl ammonium (TOPA) thiocyanate in decyl alcohol.

^d The sign refers to the more dilute solution.

(obtained from New England Nuclear and ICN Pharmaceuticals, Inc.), so that the tagged solutions used in the apparatus of Fig. 3 (about 190 ml) had radioactivities of about 0.1 mCi of $^{86}Rb^+$ and $S^{14}CN^-$. This means that the ratio of radioactive tracers to the nonradioactive ion of the same species varied in the different experi-

ments according to the concentration of the tagged solution. Correspondingly, the fractions of the tracers, which would exchange if the final distribution equilibrium were reached, vary widely, according to the ratio of the concentrations of each pair of solutions in the various experiments.

The quantities of radioactive tracer salts added to our solutions were so small that the concentrations of the latter were not altered significantly. In addition, the Na^+ or K^+ ions virtually do not replace any Rb^+ in the cation selective membrane since the latter ion is more strongly absorbable on porous cation exchangers; likewise, the SCN^- ion is vastly preferred over the Cl^- ion by the liquid ion exchangers.

For the dual label determinations of ^{86}Rb and ^{14}C , a Packard Tri Carb scintillation counter in the National Institutes of Health Radiation Laboratory was used.

The anion exchanger used in the liquid membrane was trioctyl propyl ammonium (TOPA) thiocyanate, the solvent 1-decanol, with a dielectric constant of 8.1.

The liquid membranes used in the model of Fig. 3 consisted of 30 ml of 0.02 M non-radioactive TOPA thiocyanate in 1-decanol equilibrated with 0.075 N tracer-free KSCN solution. Its specific resistance was about $5.15 \times 10^5 \Omega^{-1} \text{cm}^{-1}$. The membranes were not doped with radioactive tracer prior to the experiment proper, in order to make sure that any radioactive tracer showing up in the originally untagged solution could have originated only from the other solution and not from the membrane. This precaution, of necessity, reduces the experimentally determinable rate of thiocyanate self-exchange during a short initial phase of the experiment.⁴ Any error which might be introduced is of no significant consequence in the present context, since it would only tend to reduce the effect which is to be demonstrated, namely, the overwhelmingly high rate of the self-exchange of the thiocyanate ion as compared to that of the rubidium ion.

Before assembling the model, the porous membrane, polystyrene sulfonic acid colloid matrix membrane [19], was always brought into the rubidium form, but ordinarily it was not brought into a stationary state between appropriate radioactive and non-radioactive solutions, except in those experimental runs where the same, already mounted, membrane was used again. These procedures did not cause any significant errors because the exchange capacities of the high resistance membranes used are minimal [19], and furthermore, the periods required for measurable quantities of radioactive rubidium to exchange across the membranes are very long compared to the time in which the membranes reach the (quasi-)stationary state with respect to the tracer.

The model experiments proper were carried out without the use of a thermostat in an air-conditioned room in which the temperature fluctuated only within a few degrees; any resulting inaccuracies therefrom are negligible for our purpose. The sequence of the main steps in carrying out these experiments was as follows:

To determine the electrochemical characteristics of the porous membrane mounted *in situ* in the model of Fig. 3, aliquots of the two aqueous solutions to be used were placed into the two solution compartments up to a level high enough to submerge the membrane, but too low to establish a contact between the two solutions across the dividing wall of the right-hand side of the cell. The concentration potential, E_1 , arising at the porous membrane, was measured in the conventional manner using saturated KCl-agar bridges and calomel electrodes and a Cary 31 vibrating reed electrometer connected to a digital DC millivolt meter; its resistance was determined by means of sheet platinum electrodes immersed close to it and a General Radio impedance bridge. The concentration potentials, E_1 , arising at the porous membranes mounted

⁴ The time lag caused by this precaution is determined mainly by the time necessary to equilibrate the stirred liquid membrane with the adjacent tagged solution. The progress of this process of equilibration is determined largely by the rate of exchange of tagged and untagged SCN^- ions across the diffusion layers at the membrane-solution phase boundary, a process which even with the limited intensity of stirring permissible at the liquid-liquid phase boundaries is known to be rather fast.

in the several cells listed in column 1 of Table 1 are given in column 2; column 3 gives the corresponding resistances of the membranes as measured *in situ*, R_1 .

For the measurement of the electrochemical parameters of the liquid membrane, the apparatus was emptied and dried, and a thin circular rim of silicone stopcock grease (which does not release any detectable quantities of electrolyte into aqueous phases) was applied around the circular opening of the dividing wall on the side opposite that to which the porous membrane is cemented. A thin glass or plastic plate was now pressed on the rim of stopcock grease as a temporary seal. The solution compartments were again partially filled with the two solutions, as before, to test conductometrically that this temporary seal over the porous membrane did not leak. Next, 30 ml of the lighter-than-water anion exchanger solution which forms the liquid membrane was added to bridge the central barrier within the cylindrical part of the cell. Additional aliquots of the aqueous solutions were added until each compartment contained about 190 ml and the liquid membrane straddled the central barrier in the proper manner, reaching about 10 mm below the top of the latter. Now the concentration potential, E_2 , arising at the liquid membrane and its resistance, R_2 , were measured using the electrode assemblies mentioned above. The E_2 and R_2 values obtained with our several model cells are listed in columns 4 and 5 of Table 1.

The intensities of the currents, I , which will flow (initially) once the cells are operational, as calculated by Eq. (3) from the data in columns 2 to 5, are listed in column 6.⁵

To bring the model cell into the operational state, the cover over the circular opening in the dividing wall was removed, exposing the porous membrane to both solutions. Immediately the potential difference, E_3 , between the two solutions in the operating mosaic cell was measured. The E_3 values measured in our several experiments are listed in column 7 of Table 1; the corresponding values calculated by Eq. (4), E_4 , are listed in column 8.

Next, the radioactive tracers were added to the desired solution, and the magnetic stirring of both solutions and of the liquid membrane phase was started. Throughout the lengthy experiments the model was always covered with Saran Wrap to prevent evaporation.

The maximum percentages of the tracer which would exchange across the membranes to reach the state of equilibrium distribution across the individual membranes are listed in column 9 of Table 1.

One minute after the one solution had been doped with the radioactive tracers, considered as the time zero, a sample was taken, the analysis of which times the volume of the solution gave the total amount of radioactivity present in the model. Thereafter, samples of the initially nonradioactive, tracer-free solution were taken periodically, and occasionally also of the originally radioactive solution, and analyzed. The volumes of the two aqueous solutions were kept constant by the addition of equal volumes of nonradioactive solution of equal concentration. Since the S^{14}CN^- ion exchanges much faster across the liquid membrane than the $^{86}\text{Rb}^+$ ion across the porous membrane, a much longer time, in some instances 10 days or more, elapsed before reasonably accurately measurable quantities of the latter ions appeared in the initially tracer-free solution. Parenthetically, it might be remarked that during these prolonged periods the initial concentration potential, E_3 , of the model decreased slowly by a few millivolts, possibly caused by the absorption of small quantities of decyl alcohol and TOPA from the solutions by the porous membranes and the concomitant swelling of the latter.

The experimental data obtained in this manner were plotted

⁵ The currents in these porous-liquid models, as expected, are much weaker — about 400 to 2000 times weaker — than those measured by Neihof and Sollner [20, 21] in analogous models with two porous membranes mentioned further above.

on graph paper against time. The initial slopes of these curves give directly the initial rates of exchange of the tracers in the model cells expressed in percent of the theoretically possible maximum exchange. These rates of exchange are listed in column 10 of Table 1 for the $S^{14}CN^-$ ion, and in column 11 for the $^{86}Rb^+$ ion. Column 12 gives the ratio of these two sets of rate data.

Discussion

The data presented in Table 1 manifestly confirm the theory developed above of the electromotive and ion permeability properties of mosaic membranes, which are composed of porous areas of extreme ionic selectivity for ions of one sign, and parts consisting of a liquid ion exchanger which are virtually exclusively permeable to ions of the opposite sign. On the basis of the well-known electromotive, resistance, and permeability characteristics of the membranes of these two types, the theory, as developed explicitly for a two-macromembrane mosaic model of concentration cells with relatively low resistance porous and relatively high resistance liquid membranes, leads to the following quantitative predictions which were tested experimentally.

A. The potential difference between the two solutions in such concentration cells, E_3 , given in column 7 of Table 1, should be, within the experimental error, the same as the corresponding theoretical value, E_4 , which is calculated by Ohm's law from the data on the concentration potentials, E_1 and E_2 , across the two membranes in the corresponding single membrane cells, which are listed in columns 2 and 4, and the corresponding resistances, R_1 and R_2 , listed in columns 3 and 5. With our cells, in which the various pairs of membranes have rather extreme ratios of membrane resistances (*compare* columns 3 and 5), it follows as a corollary that E_3 and E_4 should be only a trifle smaller than E_1 .

An inspection of the appropriate columns of Table 1 shows that these theoretical predictions concerning the electromotive properties of the porous-liquid mosaic membrane model cells are fulfilled within the limits of the experimental error.

B. The prediction that the rates of exchange of ions across the very high resistance (stirred) liquid membranes of the model should be very much higher than the rates of exchange of ions across the relatively low resistance porous membranes is verified by the data on the relative rates of exchange of $S^{14}CN^-$ and $^{86}Rb^+$ which are listed in columns 10 and 11 of Table 1. In the present context, the all-important ratios of these two rates are listed in column 12. The magnitude of these ratios confirm the theoretical prediction as to the ion permeability of mosaic membranes composed of porous and liquid parts of high ionic selectivity.

C. The facts and relationships summarized under *A* and *B* together confirm the initially stated thesis, that porous-liquid mosaic membranes may act electromotively like membranes preferentially permeable for ions of one sign of charge while being, in fact, preferentially permeable to the ions of opposite sign.

We have discussed in this paper explicitly only the properties of the simplest type of porous-liquid mosaic membranes, which consist of parts of very high ionic selectivity, in concentration cells with uni-univalent electrolytes. This situation, as was shown above, can be treated readily on the basis of the simplest possible, most clear-cut assumptions, which also lead to quantitative predictions concerning the electromotive and permeability properties of such membranes. However, it is obvious that the general effect stated under *C* could readily be obtained, to an attenuated degree, also with mosaic membranes the component parts of which have less pronounced electromotive and permeability characteristics than those that were considered above.

Various other mosaic systems could also be treated theoretically in a fairly rigorous manner and would be interesting subjects of experimental work. Among the obvious examples of such mosaic models are the following: porous-liquid mosaic cells with "leaky" membranes, membranes that show only a moderately preferential selectivity of the one or the other species of ions; or cells with two liquid ion exchanger membranes having different degrees of ionic specificity; or porous-porous mosaic model cells with highly ion selective membranes, the one of which has an intrinsic ion permeability at least roughly described by the Nernst-Einstein equation, while the permeability of the other one deviates widely from the prediction of this relationship,⁶ including cells with uni-bivalent or bivalent-univalent electrolytes. Which of these or other conceivable mosaic cells would be of particular interest from the point of view of electrobiology is a question which should be answered by investigators better versed in this field than the authors.

References

1. Botrè, C., Scibona, G. 1962. Osservazioni sul comportamento elettrochimico di soluzioni organiche di sali di trialchilammine alifatiche. *Ann. Chim. (Rome)* **52**:1199
2. Carr, C.W., Sollner, K. 1944. The structure of the collodion membrane and its electrical behavior XI. The preparation and

⁶ A model of this latter type according to the previously mentioned data of Gottlieb and Sollner [6] may be constructed using oxidized collodion or polystyrene sulfonic acid collodion matrix membranes as highly cation selective membranes, and poly-2-vinyl-N-methyl pyridinium bromide collodion matrix membranes as highly anion selective membranes.

- properties of "megapermselective" collodion membranes combining extreme ionic selectivity with high permeability. *J. Gen. Physiol.* **28**:119
3. Carr, C.W., Sollner, K. 1964. Auxiliary electrodes in mosaic membrane systems: Porosity mosaics. *Nature (London)* **204**:878.
 4. Carr, C.W., Sollner, K. 1964. The electroosmotic effects arising from the interaction of the selectively anion and selectivity cation permeable parts of mosaic membranes. *Biophys. J.* **4**:189
 5. Carr, C.W., Gregor, H.P., Sollner, K. 1945. The structure of the collodion membrane and its electrical behavior. XII. The preparation and properties of "megapermselective" protamine collodion membranes combining high ion selectivity with high permeability. *J. Gen. Physiol.* **28**:179
 6. Gottlieb, M., Sollner, K. 1968. Failure of the Nernst-Einstein equation to correlate electrical resistance and rates of ionic self-exchange across certain fixed charge membranes. *Biophys. J.* **8**:515
 7. Graham, T. 1854. On osmotic force. *Phil. Trans. R. Soc. (London)* **114**:177
 8. Gregor, H.P., Sollner, K. 1946. Improved methods of preparation of "permselective" collodion membranes combining extreme ionic selectivity with high permeability. *J. Phys. Chem.* **50**:53; Improved methods of preparation of electropositive "permselective" protamine collodion membranes. *Ibid.* **50**:88
 9. Grollman, A., Sollner, K. 1932. Experimental verification of a new theory concerning the mechanism of anomalous osmosis. *Trans. Electrochem. Soc.* **61**:487
 10. Haber, F., Klemensiewicz, Z. 1909. Über elektrische Phasengrenzkräfte. *Z. Phys. Chem.* **67**:385
 11. Helfferich, F. 1962. Ion exchange, p. 339. McGraw-Hill, New York
 12. Höber, R. 1902. *Physikalische Chemie der Zelle und der Gewebe*; (6th Ed. 1926) W. Engelmann, Leipzig.
 13. Höber, R., Hitchcock, D.I., Bateman, T.B., Goddard, D.R., Fenn, W.D. 1945. *Physical Chemistry of Cells and Tissues*. Blakiston, Philadelphia
 14. Höber, R., Hoffmann, F. 1928. Über das elektromotorische Verhalten von künstlichen Membranen mit gleichzeitig selektiv kationen- und selektiv anionendurchlässigen Flächenstücken. *Pfluegers Arch. Gesamte Physiol. Menschen Tiere.* **220**:558
 15. Katchalsky, A., Curran, P.F. 1965. Nonequilibrium thermodynamics in biophysics. p. 133. Harvard University Press, Cambridge
 16. Loeb, J. 1922. *Proteins and the theory of colloidal behavior*. McGraw-Hill, New York
 17. Meyer, K.H., Hauptmann, H., Sievers, J.-F. 1936. La perméabilité des membranes III. La perméabilité ionique de couches liquides non-aqueuses. *Helv. Chim. Acta* **19**:948
 18. Meyer, K.H., Sievers, J.-F. 1936. La perméabilité des membranes. I. Théorie de la perméabilité ionique. *Helv. Chim. Acta* **19**:649; II. Essais avec des membranes sélectives artificielles. *Ibid.* **19**:665
 19. Neihof, R. 1954. The preparation and properties of strong acid type collodion-base membranes. *J. Phys. Chem.* **58**:916
 20. Neihof, R., Sollner, K. 1950. A quantitative electrochemical theory of the electrolyte permeability of mosaic membranes composed of selectively anion-permeable and selectively cation-permeable parts and its experimental verification. I. An outline of the theory and its quantitative test in model systems with auxiliary electrodes. *J. Phys. Colloid. Chem.* **54**:157
 21. Neihof, R., Sollner, K. 1955. A quantitative electrochemical theory of the electrolyte permeability of mosaic membranes composed of selectively anion-permeable and selectively cation-permeable parts, and its experimental verification. II. A quantitative test of the theory in model systems which do not involve the use of auxiliary electrodes. *J. Gen. Physiol.* **33**:613
 22. Nernst, W. 1888. Zur Kinetik der in Lösung befindlichen Körper. *Z. Phys. Chem.* **2**:613; 1889. Die elektromotorische Wirksamkeit der Ionen. *Ibid.* **4**:129
 23. Robinson, R.A., Stokes, R.H. 1955. *Electrolyte Solutions*. p. 293. Academic Press, New York
 24. Shean, G.M., Sollner, K. 1966. Carrier mechanisms in the movement of ions across porous and liquid ion exchanger membranes. *Ann. N.Y. Acad. Sci.* **137**:759
 25. Sollner, K. 1930. Zur Erklärung der abnormen Osmose an nicht quellbaren Membranen. *Z. Elektrochem.* **36**:36, 234
 26. Sollner, K. 1932. Über Mosaikmembranen. *Biochem. Z.* **244**:370
 27. Sollner, K. 1970. The basic electrochemistry of liquid membranes. In: *Diffusion Processes*, Proceedings of the Thomas Graham Memorial Symp., University of Strathclyde, Glasgow, Scotland, 1969. Vol. II. G.N. Sherwood, editor. pp. 655-730. Gordon & Breach, London-New York-Paris
 28. Sollner, K. 1976. The use of models in the study of complex effects at mosaic membranes. *Pontif. Acad. Sci. Scripta Varia* **40**:759
 29. Sollner, K., Grollman, A. 1932. Zur Erklärung der abnormen Osmose an nicht quellbaren Membranen (Part III). *Z. Elektrochem.* **38**:274
 30. Sollner, K., Neihof, R. 1951. Strong-acid type of permselective membrane. *Arch. Biochem. Biophys.* **33**:166
 31. Sollner, K., Shean, G.M. 1964. Liquid ion-exchange membranes of extreme selectivity and high permeability for anions. *J. Am. Chem. Soc.* **86**:1901; 1967. Liquid ion exchange membranes of extreme ionic selectivity and high transmissivity. *Protoplasma* **63**:174
 32. Teorell, T. 1935. An attempt to formulate a quantitative theory of membrane permeability. *Proc. Soc. Exp. Biol. and Med.* **33**:282

Received 19 July 1979