A TEST OF THE THEORY OF THE STEADY-STATE PROPERTIES OF AN ION EXCHANGE MEMBRANE WITH MOBILE SITES AND DISSOCIATED COUNTERIONS

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ABSTRACT An experimental model system, formally equivalent to a liquid ion exchange membrane having completely dissociated sites and counterions, has been devised in order to test the steady-state properties recently deduced theoretically for such a membrane by Conti and Eisenman, (1966). In this system we have obtained quantitative experimental confirmation of the following theoretical expectations. (*a*) The current-voltage relationship is nonlinear and exhibits finite limiting currents with strong applied fields. (*b*) The mobile sites rearrange within the "membrane" under applied electric field to give a linear concentration profile and a logarithmic electric potential profile in the steady state. We have also extended the theory to consider the instantaneous conductance in the steady state. Theory and experiment indicate that in a mobile site membrane the instantaneous conductance in the steady state is *not* given by the chord conductance of the steady-state current-voltage relationship, in contrast to the situation in a fixed site membrane. This finding suggests a way of testing whether ions permeate across an unknown membrane by a fixed site or a dissociated mobile site mechanism.

INTRODUCTION

The electric properties of ion exchange membranes having mobile sites should be of interest to those concerned with the properties of biological membranes for which mobile "carriers" are certainly a conceivable mechanism for ion permeation. Recently, Conti and Eisenman (1966) have deduced the steady-state electric properties of a mobile site ion exchange membrane, which they regarded as an ion exchanger in which the usual restriction of fixation of sites, characteristic of a solid ion exchanger, had been removed. Their analysis dealt only with the simplest conceivable example of such a system, in which the membrane was assumed not only to be impermeable to coions but also to have completely dissociated sites and counterions having constant mobilities. Despite these simplifying assumptions, Conti and Eisenman's analysis can serve as a starting point for the study of the electric properties of ion exchange membranes having mobile sites; but, before using it for such a purpose, it seemed desirable to test the principal conclusions in a system in which the assumptions were unequivocally satisfied. An artificial system was therefore devised in which Conti and Eisenman's assumptions were satisfied; and this paper describes the experimentally observed properties of this system and compares them with those expected from theory.

Three principal steady-state characteristics have been studied; the concentration profile, the electric potential profile, and the current-voltage relationship. For our artificial system, in which only a single counterion species is present, Conti and Eisenman's theory indicates that a mobile site membrane should be characterized by a rearrangeability of sites and counterions under applied electric field which results in a linear concentration profile[1] and a logarithmic electric potential profile as well as a nonlinear current-voltage relationship in the steady state. The experimental results reported below will be found to be in quantitative agreement with theoretical expectations for all of these properties. These expectations may be contrasted with those for a conventional ion exchange membrane having fixed, uniformly spaced sites which is characterized by a constant concentration profile of counterions and a linear electric potential profile, together with a linear (ohmic) current-voltage (I-V) relationship.

In addition to the steady-state measurements described above we have also examined, both experimentally and theoretically, the *instantaneous conductance* in the steady state. We find that the instantaneous conductance in the steady state of a mobile site membrane is *not* the chord conductance of the steady-state I-V relationship. This, in contrast to the situation in a fixed site membrane where the instantaneous conductance in the steady state is, indeed, given by the chord conductance of the steady state I-V relationship (see Conti and Eisenman, 1965*b*). This difference comes about because the "sites" of a mobile site membrane also carry some of the electric current in any nonsteady state.

THE SYSTEM STUDIED

Conti and Eisenman's treatment should apply to a liquid ion exchange membrane, provided that counterions and sites are completely dissociated. Liquid ion exchangers are well known (Coleman, Blake, and Brown, 1962) but it is difficult to find a medium in which to dissolve them which is both immiscible with water and has a sufficiently high dielectric constant for complete dissociation to be assured.

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[1] K. S. Cole has pointed out to us that Planck (1890) first reached this conclusion in his derivation of the properties of a liquid junction [cf. equation 20 of the appendix by MacInnes (1939)]. The conditions within such a junction correspond to those of the present treatment when the system behaves ideally.

Therefore, in order to avoid the complications attendant upon the possibility of ion association, an artificial system was devised in which dissociation was known to be complete. This was accomplished by using as the "membrane" a column of dilute HCl contained between AgCl boundaries (see Fig. 1). Since the AgCl boundaries are reversibly permeable to Cl^- but not to H^+, Cl^- corresponds to the counterion; while H^+ is trapped and acts as the mobile site. This system is particularly convenient in that fine chlorided silver wires can be used for the direct measurement of the chloride concentration profiles as well as of the electric potential within the interior of the "membrane." Moreover, in the concentration range studied (molarity at no point within the system greater than 0.02 mole/liter), H^+ and Cl^- are com-

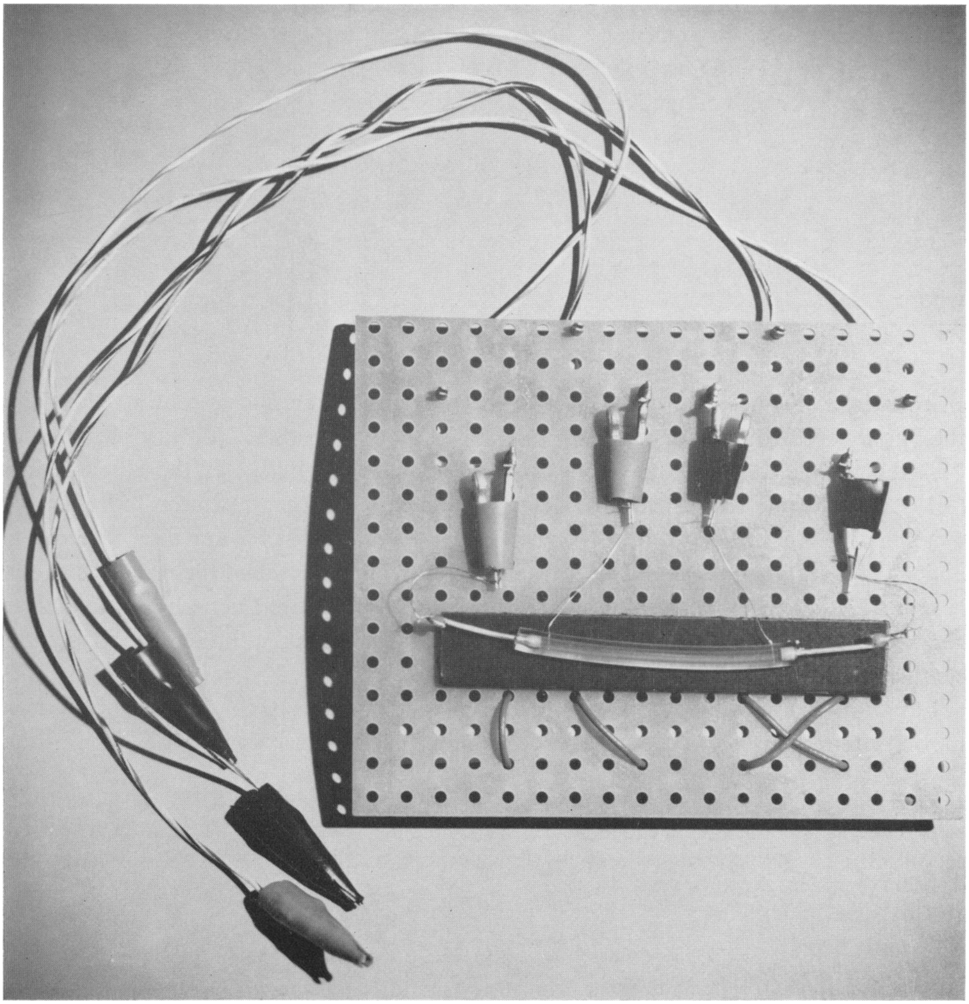

FIGURE 1 Experimental "membrane." For details see Experimental Methods.

pletely dissociated, and Conti and Eisenman's assumptions as to constancy of mobilities and negligible differences between activities and concentrations are approximately true. In fact, as is discussed later, it is neither necessary to assume constant mobilities nor to neglect activity coefficient effects since these are known functions of HCl concentration.

THE THEORETICALLY EXPECTED BEHAVIOR

The following expectations can be deduced for the steady-state behavior of our system directly from the theory of Conti and Eisenman (1966).

The Steady-State Current-Voltage Relationship. When a membrane of thickness d cm, in which Cl^- is the only permeant counterion and H^+ is the trapped (but mobile) site, is interposed between two solutions, equation (45) of Conti and Eisenman (1966) or equation (5) of Eisenman and Conti (1965) for the steady-state current-voltage relationship simplifies to:

$$I = \frac{4FRTu_{Cl}\bar{C}}{d} \cdot \frac{\exp\left[\frac{FV^*}{2RT}\right] - 1}{\exp\left[\frac{FV^*}{2RT}\right] + 1}, \tag{1}$$

where

$$V^* = V - V^0. \tag{2}$$

In equations (1) and (2), I is the electric current density in amperes centimeter^{-2}, F is the Faraday (96,500 coul equivalent^{-1}), R is the gas constant (8.317 joules mole^{-1}°K^{-1}), T is the temperature (298.2°K), u_{Cl} is the (absolute) mobility[2] of the chloride ion (8.19×10^{-9} mole cm^2 joule^{-1} sec^{-1}), $\bar{C}$ is the average concentration in moles cm^{-3}, V is the potential difference in volts between the two solutions for any electric current, and V^0 is the potential difference between the two solutions when the electric current is zero. The current density I is related to the electric current actually applied in a given experiment by $I = I_{applied}/A$, where A is the cross-sectional area in square centimeters.

Equation (1) indicates that the *steady-state* current-voltage relationship for a mobile site membrane is characterized by finite limiting current densities, or satura-

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[2] For convenience, the interrelationships between (absolute) mobility u, electrical mobility u^{el}, equivalent single ion conductance λ as usually defined by alternating current measurements, and diffusion coefficient D can be written as:

$$D = RTu = \frac{RT}{|z|\ F} u^{el} = \frac{RT}{z^2F^2} \lambda,$$

where the equivalent (ac) conductance of the salt $\Lambda_{HCl} = \lambda_{H+} + \lambda_{Cl-} = t_H\Lambda_{HCl} + t_{Cl}\Lambda_{HCl}$. The units of D are cm^2 sec^{-1}; of u^{el} are cm^2 sec^{-1} volt^{-1} and of Λ and λ are ohm^{-1} cm^{-1} equivalent^{-1}.

tion current densities, at high positive and negative applied voltages. The values of the limiting current densities, $\pm I_s$, are deducible directly from equation (1) as:

$$\pm I_s = \lim_{V^* \to \pm\infty} I = \pm \frac{4FRTu_{Cl}\bar{C}}{d}, \tag{3}$$

which for the usual experimental conditions ($\bar{C} = 10^{-5}$ moles cm^{-3}, $d = 5.00$ cm, $A = 2.11 \times 10^{-2}$ cm^2, $T = 298.2$°K) corresponds to a current of $I_s A = 3.32 \times 10^{-7}$ amp.

It is convenient to combine equations (1) and (3) to express the current-voltage relationship in terms of the fraction of saturating current, ϕ, as:

$$\phi = \frac{I}{I_s} = \frac{\exp\left[\frac{FV^*}{2RT}\right] - 1}{\exp\left[\frac{FV^*}{2RT}\right] + 1} \tag{4}$$

or

$$V^* = \frac{2RT}{F} \ln \frac{1 - \phi}{1 + \phi}. \tag{5}$$

which interrelate the current-voltage relationships for differing HCl concentration, temperature, "membrane" geometry, and current density.

The Steady-State Concentration Profile. For our system:

$$C_{Cl} = C_H = C, \tag{6}$$

for all x.

At all times after the initial "Planck charging time" (K. S. Cole, 1965) the electric current is related to the fluxes of chloride and hydrogen ions, J_{Cl} and J_H, respectively, through:

$$I = F(J_H - J_{Cl}), \tag{7}$$

where the units of J_{Cl} and J_H are moles cm^{-2} sec^{-1}. In the steady state $J_H = 0$ in our system and therefore

$$I = -FJ_{Cl}. \tag{8}$$

Combining Conti and Eisenman's (1966) equations (21) and (37) under conditions (6) and (8), the concentration profile $C(x)$ as a function of the current density, I is found to be:

$$C(x) = \frac{I}{2FRTu_{Cl}}\left(x - \frac{d}{2}\right) + \bar{C}, \tag{9}$$

where $C(x)$ is the concentration (in moles cm^{-3}) at any point x within the membrane. Introducing equations (3) and (4) into equation (9) we can express the concentration profile as a function of the fraction of saturation current as:

$$C(x) = \bar{C}\left[1 - \phi + 2\phi \frac{x}{d}\right]. \tag{10}$$

From equations (9) and (10) we deduce that the concentration profile should be linear in the steady state. Alternatively, equation (10) can be used to express the ratios of concentrations at any two points a and b as:

$$\frac{C(b)}{C(a)} = \frac{1 - \phi + 2\phi \frac{b}{d}}{1 - \phi + 2\phi \frac{a}{d}}. \tag{11}$$

Setting $b = d$ and $a = 0$ in equation (11), we immediately express the ratio of the concentrations at 0 and d in terms of the fraction of saturating current as:

$$\frac{C(d)}{C(0)} = \frac{1 + \phi}{1 - \phi}. \tag{12}$$

Using this result, equation (5) can be written as:

$$V^* = \frac{2RT}{F} \ln \frac{C(0)}{C(d)}. \tag{13}$$

The Steady-State Electric Potential Profile. On the other hand, one can integrate equation (22) of Conti and Eisenman (1966) from 0 to x, recalling their equation (37) and our equations (8) and (4), to obtain the expressions for the electric potential profile:

$$\psi(x) - \psi(0) = -\frac{RT}{F} \ln \left[\frac{1 - \phi + 2\phi \frac{x}{d}}{1 - \phi}\right], \tag{14}$$

or

$$\exp\left[\frac{F[\psi(0) - \psi(x)]}{RT}\right] - 1 = \frac{2\phi}{1 - \phi} \cdot \frac{x}{d}; \tag{15}$$

from which it can be seen that, the electric potential is expected to be a logarithmic function of x.

Alternatively, integrating Conti and Eisenman's equation (22) between $x = a$ and $x = b$, where $0 \leq a < b \leq d$, one obtains the expression for the electric potential difference $\psi(b) - \psi(a)$ between these points:

$$\psi(b) - \psi(a) = \frac{RT}{F} \ln \frac{1 - \phi + 2\phi \frac{a}{d}}{1 - \phi + 2\phi \frac{b}{d}} \tag{16}$$

Recalling equation (11), equation (16) can also be written in terms of the concentrations at a and b as:

$$\psi(b) - \psi(a) = \frac{RT}{F} \ln \frac{C(a)}{C(b)}. \tag{17}$$

This electric potential difference is in principle directly measurable by means of salt bridges, but it is more convenient to use Ag-AgCl wires for this purpose. In this latter case the observed potential V_{ab}^{obs}, is given by:

$$V_{ab}^{\text{obs}} = \psi(b) - \psi(a) + V_{ab}^{\text{Cl}}, \tag{18}$$

where V_{ab}^{Cl}, the potential difference due to the response of the AgCl electrodes to the difference of chloride ion activities at $x = a$ and $x = b$, is:

$$V_{ab}^{\text{Cl}} = \frac{RT}{F} \ln \frac{C(a)}{C(b)}; \tag{19}$$

so that, combining equations (18) and (19), we have:

$$V_{ab}^{\text{obs}} = \frac{2RT}{F} \ln \frac{C(a)}{C(b)} = \frac{2RT}{F} \ln \frac{1 - \phi + 2\phi \dfrac{a}{d}}{1 - \phi + 2\phi \dfrac{b}{d}}. \tag{20}$$

When $a = 0$ and $b = d$, equation (20) becomes:

$$V_{0d}^{\text{obs}} = \frac{2RT}{F} \ln \frac{C(0)}{C(d)} = \frac{2RT}{F} \ln \frac{1 - \phi}{1 + \phi}, \tag{21}$$

which can be seen to be identical with the expression (5), so that:

$$V_{0d}^{\text{obs}} = V^*. \tag{22}$$

The Measurement of Chloride Concentration by AgCl Electrodes. It is possible to measure the concentration profile of Cl^- within the system by locating Ag-AgCl electrodes at various points in the interior. The classical expression of Planck (1890) or Henderson (1908) for the diffusion potential under zero current conditions between any two points a and b, V_{ab}^D, is (see equations (16), (24), (25), (29) of MacInnes, 1939):

$$V_{ab}^D = \frac{u_{\text{H}} - u_{\text{Cl}}}{u_{\text{H}} + u_{\text{Cl}}} \frac{RT}{F} \ln \frac{C(a)}{C(b)} = (2t_{\text{H}} - 1) \frac{RT}{F} \ln \frac{C(a)}{C(b)}; \tag{23}$$

where t_{H} is the transference number of H^+:

$$t_{\text{H}} = 1 - t_{\text{Cl}} = \frac{u_{\text{H}}}{u_{\text{H}} + u_{\text{Cl}}}. \tag{24}$$

In the derivation of equation (23) u_{H} and u_{Cl} were assumed to be constant and activity coefficients corrections were neglected. These are reasonable simplifying assumptions over the range of concentrations (molarity ≤ 0.02) within our system but are not necessary, as is shown in the Discussion. Equation (23) is not restricted to the steady state but is valid at any time subsequent to the Planck charging process. It indicates that V_{ab}^{D} depends only on the concentration of chloride ion at $x = a$ and $x = b$, being independent of the details of the concentration profile between a and b. Equation (23) is however, restricted to zero electric current.

Adding the chloride concentration potentials of the Ag-AgCl electrodes to V_{ab}^{D}, we obtain an expression for the potential difference for zero current between two Ag-AgCl electrodes, $V_{ab}^{\text{obs}*}$

$$V_{ab}^{\text{obs}*} = \frac{2u_{\text{H}}}{u_{\text{H}} + u_{\text{Cl}}} \frac{RT}{F} \ln \frac{C(a)}{C(b)} = 2t_{\text{H}} \frac{RT}{F} \ln \frac{C(a)}{C(b)}. \tag{25}$$

This expression is valid for any time after the Ag-AgCl electrodes have reached their steady potentials, which has been found experimentally to be a matter of seconds. It can therefore be used to calculate the concentration ratios of Cl^- from measurements of potential under zero current conditions with AgCl electrodes at various points and times during an experiment. When such measurements are desired while a current is being applied, they have been carried out by interrupting the current for about 30 sec, during which time local Cl^- concentrations are essentially constant in our system. Under these conditions it should be noted that when a given steady-state applied current is first turned off, the concentrations $C(a)$ and $C(b)$ are the same for equation (25) as for equation (20), so that equations (25) and (20) can be combined to give the simple relationship:

$$V_{ab}^{\text{obs}*} = t_{\text{H}} V_{ab}^{\text{obs}}. \tag{26}$$

Some Simple Interrelationships among the Various Calculated and Measured Voltages. In concluding this section, it will be useful to note that some simple interrelationships are apparent among the various calculated and observed steady-state voltages. These are summarized in equation (27).

$$V^* = V_{0d}^{\text{obs}} = \frac{V_{0d}^{\text{obs}*}}{t_{\text{H}}} = \frac{2\, V_{0d}^{D}}{(2t_{\text{H}} - 1)} = 2\, V_{0d}^{\text{int}}, \tag{27}$$

where $V_{0d}^{\text{int}} = \psi(d) - \psi(0)$ is the "internal potential" observed during current flow. Moreover, the difference between the internal potential and the diffusion potential between two points at $x = a$ and $x = b$ is the resistive (IR) drop of the system between these points; so that from equation (26) we also have:

$$IR_{ab} = V_{ab}^{\text{obs}} - V_{ab}^{\text{obs}*} = (1 - t_{\text{H}})\, V_{ab}^{\text{obs}} = t_{\text{Cl}}\, V_{ab}^{\text{obs}}. \tag{28}$$

EXPERIMENTAL METHODS

The system used as a model for a mobile site membrane has been illustrated in Fig. 1. It consists of a length of polyvinyl (tygon) tubing of nominal 1/16" I.D., which was filled with HCl solution of known concentration. The ends of the tube were plugged with Ag cylinders of 0.17 cm diameter which were used to deliver current. At various distances along the length of the tubing Ag wires (0.018 cm diameter) were inserted for recording the potential and chloride concentration within the membrane. Guide holes were made through the wall of the tubing at right angles to the lumen with a 7 mil steel wire prior to inserting the fine Ag wires; the wires were inserted under a disecting microscope and placed with an accuracy of ±0.01 cm, distances being measured from the center to center of the wires. Ag wire of better than 99.9% purity was used. After all recording electrodes were in place, they were electrolytically chlorided in 0.1 N HCl using a heavily chlorided silver wire as the cathode. Each recording electrode was chlorided individually by applying 22.5 v for 5 sec with the cathode first at one end of the tube and then for 5 sec with the cathode at the other end. Immediately after chloriding, the chamber was rinsed with deionized distilled water. Electrodes prepared in this way had a slightly rough, light gray AgCl coat, which was mechanically stable. Any two electrodes so prepared showed a potential difference steady (over the course of an experiment) to within ±0.75 mv. (cf. the columns of Table I headed V_{ab}^{0} (initial) and V_{ab}^{0} (final), which give the values of the electrode potential differences in 0.01 N HCl concentration at the beginning and the end of each experiment of the definitive series. These measurements served as controls for the measurement of Cl^- concentration during the experiment.)

The polarizing electrode plugs were made from silver wire (0.116 cm O.D.) which was melted in a gas flame and shaped into cylinders having a diameter slightly larger than the lumen of the tube so as to give a tight mechanical seal. The surfaces facing the interior of the tubing were ground flat so as to be orthogonal to the axis of the tubing. Prior to insertion into the tubing for a given experiment, each of these surfaces was chlorided lightly at low current densities in 2N HCl using a 1 cm length of tygon tubing as a chloriding chamber and a cathode previously coated with molten AgCl (reagent grade). In order to apply the same amount of AgCl to both plugs, two chloriding chambers were connected in series and both polarizing electrodes were chlorided simultaneously. We found empirically that, since the steady state was attained by 72 hr with a 5 cm long chamber, it was convenient to chloride for 1 hr using a constant current density 100 times that to be used in the experiment. In this way we deposited about 30% more chloride than was removed during the experiment. AgCl so deposited formed a smooth, uniform dark brown layer, which was immediately rinsed with deionized distilled water.

The HCl used for the experiments was prepared by dilution from standardized 5.0N reagent grade HCl (E. H. Sargent Co.) using deionized distilled water, having a conductivity not exceeding that of a solution containing 0.05 ppm NaCl. A few granules of reagent grade AgCl was added to this solution, and it was stored in a tightly closed polyethylene bottle. After preliminary experiments using 0.001N and 0.1N HCl showed that the general characteristics of the membrane did not depend on HCl concentration, we standardized our procedure to use 0.01N HCl for all the experiments reported here. The literature on the transference number measurements in HCl (cf. Jones and Dole, 1929, and MacInnes and Dole, 1931) indicated that exclusion of oxygen from the solution was desirable in order to minimize secondary electrode reactions which might result in the undesirable introduction of OH^- into our system. Accordingly, in early experiments we deoxygenated the solution by bubbling it with tank nitrogen. This procedure was subequently abandoned when it was found that it did not significantly affect the experimental results. As a control that neither H^+ nor OH^- were produced during an experiment we measured as routine the conductivity of our system before and after an experiment, with the finding that the HCl concentration was constant to better than 3% (compare columns G_{inst} (before) and G_{inst} (after) of Table I).

A precise calibration of the cross-sectional area was carried out by measuring the resistance of a 5 cm length of tubing containing an HCl solution of known conductivity with the result that I.D. was found to be 0.164 cm, in good agreement both with the nominal

I.D. (0.159 cm) of the tubing and with a direct optical measurement of 0.16 ± 0.008 cm. The cross-sectional area of the tubing, A, was therefore taken to be 2.11×10^{-2} cm^2 for all calculations.

A major problem encountered in initial experiments was that of convective mixing of the HCl column which disturbed the establishment of concentration profiles of HCl under an applied electric field. The principal cause of convection was found to be temperature gradients introduced into the membrane by the silver electrodes. This problem was eliminated by making the tube long and thin and by placing the entire system in a polyethylene bag which was immersed in a large water thermostat. Convection was still a problem with tubes less than 1 cm in length, but the agreement between theoretical expectations and experimental results indicates that with the 5 cm long tube, convection was effectively eliminated in a system in which a steady state could be attained within a reasonable time.

The recording electrode nearest to one end of the tube was grounded and used as the reference electrode for all potential measurements. The remaining electrodes were connected to the input of a Cary model 21 vibrating reed electrometer by way of a high quality, nonshunting single pole multiposition switch. The output of the electrometer was read directly and also usually monitored by recording on a Rustrak strip chart recorder with a chart speed of 1″/hr.

Constant electric current was delivered through the polarizing electrodes from dry cell or nickel-cadmium batteries (isolated from ground) in series with a calibrated resistor having at least 100 times the maximum resistance of the "membrane" at any time. The current was monitored, at first continuously and later intermittantly, during an experiment by measuring the voltage drop across a second, smaller series resistor of value calibrated to within ± 0.05%. The batteries were found to deliver very stable currents over long time periods (weeks) with the small currents used for the experiments. The current to be used for each experiment was calculated from equations (3) and (4).

For measuring "instantaneous" conductances, a second battery was switched into series with the constant current for delivering brief pulses of constant current; and the "instantaneous" voltage changes at various points in the "membrane" were measured with a high input impedance, amplifier (linear dc to 20 kc) designed by Harry Fein (1964) and built by Roland Wyatt, in conjunction with a cathode ray oscilloscope (Tektronix type 502). The "instantaneous" voltage change was observed to be time independent from 250 msec to more than 15 sec after the current step was made and was read, as routine, 2 sec after the start of the current pulse.

The temperature of the water bath was held at 25° ± 0.2° C in the definitive series of experiments. In earlier experiments, temperatures in a given experiment were held constant to within ±0.2°C but varied from 20° – 25°C from experiment to experiment. The data from these experiments were found to be in good agreement with the definitive results after the ionic mobilities were corrected to the temperature at which the individual experiments were conducted.

THE EXPERIMENTALLY OBSERVED BEHAVIOR IN THE STEADY STATE

Even though this paper is restricted to the steady state it was necessary to characterize the nonsteady-state behavior of the system to establish the conditions for the steady state. The results of these studies will be presented later, together with a theoretical analysis (Walker, Sandblom, and Eisenman, manuscript in preparation).

Before comparing the experimental steady-state observations with those expected from theory, it will be helpful to show the time course of the potential in a typical series of experiments. Fig. 2 presents the time course of potential difference between points $a = 0.04$ cm and $b = 4.96$ cm in a "membrane" of thickness $d = 5.0$ cm. The upper portion is a tracing of part of an experimental record; in the lower portion the data from the same experiment have been replotted in order to show the entire time course of the experiment. From these records it can be seen that, in response to a step application of constant current, a potential difference is observed which consists of an initial "on" step followed by a slower process which reaches a steady state by about 72 hr. When the current is turned off, a similar step followed by a slow decay is seen. The "on" voltage step is proportional to the applied current with a slope in agreement with that expected from the (ac) conductivity of 0.01 N HCl solution, as is discussed in relation to equation (30). The "off" voltage step is also proportional to the applied current but corresponds to a resistance different from that of the "on" step. The reason for this is discussed later.

From data of which Fig. 2 is entirely typical, the results summarized in Table I were obtained. The first column presents the value of the current; while the second gives the fraction, ϕ, of saturating current which this represents. The third and fourth columns give the values of potential observed between points a and b at the beginning and end of the experiment (in both of which situations the concentration profile of HCl was uniform). The fifth column presents the potential difference observed in the steady state between points a and b; while the sixth column gives for

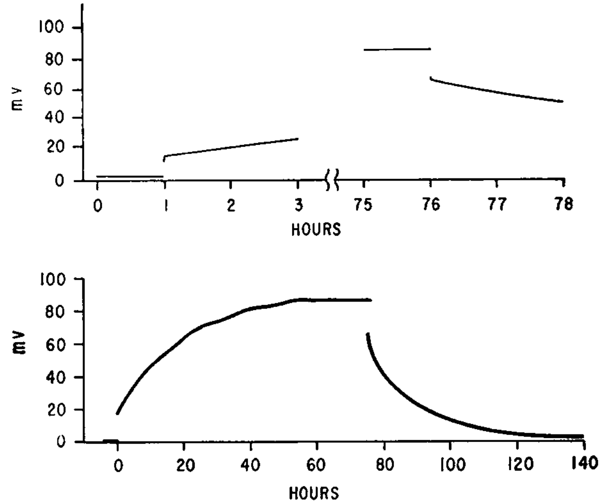

FIGURE 2 Upper: Part of an experimental record showing the time course of the potential change when the fraction of saturation current is $\phi = 0.724$. Lower: Data from the same experiment replotted to show the complete time course of the experiment. Ordinate: millivolts. Abscissa: hours.

TABLE I

	I		V_{ab}^{obs*}		V_{ab}^{obs}		V_{ab}^{off}		$C(b)/C(a)$	
Date	x 10^7	ϕ	before	after	measured	theoretical	measured	theoretical	measured	theoretical
4/23/65	2.03	0.612	−0.5	+1.0	66.0	65.3	54.0	53.6	3.63	3.56
4/30/65	3.20	0.964	−1.0	−1.0	145.	144.	119.0	118.0	17.0	16.7
5/10/65	2.63	0.792	+0.0	−1.0	94.0	94.9	76.5	77.8	6.21	6.42
5/17/65	1.39	0.419	−0.1	+0.0	40.1	41.7	32.2	34.2	2.11	2.26
5/24/65	0.685	0.206	+0.0	−0.1	18.8	19.6	16.6	16.1	1.54	1.60

	G_{inst} x 10^5			G_{inst}^{**} x 10^5		Intercept x 10^7 A		t_H	
Date	before	after	theoretical	measured	theoretical	measured	theoretical	measured	theoretical
4/23/65	1.87*	1.81	1.87	1.58	1.73	−8.76	−9.25	0.812	0.82
4/30/65	1.88	1.78	1.87	1.21	1.23	−11.25	−14.6	0.779	0.82
5/10/65	1.90	1.88	1.87	1.54	1.54	−11.82	−12.1	0.818	0.82
5/17/65	1.91	1.87	1.87	1.85	1.69	−5.91	−6.34	0.810	0.82
5/24/65	1.97	2.03	1.87	1.95	1.94	−2.95	−3.12	0.806	0.82

$T = 25.0°C \pm 0.2°C$; $d = 4.98$ cm.; $a/d = 0.04$; $b/d = 0.96$. Electric currents are expressed in amperes, voltages are expressed in millivolts; conductances in ohms^{-1}. The values of V_{ab}^{obs} have been corrected for the average value of V_{ab}^{obs*}. The measurement of G_{inst} of 4/23/65 marked with the asterisk was used to calibrate the cross-sectional area of the tube.

comparison, the theoretically expected potential difference between these points. The remaining data of Table I will be discussed individually below.

The Concentration Profile. As mentioned in the Introduction, one conclusion of Conti and Eisenman's theory is that in the steady state a mobile site membrane will show a linear concentration profile of its "sites" (and also of its counterions when only one counterion species is present). Fig. 3 compares the experimentally measured steady-state concentration profiles of Cl^- (dots) with theoretical curves calculated from equation (10) for the various indicated magnitudes of applied currents. The abscissa is the fraction, x/d, of the total distance ($d = 4.98$ cm); while the ordinate is the ratio of the Cl^- concentration at x/d to that at $b/d = 0.96$. The values of the concentration ratio were calculated by equation (25) from the potential difference observed between the various AgCl recording electrodes immediately after the current was turned off (e.g. from records of the type of the "off" records of Fig. 2). Since the mean HCl concentration is 10^{-2} N and the maximum theoretically expected HCl concentration is 2×10^{-2} N, activity coefficient corrections were neglected and the measured activity ratio taken as equalling the concentration ratio (see the Discussion for the justification of this procedure). The experimental observations can be seen not only to bear out the expectation of a linear HCl concentration profile but, moreover, to be in excellent quantitative agreement with the theoretically expected concentration ratios.

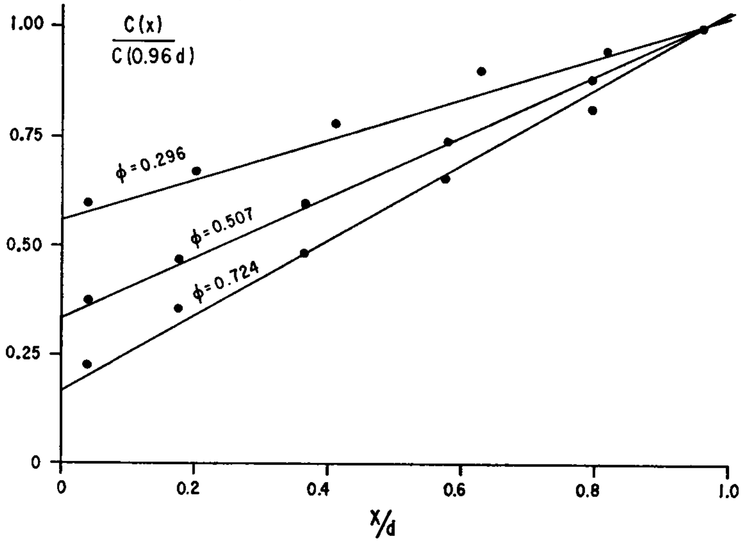

FIGURE 3 Concentration profile. Ordinate: concentration ratio, $C(x)/C(0.96d)$. Abscissa: normalized distance, x/d.

The Current-Voltage Relationship. Equations (4) and (5) indicate that the steady-state current-voltage relationship in a mobile site membrane should be nonlinear and in particular should manifest a finite limiting or "saturation" current for strong applied voltages. Fig. 4 compares the voltages observed in the steady state (large dots) between points near the ends ($a=0.04d$, $b=0.96d$) of the membrane with those calculated from equation (20) (solid curve) for the indicated applied steady-state currents; while Fig. 5 compares the theoretical value of $V^* = V_{od}^{\text{obs}}$ with that calculated between $x=0$ and $x=d$ from the data of Fig. 4. The calculated value of V_{0d}^{obs} is given by $V_{0b}^{\text{obs}}\cdot(V_{0d}^{\text{theor}}/V_{ab}^{\text{theor}})$. The agreement between theoretical expectation and the experimentally observed values is satisfactory in Figs. 4 and 5 and is particularly impressive when one compares the steady-state values with those observed for the instantaneous I-V relationship before any current was applied to the system (open circles) and at the end of a typical experiment (1 week later) after the current had been turned off and the HCl concentration profile had again become uniform (small dots). It was helpful to us to realize when doing the experiments that the instantaneous I-V relationship of Fig. 4 is given by the equivalent conductance of HCl while the slope of the steady-state I-V curve at the origin is given by the equivalent conductance of the chloride ion alone. This is because Cl^- is the only current carrying species in the steady state while instantaneously H^+ is also a current carrying species.

The Electric Potential Profile. Equations (14), (15), and (16) indicate that the potential profile in the interior of the membrane should be logarithmic in the steady state. Fig. 6 presents the experimentally observed steady-state potential

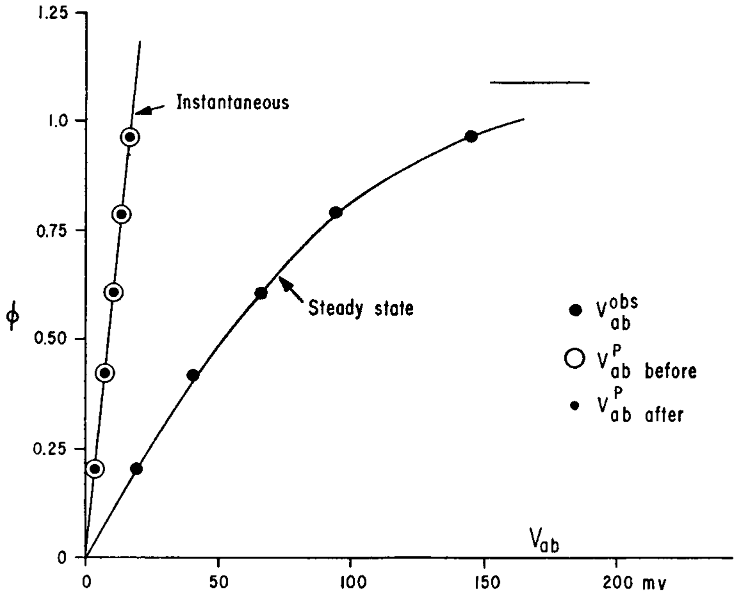

Figure 4 Instantaneous and steady-state current-voltage relationships. Ordinate: fraction of saturation current, ϕ. Abscissa: V_{ab} millivolts. Lines are theoretical. Points are experimental.

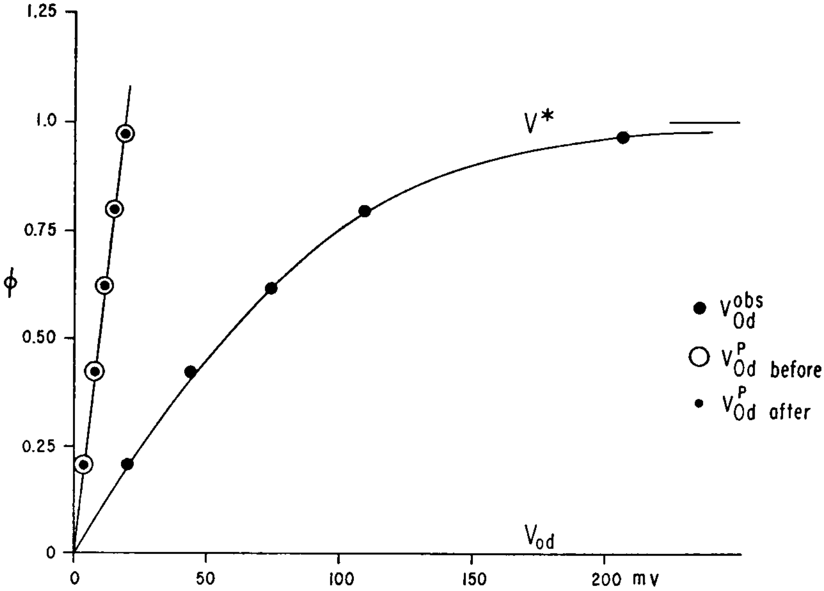

Figure 5 Instantaneous and steady-state current-voltage relationships. Ordinate: fraction of saturation current, ϕ. Abscissa: V_{0d} in millivolts.

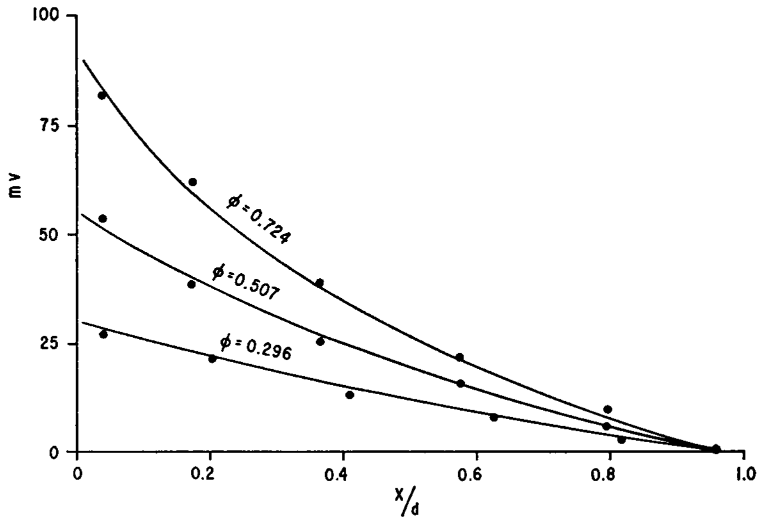

FIGURE 6 Potential profile. Ordinate: millivolts. Abscissa: normalized distance, x/d.

profiles for the indicated applied currents (dots) for comparison with the logarithmic steady-state curves expected theoretically from equations (16) or (20). (Note that the potential difference measured between points *a* and *b* with AgCl electrodes is twice the electrostatic potential difference between these two points.)

The Instantaneous Conductance. When a succession of brief current pulses is applied to our "membrane," a linear I-V curve is invariably observed, even in the nonsteady state. This is to be expected theoretically as will become clear presently. Typical measurements of such conductances are illustrated as dots in Fig. 7. For comparison, the steady-state I-V relationship of Fig. 5 has been redrawn as the heavy curve.

The instantaneous conductance expected theoretically in the steady state can be calculated for comparison with the above observations. In general, the instantaneous conductance between any two points ($x = a, x = b$) is given by [see Teorell, 1953, equation (30)]

$$\frac{1}{G_{\text{inst}}} = \int_a^b \frac{dx}{C(x)\Lambda_{\text{HCl}}(x)} \tag{29}$$

where $C(x)\Lambda_{\text{HCl}}(x)$ is the product of HCl concentration and equivalent conductance at x. In obtaining this result we have assumed implicitly that, for any instantaneous change of voltage, H^+ and Cl^- will each carry its share of the resulting current in proportion to its transference number in solution (as measured in the audio frequency range). Now $C(x)$ is given in terms of the fraction of saturating current by equation (8); and it can be seen therefore that $C(x) = \bar{C}$ for zero current. In this case $\Lambda_{\text{HCl}}(x)$ is also constant, being the equivalent conductance of 0.01 N HCl. Equation

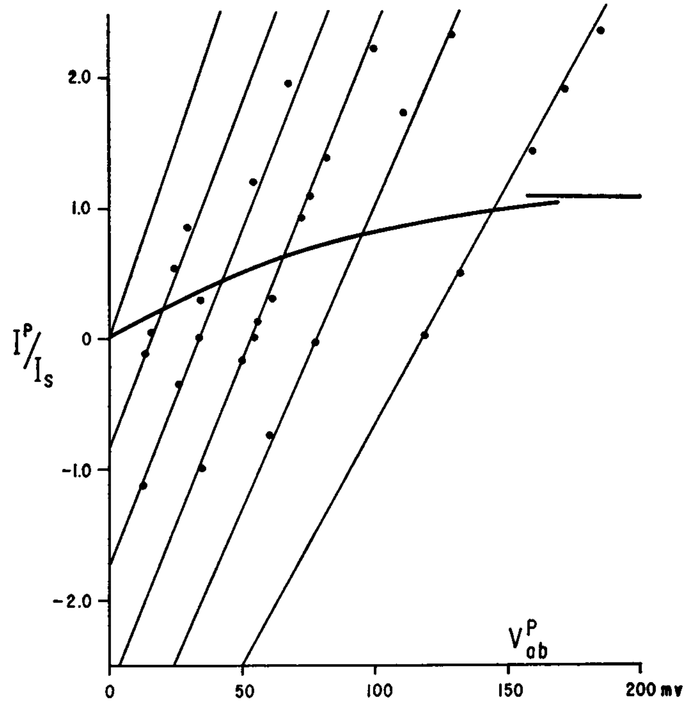

FIGURE 7 Instantaneous current-voltage relationship in the steady state. Ordinate: ratio of pulse current, I^p, to saturation current I_s. Abscissa: pulse voltage, V^p_{ab}, in millivolts.

(29) can be integrated directly to give the instantaneous conductance per unit area as:

$$\frac{1}{G_{\text{inst}}} = \frac{(b-a)}{\bar{C}\Lambda_{\text{HCl}}}. \tag{30}$$

For our particular geometry and HCl concentration this corresponds to a resistance of [1.15 × 10^4 $(b - a)$] ohms. The theoretical line, labeled "Instantaneous," corresponding to this conductance has been drawn in Figs. 4 and 5 and can be seen to be in excellent agreement with the experimentally observed data (see equation (36) for the full equation of this line).

On the other hand, when the steady-state current is not zero, if we assume $\Lambda_{\text{HCl}}(x)$ to be constant, then we can insert $C(x)$ from equation (8) into equation (29) and integrate to obtain the expression for the instantaneous conductance in the steady state, G^{ss}_{inst}, as a function of the applied current as:

$$\frac{1}{G^{ss}_{\text{inst}}} = \frac{d}{\bar{C}\Lambda_{\text{HCl}}}\,\frac{1}{2\phi}\ln\frac{1-\phi+2\phi\frac{b}{d}}{1-\phi+2\phi\frac{a}{b}}. \tag{31}$$

In the limit as ϕ approaches zero, equation (31) reduces to equation (30). Equation (31) also indicates that the value of the instantaneous conductance in the steady state should depend on the magnitude of the steady-state applied current.

We can now write the equation for the instantaneous current-voltage relationship in the steady state of any applied current. Let us define the current density during the current pulse as I^P and the observed voltage between $x = a$ and $x = b$ during the pulse as V^P_{ab}. The instantaneous conductance per unit area is then given by:

$$G^{ss}_{inst} = \frac{I^{P_1} - I^{P_2}}{V^{P_1}_{ab} - V^{P_2}_{ab}}, \tag{32}$$

where the $V^{P_1}_{ab}$ and $V^{P_2}_{ab}$ are the voltages for two different currents I^{P_1} and I^{P_2}. The $I^P - V^P_{ab}$ relationship is given by a straight line:

$$I^P = m V^P_{ab} + b, \tag{33}$$

of slope:

$$m = \frac{I^{P_1} - I^{P_2}}{V^{P_1}_{ab} - V^{P_2}_{ab}}, \tag{34}$$

and I^P intercept:

$$b = I^{P_2} - m V^{P_2}_{ab}. \tag{35}$$

Two points lying on the line are the points (V^{obs}_{ab}, I) and $(t_H V^{obs}_{ab}, 0)$, where the former is the value of V^P_{ab} when $I^P = I$ and is given directly by the steady-state current-voltage relationship [equation (20)] and the latter is the voltage, V^{obs}_{ab}, observed in the steady state immediately upon reducing I to zero, as given by equation (26). Inserting these values in equations (34) and (35), equation (33) becomes:

$$I^P = \frac{I}{t_{Cl} V^{obs}_{ab}} V^P_{ab} - \frac{t_H}{t_{Cl}} I. \tag{36}$$

The solid lines on Fig. 7 have been drawn according to equation (36) and can be compared directly with the experimentally observed data. Further comparison of the observed and theoretical values is offered in Table I, where the measured values of G^{ss}_{inst} and the intercept have been calculated from the data by the method of least squares. Note that when $a = 0$ and $b = d$, the slope of the instantaneous I-V relationship is $I/(t_{Cl}V^*)$.

Equation (36) provides an interesting method for measuring transference numbers by direct electrometric means without necessity for gravimetric procedures. It also provides an additional test of the Conti and Eisenman theory; and the excellent agreement between experiment and theory can be seen in the appropriate columns of Table I.

DISCUSSION

For the present system in which we have a single counterion species, two of the idealizing assumptions made by Conti and Eisenman (1966) [and also by MacInnes

(1939) in relation to equation (23)] can be removed. First, activities need not be assumed to be equal to concentrations because the known activity coefficients can be introduced. Second, it is not necessary to assume individual mobilities to be constant; instead we can be somewhat more general by assuming a constant transference number which is equivalent to assuming a constant *ratio* of counterion to site mobilities. This assumption can be justified by examining the values for the mobilities and transference numbers as functions of concentration (Table II). It can be seen that over the concentration range listed, the mobilities change by more than 8% while the transference numbers change by only slightly more than 1%.

TABLE II

Concentration	t_H	u_H^* (x 10^9)	u_{Cl}^* (x 10^9)
mole/liter			
0	0.821	37.4	79.9
0.005	0.824	36.7	76.7
0.01	0.825	36.4	75.8
0.05	0.830	35.4	71.3
0.1	0.832	34.8	68.7

* Calculated from equivalent conductance data Table (6-2-1A), p. 697, Harned and Owen (1958).

For the range of concentrations encountered in these experiments equation (37) accurately represents the mean activity coefficients as a function of concentration (cf. Harned and Owen, 1958),

$$\ln \gamma_{\pm}(x) = -AC^{1/2}(x) + DC(x). \tag{37}$$

Under the assumption of a constant transference number, the mobility of the counterion can be written as a function of the equivalent conductance as shown in equation (38),

$$u_{Cl} = t_{Cl}(u_{Cl} + u_H) = t_{Cl}\,\frac{\Lambda_{HCl}}{F^2}. \tag{38}$$

The equivalent conductance, however, is given as a function of concentration by the Onsager equation (Harned and Owen, 1958, 178) which means that the mobility can be written as a function of concentration as follows:

$$u_{Cl}(x) = \frac{t_{Cl}}{F^2}\,[\Lambda^{\circ} - (M + N\Lambda^{\circ})C^{1/2}(x)]. \tag{39}$$

The steady-state flux equations for the single ion case are:

$$J_{Cl} = -u_{Cl}(x)C(x)\left\{RT\,\frac{d}{dx}\,[\ln a(x)] - F\,\frac{d}{dx}\,\psi(x)\right\}, \tag{40}$$

$$J_{\mathrm{H}} = 0 = RT\frac{d}{dx}[\ln a(x)] + F\frac{d}{dx}\psi(x). \tag{41}$$

Combining equations (40) and (41) to eliminate $\psi(x)$, and recalling that by definition, $\gamma_\pm^2 = \gamma_+\gamma_-$ (Harned and Owen, 1958), we obtain:

$$J_{\mathrm{Cl}} = -2RTu_{\mathrm{Cl}}(x)C(x)\left[\frac{d}{dx}\ln C(x) + \frac{d}{dx}\ln\gamma_\pm(x)\right]. \tag{42}$$

Equations (37) and (39) can then be substituted in equation (42) and the result integrated to give:

$$\begin{aligned} C(x)\Bigg\{1 - \left[\frac{A}{3} + \frac{2(M + N\Lambda^\circ)}{3\Lambda^\circ}\right]C^{1/2}(x) + \left[\frac{D}{2} + \frac{A(M + N\Lambda^\circ)}{4\Lambda^\circ}\right]C(x) \\ - \frac{2D}{5\Lambda^\circ}(M + N\Lambda^\circ)C^{3/2}(x)\Bigg\} = \frac{IFx}{2t_{\mathrm{Cl}}RT\Lambda^\circ} \\ + C(0)\Bigg\{1 - \left[\frac{A}{3} + \frac{2(M + N\Lambda^\circ)}{3\Lambda^\circ}\right]C^{1/2}(0) \\ + \left[\frac{D}{2} + \frac{A(M + N\Lambda^\circ)}{4\Lambda^\circ}\right]C(0) - \frac{2D}{5\Lambda^\circ}(M + N\Lambda^\circ)C^{3/2}(0)\Bigg\}, \end{aligned} \tag{43}$$

or

$$C(x)f[C(x)] = kIx + C(0)f[C(0)]. \tag{43a}$$

where Λ° is the value of the equivalent conductance in the limit as $C \rightarrow 0$. Equation (43) is completely general and the values of the constants are tabulated for various electrolytes (cf. Harned and Owen, 1958, 179 and 469). Our A corresponds to Harned and Owen's $\mathcal{S}_{(f)}$; similarly $D = \mathcal{S}_{(f)}A' + B$, $M = \beta^*$ and $N = \alpha^*$. For our calculations we have used the values for HCl at 25°C.

In equation (43a) the terms $f[C(x)] \leq 1$ and $f[C(0)] \leq 1$ can be thought of as correction coefficients for nonideal behavior. If $f[C(x)]$ and $f[C(0)]$ are each set equal to 1 equation (43a) becomes identical with equation (22) of Conti and Eisenman in the present single counterion species case.

Recalling that at the saturating current either $C(0) = 0$ or $C(d) = 0$ and also that equation (44) must be satisfied for all currents:

$$\frac{1}{d}\int_0^d C(x)\,dx = \bar{C} \tag{44}$$

the saturating current density under the conditions of nonideal behavior I_s' can be calculated by a method involving successive approximations.

Doing this, we find that the shape of the steady-state I-V curve is not altered for the conditions of our experiment. The principle difference is a change in the saturating current density from $I_s = 1.58 \times 10^{-5}$ A cm^{-2} to $I_s' = 1.55 \times 10^{-5}$ A cm^{-2}. The fact that I_s' is 98.6% of I_s makes it apparent that the nonideal terms $f[C(x)]$ and $f[C(0)]$ do not cause a major change in the current-voltage relationship.

As to the details of the concentration and potential profiles, it is interesting to examine the predictions made from the nonideal theory. The maximum discrepancy between the ideal and nonideal predictions will occur at the highest current and then decrease monotonically to zero as the current decreases to zero. Consequently a comparison will be made here for the case $I = I' = 0.95\, I'_s$. For the points $a/d = 0.04$ and $b/d = 0.96$, the activity and concentration rates are 14.4 and 13.4 for the nonideal and ideal treatments, respectively. The maximum error in the predicted concentration ratio due to the idealizing assumptions of Conti and Eisenman is therefore,

$$\frac{14.4 - 13.4}{14.4} \times 100 = 6.9\% \tag{45}$$

The corresponding error in the predicted potential is:

$$\frac{\log 14.4 - \log 13.4}{\log 14.4} \times 100 = 2.7\% \tag{46}$$

It is of interest also to assess the complications to be expected from the nonzero partial molal volumes of HCl.

The mean apparent partial molal volume of a dilute solution is given by (Harned and Owen, 1958)

$$\Phi_v = \Phi_v^\circ + S_v \sqrt{C} \tag{47}$$

where Φ_v is the mean apparent partial molal volume at concentration C, Φ_v° is the mean apparent partial molal volume at infinite dilution and S_v is a constant. For HCl at 25°C, $\Phi_v^\circ = 18.2$ and $S_v = 8.3 \times 10^{-1}$. For $C = 2 \times 10^{-2}$ N

$$\Phi_v = 18.2 + 1.17 \times 10^{-7} = 18.3 \tag{48}$$

Inserting these figures in equation (20) of Conti and Eisenman we see that their condition (20) is fulfilled in our system to within an error of 7×10^{-4}. The maximum possible effect of the partial molal volumes that can be encountered in these experiments is therefore of the order of 0.07%.

These maximum error calculations make apparent the reason for good agreement between the experimental results and the predictions made from the theory based on Conti and Eisenman's idealizing assumptions.

It should be apparent from the Conti and Eisenman (1965 *a* and *b*) treatment of the steady-state properties of membranes and from the present results on instantaneous properties that there are differences between fixed site and dissociated mobile site systems which in principle provide means of characterizing an unknown membrane. For example, Eisenman and Conti (1965) have noted that the difference in steady-state relationships for fixed site versus dissociated mobile site membranes provides a means for distinguishing by which of the two mechanisms ions permeate an unknown membrane. The present finding that the instantaneous conductance in the steady state has different characteristics in fixed site versus dissociated mobile site membranes provides another possible test, which could conceivably be more easily carried out.

It should be emphasized that we have tested the Conti and Eisenman theory only for the case of a single counterion species. One could devise an experimental system in which to test the theory for more than one counterion species; but we believe, in the light of the excellent agreement between experiment and theory found here, that one can safely accept their conclusions for the properties of a system having more than one counterion species. It seems to us more important to remove the present restriction to completely dissociated systems and to examine the effects of association both theoretically and experimentally. Such work is now in progress in collaboration with Dr. John Sandblom, who has successfully generalized the theory to include the effects of incomplete dissociation.

SUMMARY

The salient predictions of the Conti and Eisenman theory for the steady-state properties of an ion exchange membrane with dissociated mobile sites have been tested experimentally in a system in which their assumptions are valid. The system consists of a thin column of dilute aqueous HCl bounded by Ag-AgCl electrodes. In this system theory and experiment are in good quantitative agreement. In addition, we have extended the theory to considerations of the instantaneous conductance in the steady state; the experimental data are again found to be in good quantitative agreement with the theory. Certain idealizing assumptions made by Conti and Eisenman are assessed for the experimental system where activity coefficients and mobilities are known functions of concentration.

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