ION~SELECTIVE Electrodes, 5

EDITED BY E. PUNGOR

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ION-SELECTIVE ELECTRODES, 5

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Proceedings of the Fifth Symposium held at Mátrafüred, Hungary, 9–13 October, 1988

Edited by

Prof. E. PUNGOR, Ph. D., D. Sc. Member of the Hungarian Academy of Sciences



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PREFACE

About 30 years ago, at the time when Miss E. Rokosinyi and I started the development of the iodide electrode, the glass electrode was the only real ion-selective electrode. No one guessed the great progress that occurred in the research of chemical sensors during this 30-year period. Particularly in the last decade, our knowledge increased greatly in understanding the behaviour of ion-selective electrodes and other sensors, in extending their application and in finding the more and more novel types of sensors.

The 5th Symposium on Ion-Selective Electrodes at Mátrafüred is, in many respects, an important event. Several details of the operation mechanism of electrodes have been elucidated by theoretical researchers working at different parts of the world, the picture is clearer as ever to show how the potentiometric signal develops and thus this Symposium can be the end of a period. Now, at this Symposium, the major trends of future have already been introduced, and the field of earlier potentiometric sensors has been extended.

Like the earlier Symposiums at Mátrafüred, this volume contains not only the lectures, but the discussions are also included. This allows to get a picture on the way of thinking of scientific workshops and the leading principles can be understood.

The book is published in the hope to serve the information of experts working in the field of ion-selective electrode research.

Ernő Pungor

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INVITED LECTURES

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Pergamon Press, Oxford Akadémiai Kiadó, Budapest 1989 5th Symposium on Ion-Selective Electrodes Mátrafüred, 1988

ELECTROCHEMISTRY OF PASSIVE MEMBRANES WITH NEUTRAL CARRIERS T.R. BERUBE, R.P. BUCK, E. GRAF², G. HORVAI², M.L. IGLEHART¹, E. LINDNER², Zs. NIEGREISZ², E. PUNGOR², J.R. SANDIFER³ and

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ABSTRACT

к. то́тн²

The K -valinomycin permselective membrane provides a standard system for describing normal current-voltage and current-time responses of the "closed circuit shuttle" carrier mechanism. A selection of ion-cyclic- and ion-acyclic-carrier system responses have been measured and are reported and compared with the standard responses. Deviations from expected normal behavior suggest Donnan exclusion failure is caused by use of high dielectric constant plasticizers and too few fixed sites in the membrane supports. The closed circuit shuttle model has been extended to allow for Donnan failure, consumption of free carriers, and additional transport by extracted salts. Predicted limiting currents and current-time responses show many features of Donnan exclusion failure.

The I-t curves require numerical solutions of transport equations. Best fits are not found with reversible ion exchange boundary conditions. Slow, potential-independent kinetics for the forward reaction of K^{+} + val(membrane) -> Kval⁺(membrane), and more rapid potential-dependent exit kinetics are satisfactory. We have attempted a global fit for all experiments, but with only modest success. The problem of surface resistances from external films or internal inhomogeneous distribution of sites at the inner surface has been addressed in connection with difficulties in identifying true interfacial kinetics. Two types of membranes have been studied by impedance and activity step methods: silicone-based and PVC-based.

INTRODUCTION

Neutral carriers or neutral ionophores are uncharged, hydrophobic complexing agents that selectively extract ions into inert, passive, fixedsite and mobile-site membranes, typically PVC = poly(vinylchloride). Preferred compositions of "normal" membranes are 33 wt % PVC, 66 wt% plasticizer, and 1 wt % neutral carrier with a choice of plasticizer: a low dielectric constant, oil soluble ester such as DNA = dinonyl adipate, or a high dielectric constant nitrocompound e.g. o-nitrophenyl octyl ether (o-NPOE). The extraction reaction can be ion-dipole outer sphere or adduct formation inner sphere reactions. The literature is extensive (1-8). Recent interpretations of transport, consistent with this study, are by Armstrong and Todd (9,10) and Morf and Simon (11).

Studies of ion transport with or without carriers require perturbations of equilibrium or steady state systems. The many prior studies of potentiometric responses of carrier-based ion selective electrodes are only indicative of possible transport mechanisms. The first publications of neutral carrier induced selective cation transport in an electric field used radio-labelled carriers and ions, and a macrotetralide mixture: 72% nonactin, 28% monactin for K (12,13). There are many more studies (14-18). Recently, the carrier ETH 149 for Li⁺ transport has been investigated (11).

New results on carrier-induced ion transport, using steady state I-V curve and transient I-t analyses, are reported for acyclic carriers: tridodecylamine and ETH 1001, and for the cyclic carrier: nonactin. These results are compared with older, established behavior for the cyclic carrier valinomycin low dielectric constant plasticizers. Ideal responses were not uniformly found for the acyclic carriers or for cyclic carriers in plasticizers. There high dielectric constant are transport new characteristics for all carriers, when used in high dielectric constant solvents. Revision of the shuttle mechanism to include Donnan exclusion failure and inclusion of Butler-Volmer kinetics by digital simulation are the theoretical contributions of this paper.

CLOSED-CIRCUIT SHUTTLE CARRIER MECHANISM AND NORMAL BEHAVIOR

The Model

An ideal, homogeneous, fixed-uninegative site or mobile-site membrane is assumed to contain site-equivalent or excess carrier with complex formation constant large enough (about 10 for Kval) so that nearly all

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counterions are M-C in the unipositive case, and n is often 1. M is typically K and C = valinomycin. The membrane is plasticized and counterions are substantially ionized, i.e. Kval is only partially ionpaired with sites S (called S in Fig. 1 left), so that current is carried by M-C or M-C. Donnan exclusion holds and virtually no anions from the electrolyte are present in the membrane. The membranes are ideally permselective for cations, and surface ion exchange reactions are rapid and reversible. Potentiometric responses are Nernstian or, in the presence of interferences, expressed by the Nicolsky-Eisenman equation. Transport theory, in somewhat different terms, was originally laid out by Morf, Wuhrmann and Simon(17).

Under an applied electrical perturbation, current is carried by M-C hopping from site-to-site without dissociation, and without jumping of free M^+ ions. Wipf et al. (19) have suggested that dissociation contributes some free K that can also carry current. Our calculations suggest this is a very small effect and we find no experimental evidence for it in normal membranes. Carrier is released at the interface where M^+ exits the membrane, but remains trapped in the membrane and is subject to back diffusion across the membrane according to Fick's Laws. The model system in Fig. 1, is basically a simple concentration polarization of carrier such that the carrier, under DC current, has high concentration at the exiting interface and a much lower concentration at the M^+ -entering interface. For fixed-site membranes, the AC resistance is determined by the charge carrier mobility. At DC, there is a constant, limiting current. The differential resistance (dV/dI) is infinite.

Electrochemical Expectations from the Model

Consequences of the theory can be summarized for impedance, steady state I-V curves, current-time transients at constant applied voltage and voltage-time transients at constant forced current. Many of the points here are conclusions from theory and experiment (1-8). Impedance plane plots are expected to show a single geometric semicircle for fixed-site cases and an additional finite Warburg impedance at lower frequencies, when mobile sites are present; although the Warburg impedance can also appear for fixed-site membranes when the carrier concentration is only slightly larger than the fixed site value. I-V curves are expected to be ohmic at low applied voltages with resistance independent of excess carrier. The following



FIGURE 1 (Left) Schematic of Concentration Profiles of Species in an Ideal Permselective Carrier Membrane at zero and at Limiting Current (Middle) Schematic of Concentration Profiles of Species in a Symmetrically Bathed, Donnan Failing Carrier Membrane (Right) Schematic of Concentration Profiles of Species in an Asymmetrically Bathed Donnan Failing Carrier Membrane at zero and at Limiting Current

observations are illustrated in Fig. 2. At moderate voltages, currents deviate negatively from ohmic response, and show a transition region followed by a limiting current at high applied voltages. The limiting currents should be independent of the bathing electrolyte concentrations by Donnan exclusion, since ion-carrier complex concentration cannot exceed the site concentration. Limiting current should be dependent on the excess quantity of carrier since concentration polarization of carrier determines the limiting current value. Current-time transients depend on the applied voltage value, but can be constant in time (at low applied voltages in the ohmic range), or initially constant (at the ohmic value) followed by an exponential decay to the steady state current limiting current. At constant applied current(20), voltages can be constant (at low currents well below the limiting current), or can look somewhat like a chronopotentiogram with an initial voltage that increases to a new constant value (for intermediate



FIGURE 2 Composite View of Carrier Concentration Profiles, I-t curves and steady state I-V curves: upper panels A-D, concentrationdistance plots; mildle panels A-D, current-time curves; lower, current-voltage.

currents) or become very large at currents equal to, or greater than the limiting, diffusion-controlled current.

The distribution of applied voltage across the membrane requires further comment. When a constant voltage is applied and current decays to the steady state value, the voltage appears in three clear-cut segments: two interfacial components and an internal or bulk phase diffusion potential. At these high applied voltages, most of the potential drop is at the interface where cations enter, because of the low carrier concentration. The diffusion potential is simply IR , where the resistance is calculated from the uniform site concentration and the mobility of $\ensuremath{\mathsf{M-C}}$.

The IR value becomes **constant** for high applied voltages on the ideal, ∞^{∞} constant limiting current plateau because the current is constant over a wide voltage range. All of the excess applied voltage appears at the depletion interface according to this classical, reversible interface, diffusion-controlled model.

AN EXPERIMENTAL EXAMPLE SHOWING NEARLY IDEAL BEHAVIOR

K⁺-Valinomycin in Plasticized, Fixed-Site Membranes

The K - valinomycin system behavior is remarkably close to the model described above, although there are noteworthy deviations. PVC is notoriously impure even when purified by extraction and filtration(2). There are fixed-sites, typically 0.05 - 5 mM, values that can be determined chemically(6), and further residual, trace, mobile sites that contribute a mobile-site diffusional Warburg impedance(2). Membranes are plasticized, but not uniformly, and cannot be considered homogeneous. They develop inhomogeneous regions, as deduced from dielectric constant measurements(2). Recent results by Armstrong(21) show that our reported results are too large by virtue of incomplete correction for stray capacitance. Nevertheless the dielectric constants vs plasticizer content do pass through a maximum value of about 7-8. Membranes are also susceptible to water uptake. Resistances are nonlinear functions of plasticizer content and carrier loading. Upon exposure to electrolytes, membranes develop additional, inhomogeneous, high-resistance, surface layers of exuded plasticizer or plasticizer impurities and carrier(3). Although the layers can be partially removed, there seem to remain inhomogeneous surface regions in the bulk membrane with abnormally low species mobilities compared with homogeneous, bulk values. After subtracting surface film resistances, bulk resistances of dummy membranes increase with aqueous solution exposure. It is likely that some charge carriers and trace mobile sites are affected, perhaps trapped or impeded, by absorbed water. The effect is less pronounced for normal membranes with carriers because sequestered ions can reside stably in the plasticized regions.

Because of the naturally low concentration of sites, carrier membranes can be close to Donnan exclusion failure which means that high bathing concentrations of the sensed ion M^+ will allow admission of salt into the membranes. The membrane loses permselectivity; potentiometric responses deviate absolutely negatively from Nernstian expectations, and the responses become sensitive to the bathing electrolyte anion according to the Hofmeister hydrophobicity sequence(4). Addition of mobile sites, such as TPB (tetraphenylborate), improves the Nernstian response; inorganic TPB salts, e.g. NaTPB, must not exceed the total carrier concentration. Otherwise the membrane loses specific carrier selectivity and begins to act as a simple mobile site membrane with more general response to cations. Addition of hydrophobic cation TPB , e.g. tetraalkylammonium TPB, avoids problem(22). The theory has been tested with this interference independently determined medium effect coefficients, and used to fit experimental data for many potassium salts using valinomycin carrier(4).

Electrochemistry of K[†]--Valinomycin in Membranes

Current-voltage curves in the steady state have been extensively determined over a 55 volt range in each direction(1,5). Ohmic character at low voltages is obeyed and the values agree with independent determinations from impedance data. Likewise, limiting currents obey the theory and give reproducible values for the carrier diffusion coefficient that agree with independent determinations. However at high applied voltages, voltage-induced Donnan failure occurs: currents rise linearly with voltage above the limiting value. The extent is dependent on the hydrophobicity of the bathing anion. Normal behavior can be recovered by removing the offending anion and soaking in more dilute solutions of chloride, fluoride or hydroxide. Since excess carrier is available this behavior is limited ultimately by complete conversion of the membrane to the complex salt form. This carrier assisted Donnan failure is a basic consequence of Morf's theory(17) as elaborated by Buck et al. (4), to explain responses of bathing solutions containing dilute K TPB.

Current-time curves, while mathematically difficult to write in closed form, predict ohmic initial values found experimentally for the Kval⁺ system (6). There is a characteristic transition time followed by a exponential current decay to the steady state value. Experimentally the carrier diffusion coefficient can be determined from the transition time and from the decay time constant. Both of these agree with the value from the limiting current and provide an adequate test of **normal** behavior and a test of the approximate theory(6).

OMISSIONS FROM THE IDEALIZED THEORY

Three major omissions from this ideal theory are: slow interfacial ion exchange kinetics (or presence of a resistive surface layer); breakdown of Donnan exclusion so that anions enter the membrane at high applied voltages or at high bathing concentrations; membrane instability, including loss of plasticizer, carrier, or mobile sites, or uptake of water. Most recently, Armstrong and Todd have commented on instabilities(23). Effects of Donnan failure on limiting currents and a simplified theory have been recently given(24). Interfacial ion transfer described by Butler-Volmer kinetics have been stressed consistently by Cammann(25,26). However. slow interfacial kinetics have always been difficult to prove when the interface is bathed in a high resistance medium, or when the underlying phase is highly resistive. Nevertheless, evidence of measureably slow interfacial ion transfer rates in polymers and ionic conductors continues to accumulate(8,27), and may reflect either true surface kinetics or a resistive surface layer. Measureably slow rate constant means heterogeneous 3 -5 to 10 cm/s. Larger values contribute rate constants with values of \approx 10 immeasurably small surface resistances, and smaller values would be inconsistent with rapid, nearly reversible responses of membrane potentials to step changes in the activities of bathing solutions.

DONNAN EXCLUSION FAILURE

Classical carrier transport theory includes the possibility of extensive Donnan failure as bathing activities are increased. Instead of steady state limiting current being independent of bathing activities of the possibility exists that salt extraction will occur with salt. consumption of the excess added carrier. The ability of excess carrier to back diffuse is jeopardized; limiting currents could rise or fall, depending on the relative mobilities of carrier complex and encroaching anion, as carrier is consumed by ever increasing concentrations of the encroaching bathing electrolyte. Decreasing limiting currents were observed for the Ca ETH 1002 carrier system(17). The result was expected because the high dielectric constant plasticizers, required for divalent systems, encouraged Donnan failure. Donnan exclusion failure and the extension of classical theory to neutral carrier systems were explained in detail earlier(4) and the new theory for I-V curves with anion-encroachment by Donnan failure is in press (24).

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For Symmetric Bathing, Reversible Ion Exchange

For all symmetric bathing concentrations of KX, there is a small amount of X in the membrane, and the Kval concentration is in excess of S. When K or the external activity of KX, a, is very large, the membrane is flooded uniformly with KvalX, until all of the carrier is consumed as complex. The concentration profiles before and after Donnan failure are illustrated schematically in Fig. 1. Curiously, the partial limiting current carried by Kval decreases and becomes zero when carrier is totally depleted, because this ion cannot move unless carrier is returned by diffusion across the membrane. However, anions carry an increasing portion of current during Donnan breakdown, but cannot carry more current than is allowed by the diminishing internal diffusion-migration electric field. The latter is determined by the partial limiting current carried by Kval⁺.

Free K concentration is small when the membrane contains excess carrier, by virtue of the large complex formation constant for Kval⁺. When all the carrier is converted to Kval⁺ Cl⁻, and still higher bathing concentrations of KCl are used, then even more KCl is extracted into the membrane; the resistance drops further, and more current can pass the membrane. Since the mobility of free K⁺ is greater then that for Kval⁺, the limiting current may continue to increase at all higher bathing activities, even though the complexed species are not a significant current carrier, i.e. the transferrence number of Kval⁺ decreases while that of K⁺ increases to the value for KCl in the membrane. The flux of Kval⁺ is determined by the flux of free carrier. Since there are no diffusion terms, ion fluxes are determined by the constant field term in the Nernst-Planck equation.

For Asymmetric Bathing

If the Donnan failure occurs at x = d, but not at x=0, the situation is a bit more complicated. It has been worked out (24). To illustrate these cases very simply, the activity coefficients, S, and K were assigned value 1. External concentrations were varied from zero to 10. Because small anions move faster than bulky Kval⁺, D /D = 5 was selected. In Fig. 3a, for symmetric bathing, the total current, anion partial current, cation partial current are illustrated. At low concentrations below one unit, Donnan exclusion holds; cation current remains constant and anions contribute nothing initially. This calculation can be scaled along the bathing concentration axis by letting K be a smaller number.



FIGURE 3 Predicted Limiting Current vs Bathing Concentration Behavior: Total Current, Anion Current, Cation Current, and Electric Field Fig. 3a: Symmetric Bathing, Flooded Membrane

Fig. 3b: Asymmetric Bathing Calculations used S = 1, K = 1, \bar{V} = 10, D_X/D_{Kval} = 5 Fig. 3b: Asymmetric Bathing Calculations used the same parameters I_T = total current; Field (-E) is (Fd/RT)d ϕ /dx Reduced currents are (-Id/FAD)

For asymmetric bathing, the results are illustrated in Fig. 3b. Consequences of Donnan exclusion failure are:

> When coion (anions in the following examples) diffusion coefficients are comparable or larger than that of the counterion, limiting currents increase.

- Increasing limiting current occurs after onset of Donnan failure. The required bathing concentration is a complicated function of D D , K and bathing activities. For normal symmetric bathing, X car a maximum in the limiting current is expected.
- 3) When the dielectric constant is large, KX can be extracted into the membrane without carrier. Then limiting current may further increase because the decreasing transferrence number of complex is replaced by a comparable transferrence number of free cation.
- 4) For symmetric bathing, concentration profiles should be uniform throughout the membrane. I-V curves at increasing applied voltages should be linear, e.g. ohmic.

The ionophores examined in this paper are nonactin (Non), tri-n-dodecy]amine (TDA), and (-) - (R,R)-N,N'-Bis[11-(ethoxycarbonyl)undecyl]-N,N'-4,5-tetramethyl-3.6-dioxaoctane-diamide (ETH 1001).

EXPERIMENTAL

The cell, electrodes and associated experimental apparatus are already described in ref: 7. Nonactin was purchased from Sigma; ETH 1001 was obtained from Fluka and tri-n-dodecyl amine was obtained from Alfa. The membranes were produced by the method described in our earlier papers (2,3). Nonactin and TDA membranes were plasticized with dinonyladipate (DNA). The ETH 1001 was plasticized with o-nitrophenyloctylether (o-NPOE).

RESULTS

A. Steady State Responses-Nonactin

Steady state I-V curves reveal that the mode of cation transport is nearly the ideal neutral carrier mechanism found for valinomycin. This conclusion can be reached from, among others, the proportionality of the limiting currents with the carrier concentration. Figure 4 shows the curves for two carrier concentrations, 14.9 and 2.79 mM Non. Data on limiting currents from a number of measurements are in Ref. 24. The diffusion coefficient for nonactin is found to be 1.3×10^{-8} cm²/s. The same limiting current (for the same membrane) when bathed in 0.001 and 0.0001 M NH Cl implies that there is neither significant bathing solution-induced carrier consumption nor substantial loss of the ionophore to the solution.

There is a 1:1 ratio between the cation and ionophore in the ammoniumnonactin complex (28). The charge is presumably passed by the NH Non complex through the fixed sites, consistent with the equality of the high frequency and DC resistivity (24). This property of fixed site membrane transport has been mentioned before(29). The lack of membrane resistivity change at different bathing concentrations supports ideal behavior, as well. Upon application of high voltages and, depending on the concentration of the bathing solution, currents increase above limiting values by Donnan failure. This result is completely analogous to the valinomycin membrane. Further confirmation of ideal behavior is given by the transient behavior in a later section.

Another similarity between nonactin and valinomycin is found from the impedance data. A 1 wt.% nonactin membrane has a typical specific resistivity, ρ of 215 MΩ-cm, a permittivity of 0.876 pF/cm and a dielectric constant of 10. The second semicircle is time dependent and can be removed by exposing the membrane surface to air. A membrane soaked for 12 hours in 0.001 M NH Cl develops a low frequency semicircle with a normalized resistance of 1.55 MΩ cm. The normalized capacitance is 0.155 μ F/cm² and the time constant is 0.241 sec. The second semicircle is thought to be an exuded plasticizer impurity surface film resistance, analogous to the Kval⁺ film(2,3).

2. Tri-n-dodecyl amine.The I-V curves for TDA membranes have limiting currents that depend on the bathing solution concentration as well as the carrier loading. This is an illustration of the abnormal behavior anticipated theoretically when Donnan exclusion failure occurs by virtue of the carrier hydrophobicity and a large ion-carrier complex formation constant. In Figure 5, a 5.39 mM TDA membrane gives constant (within experimental error) limiting currents at lowest bathing activities, followed by diminishing plateau currents at increasing HCl concentrations. The limiting current is 3.75 μA for 0.0001 M, 3.78 μA for 0.001 M, 2.98 μA for 0.01 M and approximately 0.6 μ A for 0.1 M HCl. This dependence is consistent with the simple theory. In the vicinity of 0.001 M HCl, Donnan failure has become signicant. As the membrane extracts more protons, as HCl, more carrier is consumed. The amount of bound carrier is no longer negligible, and the cation limiting current decreases. This loss of permselectivity and the resultant carrier consumption may very well be the cause of this sensor's potentiometric failure at high acid concentrations.

When Donnan failure occurs, limiting currents are no longer proportional to total carrier content. Experimentally one would expect limiting currents to increase with, but not necessarily be proportional to, carrier loading at fixed bathing activities in excess of about 0.001 M HCl.



FIGURE 4 I-V Curves of Different Nonactin Membrane Concentrations. Sweep in the Direction of Increasing Voltages. o 14.8 mM Nonactin + 2.79 mM Nonactin



FIGURE 5 Electrolyte Concentration Studies on the Steady State I-V Properties of TDA Membranes. Sweeps are in the Direction of Increasing Voltages. o 0.1 M HCl

* 0.01 M HCl + 0.001 M HCl x 0.0001 M HCl

Observed currents are not proportional when 22.6 and 5.39 mM TDA membranes are compared. The limiting currents are 7.71 μ A and 3.78 μ A for the two carrier loadings, respectively, in 0.001 M HCl. Evidently these concentrations do not produce excessive amounts of salt extraction as judged by the nearly equal limiting currents when bathed in 0.001 and 0.0001 M HCl. However, one can prove from bulk resistivity measurements (below) that the system is on the verge of Donnan failure. There seems to be sufficient excess current contribution from coions to cause high apparent diffusion coefficients of TDA as judged from the 22.6 mM concentration (2.7 x 10 cm²/s) and even greater value for the 5.39 mM membrane, 5.6 x 10 cm²/s.

The initial DC resistances agree with the high frequency resistances for 0.001 M HCl (and lower concentration) bathed membranes. As Donnan failure begins at bathing solutions exceeding 0.001 M HCl, we find that the bulk resistivities of TDA membrane decrease with increasing acid concentration: 314 MQ-cm in 0.001 M HCl, 54.4 MQ-cm in 0.01 M HCl and 41.6 MQ-cm in 0.1 M HCl for 5.39 mM TDA membranes.

TDA membranes, dried in air after exposure to solutions, show an unusal growth of the surface film impedance, illustrated in Ref. 24. This behavior is unlike that found for valinomycin membranes. A 22.6 mM TDA membrane soaked in 0.001 M HCl, has well-resolved bulk and surface semicircles. Upon exposure to air, the surface semicircle appears to grow, but merges into the bulk semicircle. Before exposure to air, the bulk semicircle's specific resistance was 156 MO-cm with time constant, au_{\perp} , of 0.123 msec. The normalized low frequency semicircle resistance was 0.286 M Ω cm and $au_{
m p}$ was 0.0454 msec. After air exposure, the bulk resistivity decreased 10% to 133 MQ-cm with time constant 0.111 msec. The second semicircle resistance grew to 1.26 MQ cm² with time constant 1.75 msec. The behavior may be the result of TDA's surfactant properties at high membrane loadings. Merging of two semicircles is not found when the membrane is bathed in 0.0001 M HCl. This normal behavior, as judged from valinomycinloaded membranes, is collowed and the second (low frequency) semicircle disappears. This phenomenon is also carrier concentration dependence and no merging of the two semicircles is observed for 5.39 mM TDA membranes in 0.001 M HCl.

3. ETH 1001 I-V curves for a wide range of CaCl bathing 2+ 2 concentrations were determined for a Ca -selective PVC membrane, plasticized with o-NPOE, containing the ionophore, ETH 1001. As carrier

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consumption occurs, beginning at about 0.001 M, limiting currents increase as anticipated from the simple theory. This result, in Fig. 6, is expected in view of the high dielectric plasticizer. Only the lowest bathing concentration gives reliable data for pure Ca-C²⁺ transport. Data for 0.0001 M was used to calculate a steady state diffusion coefficient of 5.0 $x = 10^{-8}$ cm²/s. Rising limiting currents with increasing KCl were also observed for the Kval⁺ electrode when it was plasticized with o-NPOE (5).

The I-V results for ETH 1001 membranes are different from, but complementary to, the observations for a structurally similar ionophore, ETH 1002(17). Using ETH 1002 in place of ETH 1001, I-V curves show decreasing limiting currents with increasing CaCl bathing solutions as a result of extensive carrier consumption. Our conclusion is that the earlier results(17) correspond to greater Donnan failure so that the limiting currents are on the high concentration side of the response maximum. These ligands differ by two methyl groups, and the structures are described by Morf(30) as ligands 8, ETH 1001, and 15, ETH 1002. ETH 1002 is nearly the same molecule as ETH 1001, but without methyl groups in the 4,5 positions. The implication is that ETH 1002 forms a stronger complex and K for ETH 1002 is larger than K for ETH 1001.



FIGURE 6 Steady State I-V Curves of a ETH 1001 Membranes Bathed in Different Concentrations of CaCl₂. + 16.0 mM ETH 1001 membrane in 0.1 M CaCl₂

* 16.0 mM ETH 1001 membrane in 0.01 M CaCÍ o 16.0 mM ETH 1001 membrane in 0.001 M CaCÍ x 10.1 mM ETH 1001 membrane in 0.0001 M CaCÍ Figure 6 is thought to be an accurate representation of the I-V curve for two reasons. First, voltage induced membrane change was minimized by initially applying small voltages. Voltage assisted salt extraction occurs mainly at higher voltages. In this way, all points measured experienced the lowest applied bias possible (i.e. the least possible membrane change). Secondly, our steady state data were measured as a constant current for 16 minutes.

Steady state resistivities confirm that salt extraction is occurring. The DC resistivities for a 16 mM ETH 1001 membrane are 10.7, 13.7, 16.5 and 29.6 MQ-cm for membranes bathed in 0.1, 0.01, 0.001 and 0.0001 M CaCl, respectively. In all the solutions, resistances decrease during I-V measurement and reach steady values after about 16 minutes. These resistivity drops are much more pronounced than the small drops found for low dielectric constant DNA plasticized membranes (1). The great amount of voltage assisted salt extraction required to reach steady state is a consequence of the o-NPOE's higher dielectric constant.

The high frequency bulk resistance is also dependent on the bathing electrolyte and provides further confirmation of Donnan failure. Impedance values for a 1% membrane over a wide bathing concentration range are in Ref. 24. The bulk resistivities increase with decreasing solution concentration until the membrane is bathed in 0.0001 M CaCl. Similar behavior is also found for the surface film resistances. Toth et al. (3), have interpreted this behavior as concentration dependent salt extraction into the exuded film. This film's properties are similar to other plasticized PVC membranes with the exception of TDA based films, above.

B. Current-Time Behavior-Nonactin

Fixed-site systems loaded with large excess of neutral carrier should display current-time responses to constant applied plateau voltage that have three characteristic regions: 1) the nearly constant initial current, 2) a monotonic exponential decay and 3) a steady state current(7). The I-t transient of a 2.79 mM Non membrane is illustrated in Figure 7. All three regions are observed. The initial current is exactly given by - $V_{Appl} \sim (R)$. The nearly constant initial current reflects transport of NH Non $Appl \sim 4$ through fixed sites of the membrane. At the transition time, surface concentrations of the carrier at the NH + 4membrane are zero and 2V. The transition time can be used to calculate the diffusion coefficient of Non in the membrane. For 1% Non membranes, the calculated diffusion coefficient is 1.6 x 10^{-8} cm²/s. The current decay is

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