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VALIDATION OF CARRIER-MEDIATED TRANSPORT OF H^+ AND Na^+ THROUGH MOBILE-SITE MEMBRANES

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Summary—The response of membranes containing neutral ion carriers of either H^+ or Na^+ to an externally-applied potential step was investigated using previously developed techniques for the analysis of charge and mass transport in ion-selective membranes. The results from constant-resistance membranes, *e.g.* membranes with unperturbed negative site concentration profiles, showed that tridodecylamine behaved as a carrier for H^+, and there was no evidence for proton hopping from stationary carriers. In addition, the experimental outcome supported the assumption of a failure of the Donnan exclusion principle at very low pH levels in these membranes. The results from membranes containing the Na^+ carrier illustrated the significant concentration polarization of ionic species, which was related to significant changes in bulk membrane resistance.

Earlier studies presented theoretical and experimental verification of carrier-mediated transport of a selected ion, K^+, through a permselective membrane containing mobile sites.[1] Two types of response to an externally applied potential step were isolated, depending on whether the carrier or the ionic species (both negative sites and positive ion complexes) inside the membrane restricted the transport process of the counter ion. The experimental verification of the theoretical transient and steady-state responses was accomplished using plasticized PVC membranes containing valinomycin (K^+ carrier) and tetraphenylborate (TPB)-type mobile sites.[1] In addition, spectroscopic evidence from membranes containing chromoionophores qualitatively related two different chronoamperometric (current *vs* time) and transient-resistance responses to significant concentration perturbation of either carriers or ionic species.[2]

Both of these investigations benefitted from previous knowledge of diffusion coefficients[1] or the ability to trace and measure the concentration of the carrier species inside the membrane.[2] However, under most circumstances, there is no prior knowledge of the transport parameters, and the most convenient measurement is the response of the system to an external electrical excitation. In this work, transient and steady-state responses of two other carrier-type membranes to an applied potential step are interpreted using results from the above model systems.

The first example is of a plasticized PVC membrane containing tridodecylamine (TDDA)—one of the most frequently-used carriers in the fabrication of pH ion-selective electrodes.[3] The high selectivity of TDDA towards H^+ is explained by the presence of a tertiary amine in the center of the molecule. An earlier investigation showed a peculiar chronoamperometric response from membranes made with this species.[4] Unlike the results obtained from fixed-site plasticized PVC membranes containing common cyclic ionophore/carriers, such as nonactin and valinomycin, the transient currents did not show the characteristic current break, which is related to the depletion of carrier at one interface.[5] In addition, the steady-state current *vs* voltage plots showed several limiting currents, depending on the pH of the contacting aqueous solutions. One of the intriguing questions that this work addresses is whether the carrier mechanism exists in this membrane at all.

The second example is a sodium ionophore, bis[(12-crown-4)methyl]dodecylmethylmalonate (Na VI).[6] Unlike valinomycin, it is not monocyclic, and the two crown units cooperate to bind a single sodium ion. The results shown here confirm both the carrier mechanism and the transport processes of the ionic species in membranes containing this acyclic ionophore.

EXPERIMENTAL

Reagents and solvents

PVC, tridodecylamine (TDDA) and bis[(12-crown-4)methyl]dodecylmethylmalonate (Na VI) were purchased from Fluka. Sodium tetraphenylborate (NaTPB) was obtained from Aldrich. Citric acid, concentrated NaOH, NaCl and tetrahydrofuran (THF) were from EM Sciences. Concentrated hydrochloric acid was from Fisher. Di(2-ethylhexyl)sebacate (DOS) was bought from Sigma. Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaT*m*FMPB) was a gift from Dr Maurice S. Brookhart (UNC).

Membrane preparation

THF solutions of PVC and DOS (at 1:2 weight ratio, respectively) were prepared several days in advance, and mixed with desired amounts of fresh THF stock solutions of TDDA or Na VI and fresh THF stock solutions of mobile-site salt. The membranes were cast using the procedure described by Craggs *et al.*,[7] and were approximately 100×10^{-6} m thick.

Apparatus

The membranes were placed between two aqueous pH 5 citrate buffer (for TDDA membranes) or 0.01*M* NaCl (for Na VI membranes) solutions in an electrochemical cell, designed for the purpose of ionic transport analysis, similar to that described earlier.[5,8] Desired voltage steps were applied by a Solartron 1250 frequency analyzer (Solartron Instrumentation Group, Farnborough, U.K.) through an EG&G 363 potentiostat (Princeton Applied Research, Princeton, NJ, U.S.A.), controlled by a Zenith XT computer equipped with a CEC IEEE 488 interface (Capital Equipment Corporation, Burlington, MA, U.S.A.). This equipment was also used to perform impedance spectroscopy analysis of the membranes. Current *vs* time data were collected by the same computer using a Data Translation DT2801 A/D board (Data Translation, Marlborough, MA, U.S.A.).

RESULTS AND DISCUSSION

Tridodecylamine (TDDA)

The first goal was to determine whether TDDA exhibited chronoamperometric behavior which was consistent with a carrier mechanism. Therefore, a series of potential-step experiments on plasticized PVC membranes containing tridodecylamine and no additional mobile sites were conducted. In these systems, the sources of negative sites are assumed to be anionic groups attached to the PVC matrix, unbound emulsifier residues, and others.[9,10] Since earlier investigations[8] demonstrated their relative immobility, they are usually called fixed sites. Figure 1(a) shows a current *vs* time plot obtained from several potential-step experiments on a fixed-site plasticized PVC membrane containing 0.5 m*M* carrier (TDDA), which was immersed between two pH 5 citrate buffer aqueous solutions. Each voltage was applied after the membrane had been allowed to relax and equilibrate at 0 V for several hours. The clearly observed characteristic current drop (*e.g.* near 150 sec at 7 V) is due to the increase in the interfacial potential drop, given by

$$V_{\text{int}} = \left| \frac{RT}{F} \ln \frac{a_{\text{H}^+}^{\text{interface 1}}}{a_{\text{H}^+}^{\text{interface 2}}} \right| = \left| \frac{RT}{F} \ln \frac{a_{\text{TDDA}}^{\text{interface 2}}}{a_{\text{TDDA}}^{\text{interface 1}}} \right| \quad (1)$$

where R is the universal gas constant; T is the temperature; F is the Faraday constant; and a_i^x is the activity of species i at location x inside the membrane.[5] The magnitude of V_{int} becomes large, when the carrier is depleted at the membrane/aqueous solution interface where H^+ enters the membrane, due to the reaction $TDDA_{(\text{memb})} + H^+_{(\text{aq})} \rightleftarrows HTDDA^+_{(\text{memb})}$. The break in the current also appears earlier at higher potentials, as predicted theoretically.[5] From these results, the diffusion coefficient of TDDA was calculated to be 1.3×10^{-11} m^2/sec. This relatively high value is supported by results from a Cottrell plot analysis of the I–t curve at 7 V, shown in Fig. 1(b), which yields a value of 3×10^{-11} m^2/sec.

The observed initial current decline, *e.g.* during the initial 25 sec in Fig. 1(a), is not understood at this point. This feature was often observed in chronoamperometric experiments on membranes containing other ionophores, and an attempt was made to explain such experimental results for fixed-site valinomycin membranes, if there were limits on interfacial reaction kinetics.[11] However, in this investigation, these initial current drops could not be reproduced consistently. Therefore, this study does not attempt to resolve such observations.

A similar chronoamperometric analysis was done in membranes containing 7.4 m*M* TDDA (total species concentration) and additional 1.0 m*M* tetraphenylborate negative sites (total concentration). Earlier work showed that these systems exhibited constant resistances which

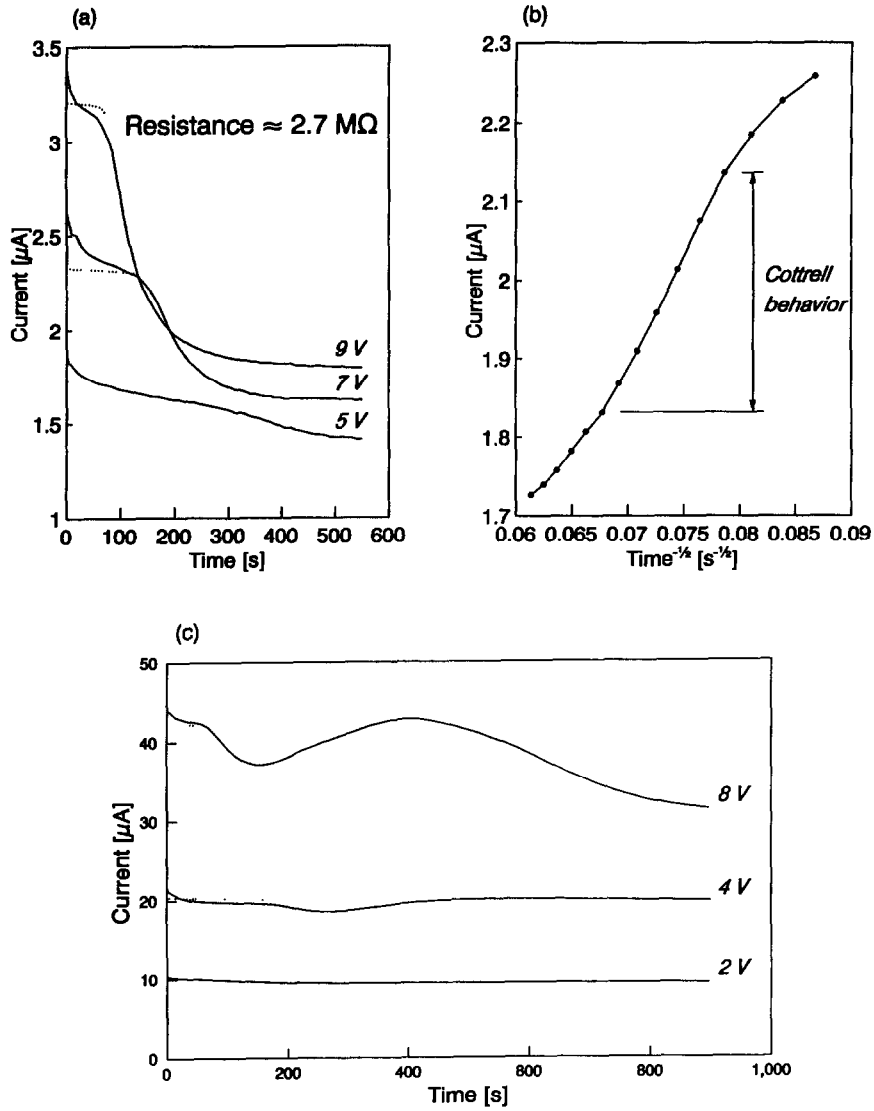

Fig. 1. Transient current responses of constant-resistance membranes containing TDDA. (a) Response of a fixed-site membrane to several potential steps of different magnitudes. (b) Cottrell plot of the results from the 7 V potential step in (a). (c) Transient current responses of a mobile-site membrane containing additional TPB. (The solid lines in (a) and (c) are experimental observations, and the dotted lines are from the approximate solution in Ref. 5).

were lower than those observed in fixed-site membrane.[1-2] Figure 1(c) presents the chronoamperometric results from the application of a series of potential steps. Although the currents are an order of magnitude higher than those measured in the fixed-site case, the distinct current break (in the current–time response curve) is evident at 4 and 8 V. A diffusion coefficient value of 1.0×10^{-11} m^2/sec for TDDA was again calculated using the approximate solution developed in Ref. 5.

An interesting behavior is noticed in Fig. 1(c) when an 8 V potential step is applied. After the sharp current drop, the current does not fall to a low limiting value, but starts to rise. This can be interpreted as the failure to maintain the H^+ selectivity at the interface (failure of the Donnan exclusion principle). Therefore, the magnitude of the interfacial potential drop, given by equation (1), cannot be expressed simply by using the carrier concentrations, but requires a full accounting of all of the ionic concentrations. Under these circumstances of decreased interfacial potential drop, the ohmic potential drop gradually increases to maintain the constant total applied voltage, and the cur-

rent becomes larger, as long as the resistance of the membrane remains constant. From approximately 400 sec, there is a decline in the current that is related to the slow increase in bulk membrane resistance due to the polarization of ionic species inside the membrane. The resistance at 1000 sec measured using impedance spectroscopy, reaches 250 kΩ (up from 180 kΩ initially), and the calculated ohmic potential drop is approximately 8 V. This is direct evidence for the decreased, almost insignificant contribution of the interfacial component to the total fixed membrane potential drop, as predicted for Donnan failure.

Steady-state currents may be plotted *vs* applied voltages using the final values of transient current results such as shown in Figs 1(a) and (c). Obviously, the limiting currents, that should be identical in all cases of high voltage, are not constant. Under the assumed circumstances of carrier concentration-polarization control, the steady-state current should be the limiting current, since the steady-state concentration gradients of TDDA are at their highest possible value:

$$I_l = FAJ_{\text{carrier},l} = FAD_{\text{carrier}} \frac{2c_{\text{carrier,tot}}}{d}, \qquad (2)$$

where I_l is the limiting current; A is the membrane cross-section area; $J_{\text{carrier},\,l}$ is the steady-state flux of the carrier when this species is completely depleted at one end of the membrane; $c_{\text{carrier, tot}}$ is the initial net carrier (*i.e.* uncomplexed neutral carrier species only) concentration; and d is the membrane thickness. The lack of constant steady-state currents at high applied voltages implies the breakdown of interfacial permselectivity.

Finally, the membrane failure, when it was contacted by very acidic solutions, was investigated. At very low pH (below pH 3 for TDDA), it has been assumed that coions, such as chloride, may enter the membrane from the aqueous solution together with H^+ ions (*i.e.* failure of the Donnan exclusion principle). In addition to rendering equation (1) inappropriate, because anion transport across the interface is not included in it, this event will disrupt the ionic balance, which is controlled under normal conditions (*i.e.* higher operating pH) by the amount of negative sites inside the membrane. Consequently, two major changes in the membrane are anticipated at these very low pH conditions: (i) the amount of neutral TDDA will decrease due to the reaction with H^+ to form additional positive $HTDDA^+$ ion complexes (which are produced to balance the charge of the extra negative chloride ions) and (ii) the membrane resistance will decrease due to the presence of more ions. Figure 2(a) clearly shows the decrease in the resistance of the 0.5 m*M* TDDA fixed-site membrane initially immersed in a pH 5 buffer solution, as a function of time from the moment of immersion in 0.01*M* $HCl_{(aq)}$. It should be noted, however, that relative to the present measurements, which were taken while

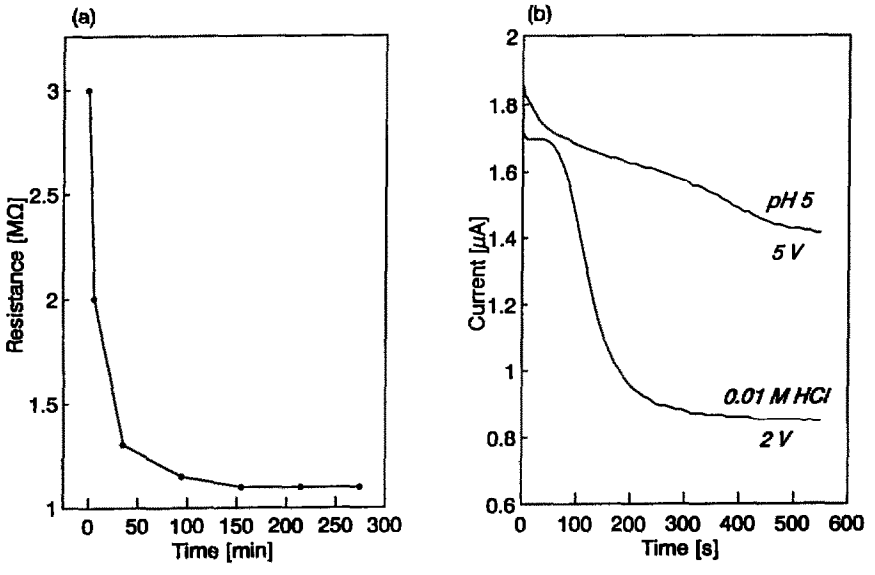

Fig. 2. Effects of changing contacting solution from pH 5 to 0.01*M* HCl on a fixed-site TDDA membrane. (a) Transient change in bulk membrane resistance. (b) Current *vs* time plots of the same membrane but at different pH levels.

potential steps of approximately 2 V were being applied, the rate of change of the membrane resistance may be slower when the membrane is simply soaked and equilibrated in the solution. Figure 2(b) presents the change in transient current behavior as a result of an applied potential step after approximately 3 hr of soaking in a pH 2 solution. The shorter time that was needed to reach the point at which the interfacial TDDA was almost completely depleted (*i.e.* when the current break is observed at ~60 sec *vs* ~350 sec at pH 5), is evidence for the lower net concentration of the carrier in the membrane. Using the magnitude of the diffusion coefficient determined earlier, the concentration of remaining TDDA at equilibrium with $0.01M$ $HCl_{(aq)}$ was calculated to have dropped to approximately half of its original value. When the membrane was replaced into a pH 5 buffer (at 0 V applied potential), there was only a slight increase in the resistance during a period of several hours. This could be attributed to the inability of the coions to be extracted out of the membrane (for example, Cl^- ions may be trapped in water clusters inside the polymer) and the change due to immersion in the very low pH solution was probably irreversible.

Bis[(12-crown-4)methyl]dodecylmethylmalonate (Na VI)

The diffusion coefficient of the neutral carrier, Na VI, was determined using potential-step experiments in constant-resistance membranes containing additional tetraphenylborate (TPB) mobile sites, which were similar to the tests on TDDA membranes shown in Fig. 1(c). These studies yielded a value of 5×10^{-12} m^2/sec, which is greater than that measured for valinomycin.

Using a different type of mobile site, T*m*FMPB, the diffusion coefficients of the ionic species and the related ionic dissociation constant could be determined by applying the method illustrated earlier.[1] The steady-state results, for a variable-resistance membrane containing 12.4 mM Na VI (total concentration) and 2.0 mM sites (total concentration), are shown in Fig. 3. Both current *vs* voltage (a) and resistance *vs* current (b) plots show that the limiting current is near 2.4×10^{-6} A. At higher currents, breakdown of membrane selectivity and failure of Donnan exclusion are responsible for the rise in the magnitude of the steady-state currents.[12] In addition to the limiting current value, the initial resistance and the total site concentration allow the calculation of a range of diffusion coefficients of the participating species, as well as dissociation constants of the ion pair [Na(Na VI)]–[T*m*FMPB]; all of which yield theoretical steady-state plots in agreement, within experimental error, with those shown in Fig. 3 (up to limiting current values). The screening of these possible sets was done using the steady-state analysis developed by Sandblom *et al.*[13]

The transient responses to various potential

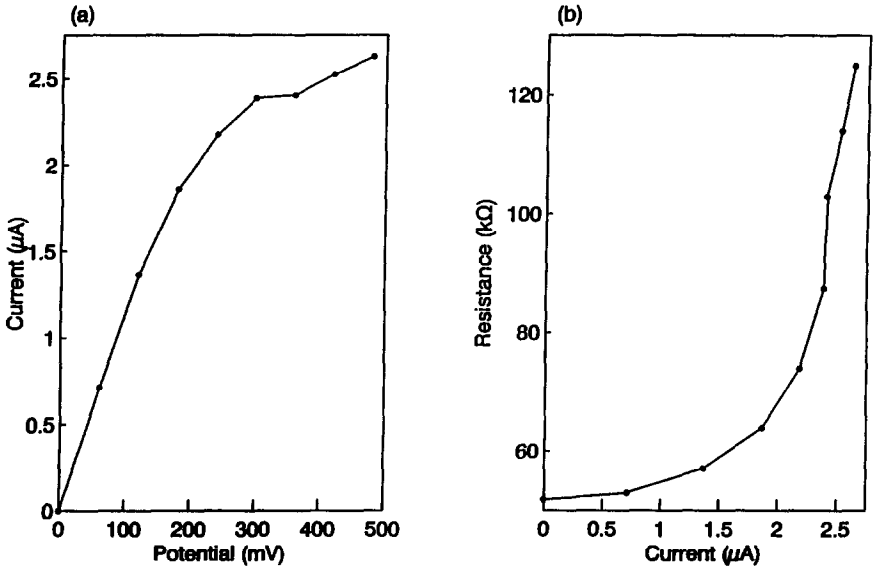

Fig. 3. Experimental steady-state (a) current *vs* potential and (b) resistance *vs* current for a membrane containing Na VI and T*m*FMPB mobile sites.

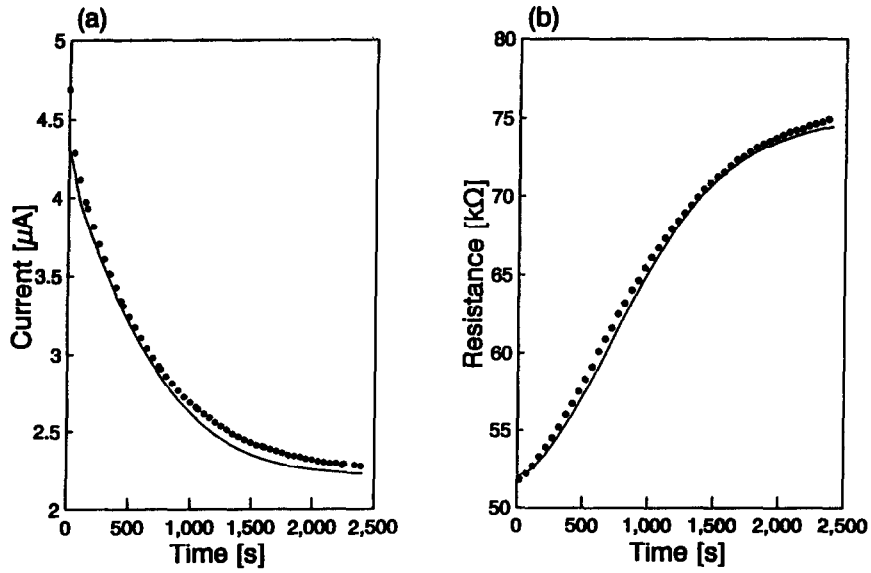

Fig. 4. Transient (a) current and (b) resistance plots for a membrane containing Na VI and T*m*FMPB mobile sites. The circles are experimental results (0.24 V potential step) and the lines are from digital simulations.

steps were measured individually with a period of relaxation between the application of each potential. The steady-state values were obtained after approximately 1 hr at each step. The transient results allow for the discrimination between the various sets of parameters obtained from the steady-state analysis. The best fit, presented in Fig. 4, was obtained using a dissociation constant of 2 m*M* and diffusion coefficients of 1.8×10^{-12}, 0.7×10^{-12} and 1.1×10^{-12} m^2/sec for the Na ion complex, mobile site and corresponding ion pair, respectively.

Similar to the initial response measured in TDDA membranes, there was a noticeable drop in the current during the first few seconds of the potential step experiment. To overcome this problem, the applied potential used in the simulations, whose results are shown in Fig. 4, was 0.225 V instead of the actual 0.24 V step. This proved to be the only way to fit the simulation results to the experimental data, which supports the existence of an additional potential drop (besides the interfacial and bulk ohmic contributions already included in the model).

CONCLUSIONS

In this work, the application of the carrier mechanism to membranes other than those containing valinomycin, exhibited the usefulness of the theoretical models suggested previously.[1,5] The identification of limiting processes and the determination of important transport parameters such as diffusion coefficients and dissociation constants were achieved in plasticized PVC membranes containing TDDA or Na VI ionophores. This analysis of transport mechanisms was possible, even though the results did not always show the complete, theoretically-expected transient and steady-state responses to an externally applied potential step.

The results from TDDA membranes illustrated the correlation between the failure of the membrane in very acidic solutions (pH < 3) and an alteration of transport properties such as a decrease in bulk resistance. In addition, there was no evidence to support proton-hopping in these pH membranes.

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