

## 23. Transport Properties of H<sup>+</sup>-Selective Membranes Containing Amine-Derivative Ionophores and Mobile Sites

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Transport processes in plasticized PVC membranes containing the H<sup>+</sup> chromoionophore *ETH 5294* and additional tetraphenylborate-type mobile sites were analyzed by employing the potential-step method. Using chronoamperometry, impedance spectroscopy, and UV/VIS absorbance measurements, it is shown that the ionophore behaves as a carrier for protons, when the membranes are immersed between two aqueous solutions. It was possible to document the changes in the concentration profiles of both free ionophores and ionic species in some of the membranes. There is no evidence of proton hopping between the ionophores.

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**Introduction.** – A common technique for the measurement of concentrations of cations in aqueous solutions involves the use of ion-selective electrodes (ISE's) made of plasticized PVC membranes containing large lipophilic ionophores and additional anionic sites [1]. Most ionophores are assumed to form a cavity or a 'sandwich' into which the cation is incorporated [2] [3]. This reaction facilitates the transfer of the ion across an aqueous solution/hydrophobic membrane interface and its further transport in an ion-complex form through the bulk membrane by the carrier mechanism [4–10]. In contrast, pH sensors of this general design use ionophores which provide an amine site (instead of a cavity) where H<sup>+</sup> can react to form a protonated complex inside the membrane [11–13]. In light of a report of a pH sensor made of plasticized PVC membranes containing immobilized aminated sites [14] and mixed results from earlier transport studies of tridodecylamine (TDDA) as a proton ionophore in plasticized PVC membranes [15], it has become important to establish whether protons can be 'carried' by the ionophores or, perhaps, 'hop' between amine sites.

Another goal of this work is to demonstrate transport phenomena in membranes containing negative *mobile* sites. Usually, transport studies done in PVC membranes take advantage of the endogenous *immobile* anionic sites [16] (a major exception is the study of anion transport [17]). Common cation ISE's, however, incorporate additional negative sites, usually from tetraphenylborate (TPB)-type compounds [18]. Upon the application of a field across the latter membranes, a complicated transport process will be initiated, since the ionic concentrations may be significantly different at various regions in the membrane, and ion pairs will be found, especially in matrices containing low-dielectric-constant plasticizers (*e.g.* di(2-ethylhexyl)sebacate (DOS)) [19]. Therefore, the results from these new electroanalytical studies may not be as easily interpreted as corresponding experiments with fixed anionic site membranes.

The transport of a cation through a mobile-site ion-selective membrane by the carrier mechanism is shown in *Fig. 1*. Upon the application of a voltage difference,  $V_{\text{appl}}$ , across

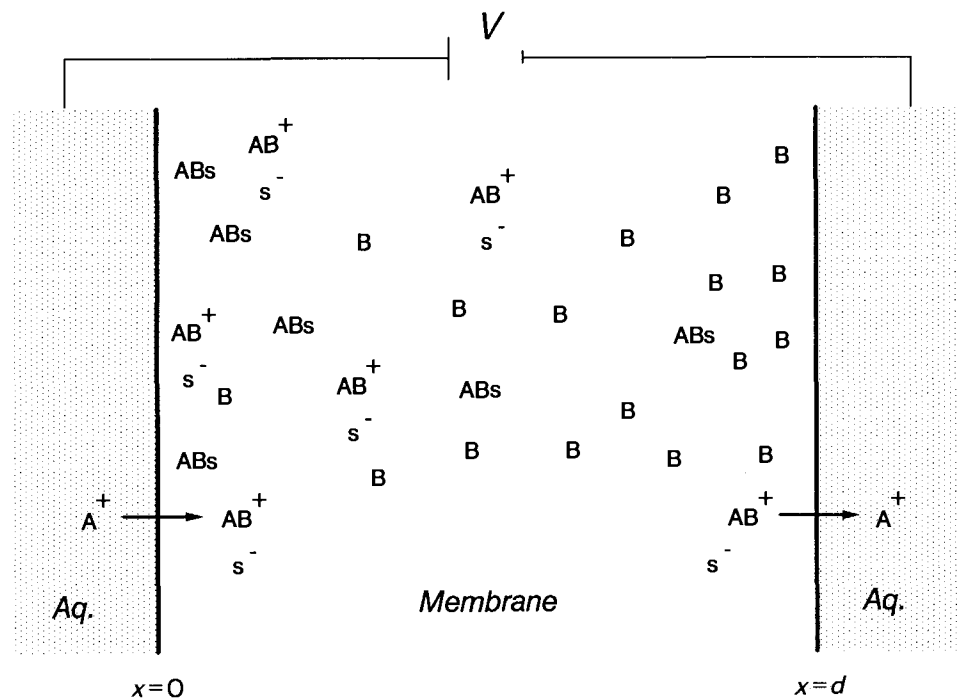


Fig. 1. Transport of an ion  $A^+$  through a membrane which contains an ionophore/carrier  $B$  and negative sites  $s^-$  and is subject to an externally applied voltage step  $V_{app}$ .

the system, the ion  $A^+$  will cross the interface between the aqueous solution and the membrane into the membrane, and immediately react with the ionophore/carrier  $B$  (which is present in a large excess of  $s^-$  to preclude the existence of any significant amount of  $A^+$  in the membrane) to produce a positive ion complex  $AB^+$ . To satisfy electroneutrality, a negative site  $s^-$  will migrate from the bulk towards the interface. At the interface where  $A^+$  exits, the reverse process occurs. In addition, uncharged ion pairs  $ABs$  may form and diffuse from left to right, and the neutral carrier  $B$  will diffuse from right to left, according to the direction of their respective concentration gradients.

Since the ionic concentrations in plasticized PVC ISE's are at the mM level and typical diffusion coefficients are near  $10^{-12}$  m<sup>2</sup>/s, the membranes exhibit relatively low conductivities. The magnitude of the resistance of the bulk of a membrane containing two ions of single but opposite charges is given by:

$$Res = \frac{RT}{AF^2} \int_{x=0}^{x=d} \frac{dx}{\sum_i D_i C_i(x)} \quad (1)$$

where  $R$  is the gas constant;  $T$  is the temperature;  $A$  is the area;  $F$  is the faraday;  $d$  is the thickness of the membrane;  $D_i$  is the diffusion coefficient of ion  $i$ , and  $C_i(x)$  is the ionic concentration of either positive ion-complexes or negative sites at  $x$  inside the membrane. Whether the membrane resistance is constant or variable depends on the extent of change

in ionic concentration profiles, as the potential-step experiment progresses [20] [21]. The absence of change in resistance may be due to several factors pertaining to experimental conditions and membrane properties such as *i*) small currents in a system where both ionic species ( $AB^+$  and  $s^-$ ) have large diffusion coefficients, *ii*) high ionic concentrations, *iii*) immobility of sites and consequential no change in ionic concentration profiles due to electroneutrality requirements (*e.g.* ‘fixed-site’ membranes), and *iv*) a small ion-pair dissociation constant, which produces a buffering effect during the accumulation or depletion of ionic species at the interfaces. An observed gradual increase in resistance is usually attributed to the significant concentration polarization of ionic species in the membranes.

In this paper, the transport process of protons across a membrane containing  $H^+$  ionophores and additional mobile sites is investigated. The study monitored both neutral and protonated forms of the chromoionophore *ETH 5294* (usually used in pH sensors [22] or in combination with another cation-selective ionophore to produce an optode [23]), during an electro dialysis experiment. The results confirm the presence of the carrier mechanism, and document the concentration polarization of the free neutral carrier, as well as the change in ionic-concentration profiles in these pH membranes. Specifically, two different cases of mobile anion site behavior are shown to be consistent with the presence, or absence, of concentration polarization of ionic species, *e.g.*, protonated species and mobile anionic sites.

**Results and Discussion.** – *Absorption Analysis.* UV/VIS Absorbance measurements revealed two main features in the absorption spectrum of solutions containing *ETH 5294*.

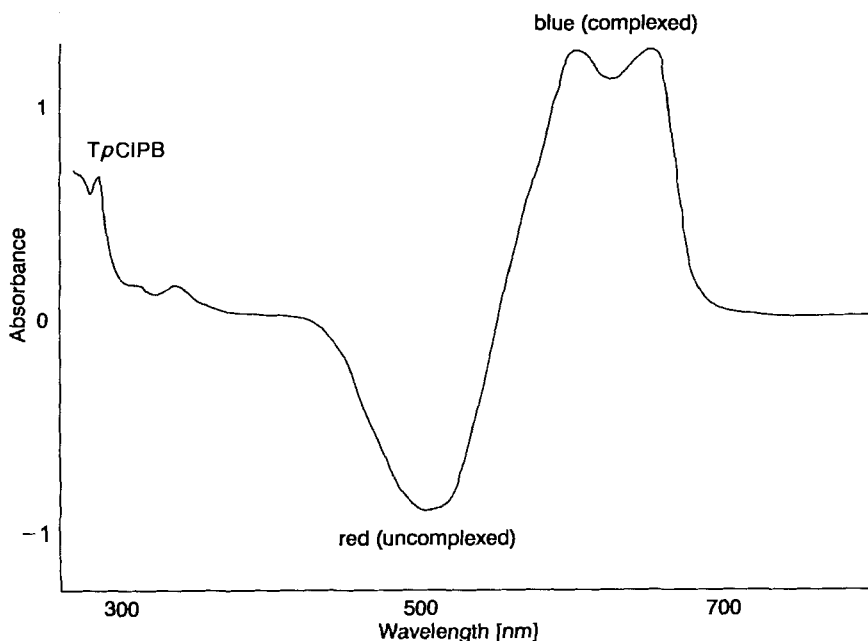
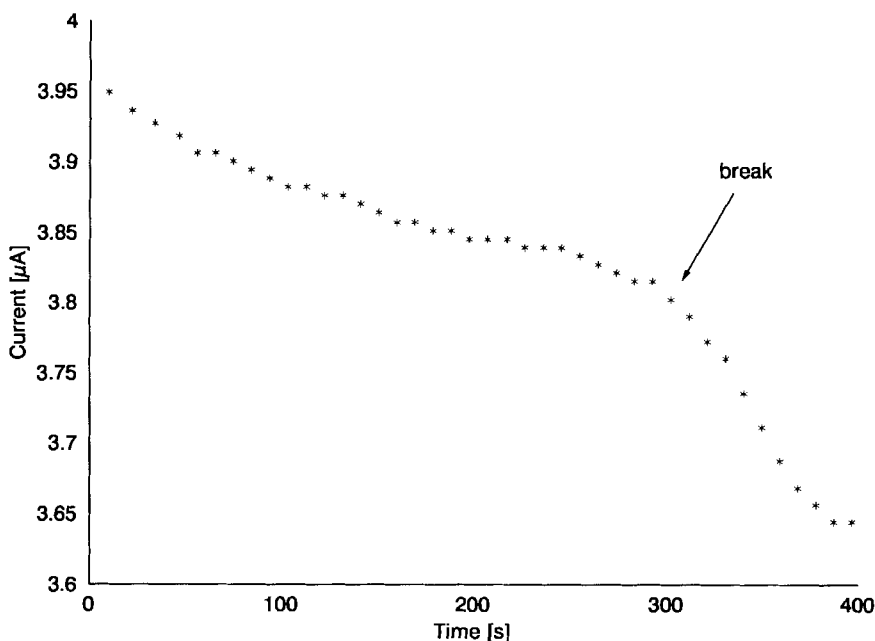


Fig. 2. UV/VIS Spectrum of a sample containing *ETH 5294* and *KTpCIPB* in *DOS* vs. a reference containing *ETH 5294* in *DOS*

A red solution color (and a single peak at 535 nm) is associated with the neutral, uncomplexed chromoionophore. A blue solution (related double peak at 610 and 655 nm) has been seen on several occasions, *e.g.* while stirring a mixture of *ETH 5294* in a DOS solution and an aqueous solution at  $\text{pH} < 3$ , and when the ionophore is dissolved with a substantial amount of potassium tetrakis(4-chlorophenyl)borate (KTPClPB) in dry DOS. The UV/VIS spectrum of a sample with the latter composition *vs.* a reference containing only *ETH 5294* in DOS is shown in *Fig. 2*. The peak near 290 nm is probably due to TPClPB [24]. Since the membranes considered in this work contained both *ETH 5294* and TPB-type salts (in ionic or ion-pair forms), their color was purple-magenta, regardless of whether they were in contact with an aqueous solution or not.

*Constant Resistance Membranes.* Four thin plasticized-PVC membranes containing 5.2 mM formal (or total) concentration of *ETH 5294* and 1.0 mM of sodium tetraphenylborate (NaTPB) were tested according to the procedure described below. Upon the application of 5 V across the system, the characteristic chronoamperometric features of a carrier-controlled transport mechanism [25] were noted (*Fig. 3*): *i*) the initial current is



*Fig. 3.* Current vs. time response of a membrane with a constant resistance ( $1.25 \text{ M}\Omega$ ) subject to a potential step of 5 V

approximately  $V_{\text{appl.}}/R_{\text{es}}$  (the resistance was measured by impedance analysis), and *ii*) the break in the current, after a characteristic time, is an indication of the depletion of the carrier at the interface where  $\text{H}^+$  enters, since the current is given by

$$I = \frac{1}{R_{\text{es}}} (V_{\text{appl.}} - V_{\text{interface}}) \quad (2)$$

and the interfacial potential difference in this case is

$$V_{\text{interface}} = \frac{RT}{F} \ln \frac{C_{\text{carrier}}^{\text{right}}}{C_{\text{carrier}}^{\text{left}}} \quad (3)$$

The log term, which represents a potential drop contribution at the interfaces, becomes large when the concentration of the carrier at the side where  $\text{H}^+$  enters is small, and the magnitude of the current must decrease.

The results from UV/VIS spectrophotometry of the individual membranes confirm both the existence of a carrier process and the lack of polarization of ionic species. Fig. 4 shows the changes in the absorbance of the deprotonated (*left*) and protonated (*right*) forms of ETH 5294 immediately after the application of an external potential step, and after a relaxation period of 3 h in which the membranes were re-stacked and allowed to equilibrate with each other. The normalized initial absorbance corresponds to 4.2 mM free carrier and 1.0 mM total ion-complex species. Normalization also allowed to correct for slightly different membrane thicknesses.

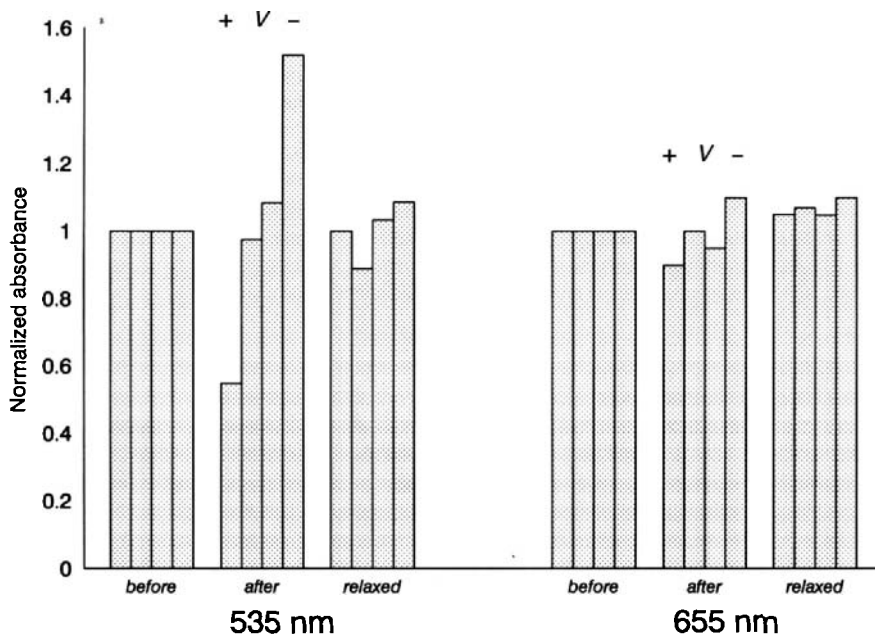


Fig. 4. Absorbance of individual membranes before, immediately after a potential step, and after an equilibration period (relaxed), from a stacked membrane exhibiting a constant resistance. On the left is the 'red' peak, related to the neutral ETH 5294, and on the right is the 'blue' peak, related to the complexed ETH 5294. The direction of applied voltage is also shown.

These data demonstrate a classical constant resistance, *e.g.*, a behavior marked by concentration polarization of free neutral carriers. Thus, the systems behave like a constant-resistance 'fixed-site' membrane because of strong ion pairing and a virtual absence of ionic species polarization.

*Variable Resistance Membranes.* In marked contrast with the results from constant-resistance membranes, the results from a stack of four membranes made of 3.5 mM

*ETH 5294* (total concentration) and 0.34 mM sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ( $\text{NaTmFMPB}$ ) show a monotonous decrease in a current vs. time plot. Concurrent results from impedance spectroscopy measurements show a gradual increase in the bulk membrane resistance during current flow (Fig. 5). Initially, the magnitude of the product  $IRes$  (the potential drop due to bulk membrane resistance) is very close to  $V_{\text{appl.}}$  (3 V). However, as the experiment proceeds, an increasingly larger discrepancy between these two quantities is noted. From Eqn. 2, this can be attributed to additional interfacial potential drop contribution.

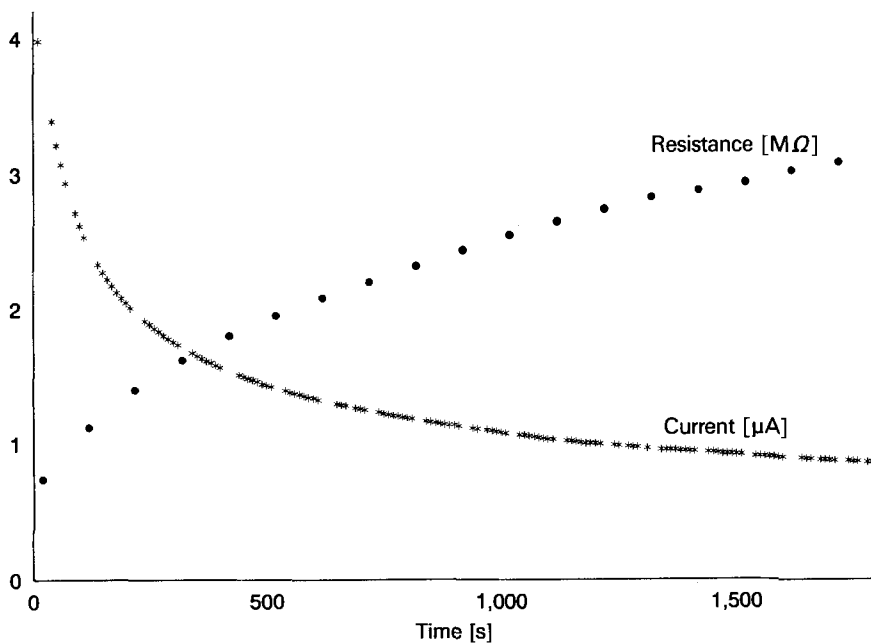


Fig. 5. Current and resistance vs. time response of a membrane with a variable resistance subject to a potential step of 3 V

Spectroscopic analysis (Fig. 6) shows a moderate change in the concentration profile of neutral *ETH 5294*, similar to that observed in the constant resistance case. This result is evidence of the existence of a carrier mechanism in this membrane, too. A new feature is the change in the concentration profile of the protonated species, which presents a concentration gradient in the predicted opposite direction of that for the neutral carrier. This result is anticipated by the model of a mobile-site membrane [21].

An interesting result is the relatively large absorbance observed at 655 nm in the membrane section contacting the interface where  $\text{H}^+$  exits, immediately after the application of a voltage step (Fig. 6). This can be explained by a *Donnan* failure, which implies the entrance of anionic species from solution into the membrane on the depletion side, thus providing a way to move more complexed  $\text{H}^+$  into the membrane as an extracted salt from the bathing solution [26].

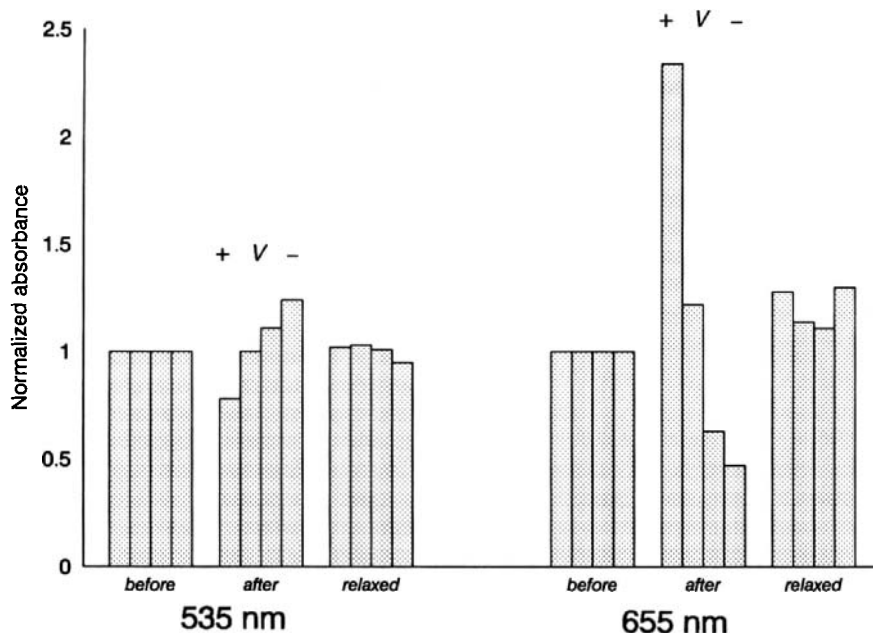


Fig. 6. Absorbance of individual membranes from a stacked membrane exhibiting a variable resistance. See Fig. 4 for details.

The difference in transport behavior between the constant-resistance and variable-resistance cases is due to the incorporation of different types of mobile sites in each membrane. Studies of membranes, which contained equal total amounts of both ionophores and mobile sites, revealed the same pattern of chronoamperometric results as shown in Figs. 3 and 5 [28]. It is not, therefore, the total amount of the mobile-site which is responsible for this behavior, but the more hydrophobic nature of the *Tm*FMPB sites compared with TPB. Since *Tm*FMPB is probably more sluggish than TPB, this larger anion is anticipated to cause a slower ionic-concentration polarization process, and a more moderate increase in resistance with time is anticipated (the extreme case of a fixed-site membrane shows no significant change in resistance). Also due to the difference in diffusion coefficients, one expects that, at zero current, *Tm*FMPB membranes will show larger resistances than otherwise identical TPB membranes. In both cases, the measurements here show opposite results, which lead to ruling out the effect of the magnitude of the ionic-species diffusion coefficients.

Clearly, another explanation is required. Since the dissociation constant of the *ETH*-5294-*H-Tm*FMPB ion pair should be larger than that of *ETH*-5294-*H*-TPB, the latter species may exhibit a greater buffering capacity and prohibit a significant ionic-concentration polarization; *e.g.*, the TPB anion response is similar to that in a fixed-site system, and no change in resistance is expected. Furthermore, the smaller *ETH*-5294-*H*-TPB ion pair should be diffusing more quickly in the membrane to eliminate the build-up of significant concentration gradients of both ionic species and ion pairs. The overwhelming importance of these considerations is supported by the results from this work.

**Conclusions.** – The results from chronoamperometric studies of mobile-site plasticized PVC membranes, containing the H<sup>+</sup> ionophore *ETH 5294*, show that protons are carried across the bulk membrane, and that polarization of neutral, deprotonated species takes place simultaneously. In addition, it has been shown that, depending on the added mobile sites, polarization of the ionic species in the membranes can take place, and that mobile sites with strong ion-pairing capabilities show less tendency to permit concentration polarization of ionic species. The electrochemical analysis was supported by the results from UV/VIS spectrophotometry, which allowed the distinction between the neutral and charged/complexed forms of the ionophore, and their individual distributions across the polarized membranes. These observations are general, and should apply to many systems which exhibit substantial resistances and concentration polarization phenomena of neutral and ionic species.

**Experimental.** – *Reagents and Solvents.* PVC, potassium tetrakis(4-chlorophenyl)borate (KTPClPB), and *ETH 5294* were purchased from *Fluka*. Sodium tetraphenylborate (NaTPB) was obtained from *Aldrich*. Citric acid, conc. NaOH, and THF were from *EM Sciences*. Di(2-ethylhexyl)sebacate (DOS) was bought from *Sigma*. Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTmFMPB) was a gift from Dr. *Maurice S. Brookhart* (UNC).

*Membrane Preparation.* THF solns. of PVC and DOS (at 1:2 weight ratio, resp.) were prepared several days in advance, and mixed with desired amounts of fresh THF stock solns. of *ETH 5294* and fresh THF stock solns. of mobile-site salt. The membranes were cast using the procedure described by *Craggs et al.* [28], and were ca. 50  $\mu\text{m}$  thick.

*Apparatus.* The membranes were placed between two aq. pH 5 citrate buffer solns. in an electrochemical cell, designed for the purpose of ionic transport analysis, similar to that described earlier [8]. Desired voltage steps were applied by a *Solartron 1250* frequency analyzer (*Solartron Instrumentation Group*, Farnborough, England) through an *EG&G 363* potentiostat (*Princeton Applied Research*, Princeton, NJ, USA), controlled by a *Zenith XT* computer equipped with a *CEC IEEE 488* interface (*Capital Equipment Corporation*, Burlington, MA, USA). 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, USA). UV/VIS Spectrophotometry was performed with an *IBM 9240* spectrophotometer.

*Procedure.* Four membranes with identical chemical composition were individually analyzed using UV/VIS spectrophotometry. Then, they were stacked back-to-back and placed in the electrochemical cell which was filled with 50 ml of 0.1M (pH 5) citrate buffer and 2 ml of 0.01M KCl soln. A potential step was applied to the system, and current and impedance measurements were recorded. Immediately at the end of this stage, the cell was taken apart, and the membranes were separated from each other. This took less than 1 min. The membranes were reexamined by UV/VIS spectrophotometry and then restacked together for a few h to equilibrate with each other (outside the cell). Finally, the spectrum of each membrane was retaken.

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