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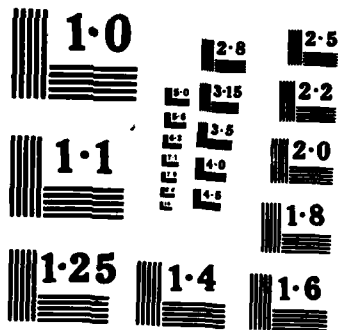
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Luminescence Probe Studies of Ionomers. I. Steady-State Measurements from Nafion Membrane.

by

Marilyn N. Szentirmay, Nelson E. Prieto and Charles R. Martin

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Steady-State Measurements From Nafion Membrane

Marilyn N. Szentirmay, Nelson E. Prieto and Charles R. Martin*

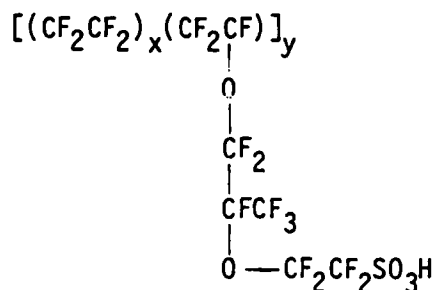
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Abstract

Steady state luminescence probe methods were used to study the polarity of the ionic cluster phase within Nafion 117 membrane. Three probes, pyrene, a cationic dansyl derivative and $\text{Ru}(\text{bpy})_3^{2+}$ were used. In fully hydrated Nafion membranes (ca. 40% water by weight), these probes report back microenvironment polarities significantly lower than bulk water. In addition, these probes show that the $-\text{SO}_3\text{H}$ sites are chemically heterogeneous. The effects of water content and counterion on cluster phase polarity were also evaluated. The cluster phase can become quite nonpolar when water is removed and/or when a hydrophobic counterion is added. The effects of the Nafion chemical environment on the dynamics and thermodynamics of chemical processes occurring within the polymer are discussed and demonstrated.

Introduction

Nafion (I) is a family of perfluorosulfonate polymers marketed by Du Pont (1,2). While these polymers were developed for use as separator



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membranes in chlor-alkali cells (2), they have in recent years been used in a number of other electrochemical processes and devices. For example, Nafion membranes have been used in fuel cells (3), batteries (4) and water electrolyzers (5). In addition, considerable recent research efforts has been devoted to studies of the electrochemical properties of Nafion-based chemically modified electrodes (6).

The concept of developing integrated chemical systems (ICS's) (7) based on Nafion films or membranes is one of the most promising outgrowths of the fundamental modified electrode research. Bard defines ICS's as "heterogeneous systems consisting of several components acting in a synergistic way to carry out a particular process" (7b). An electrocatalytic ICS based on a Nafion film-modified electrode has been recently described by Buttry and Anson (7a). This system incorporates an oxygen reduction catalyst and an electron shuttling redox couple, and converts substrate (O_2) to product (H_2O_2), within a Nafion film. A variety of chemical and electrochemical processes including heterogeneous and homogeneous electron transfer, diffusion, substrate-catalyst complex formation,

complex reduction and catalyst regeneration occur within the film (7a).

It is important to point out that the Nafion film in such a system is more than just a passive host in which the various chemical and electrochemical processes occur. This point is emphasized by recently reported ion exchange data which suggest that ion exchange in Nafion is thermodynamically more akin to ion pair extraction into a nonpolar organic solvent than to a conventional ion exchange process (8), and by Reisen's recent observation that metal ion carbonylation reactions are much more facial in Nafion than in conventional media (9). These results (and results presented here) suggest that Nafion must be regarded as a chemical phase whose properties can influence the dynamics and thermodynamics of chemical processes occurring within this phase.

The preceding discussion suggests that if Nafion-based ICS's are to be developed, the nature of the chemical environment within the membrane phase must be discerned. Indeed, because ionomers have so many, varied applications ranging from electrochemistry, to chemical synthesis (9,10), to separation science (8,11), an elucidation of the chemical properties of ionomers is important to a wide range of chemical subdisciplines. Such an elucidation is not, however, a trivial matter because the charged groups in Nafion and other ionomers (2) aggregate to form complex micelle-like domains called ionic clusters (12). Thus, a study of the chemical properties of the membrane interior must entail an investigation of the microenvironment within these micelle-like clusters.

The similarities between the ionic cluster and the micelle (13) suggest that the chemical methodologies used by micelle chemists (14) might be useful for discerning the chemical and structural features of the cluster. Luminescence spectroscopy has proved to be one of the most powerful of these chemical methodologies (15). For this reason, we are

using luminescence probe methods (15,16) to study the ionic cluster phases in ionomers. Our first set of experiments has addressed the questions — what is the polarity of the microenvironment(s) within Nafion membrane and how do parameters such as water content and counterion affect this micro-polarity. The results of these and related studies are reported here. While there have been a handful of prior luminescence studies of Nafion (17,18), none have systematically addressed the questions posed here.

Experimental Section

Materials. Nafion 115 membrane (proton form) was donated by the E. I. Du Pont Company. 5-Dimethylaminonaphthalene-1-sulfonamidoethyl-trimethylammonium perchlorate DAClO_4 was obtained from Sigma. $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ ($\text{bpy} = 2,2'$ -bipyridine) was obtained from G. F. Smith. Tetrabutylammonium bromide was obtained from Kodak. Pyrene (Py) (99+%) was obtained from Aldrich. All other chemicals were of reagent grade. Water was triply distilled or circulated through a Milli-Q water purification system (Millipore Corp.). Glassy carbon rods were obtained from Atomergic.

Procedures. Prior to use, the Nafion membranes were cleaned ultrasonically in 50:50 ethanol-water for 1 hr. and then boiled in water for 4 hr. Na^+ form membranes were prepared by stirring the pretreated Nafion in several portions of concentrated NaOH or NaOH/NaCl solutions for at least 1 day. Excess base was then removed by stirring the membranes in several portions of pure water. Nafion solutions were prepared using the procedure of Martin et al. (6d). Nafion film-modified glassy carbon electrodes were prepared as described previously (6e).

The luminescent probes (Py, DA^+ , $\text{Ru}(\text{bpy})_3^{2+}$) were incorporated (loaded) into Nafion by stirring the membranes in aqueous solutions of the probes.

The quantity of $\text{Ru}(\text{bpy})_3^{2+}$ and DA^+ loaded was determined by monitoring the UV/visible absorbance of the probe solutions. The quantity of Py incorporated was estimated by measuring the absorbance of the Py-loaded membranes. Loading levels were kept low (DA^+ and $\text{Ru}(\text{bpy})_3^{2+}$ usually less than 3 probe ions per 100 $-\text{SO}_3^-$ sites, pyrene ca. 0.03 probe molecules per 100 $-\text{SO}_3^-$ sites).

The effects of membrane water content on the emission characteristics of the probes were investigated by gradually drying the membranes first by exposure to ambient air, then in a desiccator and finally in a vacuum oven (temperature $< 70^\circ\text{C}$). The water content of each membrane was determined from the average of weights recorded immediately before and after each spectrum was acquired. Water content is reported as percent by weight ($100 \times \text{wt. H}_2\text{O}/\text{wt. dry polymer}$) and as the number of water molecules per $-\text{SO}_3^-$ site. Membranes dried in a vacuum oven at 100°C for 1 to 3 days served as "zero" water content references.

Membranes containing various amounts of tetrabutylammonium, Bu_4N^+ , were prepared by stirring the membranes in aqueous solutions of Bu_4NBr . Uptake of Bu_4N^+ was monitored by titrating the released protons with NaOH . Bu_4N^+ uptake by Na^+ membranes was assumed to be the same as uptake by acidic form membranes, an assumption justified by Nafion's remarkable ion exchange affinity for such hydrophobic cations over both Na^+ and H^+ (8). The water contents of membranes containing various quantities of Bu_4N^+ were determined by weight, with correction for the weight of added Bu_4N^+ .

Spectroscopy. Emission spectra were obtained with a Spex Fluorolog 2 spectrofluorometer. The Spex solid sample holder (front surface viewing geometry) was used. Unless otherwise noted, excitation wavelengths for Py, $\text{Ru}(\text{bpy})_3^{2+}$, DA^+ (Na^+ -form membranes) and DA^+ (H^+ -form membranes) were

310, 455, 340 and 300 nm, respectively. Emission slit widths of 0.8 nm (Py spectra) and 4.1 nm ($\text{Ru}(\text{bpy})_3^{2+}$ and DA^+ spectra) were used. Absorption spectra were recorded on a Beckman Model 26 spectrophotometer. Nafion does not absorb light of wavelengths greater than 230 nm. If probes were not incorporated, no luminescence was observed from the Nafion membranes.

Results and Discussion

The Probes and the Method. Three different luminescent probes, Py, DA^+ and $\text{Ru}(\text{bpy})_3^{2+}$, were used to study the chemical properties of the micro-environments within Nafion membrane. These probes were chosen because their emission characteristics have been extensively studied and because they (or their derivatives) have been used in luminescence probe studies of other types of microdomains and structures. Fluorescence spectra of Py show vibronic fine structure in most solvents (19a). Because of solvent dipole-excited state dipole interactions, the relative intensities of the vibronic bands vary with solvent polarity. In general, an increase in the solvent polarity results in a decrease in the ratio of the third to first vibronic band intensities (I_3/I_1) (19). This effect is demonstrated by the data in column 4 of Table I (19b). Thus, Py may be used as a polarity probe.

Derivatives of dimethylaminonaphthalenesulfonate (DNS) have been used as probes for proteins and other macromolecules (20). Hercules et al. (21) have shown that the wavelengths of maximum emission intensity (λ_{Max}) for 1,5-DNS derivatives are sensitive to solvent polarity, showing blueshifts, relative to water, in nonpolar solvents (see column 2 of Table I). The fluorescence quantum yields for these compounds are also solvent sensitive; of particular interest to the present study is the fact that water produces one of the lowest quantum yields for 1,5-DNS

derivatives (21). The solvent sensitivities of these compounds have been explained in terms of a polar solvent induced inversion of the energy levels of two closely spaced excited states (21). Because of their solvent sensitivity, 1,5-DNS derivatives may also be used as polarity probes (20).

The acid-base characteristics of DNS derivatives complicate their spectroscopic properties (22). This is of particular significance for studies of Nafion since it is a strong acid. The basic (unprotonated) form of the DNS derivative used here (DA^+) shows absorption maxima at ca. 325 and 245 nm (aqueous solution, pH 6.8 phosphate buffer) while the acidic form, HDA^{2+} , shows maxima at ca. 283 and 221 nm (aqueous solution, pH 2.2 phosphate buffer). These spectral characteristics are similar to those reported for related compounds (20a,22a,b). Upon excitation, both of these ground state forms produce luminescence at ca. 570 nm (aqueous solution, see column 2 of Table I) which is attributable to emission from the deprotonated excited state DA^{+*} (22b). In addition, in strongly acidic solutions a higher energy fluorescence band at ca. 340 nm is observed which is attributable to emission from the protonated excited state, HDA^{2+*} (22b). It is the DA^{+*} emission which is solvent sensitive (21).

The emission characteristics of $Ru(bpy)_3^{2+}$ have been extensively studied (23). In general, the energy of its emission does not correlate in an easily interpretable manner with solvent polarity (column 3, Table I). However, our luminescence probe studies of aqueous solutions of Nafion polyelectrolytes have shown that a blueshift and an increase in emission quantum yield result when $Ru(bpy)_3^{2+}$ is taken from a purely aqueous environment to an environment where interaction with fluorocarbon chain material is possible (17c,d). A similar effect is observed when $Ru(bpy)_3^{2+}$ is solubilized in fluorocarbon micelles (17b). In addition, Lee and Meisel,

in a prior study of $\text{Ru}(\text{bpy})_3^{2+}$ emission from Nafion, observed a blueshift in λ_{Max} (17b). These studies show that both λ_{Max} and emission yield can be used to determine the relative contributions of water and chain material to the chemical properties of the microenvironment in Nafion membrane.

It is important to emphasize that we have already investigated the nature of the interactions between $\text{Ru}(\text{bpy})_3^{2+}$ and Nafion and between DA^+ and Nafion through luminescence probe studies of aqueous solutions of Nafion polyelectrolytes (17c,d). In aqueous solution, both of these probes are strongly bound to Nafion via concerted hydrophobic and electrostatic interactions (17c,d). The strong electrostatic interaction results from the well known polyelectrolyte-counterion condensation effect (24) and the hydrophobic interaction occurs because both polymer and probe are quite hydrophobic. It is of interest to note, however, that both DA^+ and $\text{Ru}(\text{bpy})_3^{2+}$ seemed to respond only to the hydrophobic component of the interaction (i.e., blueshifts and increased emission yields) and showed no clearly discernable response to the electrostatic component. In the case of $\text{Ru}(\text{bpy})_3^{2+}$, this is illustrated by the fact that polyelectrolytes which can interact only electrostatically exert no effect on $\text{Ru}(\text{bpy})_3^{2+}$ emission (25). In effect, these polyelectrolyte studies served to calibrate our probes so as to render their emission characteristics from Nafion membrane more easily interpreted.

Extent of the Domain Sampled by the Excited Probe. Prior luminescence probe studies of Nafion have not commented on the extent of the domain sampled by the probe during the excited state lifetime. The extent of the domain sampled could be calculated if D_{App}^* , the apparent diffusion coefficient associated with intra-cluster exciton migration were known (26). The term apparent diffusion coefficient is used here because exciton migration by both physical diffusion and exciton exchange (27) is possible. The quenching

data of Buttry and Anson (6c) can be used to provide an estimate of D_{App}^* for $Ru(bpy)_3^{2+}$ in Nafion.

Buttry and Anson measured k_q , the second order rate constant associated with the quenching of $Ru(bpy)_3^{2+}$ by $Ru(bpy)_3^{3+}$, in Nafion (6c). Following the development of Majda and Faulkner (27), this k_q can be used to estimate D_{App}^* via use of the Smoluchowski equation (27), $k_q = p4\pi N'R D$, where p is the probability that an intra-cluster $Ru(bpy)_3^{2+} - Ru(bpy)_3^{3+}$ encounter will result in quenching, N' is Avagadro's constant per millimole, R is the encounter radius (ca. $14 \times 10^{-8} \text{ cm}$) (27b) and $D = D_{App}^* + D_{App}^{III}$; D_{App}^{III} is the apparent diffusion coefficient for intra-cluster movement of $Ru(bpy)_3^{3+}$. Using Buttry and Anson's $k_q = 5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ a value for D of $4.7 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ is obtained. This is the lower limit for D since $p = 1$ was used (27). As noted by Majda and Faulkner, it is quite reasonable to assume that $D_{App}^* = D_{App}^{III}$ (27); thus, $D_{App}^* = D_{App}^{III} = 2.4 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. Plugging this D_{App}^* and the excited state lifetime for $Ru(bpy)_3^{2+}$ in Nafion (17b) into the Einstein-Smoluchowski equation (28) gives 6.6 Å for the distance traversed by the probe during the excited state lifetime. Again, this represents the minimum value.

Because the ionic clusters in Nafion are approximately 40 Å in diameter (12), the above calculation suggests that $Ru(bpy)_3^{2+}$ can sample a fraction, although probably not all of the ionic cluster during its lifetime. Therefore, the microenvironment reported back by a probe is not necessarily representative of the entire ionic cluster. On the other hand, the environment experienced by the probe will be a good indicator of the chemical environment experienced by an additive (e.g., a catalyst, electroactive species, etc.) of similar structure and charge. A global picture of the cluster could be obtained by using probes of widely different sizes, charges, hydrophobicities, etc. so that all "corners" of the cluster could be sampled. The use of monovalent,

divalent and neutral probes in this study is a step in this direction.

It is worthwhile to return momentarily to the question of intra- vs. inter-cluster exchange processes. Note that the value of D_{App}^{III} (calculated above) describing intra-cluster movement of $Ru(bpy)_3^{3+}$ is an order of magnitude larger than D_{App}^{III} obtained via electrochemical experiments on identical polymer films. Majda and Faulkner would argue that this difference is due to slow counter/coion migration, which must accompany the electrochemical event in the polymer film (27). However, the studies of Martin et al. (6b) clearly show that counter/coion migration is not the rate determining step for $Ru(bpy)_3^{3+/2+}$ electrochemistry in Nafion. The difference between the luminescence and electrochemical D_{App}^{III} values arises because the luminescence experiment produces an intra-cluster value and the electrochemical experiment produces an inter-cluster value (because charge must be transported across the entire length of the film in the electrochemical experiment). Inter-cluster charge transport is less facile because of the constriction presented by the narrow channels which interconnect the clusters (12).

The above discussion brings out two important points. First, Majda and Faulkner suggest that a difference between an electrochemical D_{App} and a luminescence D_{App} can be used as a diagnostic for slow counter/coion diffusion. This is only true if the charged groups are homogeneously distributed throughout the film so that both methods are monitoring the same process. Second, if the luminescence and electrochemical methods produce different values of D_{App} and if independent measurements show that counter/coion diffusion is not rate-determining in the electrochemical step (6b), some degree of charge aggregation must be extant. Hence, it would appear that non-equal luminescent and electrochemical D_{App} values could be used as a diagnostic for ion clustering. We are currently exploring this possibility.

Emission from Fully Hydrated Membranes. Fully hydrated membranes are those

which have been pretreated in the manner described in the experimental section. In the Na^+ or H^+ forms, these membranes contain about 40% water, by weight. In spite of these very high water contents, the probes used here report back microdomain polarities significantly lower than that of bulk water (Table II). For example, I_3/I_1 for Py is about 0.75 in Nafion as opposed to 0.58 in water and λ_{Max} values for DA^+ are significantly blueshifted in Nafion relative to λ_{Max} for DA^+ in water (ca. 570 nm). Kuczynski et al. have recently observed I_3/I_1 values for Py in H^+ and Na^+ form Nafion of 0.8 and 1.6, respectively (18). These values suggest that Py in their Nafion is in a significantly more nonpolar microenvironment than Py in our Nafion. It is important to point out, however, that they used methanol solutions of Py to incorporate the probe into the membrane. Given the tremendous affinity of Nafion for methanol (29), it seems likely that their values are not representative of native Nafion membrane or of Nafion after exposure to water or water vapor.

These results show that there are microenvironments within Nafion which, in spite of the high water content, are rather apolar. As noted by Lee and Meisel, this suggests that the excited probe is exposed to both water and polymer chain material (17b). This interpretation is strengthened by the Py data in that I_3/I_1 is intermediate between values expected for fluorocarbon and aqueous environments (19a). This interpretation is also strengthened by our luminescence probe studies of Nafion solution. These studies showed that, given the choice of a purely aqueous environment or an environment where interaction with Nafion chain material is possible, both $\text{Ru}(\text{bpy})_3^{2+}$ and DA^+ chose the latter (17c,d). Prior studies have not addressed the question of how the microenvironment polarity might be affected by changes in the relative concentrations of water and chain material. This

question is addressed in the next section of this paper.

Prior luminescence probe studies of Nafion have also not addressed the question of the chemical homogeneity of the ionic cluster. Homogeneity may be studied by following the emission characteristics of the probe as a function of loading. As shown in Table II, $\text{Ru}(\text{bpy})_3^{2+}$'s λ_{Max} increases sharply with the quantity of $\text{Ru}(\text{bpy})_3^{2+}$ loaded. These data indicate that the first $\text{Ru}(\text{bpy})_3^{2+}$ ions to enter the membrane preferentially occupy sites which have much lower local water activities than sites occupied by $\text{Ru}(\text{bpy})_3^{2+}$ ions subsequently loaded. Thus, the cluster phase is chemically

heterogeneous and cannot be characterized by a single effective dielectric constant value. It is of interest to note that both infrared (30) and NMR (31) studies of water in Nafion suggest that the ionic cluster is chemically heterogeneous.

Studies of the effect of loading on DA^+ emission produce different results. Emission spectra from an H^+ -form and an Na^+ -form membrane are shown in Figures 1a and 1b, respectively. The H^+ -form membrane shows emission from both DA^{++} (ca. 545 nm) and HDA^{2++} (ca. 340 nm) as would be expected from an environment having a high H_3O^+ activity (22). As noted above, the DA^{++} emission is strongly blueshifted relative to water indicating that DA^+ 's microenvironment is much less polar than bulk water. While DA^{++} 's emission is the most prominent feature from the Na^+ -form membrane (Figure 1b), some emission is observed at ca. 340 nm. Furthermore, if the DA^+ loading level is decreased, the emission from HDA^{2++} increases at the expense of that from DA^{++} (Figure 2) until at very low loadings, it is by far the most prominent feature (Figure 2c).

Figures 1 and 2 show that in spite of the exposure and equilibration with concentrated NaOH solution, there are residual $-\text{SO}_3\text{H}$ sites which are donating protons to DA^+ to produce HDA^{2+} in

these membranes. Absorbance measurements produce analogous results and indicate that about 1% of the DA^+ becomes protonated. This seemingly enigmatic protonation can be explained through consideration of the ion exchange properties of the polymer. When a membrane is fully equilibrated with excess concentrated NaOH, it undoubtedly becomes 100% neutralized. However, in our procedure, the membrane is then equilibrated with several portions of pure water to remove any excess base. If it is assumed that the final rinse has a pH of 7.0 and contains no Na^+ , the known ion exchange selectivity coefficient for the replacement of H^+ with Na^+ (32) may be used to calculate the equilibrium quantity of H^+ in the membrane. A value of ca. 1 mole percent is obtained. Because of the limited volume within the ionic cluster, this 1 mole percent of $-SO_3H$ sites makes the local pH very low. This, combined with the high mobility of the proton within the membrane (33) insures that an equivalent quantity of DA^+ is protonated. The agreement between the calculated and experimentally observed amounts of HDA^{2+} is quite good.

Effect of Water Content on Microenvironment Polarity. If the luminescent probe reports back a microenvironment polarity which is an average of influences of the various components of the cluster phase, it seems likely that the effective polarity could be modified by changing the relative concentrations of these components. For example, it seems likely that the cluster should become less polar when water is removed from the membrane. Figures 3 and 4 show that this is indeed the case. $Py\ I_3/I_1$ increases sharply at low water contents (Figure 3); its value in the driest membranes studied here (ca. 1.1) suggests that Py's microenvironment is similar to that for Py dissolved in a high molecular weight alcohol (Table I) (34). DA^+ 's emission intensity increases (Figure 4a) and

λ_{Max} blueshifts (Figure 4b) as water is removed; both effects are indicative of a decreasing environment polarity (21). The λ_{Max} value for the driest membrane studied here (503 nm) suggests that DA^+ 's micro-environment is considerably less polar than any of the solvents shown in Table I. In fact, it seems unlikely that DA^+ could be solubilized in a solvent of low enough polarity to produce a λ_{Max} of 503 nm. This is an interesting point because it suggests that a microenvironment which would be impossible to create in homogeneous solution can be created in the Nafion membrane.

Figures 3 and 4 show that little or no change in emission is observed for any of the probes, until the water content is decreased below ca. 20%. This effect could be caused by preferential solvation (35,36) of the probe by water, such that its solvation shell remains relatively constant inspite of the change in bulk solvent composition (i.e., loss of water). Henda et. al have recently studied the emission characteristics of 1,8-anilino-naphthalenesulfonate in CH_3CN -tetrahydrofuran mixtures (37); a similar effect is observed for these systems.

An alternative explanation is at least in principle possible. Yeager and Steck have suggested that the ionic cluster in Nafion is, in fact, biphasic, these phases being an aqueous-like cluster phase and a more hydrophobic interfacial region (38). Their data suggest that the water content of the interfacial region does not change with bulk membrane water content when bulk water content varies from about 25 to 15 percent (38). If the probes used here reside in this hypothetical interfacial region, their emission characteristics would, therefore, be expected to remain constant down to about 15 percent bulk water. The up swing in λ_{Max} , I_3/I_1 , or I_{Max} observed subsequently would then correspond to the dessication of the interface which, according to Yeager's model, would occur only when the

bulk water content is very low.

Modification of Microenvironment Polarity with Bu_4N^+ . The preceding experiments have shown that the polarity of the cluster microenvironment can be varied over a considerable range through adjustment of the membrane water content. Yeager and Steck have shown that the quantity of water imbibed by Nafion is dependent on the counterion present (32). It seemed likely, then, that modification of the microenvironment polarity, as illustrated in Figures 3 and 4, could also be accomplished by changing the counterion. This contention is supported by Figure 5, which shows equilibrium water contents for a Nafion membrane as a function of the percent of the $-\text{SO}_3^-$ sites which have been converted to the Bu_4N^+ -salt form. The water content decreases as Bu_4N^+ is added to the membrane. Figure 6 shows that the probes react to the addition of Bu_4N^+ (and concurrent loss of water) in the expected manner; λ_{Max} values for DA^+ blueshift (Figure 6a) and emission intensities for both DA^+ and $\text{Ru}(\text{bpy})_3^{2+}$ increase (Figure 6b and c, respectively), indicating that the microenvironment is becoming less polar. Again, the "drying" curves are initially rather flat (vide supra).

It is of interest to compare the effects of the two drying procedures studied here on the emission characteristics of the probes. Curve A of Figure 7 shows the effect of water content on $\text{DA}^+ \lambda_{\text{Max}}$ when water is removed via evaporation and curve B shows the effect on $\text{DA}^+ \lambda_{\text{Max}}$ when water is removed by adding Bu_4N^+ . At all water contents DA^+ reports back much lower microenvironment polarities when the hydrophobic Bu_4N^+ ion is present in the film. These data show that the hydrophobic nature of Bu_4N^+ is exerting an influence on the cluster, making it less polar at all water contents than the Na^+ -form of the membrane (i.e., that interaction

of excited probe with the low dielectric constant n-butyl groups causes the probe to experience a lower effective dielectric constant microenvironment). This suggests that organic counterions can be used as chemical modifiers of Nafion membrane polarity.

Effects of Microenvironment Polarity on Chemical Processes Occurring Within the Membrane.

In the introduction, we suggested that a Nafion film or membrane should be regarded as a chemical phase whose properties can influence the courses of chemical processes occurring within this phase. We have shown here that the polarity of the cluster phase in Nafion can be varied over a considerable range via control of the membrane water content and/or counterion. Based on this observation, it is of interest to identify specific chemical processes which would be susceptible to variations in the Nafion chemical environment. Several processes come to mind.

First, it is well known that the Menschutkin (39) and related reactions (40) proceed through highly polar transition states and, as a result, the activation energies for these reactions decrease as solvent polarity increases (40). The data in Figures 3, 4 and 6 suggest that the rates of these reactions in a Nafion membrane could be varied at will by controlling water and/or hydrophobic counterion content.

Second, studies of the effect of the quantity of an electroactive organic counterion loaded, into a Nafion film, on the apparent diffusion coefficient (D_{App}) for this counterion frequently show that D_{App} decreases with the amount of the organic counterion loaded (6c,41). Single file diffusion has been suggested as a possible cause for this decrease in D_{App} (6c). An alternative possibility, suggested by the data in Figure 5, is that the film dehydrates as the organic counterion is added. Since water acts as a plasticizer for the film, water loss would be expected to cause

a diminution in the rates of diffusional processes. In addition, since the rate expression for an electron self-exchange reaction between two ions generally includes the medium dielectric constant (42), the rate of electron hopping in these films should also decrease as water is removed.

Finally, and of more direct interest to ICS's, it seems likely that through control of the appropriate chemical variables, the E° values for certain redox reactions occurring within the Nafion phase could be intentionally and predictably varied. Gritzner has shown that the E° value for a redox couple in a solvent is influenced by the relative strengths of the interactions of the solvent with the two species comprising the couple (43). The simplest example is the reduction of a cation to the amalgam; because the solvent cannot interact with the amalgamated metal, the E° for such a reduction shifts negatively as the strength of the interaction of the solvent with the cation increases (43). It seems likely that through variation in the water or hydrophobic counterion content, E° shifts for analogous redox reactions should be observed in Nafion.

Because ferricinium (Fc^+) is very strongly hydrated and ferrocene (Fc) is very weakly hydrated, it occurred to us that the E° for this couple should be sensitive to the local water concentration (44). For this reason, Fc seemed to be ideally suited for studying the effects of micro-environment on E° . Figure 8 shows voltammograms for Fc in an Na^+ -form Nafion film and in a predominantly Bu_4N^+ -form Nafion film. As would be predicted from the luminescent studies (Figures 6 and 7), E° for Fc^+/Fc in the Na^+ -form Nafion film is ca. 90 mV negative of E° for Fc^+/Fc in the Bu_4N^+ -form film. While shifts in E° values (relative to E° in water) for redox couples in polymer films have been observed (45), in

the present case, E° for the couple in one chemical form of the film is shifted relative to E° for the same couple in a second chemical form of the film. Furthermore, the E° shift was intentionally and predictably produced and would appear to be reversible (i.e., by replacing the Bu_4N^+ with Na^+). Further studies of the effects of Nafion on the dynamics and thermodynamics of chemical and electrochemical processes are in progress in this and other laboratories (46).

Conclusions

We have shown that the local microenvironments around probe molecules or ions within Nafion membrane can be quite low in spite of the very high membrane water content. This point is reinforced by results of analogous luminescence probe studies of sulfonated polyethylenes (47); these membranes contain ca. 120 percent water, yet both Py and DA^+ report back microenvironment polarities significantly lower than that of a bulk water phase (47). Because the probes used here are all rather hydrophobic, they undoubtedly preferentially occupy the most nonpolar portions of the ionic cluster. This point is reinforced by the $\text{Ru}(\text{bpy})_3^{2+}$ loading data (Table II). It is of interest to note, however, that both charged and uncharged probes produced analogous results. As noted earlier, a more global picture of the cluster could be obtained by contrasting these results with data obtained from very hydrophilic probes. To this end, we are currently studying the emission characteristics of Eu^{3+} , UO_2^{2+} and other ions from Nafion.

We have also demonstrated, for the first time, that the polarity of the microenvironments within Nafion can be intentionally and predictably altered via control of appropriate chemical parameters. Analogous results have been obtained for sulfonated polyethylene and Teflon membranes (47).

More importantly, we have shown that the thermodynamics of electrochemical processes occurring within the polymer phase can be altered via alterations of the chemical properties of the membrane microenvironment.

While these studies have shed some light on the chemical properties of the ionic cluster phase within Nafion, they have not provided further information about the structure of the ionic cluster. Earlier studies by Lee and Meisel (17b) and Okamoto et al. (48) have indicated that investigations of quenching reactions within the membrane can provide structural information. We are currently pursuing this possibility.

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Table 1. Wavelength of maximum emission intensity (λ_{Max}) for DA^+ and $\text{Ru}(\text{bpy})_3^{2+}$ and I_3/I_1 for Py in various solvents.

Solvent	DA^+	λ_{Max} (nm) $\text{Ru}(\text{bpy})_3^{2+}$	Py I_3/I_1
Water	571	613	0.58
Ethylene Glycol	544	--	0.79
Methanol	534	610	0.72
Ethanol	526	606	0.80
Butanol	522	608	0.94
Pentanol	519	616	0.98
Decanol	513	622	1.24
Hexane	--	--	1.50

Table II. Emission Characteristics of Probes in Fully Hydrated Nafion Membranes.

Counterion	Pyrene I_3/I_1^a	% Load ^b	DA ⁺ λ_{Max}^c (nm)	Ru(bpy) ₃ ²⁺ % Load ^b	λ_{Max}^c (nm)
H ⁺	0.75	3.0	545	0.01	597
				0.1	602
				1.0	607
				3.0	612
Na ⁺	0.68	3.0	527	—	—

^aRatio of the emission intensities of third and first vibronic bands. Reproducibility from membrane = ± 0.03 .

^b100 x equivalent ionic fraction of $-SO_3^-$ sites converted to probe cation form. ^cWavelength of maximum emission intensity. Reproducibility better than ± 2 nm.

Figure 1. Emission spectra of DA^+ from Nafion membrane a. H^+ -form, 2.6% DA^+ loaded, excited at 295 nm; b. Na^+ -form, 5% DA^+ loaded, excited at 285 nm.

Figure 2. Emission spectra of DA^+ from Na^+ -form Nafion a,b,c = 3%, 1%, 0.1% DA^+ loaded, respectively. Excited at 285 nm.

Figure 3. $\text{Py } I_3/I_1$ vs. water content of H^+ -form Nafion membrane.

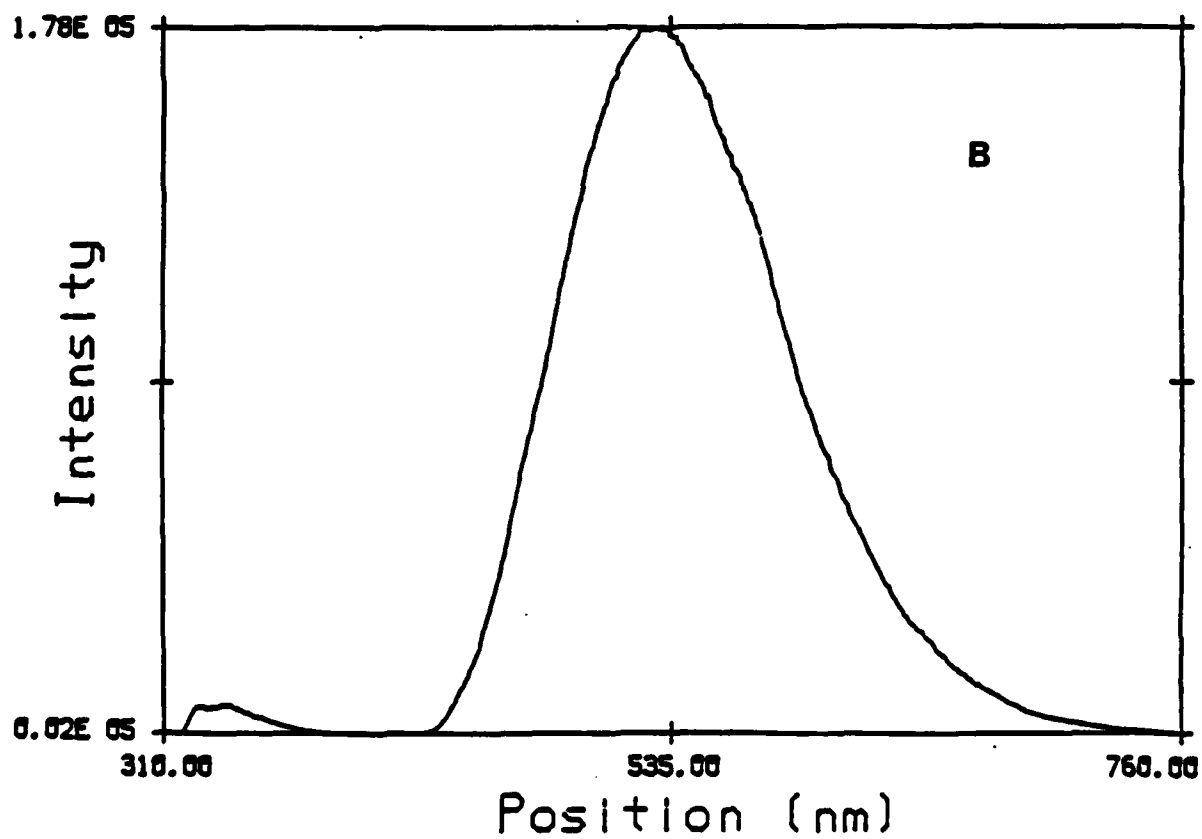
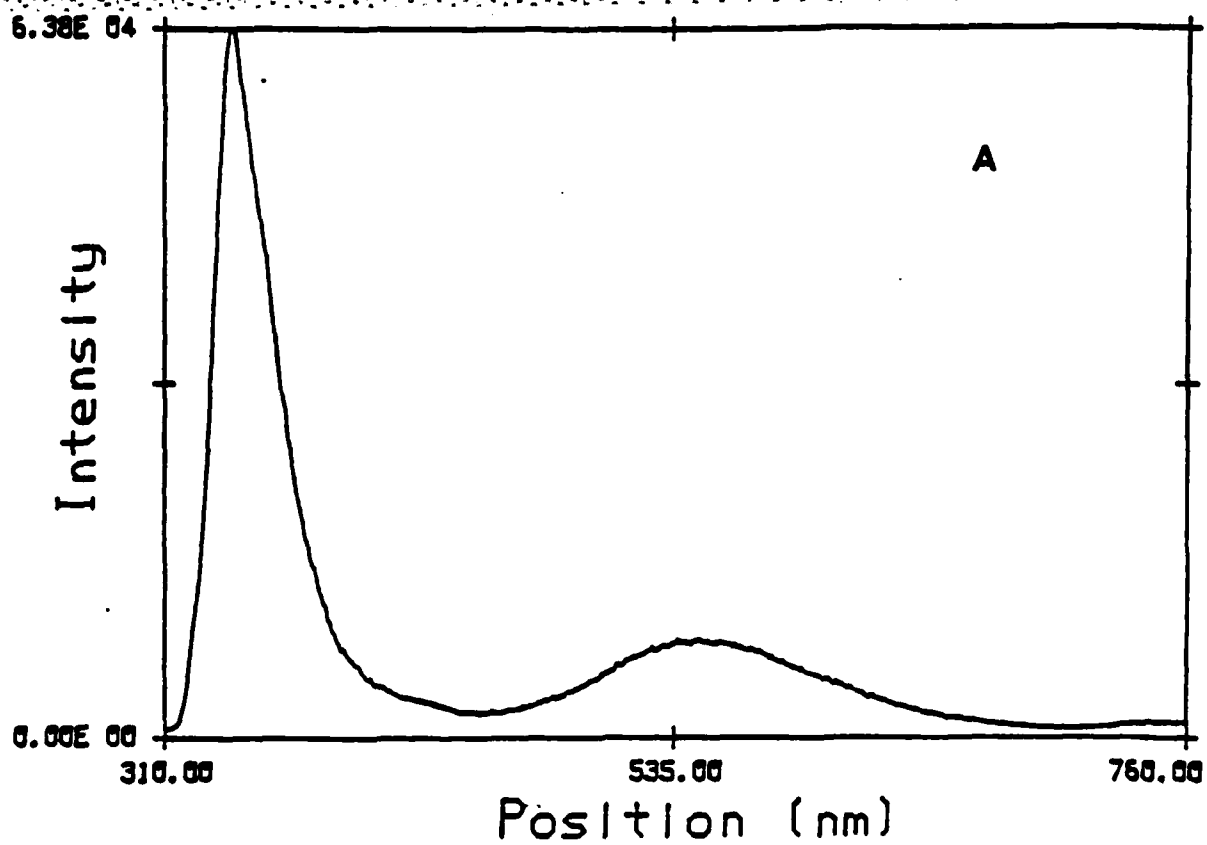
Figure 4. DA^+ emission as a function of Na^+ -form Nafion water content. a. I_{Max} ; b. λ_{Max} .

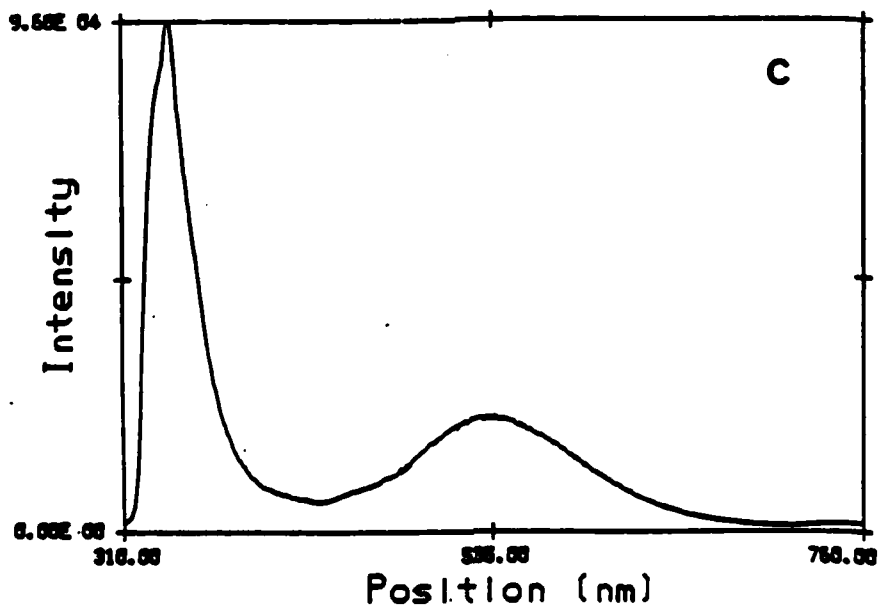
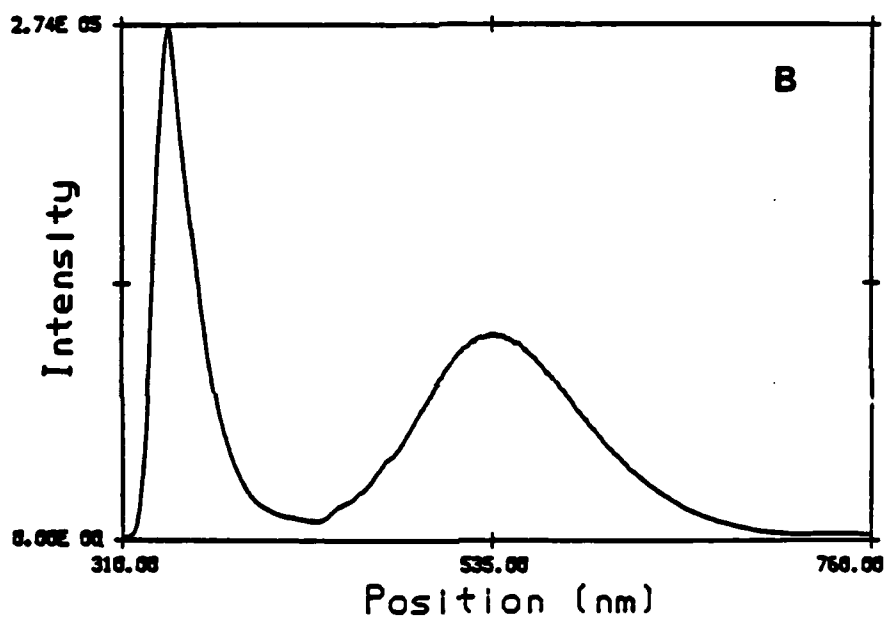
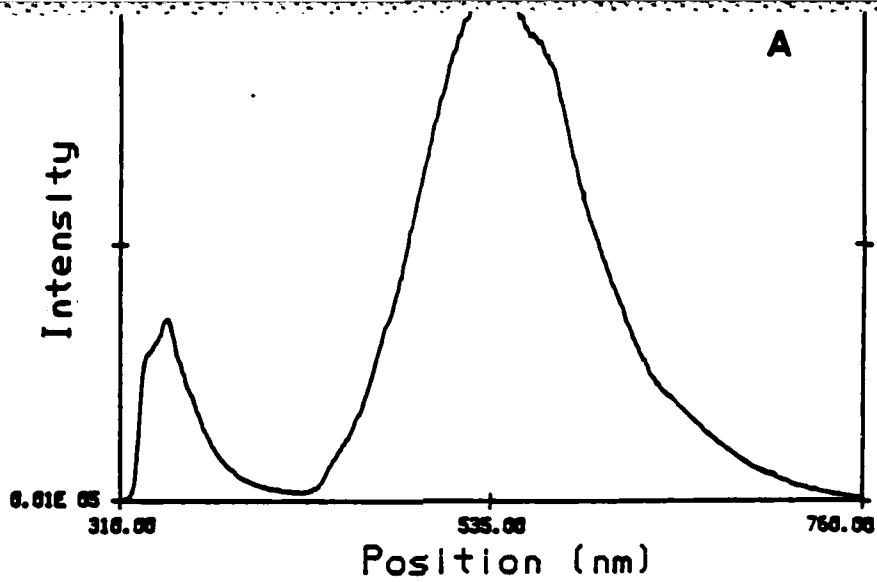
Figure 5. Equilibrium water content of a Nafion membrane vs. % of $-\text{SO}_3\text{Na}$ sites converted to the Bu_4N^+ form.

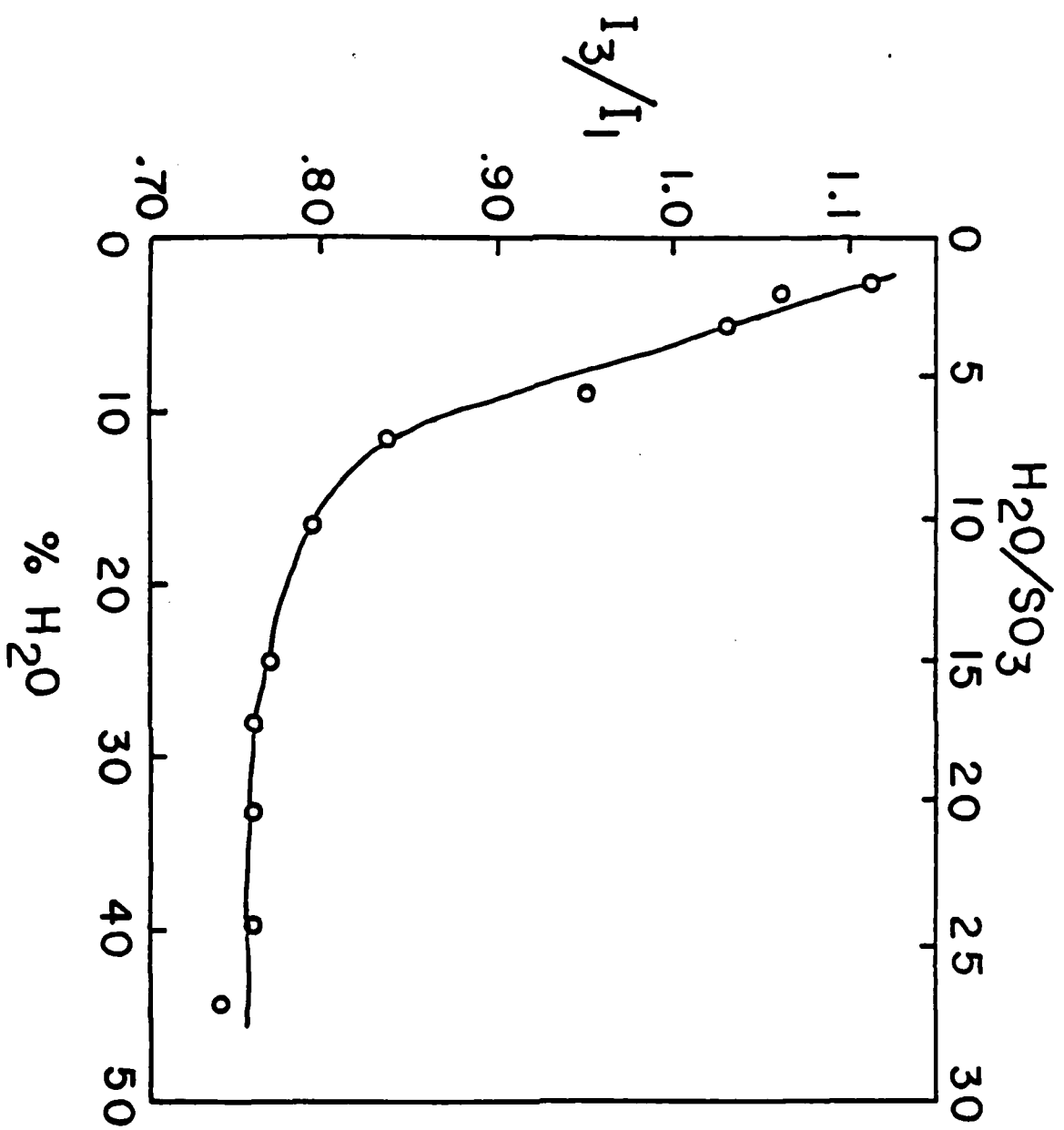
Figure 6. Effect on emission characteristics of conversion of $-\text{SO}_3^-$ groups to the Bu_4N^+ form. a. $\text{DA}^+ \lambda_{\text{Max}}$ vs. % Bu_4N^+ , Na^+ -form initially. b. $\text{DA}^+ I_{\text{Max}}$ vs. % Bu_4N^+ , Na^+ -form initially. c. $\text{Ru}(\text{bpy})_3^{2+} I_{\text{Max}}$ vs. % Bu_4N^+ , H^+ -form initially.

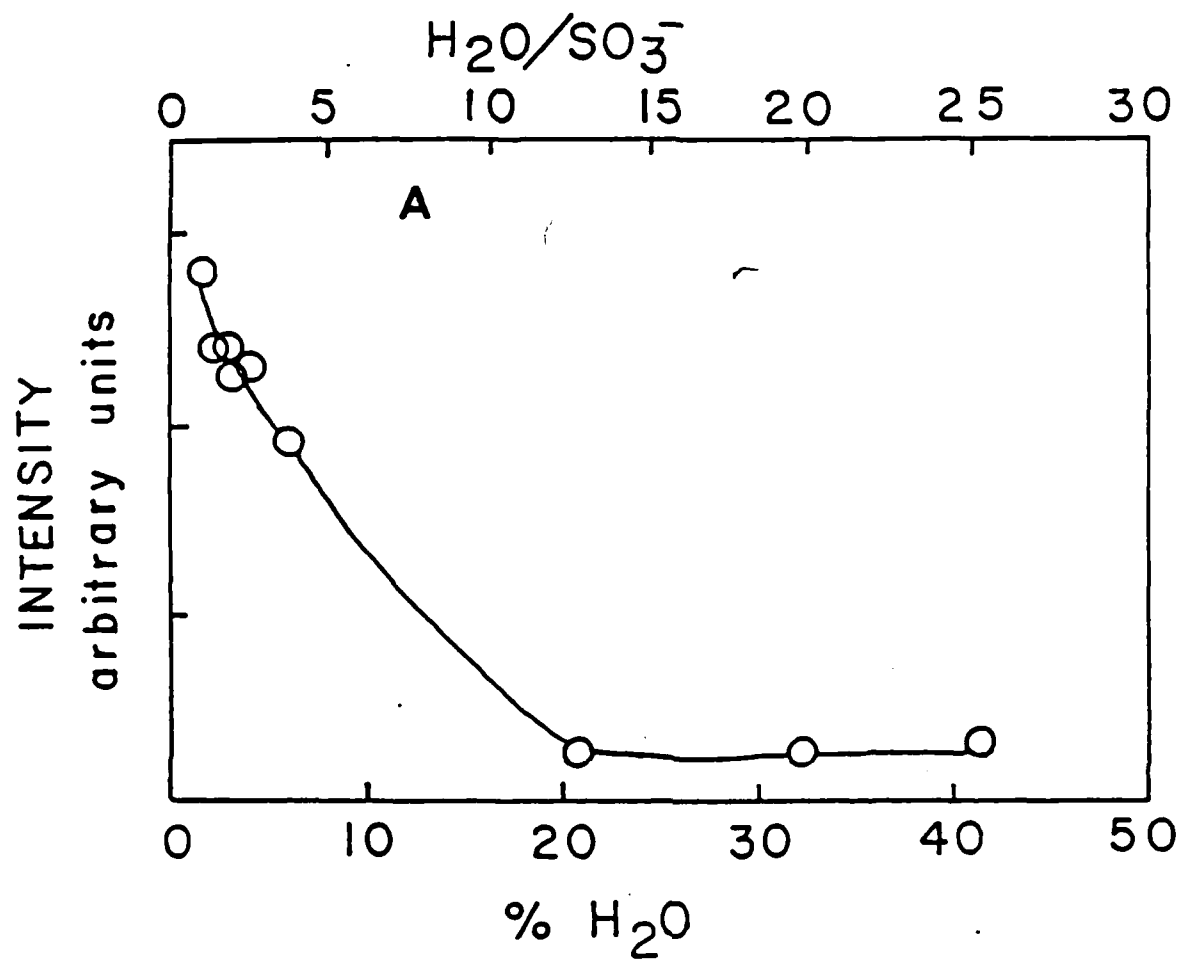
Figure 7. $\text{DA}^+ \lambda_{\text{Max}}$ vs. water content for Na^+ -form membrane. Membrane dried by, A. evaporation; B. conversion to Bu_4N^+ form.

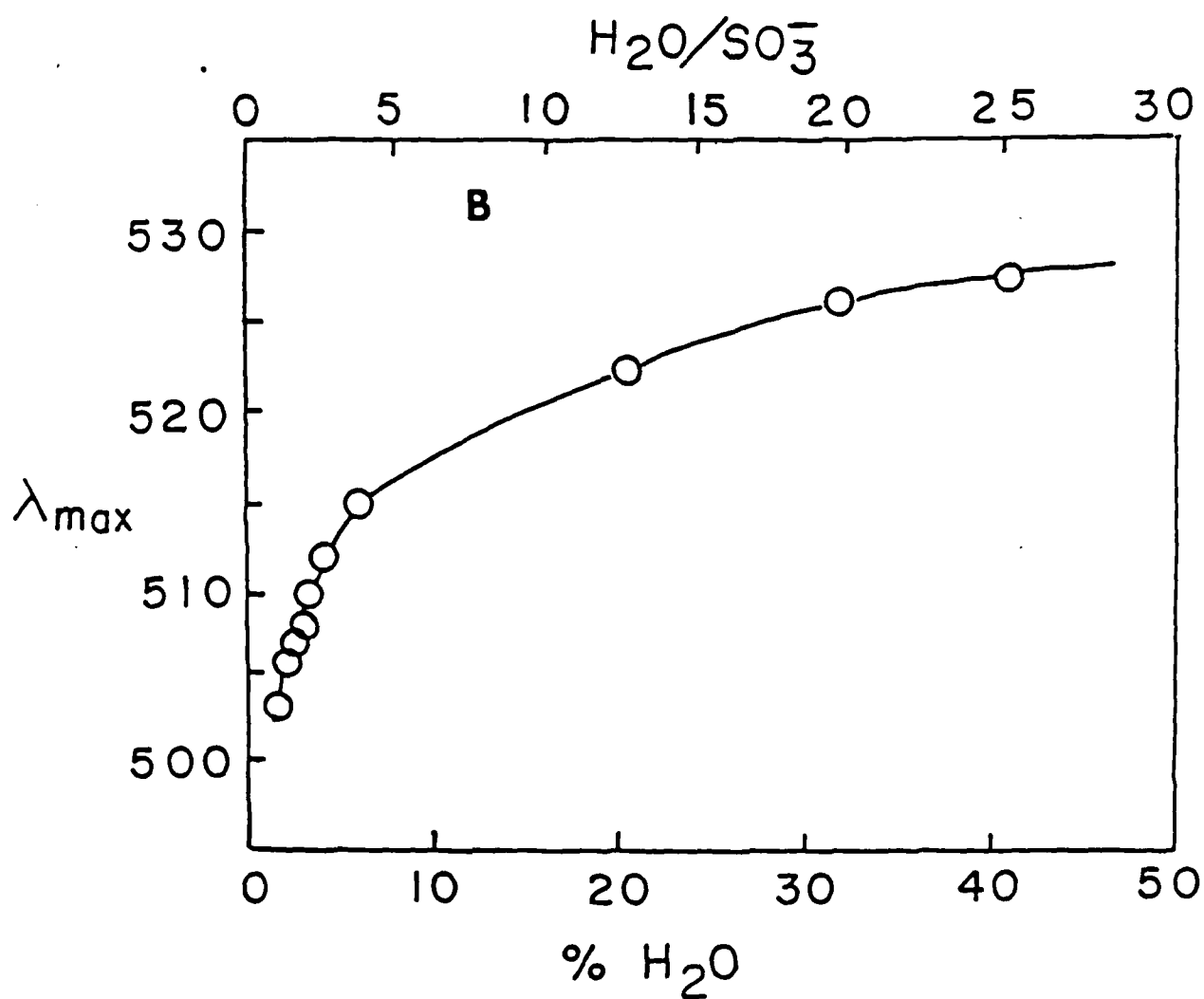
Figure 8. Steady state cyclic voltammograms of ferrocene (scan rate = 0.1 Vs^{-1}) at Nafion-coated glassy carbon electrode in saturated aqueous ferrocene solution. Supporting electrolyte = 0.2M NaOCCF_3 , pH 3.0 — Na^+ -form Nafion. ---- Bu_4N^+ -form Nafion, produced by immersing Na^+ -form Nafion-coated electrode in $1.5 \times 10^{-5}\text{M}$ Bu_4NCl for ca. 10s and making supporting electrolyte $3 \times 10^{-7}\text{M}$ in Bu_4NCl .

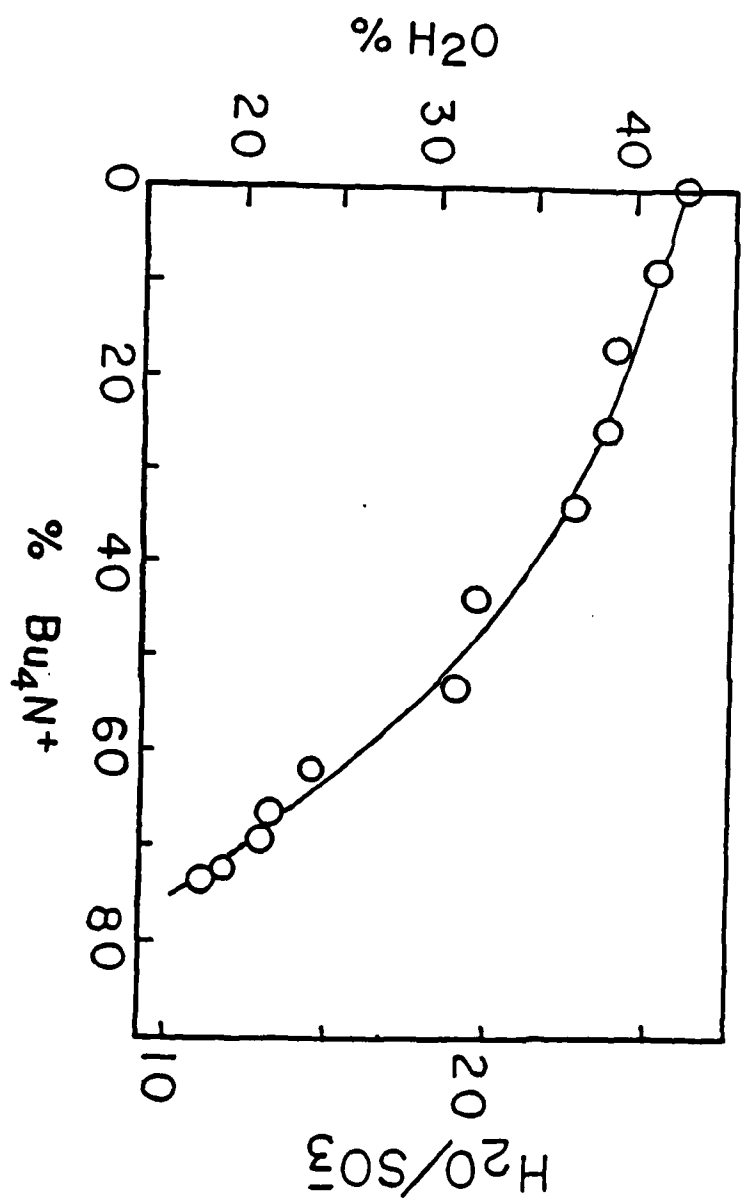


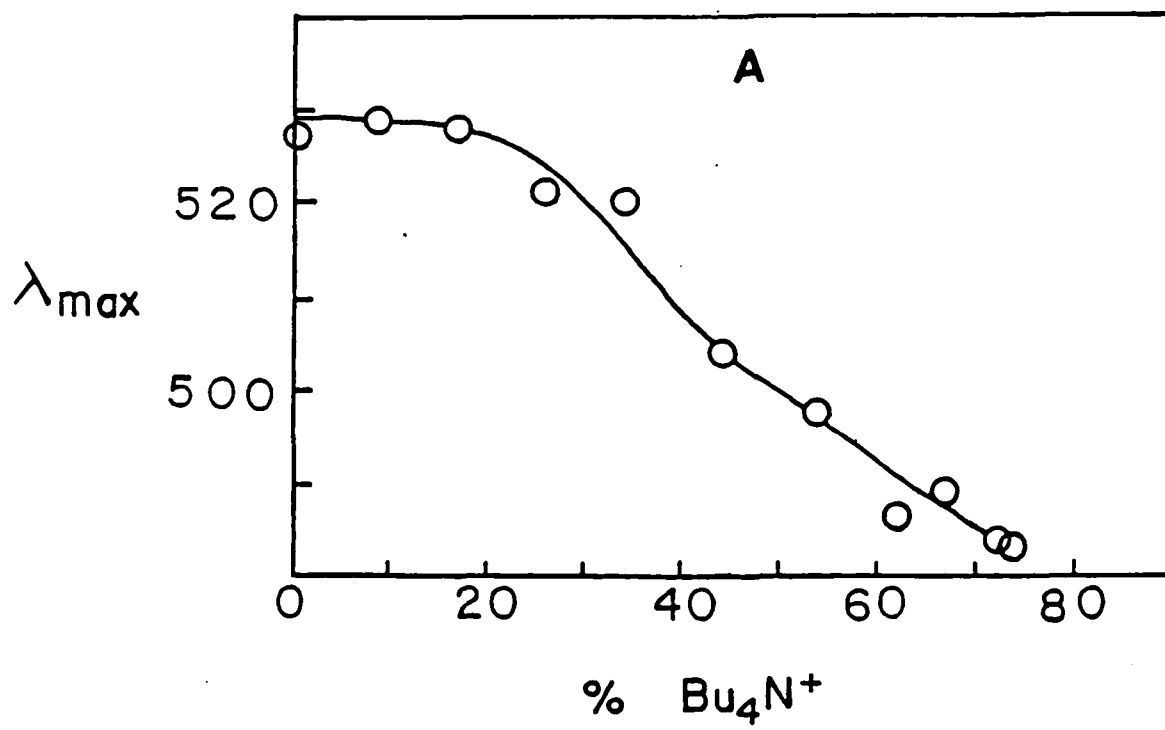


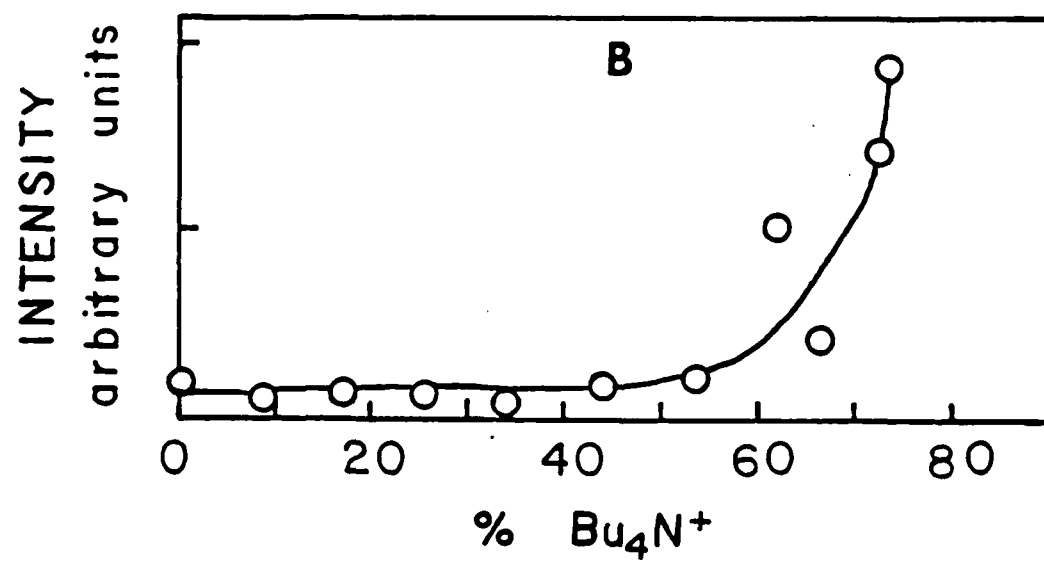


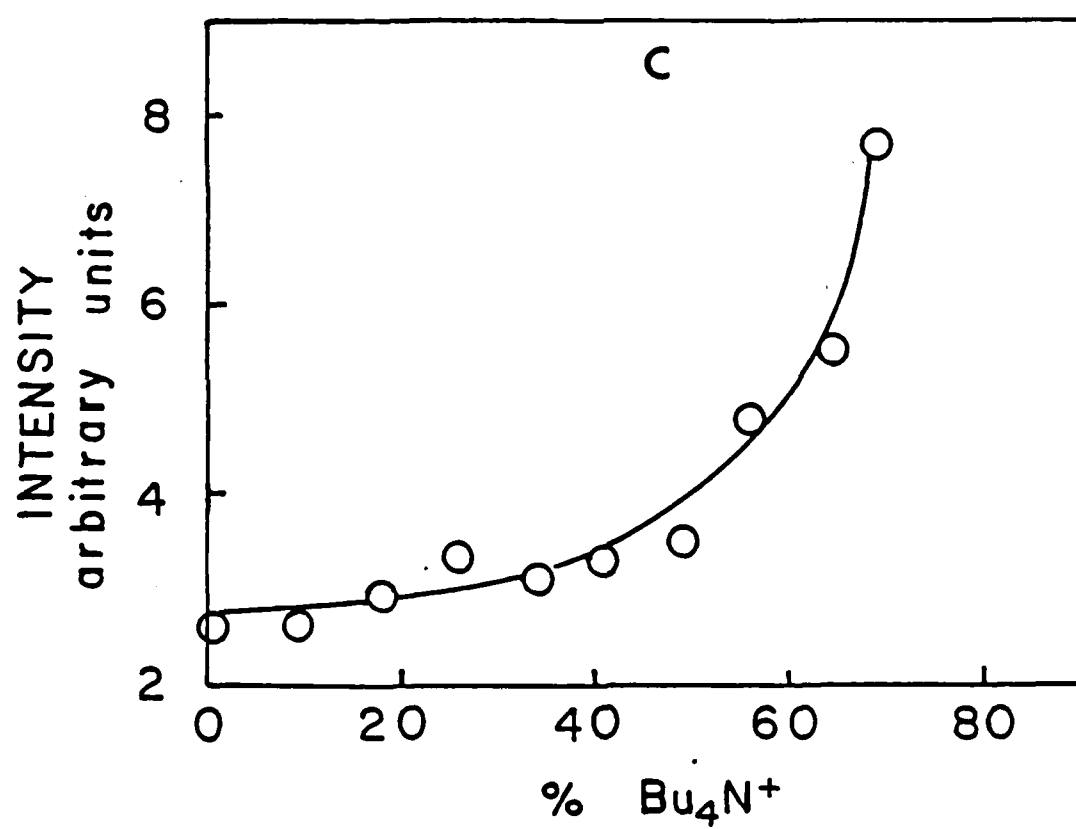


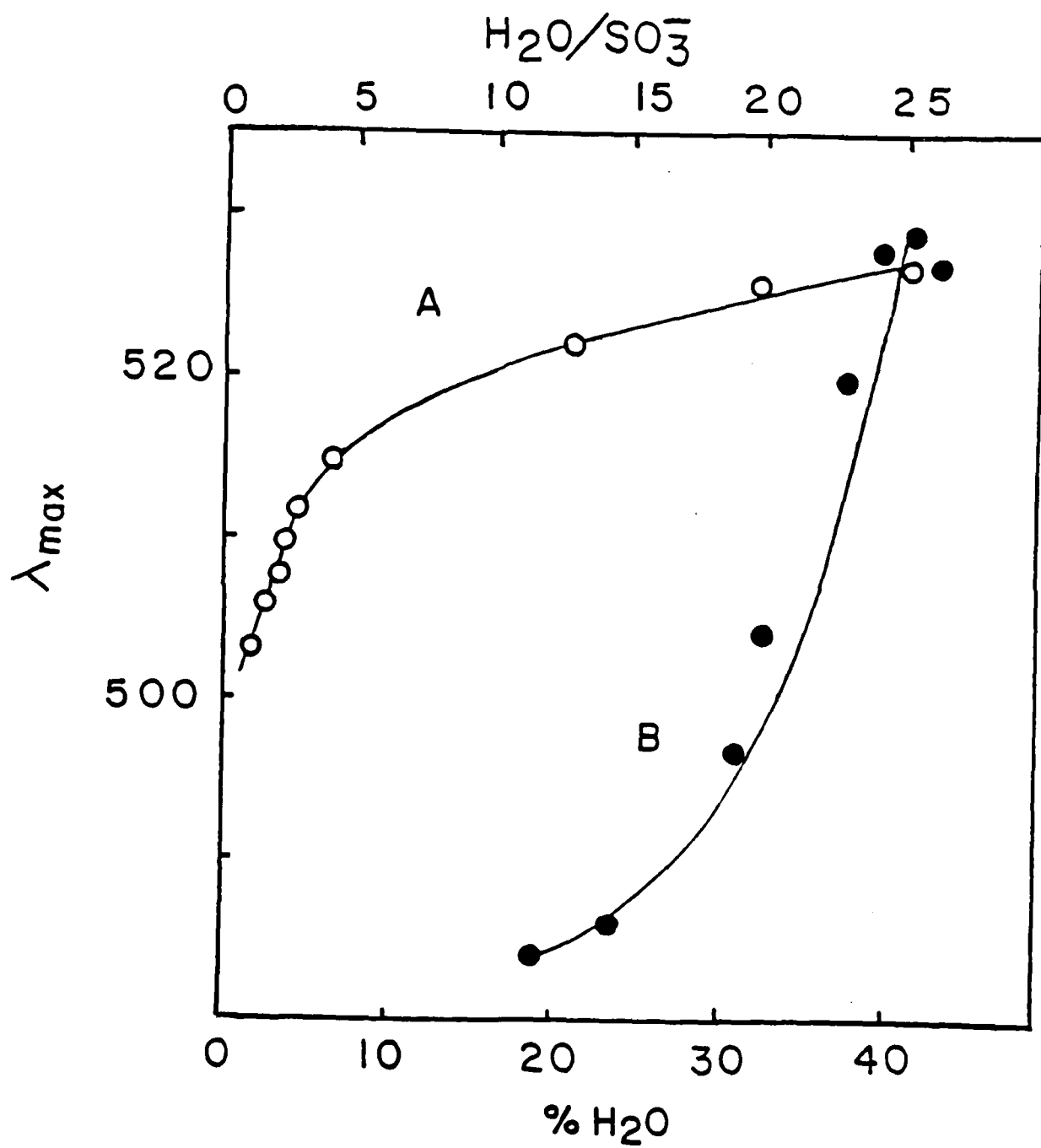


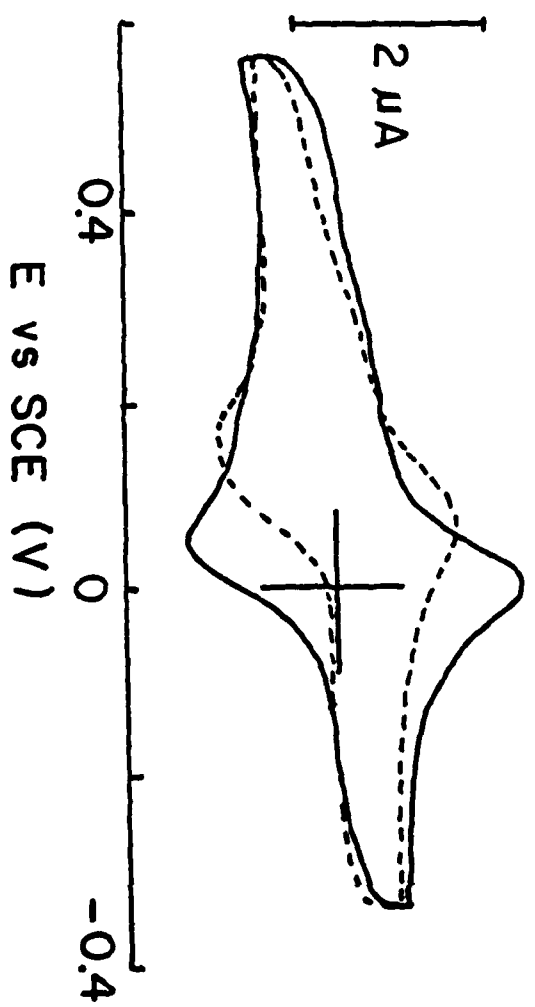












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