Near-Infrared Probe for *In Situ* Characterization of Nafion Thin Films

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SYNOPSIS

A near-infrared (NIR)-absorbing cyanine dye was used as a probe for *in situ* characterization of Nafion thin films. This NIR dye was very sensitive to changes in the hydrophobicity of the environment and proved to be very suitable for probing the Nafion coatings, which involve a two-phase structure of hydrophobic and hydrophilic zones. Sorption phenomena of water and aqueous alkali salt solutions by Nafion were investigated. For our study systems of thin-coating films prepared from 5% wt alcoholic solution of Nafion 117, the absorption spectrum was dominated by higher-order aggregates when in dry form. In pure water, the absorption maximum of the monomer dye appears at 773 nm and can be used as an indication of the swelling process of the film. The water uptake reaches saturation in only a few seconds. After the swelling process, an additional absorption band with a maximum at 555 nm appears primarily at the expense of the NIR monomer dye absorption band. The peak transition process, which is a very slow process and is a strong function of the water content inside the matrix, can be used as an indication of the establishment of equilibrium between the two-phase structure due to the water uptake. Since the absorption maximum of the study system is around 800 nm, semiconductor lasers can be used. This technique shows high potential in other applications where polymers are used as support material, e.g., *in situ* thin-film thickness measurements. In the study, the feasibility of this approach was illustrated.

INTRODUCTION

Perfluorosulfonic acid ionomer electrolytes, such as Nafion, are gaining increasing attention as a surface-film material not only on chemically modified electrodes,[1-7] but also in the fabrication of optrodes.[8] Nafion can be made to coat over a suitable system of interest simply by applying its solution to the surface. Nafion in the solution is then formed into an immobilized solid polymer electrolyte surface by evaporating the solvent. The immobilized solid-polymer electrolyte can then be further modified by ion-exchanging a cation for the proton associated with the sulfonic acid groups or merely by entrapping the molecules of interest for some specific applications. Our group has successfully used Nafion as a substrate for immobilizing a near-infrared (NIR)-absorbing fluorophore, a biscarboxylic acid derivative of a cyanine dye, to determine pH.[9] Because Nafion has the property of strongly binding hydrophobic counterions through a combination of electrostatic and hydrophobic attraction, the dye adheres strongly to the membrane without being covalently bonded to it. By combining the use of laser diodes with NIR pH-sensitive chromophores or using NIR reporting labels in immunochemical determinations, promising new techniques emerge in cases where visible probes are not useful due to interference.

In this study, we demonstrate a simple method of using an NIR probe for *in situ* characterization of the Nafion thin-film matrix. The NIR probe used in this study was very similar to that of the pH-sensitive dye only without the pH-sensitive functional group and was entrapped within the Nafion matrix following exactly the same preparation procedures as for the NIR fluorescence pH sensor.[9] Since this dye has a chemical structure and a hy-

drophobic nature similar to the pH-sensitive dye, a fundamental study of this system can provide an insight into the nature of the transport processes in Nafion films. This information can be important in expanding the applications of this material.

NIR dyes similar to the dye used in this study were found to be very sensitive to changes in the hydrophobicity of the environment and proved to be very suitable for probing the hydrophobic microenvironment in different systems, e.g., micellar assemblies, proteins, etc.[10,11] It is logical to extend microenvironmental studies to gain information on the Nafion morphology. Actually, as a result of the strongly hydrophobic backbone and highly hydrophilic terminal group, it is not surprising that some form of phase separation occurs in Nafion. Small-angle X-ray scattering studies of Yeo and Eisenberg[12] laid the foundation for the detailed model of the morphology of the swollen Nafion membrane.[13] In this model, hydrated $-SO_3^-$ head groups and counterion clusters (~ 40 Å in diameter) are interconnected by short channels (~ 10 Å in diameter) immersed in a fluorocarbon backbone network. Moreover, the analogy between this biphasic structure and the structure of reversed micelles has been noted and examined by ^{23}Na magnetic resonance[14] and luminescence quenching studies.[15] Several interesting results in the electrochemical studies of charge-transport processes in Nafion-modified electrodes were explained based on this model.[16–18] Our study provides more information and support for these explanations. The most important result is the understanding of the role fundamental properties play in future applications of similar systems using this technique, not to mention *in situ* characterization of these processes that are potentially important to all branches of science.

EXPERIMENTAL

Reagents and Chemicals

The chemical structure of the hydrophobicity-sensitive NIR dye used in this study is depicted in Figure 1. This dye, whose chemical name is 2-{4'-chloro-7'-[2"-(1"-ethyl-3",3"-dimethylindolenine)]-3',5'-(1''',3'''-propanediyl)-1',3',5'-heptatrien-1'-yl}-1-ethyl-3,3-dimethylindoleninium iodide was prepared as follows: The starting material, 1-ethyl-2,3,3-trimethylindoleninium iodide, was obtained by refluxing a solution of ethyl iodide and 2,3,3-trimethylindolenine in acetonitrile for 8 h. After cooling, the product was dissolved in methanol. It was then fil-
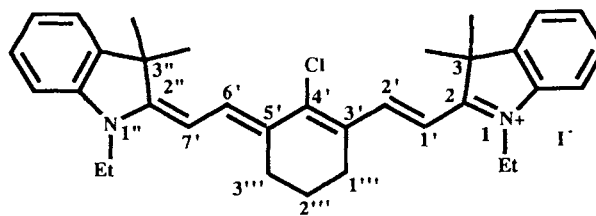

Figure 1 Chemical structure of the hydrophobicity-sensitive NIR dye used in this study.

tered and precipitated with diethyl ether (mp 221–222°C). The other starting material, (5-anilino-3-chloro - 2,4 - trimethylene - 2,4 - pentadienylidene) - anilinium chloride, was prepared according to the procedure in the literature.[17] A mixture of 0.002 mol of 1-ethyl-2,3,3-trimethylindoleninium iodide and 0.001 mol of (5-anilino-3-chloro-2,4-trimethylene-2,4-pentadienylidene)anilinium chloride was then refluxed for 1 h in 20 mL ethanol in the presence of 0.2 g anhydrous sodium acetate. After removal of ethanol, the residue was redissolved in chloroform and the unreacted sodium acetate was filtered off. The chloroform solution was purified by the chromatographic method (silica gel, 5% methanol in chloroform). The final product was washed with diethyl ether and dried under vacuum (mp 227–229°C). The structure of the dye given in Figure 1 was fully consistent with the obtained MS and 400 MHz proton NMR spectra ($CDCl_3$ as solvent). ^1H-NMR: 8.35 d (2H, $=CH-$, J = 14.4 Hz), 7.171–7.427 m (8H, aromatic), 6.25 d (2H, $=CH-$, J = 14.4 Hz), 4.28 q (4H, CH_2, J = 7.2 Hz), 2.77 t (4H, CH_2, J = 6.2 Hz), 1.99 quint. (2H, CH_2, J = 6.2 Hz), 1.72 s [12H, $C(CH_3)_2$], 1.46 t (6H, CH_3, J = 7.2 Hz). MS: 512, 100% [$M^+ - I^-$].

Nafion perfluorinated ion-exchange powder, 5 wt % solution in a mixture of lower aliphatic alcohols and 10% water, was obtained from the Aldrich Chemical Co. (Milwaukee, WI). The solution was prepared from Nafion 117 perfluorinated membrane with an equivalent weight (EW) of 1100 and in hydrogen form. HPLC-grade methanol was also obtained from Aldrich. Hydrochloric acid, sodium chloride, potassium chloride, and lithium chloride were obtained from Fisher Scientific (Pittsburgh, PA).

Method

A $10^{-3} M$ stock solution of the NIR-absorbing dye was prepared in HPLC-grade methanol. For the hydrophobicity studies, solutions were prepared by pi-

petting the required amount of the dye stock solution into a 10 mL volumetric flask. After the methanol was removed by nitrogen gas, the volumetric flask was filled with deionized water and briefly sonicated. For film preparation, the required amounts of dye stock solution and Nafion solution were pipetted into a small beaker and thoroughly mixed by sonication to form the coating solution. The coating solution was then placed on the inside wall of a polystyrene cuvette (Fisher). After being dried briefly in an oven at 80°C, the cuvette was air-dried overnight. A thin film of Nafion with the NIR dye entrapped was formed by the complete removal of the solvent. Note that in order to assure a similar film thickness the amount of Nafion is 0.035 mL for all coating solutions. The thin film formed by this method was not very uniform; however, this did not affect our results when relative measurements were used. Naturally, when absolute measurements are required, we need to prepare more uniform films.

Each freshly prepared thin-film-coated cuvette with different entrapped dye concentration was used only once in either absorbance or fluorescence measurements by adding different aqueous solutions to it. The absorption spectra were taken from time to time depending on how fast the peak transition appeared, while both the measurements of time-dependent absorbance change at 773 nm and fluorescence intensities were continuously monitored.

Instrumentation

A Perkin-Elmer Lamda 2 UV/vis/NIR spectrophotometer was used for absorption measurements. The spectrophotometer was interfaced to a Zenith 286 computer to store data and control the spectrophotometer. Each spectrum was recorded using a Perkin-Elmer program (PECSS) purchased with the Lambda 2 instrument, with a scan rate of 240 nm/min. The PECSS program was also used to monitor the time-dependent absorbance changes at 773 nm by taking the data every 0.1 s. All data were obtained at room temperature using solutions in equilibrium with air. Fluorescence intensities of the dye-entrapped Nafion thin film were excited with a simple and inexpensive laser diode (30 mW, 780 nm) along with an amplifier and measured by a digital voltmeter (DVM), which was constructed from off-the-shelf components in our laboratory as reported earlier.[20,21]

RESULTS AND DISCUSSION

Representative absorption spectra for the NIR-absorbing dye with different concentrations in water and methanol are shown in Figure 2. The observed monomer and dimer peak absorption maxima are 778 and 771 nm in methanol and water, respectively.
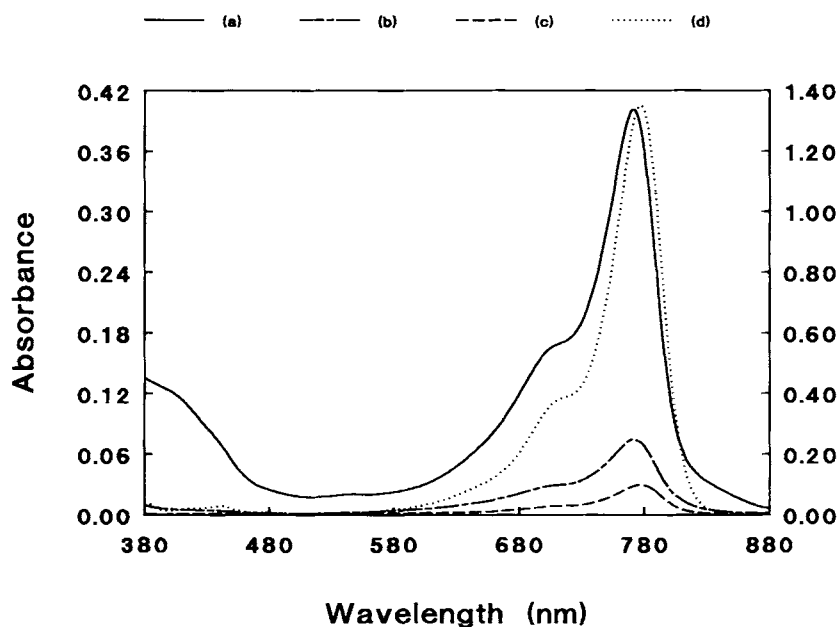

Figure 2 Representative absorption spectra of the NIR dye—in water (left scale): (a) $1 \times 10^{-5} M$; (b) $1 \times 10^{-6} M$; in methanol (right scale): (c) $1 \times 10^{-6} M$; (d) $1 \times 10^{-5} M$.

As can be seen, the dimer band is not too well resolved from the monomer band. The same phenomenon was also observed with the commercially available NIR dyes IR-144, IR-125, and DTTCI products of Eastman Kodak Company, as reported from our previous study.[22] It is well known that solutions of NIR dyes in aqueous systems, especially at higher dye concentrations, exhibit an absorption band different from the absorption band that can be observed in less concentrated solutions or in less polar organic solvents. These spectral changes have long been attributed to dye molecule aggregation. The NIR dye used in this study also displays this type of behavior in water, where there is a tendency to form dimers or higher associations because of the strong dispersion forces associated with the high polarizability of the polymethine chain. At higher concentrations, higher-order aggregates have been observed in aqueous solutions that have been identified as H and J aggregates.[23,24] Therefore, the formation of higher-order aggregates, which is clearly observable in $1 \times 10^{-5} M$ aqueous solutions at 450 nm as shown in Figure 2, can be attributed to the "H" band.

Representative absorption spectra of the dye entrapped within the Nafion matrix in different conditions are shown in Figure 3. The spectrum of the dry film was taken after the thin-film-coated cuvette was air-dried overnight. During the drying process,

the methanol inside the film was completely removed. However, a very small amount of water, which may come from either the Nafion stock solution or air moisture, is believed to remain inside the film. As can be seen, the absorption spectrum of the dry film is dominated by the higher-order aggregate. This is anticipated since the film's dimension is shrinking during the drying process. The decrease in film dimension is actually equal to the increase in the concentration of the dye inside the film. Film dimension decrease has the same effect as solvent evaporation from a solution, i.e., increased concentration of the solute. The observed higher-order aggregates for this dye in dry Nafion thin film can be attributed to the "H" band, since it appears at the same wavelength as that of the free dye in aqueous solutions, as shown in Figure 2.

Immediately after the addition of pure water into the cuvette, a well-separated absorption peak appears at 773 nm. This is because the film swells in water and the expansion of the film dimension breaks up a majority of the higher-order aggregates. The shape of the spectrum is typical of the molecular spectrum of the free cyanine and other polymethine dyes in solution, as shown in Figure 2. Interestingly, the maximum of the absorption peak at 773 nm lies between the absorption maxima of monomer (778 nm) and dimer (771 nm) for this dye in solution. Moreover, an additional absorption band with a
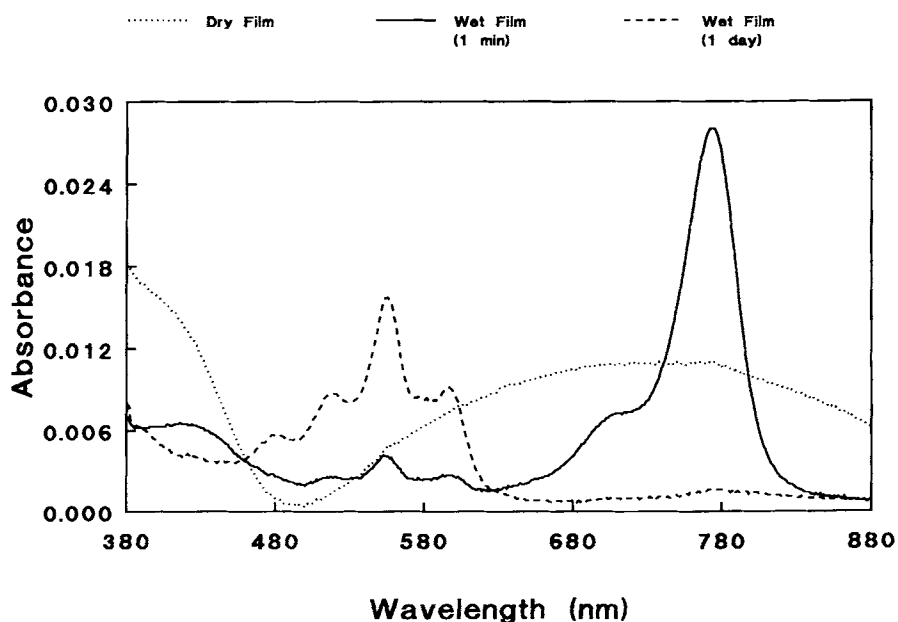

Figure 3   Representative absorption spectra of the NIR dye entrapped within Nafion thin-film matrix before and after swelling in pure water.

maximum at 555 nm appears primarily at the expense of the NIR peak at 773 nm. It takes several hours before the peak transition is completed.

Lee and Meisel used the charge-transfer excited state of $Ru(bpy)_3^{2+}$ as a probe to study the morphology of Nafion.[15] They observed a slightly blue shift (ca. 3 nm) of the absorption spectrum of $Ru(bpy)_3^{2+}$ in Nafion to that observed in aqueous solution. A more pronounced effect was observed in the emission spectrum of $Ru(bpy)_3^{2+*}$ (12 nm blue shift). After comparing the results to those of different micellar solutions, they concluded that the spectral shifts in Nafion stemmed from the interaction of $Ru(bpy)_3^{2+}$ with the fluorocarbon chain rather than with the sulfonate head groups. Taking into account that our NIR-absorbing dye is more hydrophobic than is $Ru(bpy)_3^{2+}$, the absorption peak at 773 nm can be attributed to the monomer and the minor spectral shift is due to the interaction between the dye and Nafion.

Representative time-dependent absorption spectra of the extra peak formation for the NIR dye entrapped within the Nafion thin film in pure water are shown in Figure 4. Two isobestic points, which appear at 462 and 632 nm, were observed in the family of absorption curves. According to the well-known properties of the isobestic point, all species are in equilibrium. It appears that the NIR dye significantly changes its absorption spectra depending upon the swelling process of the Nafion polymer.

The swelling process of the polymer, which is the result of the water uptake, seems to cause the change in the hydrophobicity of the environment and, hence, the change in spectra. However, after careful investigation, this is proved to be not the case, as will be discussed later. Nevertheless, the appearance of the extra absorption band did indicate that some interactions related to the dye and Nafion were taking place inside the matrix.

To further investigate the process of peak formation at 555 nm in Nafion, the effect of dye concentration was studied. Figure 5 shows the absorption spectra of three different cuvettes coated with different dye concentration immediately after addition of pure water and the results of peak transition after a specific period of time. The volume ratios between Nafion and dye of the coating solutions used to prepare the thin films on the cuvettes were (35 : 15), (35 : 10), and (35 : 5), respectively. As can be seen, the difference in absorbance at 773 nm for these three cuvettes generally follows Beer's law, which demonstrates the stability of the dye inside the Nafion matrix and the reliability of the simple thin-film preparation method. It also shows that the variation in the film thickness did not significantly affect the final results and that the time required to complete the peak transition depends on the dye concentration inside the Nafion; the higher the dye concentration inside the Nafion, the longer the peak transition time.
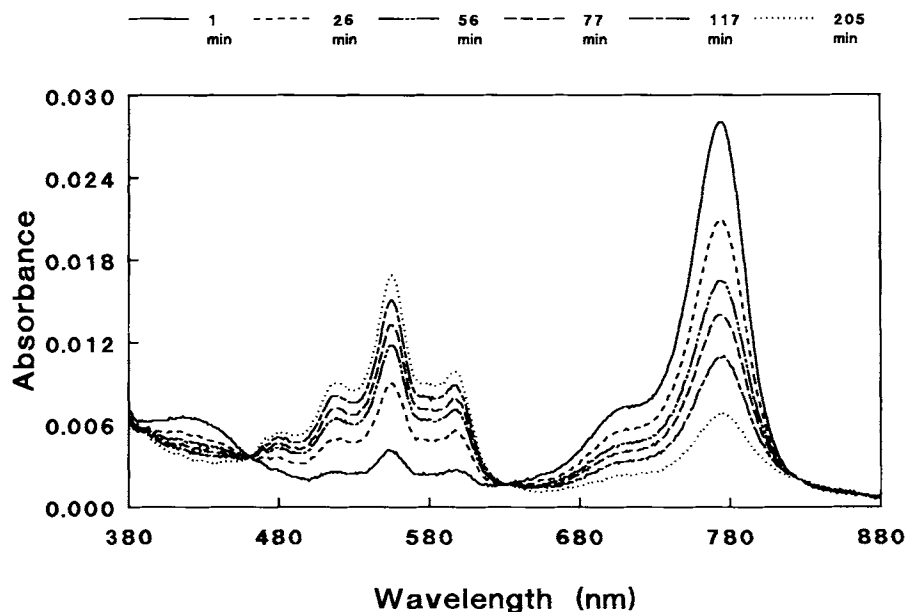

Figure 4 Representative time-dependent absorption spectra of peak transition for the NIR dye entrapped within Nafion thin-film matrix in pure water.
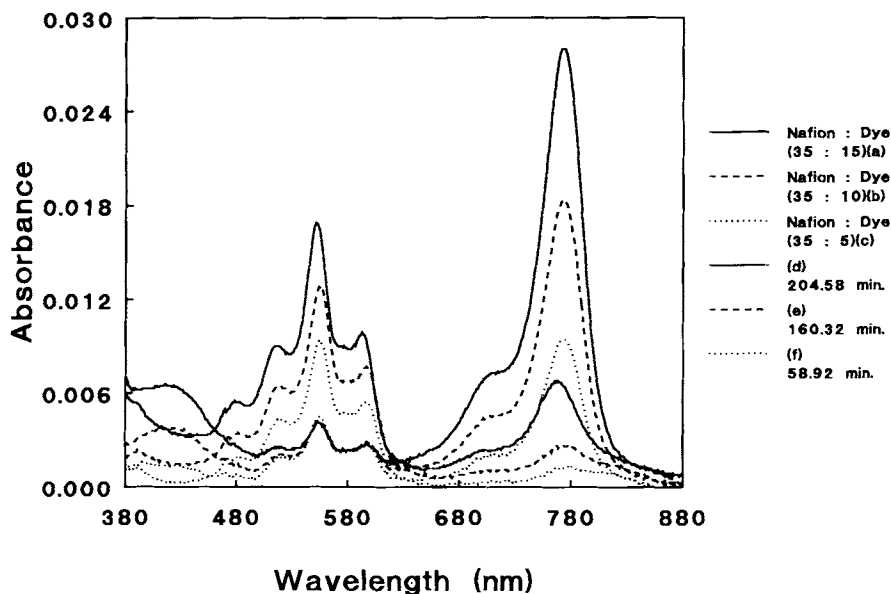
Figure 5 Typical absorption spectra of the NIR dye entrapped within Nafion thin-film matrix prepared in different dye concentrations: (a)-(c) immediately after the addition of pure water; (d) same film as (a) after 204.58 min; (e) same film as (b) after 160.32 min; (f) same film as (c) after 58.92 min. The scan rate was 240 nm/min.

The time-dependent absorbance changes for these three cuvettes were monitored at 773 and 555 nm. Figure 6 clearly demonstrates the process of peak transition for these three cuvettes. Based on the

calculation of the initial slope (i.e., before the curves level off), the transition rate for all three cuvettes is pretty similar, approximately 2.58×10^{-4} $\Delta Abs/$ min at 773 nm. Obviously, the mechanism of peak
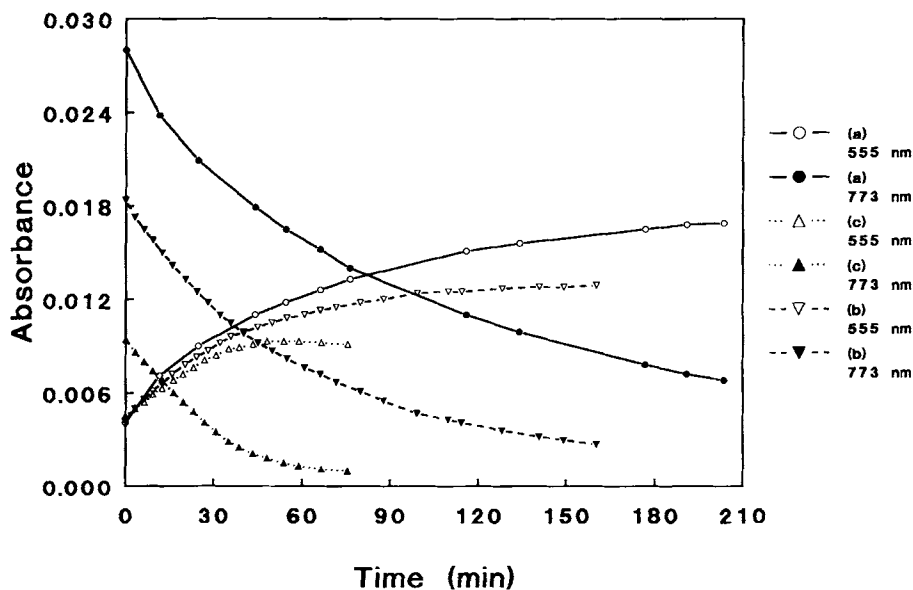

Figure 6 Typical time-dependent peak transition process for the NIR dye entrapped within Nafion thin-film matrix prepared in different dye concentrations. The absorbance values were monitored at 773 and 555 nm. The volume ratios of the coating solutions between Nafion and dye used to prepare the thin films were (a) 35 : 15, (b) 35 : 10, and (c) 35 : 5.

formation at 555 nm is the same for all three cuvettes and is independent of the dye concentration. Apparently, the probe molecule selectively binds to a specific site or preferentially partitions into an organized structure. It is proper to expect that this dye prefers to stay in the hydrophobic zone of Nafion. Therefore, the appearance of the new spectral band should provide an indication of the environment immediately surrounding the probe.

The effect of alkali ions on the process of peak formation at 555 nm in Nafion thin film was also studied. Because of the ion-exchange property of Nafion, the alkali ions should be able to exchange to some extent with H^+ so that an ion-exchange equilibrium will be established. The same experiments mentioned above were repeated in $1M$ HCl(aq), $2M$ LiCl(aq), $2M$ NaCl(aq), and $2M$ KCl(aq). Once again, the same peak transition process was observed in all solutions; therefore, it is not shown here. However, as expected, we observe very different peak transition rates in different alkali solutions. These rates are summarized in Table I. The discussion of the results has to take into consideration two factors: hydration energy and ion-exchange equilibrium constant. The order of increase in the peak transition rate follows exactly the order of increase in hydration energy, which is $H^+ > Li^+ > Na^+ > K^+$. The equilibrium constant of alkali ions in cation-exchange resin (Rel—$SO_3^- H^+$) is in the order of $K^+ > Na^+ > H^+ > Li^+$.[25] The same order is also expected for the Nafion polymer matrix, which also contains the sulfonic acid group. With the two factors almost in reverse order, the peak transition rate is actually a compromise result between the two factors. Takamatsu and Eisenberg studied the densities and expansion coefficients of alkali salt Nafion membranes (EW = 1155; thickness = 1.26 mm).[26] Their results show that after the dry membranes were immersed in water the water content for Li, Na, and K salts was 14.0, 9.4, and

1.8%, respectively (room temperature). Moreover, the diffusion coefficients of several cations (K^+, Cs^+, Ba^{+2}, and Ca^{+2}) were determined and found to be considerably smaller than that of water. Both results seem to fit with our results in Table I not only in the order of change but also in the degree of difference.

The results can be further classified by considering the very slow rate of peak transition when compared to the results in the literature about the study of the sorption phenomena in Nafion membranes. Actually, Nafion materials have been the subject of extensive research as a result of their unusual sorption properties.[27-30] The sorption phenomena of water and aqueous salt solutions in Nafion membranes were one of the topics that was thoroughly investigated. These studies have shown that the time it takes for the water uptake to approach saturation depends very much on the equivalent weight of Nafion. Also, the lower equivalent weight membranes have a higher affinity for hydration since the lower equivalent weight polymers are characterized by a greater sulfonic acid functional group concentration. It takes about 50 min for a relatively thick, 1.3 mm, Nafion membrane (EW = 1155) to approach saturation of water uptake.[31] For some perfluorosulfonic acid ionomers with lower equivalent weight (850 and 950), the time required to reach saturation of water uptake can be less than 2 s.[32] In our case, since the equivalent weight of Nafion is 1100 and the film thickness is much less than those of membranes, it is reasonable to expect that the water uptake should reach saturation in a very short period of time. Unfortunately, because the absorbance spectra were taken with a scan rate of 240 nm/min, the saturation of water uptake is apparently completed even before completion of the scan (2.5 min). Nevertheless, it is certain that the water uptake reaches saturation in less than 2.5 min, and the peak formation, at 555 nm, which takes hours to complete, is not a result of the swelling process.

A more precise study of the swelling process was done by monitoring the time-dependent absorbance changes at 773 nm within short time intervals (0.1 s). Because the manual speed of handling the process of starting the experiments was not rapid enough compared to the swelling process of the film immediately after filling in solution, the experiments were modified by injecting the solution into the cuvette after the instrument had started collecting data. With this modified technique, the results of the swelling process of Nafion thin films in different aqueous solutions are shown in Figure 7. Note that the data collected in the first second are not shown

Table 1   The Peak Transition Rate at 773 nm for the NIR Hydrophobicity-Sensitive Dye Entrapped within the Nafion Thin Film in Different Aqueous Solutions

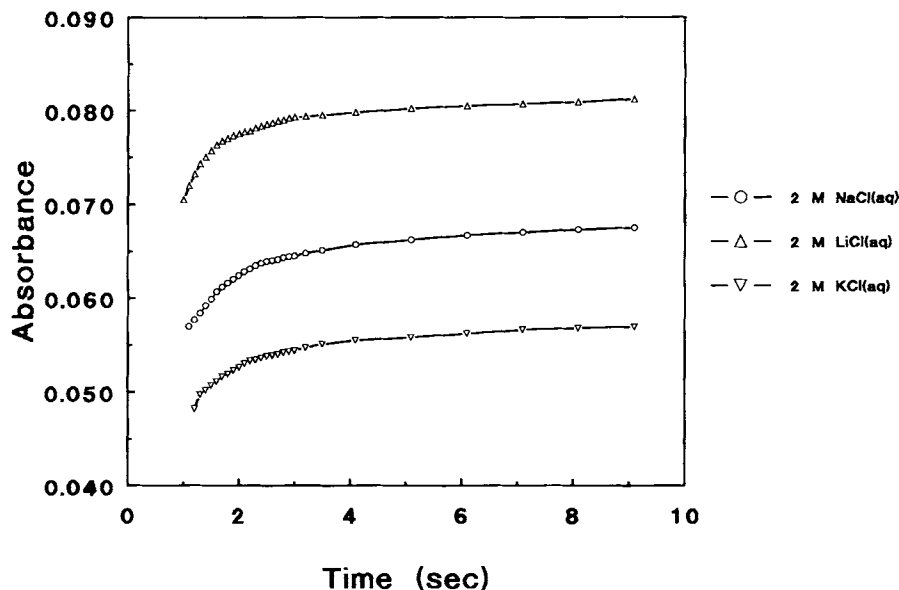| Solvent	ΔA_{773}/min
Water	2.58×10^{-4}
HCl (aq, $1M$)	6.43×10^{-3}
LiCl (aq, $2M$)	6.56×10^{-4}
NaCl (aq, $2M$)	3.05×10^{-4}
KCl (aq, $2M$)	2.33×10^{-5}

Figure 7 Typical time-dependent absorbance changes at 773 nm immediately after the injection of different alkali aqueous solutions into the dye-entrapped Nafion thin-film-coated cuvettes.

in the figure due to the perturbation of the injection process. The difference in absorbance in different aqueous solutions is only for the purpose of demonstration, since similar results of the swelling process were observed for different cuvettes coated with different dye concentrations in the same solutions. As can be seen in Figure 7, the water uptake reaches saturation in less than 4 s for all solutions. After the large increase of absorbance in the first few seconds, the absorbance is actually still slowly increased until a certain time and then starts to decrease to zero eventually. The starting times of the decrease in absorbance are 35, 40, and 65 s in $2M$ LiCl(aq), $2M$ NaCl(aq), and $2M$ KCl(aq), respectively.

The above experiments can also be done by the more sensitive NIR laser diode-induced fluorescence method. The thin-film system can be studied by a simple and inexpensive NIR laser diode system that was constructed from off-the-shelf components in our laboratory as reported earlier.[20,21] The NIR fluorescence intensity of the dye-entrapped Nafion system was determined using a laser diode excitation source of 780 nm (30 mW) in different aqueous solutions. The results are shown in Figure 8. The data show the same trend of change in the alkali solutions. However, due to the saturation of the detector, the detailed results in the first few minutes cannot be seen. To avoid saturation of the detector, the concentration of the dye inside the Nafion matrix is reduced until the maximum signal is lower than

25% of the full scale. Moreover, since the data were collected by DVM manually, it is impossible to perform precise measurements in the first few seconds. Nevertheless, this result demonstrates the sensitivity of the fluorescence method, which may be important for some other applications.

Overall, based on the above studies, the information can be summarized as follows: The NIR dye with its hydrophobic nature prefers to stay in the hydrophobic zone of the Nafion matrix. The water uptake reaches saturation in only a few seconds, which causes a large expansion of the film dimension and breaks up most of the aggregation of the NIR dye entrapped within the Nafion matrix. However, because the process of water uptake happens solely in the hydrophilic zone of Nafion, no dimer formation of the NIR dye was observed. The dimer formation is an intrinsic property of the NIR free dye when in low concentration of aqueous solution. The absorption peak at 773 nm can be attributed to the monomer, which appears between the absorption maxima of monomer (778 nm) and dimer (771 nm) of the dye in solutions. The minor spectral shift of the NIR monomer absorption maxima is due to the interaction between the dye and Nafion. The very slow peak transition process actually is a good indication of the two-phase structure of the Nafion matrix and has nothing to do with the very fast swelling process. This process, which usually takes hours to complete, actually is an indication of the
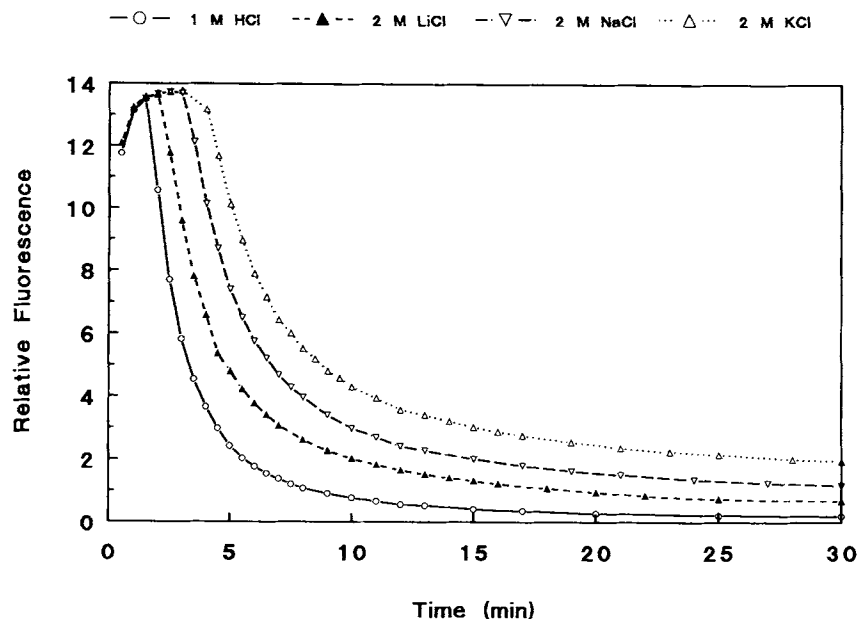
—O— 1 M HCl   --▲-- 2 M LiCl   —▽— 2 M NaCl   ···△··· 2 M KCl

Figure 8   The fluorescence intensity measured using the dye-entrapped Nafion thin-film sensor and NIR laser diode excitation in $1M$ HCl(aq), $2M$ LiCl(aq), $2M$ NaCl(aq), and $2M$ KCl(aq).

establishment of equilibrium between the hydro-phobic and the hydrophilic zones after the water uptake. The results of the peak transition process in alkali ions provide extra support for the above explanation. Taking into consideration their different hydration energies and ion-exchange equilibrium constants with Nafion, the peak transition process in alkali aqueous solutions appears to be a strong function of the moisture content inside the Nafion matrix. Therefore, the time required to establish equilibrium between the two-phase structure of Nafion depends on the water content inside.

This study demonstrates a genuine method of using an NIR probe for *in situ* characterization of Nafion thin films. The same method can also be applied to other interesting and suitable polymer thin-film systems. Future work will concentrate on the development of the more sensitive fluorescence method using NIR laser diode for *in situ* monitoring of film thickness, which is very important in several areas. The results will help to design suitable substrate for immobilizing several analytical and bioanalytical probes for NIR fluorescence spectroscopic determination of pH, metal ions, and immunochemical species.

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