

# Regulation of Dye Assembly Within Wet and Dry Nafion Films

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**ABSTRACT:** Different forms of Nafion films were prepared and used to exchange phenothiazine and phenazine dye cations. The monomer dye molecules are emissive and the protonated and aggregated dye molecules are nonemissive. A spectrophotometer and spectrofluorometer were used effectively to identify these molecules in the adsorbed state and the control of different forms of dye molecules by Nafion film was clearly established. Protonation of the dye molecules occurred mainly in the proton-exchanged dry Nafion film ( $H^+ - Nf$ ), whereas dimerization of dye molecules was predominant in the sodium-exchanged dry Nafion film ( $Na^+ - Nf$ ). The higher acidity and narrow ionic cluster and interfacial regions of the dry Nafion films were found to control the protonation and dimerization of dye molecules. The dyes were predominantly in monomeric form in the wet  $H^+ -$  and  $Na^+ - Nf$  films. When the  $Na^+ - Nf$  film was in a wet condition, the ionic cluster and interfacial regions expanded to form a more open structure. When large hydrophobic organic cations like tetrabutyl ammonium ions ( $Bu_4N^+$ ) and tetraethyl ammonium ions ( $Et_4N^+$ ) were exchanged into the Nafion film, the film structure was totally controlled by these organic cations and, consequently, controlled the monomeric and dimeric forms of dyes in the film. The dye adsorbed dry  $H^+ -$  and  $Na^+ - Nf$  films may find applications in acid-base sensors. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 777–787, 1997

**Key words:** nafion film; phenothiazine dyes; phenazine dye; acid-base sensor

## INTRODUCTION

Interest in studying the photophysical and photochemical properties of sensitizer molecules adsorbed into various kinds of solid surfaces has received much attention in recent years.<sup>1–4</sup> Among the various adsorbents used to study the adsorbed molecules, Nafion, a perfluorosulfonate ion-exchange polymer, has been used extensively to study the photophysical and photochemical properties of metal complexes and organic mole-

cules.<sup>5–13</sup> Studies on organic dyes have been carried out in homogeneous and microheterogeneous environments in relation to solar energy conversion.<sup>14–17</sup> Recently, a few reports on the photophysical and photochemical properties of organic dye molecules adsorbed into the Nafion membrane have appeared in the literature.<sup>10–13</sup>

In Nafion, a fluorocarbon backbone provides exceptional chemical and thermal stabilities while the sulfonate head groups ( $-SO_3^-$ ) are responsible for ion-exchange and swelling properties.<sup>18</sup> The sulfonate head groups present in the Nafion film impose a strong acidic environment to the incorporated molecules.<sup>19</sup> It has been found that the photophysical characteristics of many organic molecules and metal complexes have been greatly altered by the polarity of Nafion film.<sup>6,7,10</sup> Even though few reports have appeared on the dye mol-

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ecules incorporated into Nafion film,<sup>10–13</sup> the control of dye aggregation within Nafion film has not been reported so far.

The aggregation of thionine dye at higher concentration was one of the main reasons for the poor performance of the iron–thionine photogalvanic cell.<sup>20,21</sup> Attempts have been made<sup>22–24</sup> to minimize the aggregation of dye molecules and to improve the efficiency of the photogalvanic cell. In the present article, we report on the control of aggregation of thionine, methylene blue, and phenosafranine dyes using different forms of Nafion films.

## EXPERIMENTAL

### Materials

Nafion 117 (EW 1100) was purchased as a 5% solution from Aldrich and was diluted to 1% with ethanol before use. The dyes, thionine ( $\text{TH}^+\text{CH}_3\text{COO}^-$ ), methylene blue ( $\text{MB}^+\text{Cl}^-$ ), and phenosafranine ( $\text{PS}^+\text{Cl}^-$ ) (Aldrich), were purified by the reported procedures.<sup>25–27</sup> Tetraethylammonium bromide and tetrabutylammonium bromide were analytical reagents and were recrystallized using 95% ethanol.<sup>28</sup> All other chemicals were analytical grade and used as received.

### Procedures

The Nafion-coated quartz glass plate was prepared by casting 6  $\mu\text{L}$  of a 1% Nafion solution and dried at room temperature. The thickness of the dry Nafion film was calculated as 0.3  $\mu\text{m}$  using the density of 2  $\text{g}/\text{cm}^3$ . The sodium ( $\text{Na}^+ - \text{Nf}$ )- and proton ( $\text{H}^+ - \text{Nf}$ )-exchanged Nafion films were prepared by soaking a Nafion film-coated quartz glass plate in 1M NaOH and 0.5M  $\text{H}_2\text{SO}_4$ , respectively.<sup>10,11,27</sup> The  $\text{Na}^+ - \text{Nf}$  and  $\text{H}^+ - \text{Nf}$  films were then washed with distilled water and dried. The dye-incorporated  $\text{Na}^+ - \text{Nf}$  ( $\text{Na}^+ - \text{Nf}/\text{dye}$ ) or  $\text{H}^+ - \text{Nf}$  ( $\text{H}^+ - \text{Nf}/\text{dye}$ ) film was prepared by dipping the respective film in an aqueous dye solution ( $5 \times 10^{-5}\text{M}$ ) for 3 min and washed with distilled water. The effect of water content on the absorption spectral characteristics of  $\text{H}^+ - \text{Nf}/\text{dye}$  and  $\text{Na}^+ - \text{Nf}/\text{dye}$  films was studied by drying the films in air for 30 min (dry) or by dipping them in water for 30 min (wet).

The effect of water content on the spectral characteristics of dyes was also investigated by exchanging hydrophobic organic cations of  $\text{Bu}_4\text{N}^+$

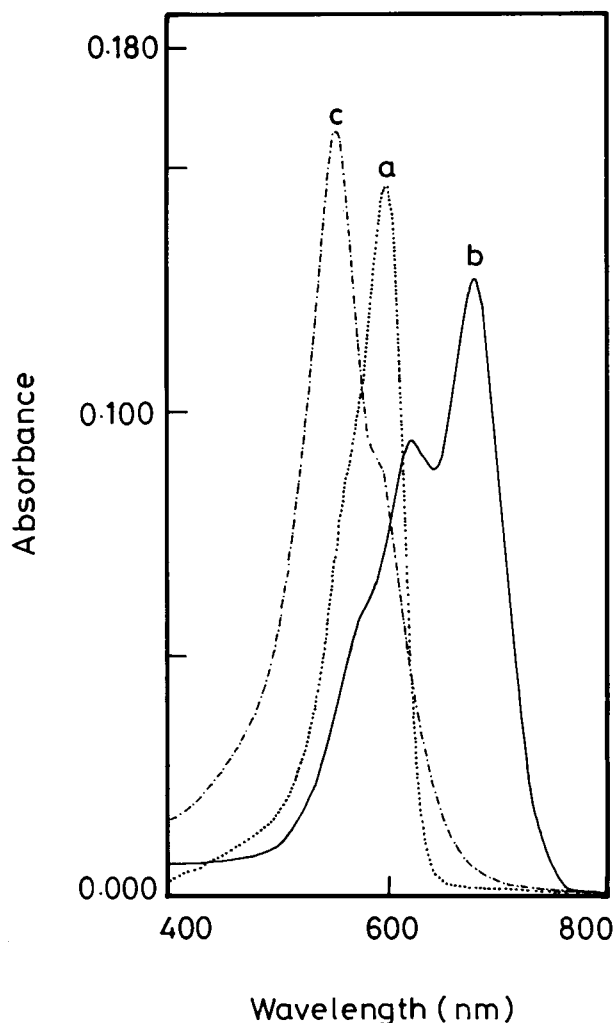
and  $\text{Et}_4\text{N}^+$ . The  $\text{Bu}_4\text{N}^+$  ( $\text{Nf}/\text{Bu}_4\text{N}^+$ )- and  $\text{Et}_4\text{N}^+$  ( $\text{Nf}/\text{Et}_4\text{N}^+$ )-exchanged forms of Nafion films were prepared by dipping the  $\text{Na}^+ - \text{Nf}$  film in a 0.1M aqueous solution of tetrabutylammonium bromide and tetraethylammonium bromide, respectively.<sup>7</sup> The above films were dipped in an aqueous dye solution ( $1 \times 10^{-4}\text{M}$ ) to obtain the  $\text{Nf}/\text{Bu}_4\text{N}^+/\text{dye}$  and  $\text{Nf}/\text{Et}_4\text{N}^+/\text{dye}$  films. Absorption spectra of the  $\text{Nf}/\text{dye}$  films were recorded on a JASCO (7800) UV-visible spectrophotometer using a Nafion-coated quartz glass plate as the reference. The emission spectra of the  $\text{Nf}/\text{dye}$  were recorded on a Hitachi F4500 spectrofluorometer by exciting at the absorption maximum of the dyes in Nafion film.

## RESULTS AND DISCUSSION

### Absorption Spectra of Dye Molecules Incorporated into Different Forms of Nafion Film

Absorption spectra of phenothiazine and phenazine dye molecules in different media were studied by several groups.<sup>25,26</sup> The aqueous solution of dye molecules at lower concentrations ( $< 10^{-5}\text{M}$ ) shows a distinct absorption band for the monomeric dye and a shoulder band on the higher-energy side for the dimer and higher aggregates. At increased concentrations, the shoulder band due to aggregates becomes the main band, and in a strongly acidic solution, a new band is observed for the protonated form of the dye molecules.

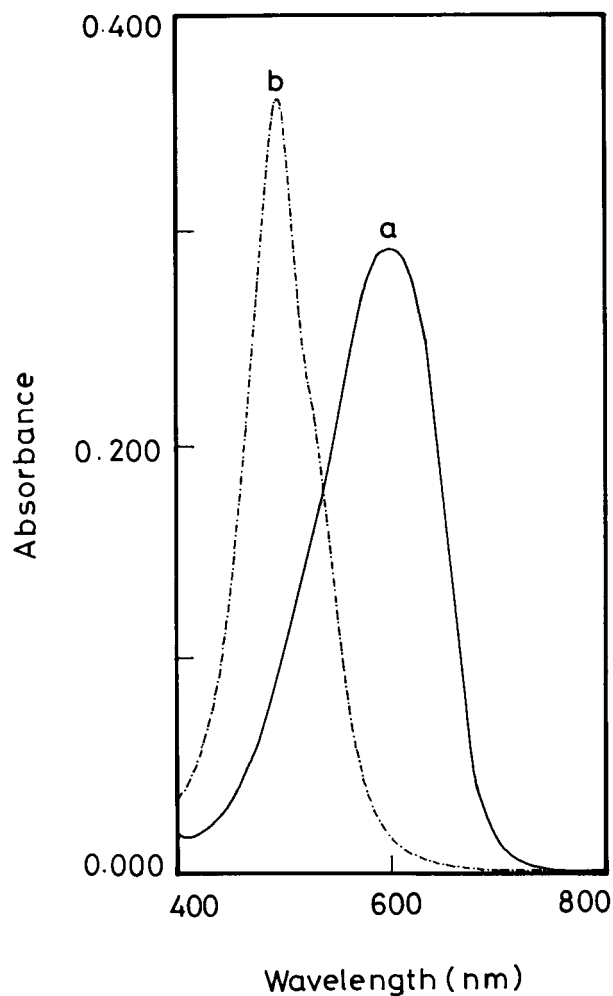
The absorption spectrum recorded for thionine in an aqueous solution is shown in Figure 1(a) and it shows an absorption band at 600 nm due to the monomer and a shoulder band at 560 nm due to the dimer. Figure 1(b) shows the absorption spectrum recorded for the dry  $\text{H}^+ - \text{Nf}/\text{TH}^+$  film and it gives two absorption bands at 680 and 610 nm with a shoulder band at 554 nm. The observed absorption bands at 680 and 610 nm correspond to the protonated ( $\text{TH}_2^{2+}$ ) and monomeric ( $\text{TH}^+$ ) forms of thionine, respectively.<sup>25</sup> A similar absorption spectrum was observed for thionine in 2.5M HCl solution and this indicates the fact that the absorbed thionine experiences a highly acidic environment in the dry  $\text{H}^+ - \text{Nf}$  film. It has already been reported that the  $\text{H}^+ - \text{Nf}$  film exhibits an acidic environment corresponding to  $-4 > H_0 > -6$  ( $H_0 =$  Hammett acidity function).<sup>29</sup> Due to the presence of high acidity in the dry  $\text{H}^+ - \text{Nf}$  film, the thionine dye undergoes protonation and shows an absorption band at 680 nm. A similar



**Figure 1** Absorption spectra of (a)  $\text{TH}^+$  in aqueous solution, (b) dry  $\text{H}^+$ -Nf/ $\text{TH}^+$  film, and (c) dry  $\text{Na}^+$ -Nf/ $\text{TH}^+$  film.

observation was reported for the emission of pyrenecarboxyaldehyde (POH) by studying its emission spectrum in  $\text{H}^+$ -Nf film.<sup>6</sup> This observation was explained on the basis of the presence of higher acidity in the  $\text{H}^+$ -Nf film than in its  $\text{Na}^+$  form.<sup>6</sup> Very similar spectral changes were also observed for  $\text{MB}^+$  and  $\text{PS}^+$  dyes adsorbed into dry  $\text{H}^+$ -Nf film.  $\text{MB}^+$  showed an absorption band at 745 nm with a shoulder band at 670 nm corresponding to the protonated ( $\text{MBH}^{2+}$ ) and monomeric ( $\text{MB}^+$ ) dyes, respectively.  $\text{PS}^+$  showed an absorption band at 600 nm due to the protonated ( $\text{PSH}^{2+}$ ) form of  $\text{PS}^+$  [Fig. 2(a)]. The dry  $\text{H}^+$ -Nf film provides a very high acidic environment to the adsorbed dyes and, hence, the dye molecules undergo protonation and exist in the protonated form.

The absorption spectrum recorded for the dry  $\text{Na}^+$ -Nf/ $\text{TH}^+$  is shown in Figure 1(c). It shows an absorption band at 554 nm with a shoulder band at 600 nm when compared to the dry  $\text{H}^+$ -Nf/ $\text{TH}^+$  film [Fig. 1(b)]. The observed absorption band at 554 nm corresponds to the dimeric form of thionine ( $\text{TH}^+$ )<sub>2</sub> in the dry  $\text{Na}^+$ -Nf film. When the Nafion film is fully equilibrated with NaOH, it becomes neutralized and results in a very low local  $[\text{H}^+]$  inside the Nafion film.<sup>7,30</sup> Even though the fully hydrated  $\text{Na}^+$ -Nf film contains 40% water, the polarity of the film was significantly lower than that of water.<sup>7</sup> For example, the emission intensity of 5-(dimethylamino)naphthalene perchlorate ( $\text{DA}^+$ ) adsorbed into dry  $\text{Na}^+$ -Nf film was increased and the emission maximum strongly blue-shifted.<sup>7</sup> This indicates that the dry  $\text{Na}^+$ -Nf film provides a less polar environment to the adsorbed molecule. Very similar spectral

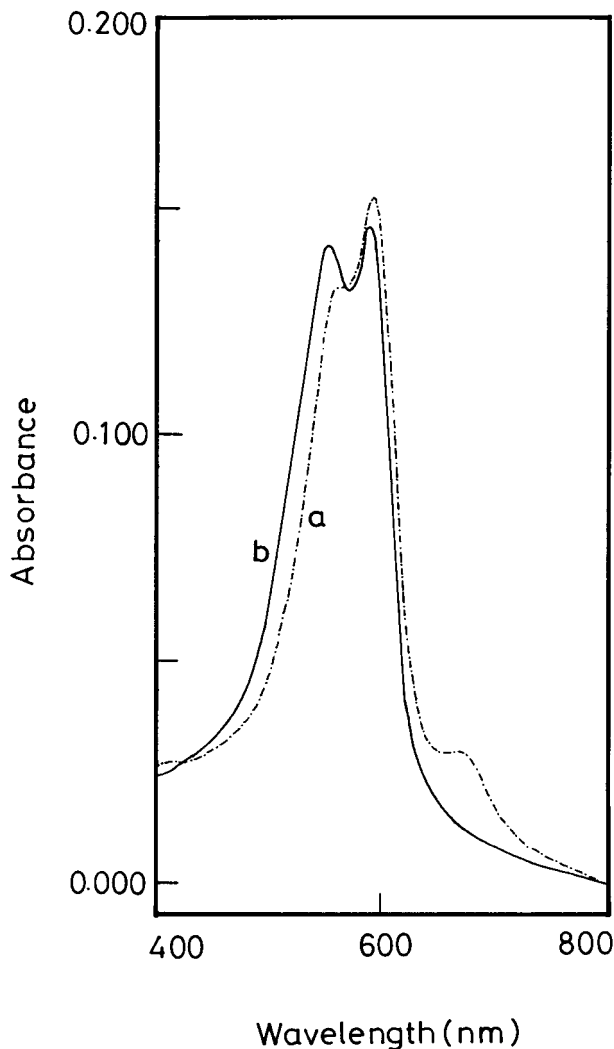


**Figure 2** Absorption spectra of dry (a)  $\text{H}^+$ -Nf/ $\text{PS}^+$  and (b)  $\text{Na}^+$ -Nf/ $\text{PS}^+$  films.

changes were also observed for  $\text{MB}^+$  in the dry  $\text{Na}^+ - \text{Nf}$  film.  $\text{MB}^+$  shows an absorption band at 600 nm with a shoulder band at 650 nm corresponding to the dimeric and monomeric  $\text{MB}^+$ , respectively.

Yeager and Steck<sup>31</sup> proposed a triphasic structure for Nafion film. The three phases are the hydrophobic fluorocarbon chain phase, the ionic cluster phase, and an interphase that separates the ionic and hydrophobic fluorocarbon chain phases. According to the above structure, water molecules and  $-\text{SO}_3^-$  sites reside in both the ionic and the interfacial regions. The interfacial region contains a higher concentration of hydrophobic chain material and has a lower void volume than that of the cluster phase. Recently, the morphological difference between dry and wet Nafion films was reported.<sup>32</sup> In the proposed model, the dried form of Nafion film is suggested to have only a narrow ionic cluster and interfacial regions when compared to the wet Nafion film. It has also been reported that the lower charge molecules would occupy both the ionic cluster and interfacial regions.<sup>33</sup> Since the dye molecules are lower in charge and hydrophobic in nature, it will occupy both the ionic cluster and interfacial regions.<sup>27</sup> In the present investigation, the dimerization of dyes was predominantly observed in the dry  $\text{Na}^+ - \text{Nf}$  film. The dry  $\text{Na}^+ - \text{Nf}$  film contains only a narrow ionic cluster and interfacial regions and, hence, the distance between the adsorbed dye molecules becomes less. Under this condition, the hydrophobic interaction/self-association between the adsorbed dye molecules will easily lead to dimerization.<sup>25,34</sup>

The absorption spectrum recorded for phenosafranine in dry  $\text{Na}^+ - \text{Nf}$  film is shown in Figure 2(b). It shows an absorption band at 500 nm with a shoulder band at 520 nm. The observed absorption band at 500 nm indicates the formation of dimerized  $\text{PS}^+$  molecules in the dry  $\text{Na}^+ - \text{Nf}$  film. At higher concentration ( $>10^{-3}M$ ), the  $\text{PS}^+$  dye in aqueous solution did not show an observable shoulder band due to aggregation when compared to thionine and methylene blue dyes. However, when  $\text{PS}^+$  was incorporated into dry  $\text{Na}^+ - \text{Nf}$  film, most of the adsorbed dye molecules dimerized [Fig. 2(b)]. Gopidas and Kamat<sup>10</sup> observed a shoulder band at 500 nm for  $\text{PS}^+$  in  $\text{Na}^+ - \text{Nf}$  film due to aggregation of  $\text{PS}^+$  and the observed shoulder band was not discussed in relation to the Nafion film structure. In the dry  $\text{Na}^+ - \text{Nf}$  film, the hydrophobic interaction between the  $\text{PS}^+$  molecules adsorbed into the narrow ionic cluster and

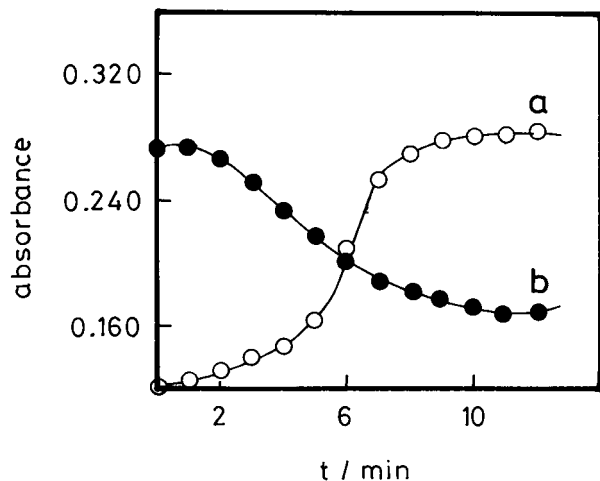


**Figure 3** Absorption spectra of wet (a)  $\text{H}^+ - \text{Nf}/\text{TH}^+$  and (b)  $\text{Na}^+ - \text{Nf}/\text{TH}^+$  films.

interfacial regions will easily lead to the formation of a dimer.

#### Role of Water Content on the Adsorbed Dyes in $\text{H}^+$ - and $\text{Na}^+$ -Nafion Films

The dry  $\text{H}^+$ - and  $\text{Na}^+ - \text{Nf}/\text{TH}^+$  films are dipped in water to convert them into a wet form. The absorption spectrum recorded for wet  $\text{H}^+ - \text{Nf}/\text{TH}^+$  film is shown in Figure 3(a). It shows an absorption band at 600 nm and two shoulder bands at 670 and 570 nm when compared to the dry  $\text{H}^+ - \text{Nf}/\text{TH}^+$  film [Fig. 1(b)]. The dry  $\text{H}^+ - \text{Nf}$  film is highly acidic and protonates the incorporated thionine molecule. However, in the wet condition, the water content present in the wet  $\text{H}^+ - \text{Nf}$  film would change the proton concentra-



**Figure 4** Plot of change of absorbance observed at (a) 745 nm and (b) 651 nm with time for the conversion of wet to dry of  $H^+$ –Nf/MB<sup>+</sup> film.

tion inside the film.<sup>11</sup> This leads to the deprotonation of the  $TH_2^{2+}$  molecule to monomeric  $TH^+$  and, consequently, shows an absorption band at 600 nm [Fig. 3(a)]. Also, the deprotonation of  $TH_2^{2+}$  leads to partial dimerization of thionine in the wet film [Fig. 3(a)]. Similar spectral changes were also observed for MB<sup>+</sup> and PS<sup>+</sup>. The plot of change of absorbances observed at 745 and 651 nm for the wet  $H^+$ –Nf/MB<sup>+</sup> film with different drying times is shown in Figure 4. This clearly shows the conversion of monomer MB<sup>+</sup> to protonated MBH<sup>2+</sup> upon drying the wet film.

The absorption spectrum recorded for wet  $Na^+$ –Nf/TH<sup>+</sup> film is shown in Figure 3(b). It shows a band at 600 nm in addition to the band at 554 nm in comparison to the dry  $Na^+$ –Nf/TH<sup>+</sup> film [Fig. 1(c)]. When the  $Na^+$ –Nf film becomes wet, due to the higher water content, the volume of the hydrophilic ionic cluster and interfacial regions expands and leads to a more open structure<sup>35</sup> with wider interconnecting channels. In the case of wet  $Na^+$ –Nf/TH<sup>+</sup> film, the expanded volume of ionic cluster and interfacial regions favors the formation of monomer dye molecules, which show an intense band at 600 nm. When the wet  $Na^+$ –Nf/TH<sup>+</sup> film is slowly dried, the intensity of the absorption band due to the monomer decreased with a simultaneous increase in the intensity of the band due to the dimer. The schematic diagram showing the monomer and dimer thionine present in the wet and dry Nafion film is shown in Scheme 1. Absorption spectra recorded at different drying times for wet  $Na^+$ –Nf/MB<sup>+</sup> film is shown in Figure 5. It shows predominantly

the formation of the MB<sup>+</sup> dimer in the dry  $Na^+$ –Nf film and monomeric MB<sup>+</sup> in the wet  $Na^+$ –Nf film. It clearly shows that the ionic cluster and interfacial regions of the Nafion film shrink during drying (Scheme 1) and the hydrophobic interaction/self-association of the dye molecules leads to dimerization. When the same dried film is converted to wet film, both the ionic cluster and interfacial regions expand and result in the formation of monomer dye molecules (Scheme 1). In addition, in wet Nafion film, the well-solvated ionic cluster region would enhance the electrostatic interaction between the anionic polymer ( $-SO_3^-$ ) and cationic dye molecules and this will reduce the hydrophobic/self-association between the adsorbed dye molecules.

In a typical experiment, the concentrations of monomer and dimer at different amounts of adsorbed MB<sup>+</sup> in the dry  $Na^+$ –Nf film were calculated by assuming that the molar absorptivity of the monomer and dimer in solution is the same for MB<sup>+</sup> in Nafion film.<sup>26,36,37</sup> The absorbances observed for MB<sup>+</sup> in Nafion film at 660 and 610 nm are given by eqs. (1) and (2):

$$A^{660} = (\epsilon_m^{660} C_m + \epsilon_d^{660} C_d) D \quad (1)$$

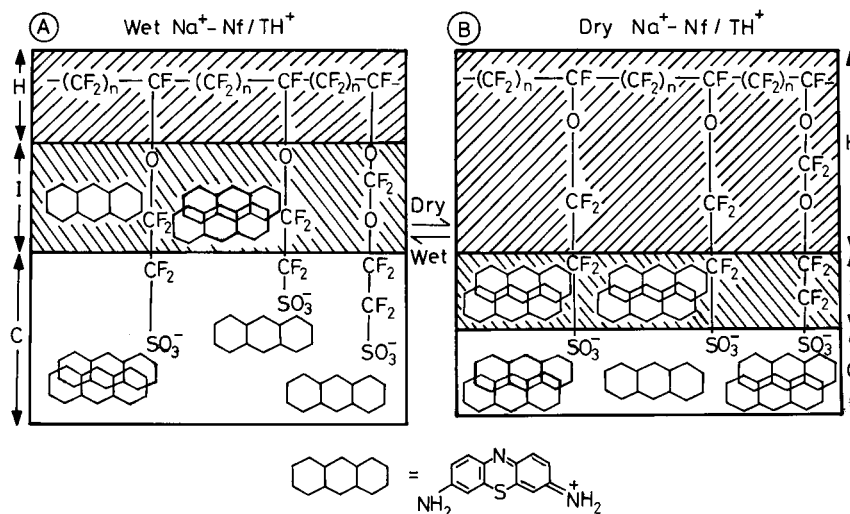
$$A^{610} = (\epsilon_m^{610} C_m + \epsilon_d^{610} C_d) D \quad (2)$$

where  $D$  is the Nafion film thickness;  $C_m$ ,  $\epsilon_m^{660}$ , and  $\epsilon_m^{610}$  are the concentration and the molar extinction coefficients of the monomer MB<sup>+</sup> at 660 and 610 nm, respectively; and  $C_d$ ,  $\epsilon_d^{660}$ , and  $\epsilon_d^{610}$  are the concentration and the molar extinction coefficients of the dimer MB<sup>+</sup> at 660 and 610 nm, respectively.  $C_m$  and  $C_d$  are calculated using eqs. (3) and (4):

$$C_m = \frac{\epsilon_d^{660} A^{610} - \epsilon_d^{610} A^{660}}{\epsilon_m^{610} \epsilon_d^{660} - \epsilon_m^{660} \epsilon_d^{610}} \frac{1}{D} \quad (3)$$

$$C_d = \frac{\epsilon_m^{660} A^{660} - \epsilon_m^{610} A^{610}}{\epsilon_m^{610} \epsilon_d^{660} - \epsilon_m^{660} \epsilon_d^{610}} \frac{1}{D} \quad (4)$$

The  $\epsilon_m^{660}$ ,  $\epsilon_d^{660}$ ,  $\epsilon_m^{610}$ , and  $\epsilon_d^{610}$  values of MB<sup>+</sup> are  $7.18 \times 10^4$ ,  $1.54 \times 10^3$ ,  $3.88 \times 10^4$ , and  $9.06 \times 10^4 M^{-1} cm^{-1}$ . The plot of concentrations of  $C_d(MB^+)_2$  vs. the square of concentrations of  $C_m(MB^+)$  is shown in Figure 5 (inset). The dimerization constant for MB<sup>+</sup> in the dry  $Na^+$ –Nf film was calculated as  $22 M^{-1}$  from the slope of the plot.<sup>36,37</sup> The calculated value was higher than the reported value of Kuwabata et al.<sup>36</sup> ( $3.4 M^{-1}$ ) and lower than the value of Guadalupe et al.



**Scheme 1** Schematic representation of the dry and wet  $\text{Na}^+ - \text{Nf} / \text{TH}^+$  films. H is the hydrophobic fluorocarbon region; I is the interfacial region and C is the ionic cluster region. (A) Wet  $\text{Na}^+ - \text{Nf} / \text{TH}^+$  and (B) dry  $\text{Na}^+ - \text{Nf} / \text{TH}^+$  films.

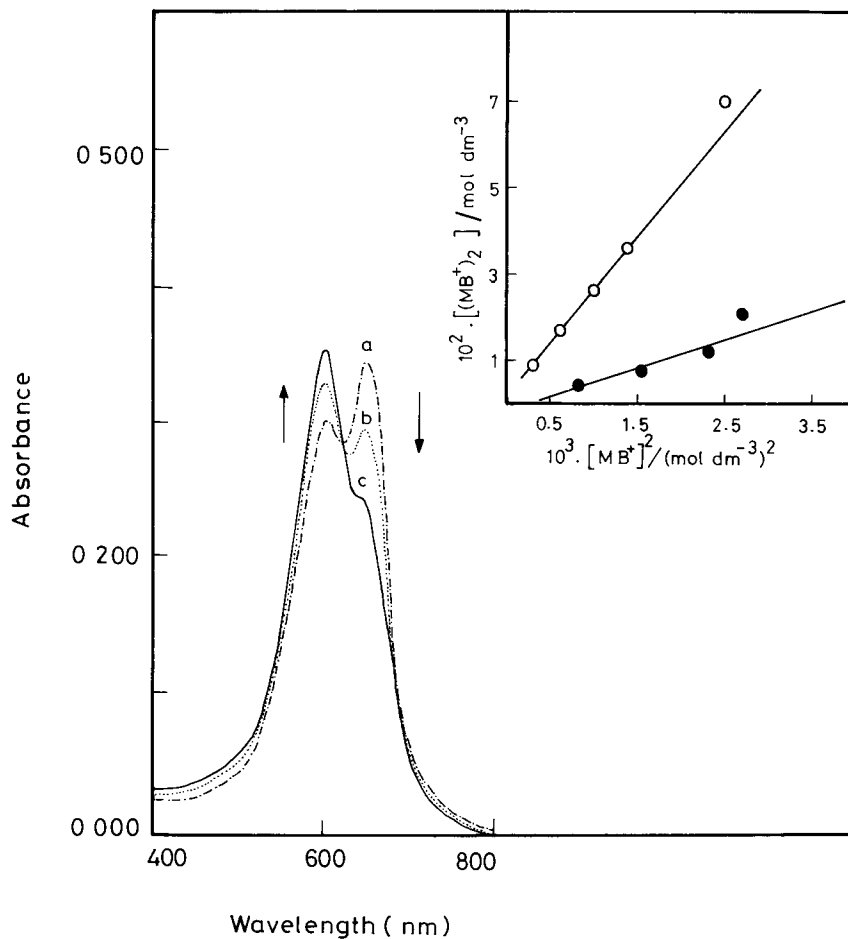
( $130M^{-1}$ ).<sup>37</sup> The difference in the values may be due to the different nature of the Nafion film and concentrations of  $\text{MB}^+$  adsorbed in the Nafion film. In the previous reports,<sup>36,37</sup> untreated Nafion film was used to calculate the dimerization constant of  $\text{MB}^+$ . In the present work,  $\text{Na}^+ - \text{Nf}$  films in wet and dry conditions were used for the determination of the dimerization constant. For the same film, the dimerization constant for  $\text{MB}^+$  in the wet form was calculated from the slope of the plot (Fig. 5 [inset]) as  $8.25M^{-1}$ , which was lower than the value calculated for  $\text{MB}^+$  adsorbed into the dry  $\text{Na}^+ - \text{Nf}$  film ( $22M^{-1}$ ). It is concluded that the presence of water in the Nafion film greatly alters the structure of the Nafion film and affects the monomer-dimer dye equilibrium in the Nafion film.

#### Emission Spectral Studies of Dyes Incorporated into $\text{H}^+ -$ and $\text{Na}^+ - \text{Nf}$ Films

The fluorescence emission spectra recorded for aqueous  $\text{PS}^+$  showed an emission maximum at 576 nm and the relative intensity of the fluorescence emission decreased with increasing concentrations of  $\text{H}_2\text{SO}_4$ . The observed decrease in the emission intensity was attributed to the very weakly fluorescing character of protonated  $\text{PS}^+$ .<sup>10</sup> The fluorescence emission spectra recorded for the wet  $\text{H}^+ - \text{Nf} / \text{PS}^+$  film at different drying times is shown in Figure 6. The fluorescence emission spectra of wet  $\text{H}^+ - \text{Nf} / \text{PS}^+$  showed an emission maximum at 558 nm. The observed blue shift for

$\text{PS}^+$  in  $\text{H}^+ - \text{Nf}$  film is due to the interaction of  $\text{PS}^+$  with the hydrophobic region of the Nafion film.<sup>10</sup> While drying the wet  $\text{H}^+ - \text{Nf} / \text{PS}^+$  film, the emission intensity decreased. The protonated  $\text{PS}^+$  in  $\text{H}^+ - \text{Nf}$  film was nonfluorescing and the emission intensity of  $\text{PS}^+$  decreased while drying. In the wet  $\text{H}^+ - \text{Nf} / \text{PS}^+$ , the presence of a higher water content decreased the proton concentration inside the Nafion film<sup>11</sup> and a part of  $\text{PS}^+$  molecules existed in the deprotonated form and showed fluorescence emission at 558 nm. The phenothiazine dyes,  $\text{TH}^+$  and  $\text{MB}^+$ , in wet  $\text{H}^+ - \text{Nf}$  showed a weak fluorescence emission.

The fluorescence emission spectra recorded for wet  $\text{Na}^+ - \text{Nf} / \text{MB}^+$  at different drying times are shown in Figure 7. The emission spectra of  $\text{MB}^+$  in wet  $\text{Na}^+ - \text{Nf}$  film showed an emission maximum at 670 nm which was blue-shifted compared to  $\text{MB}^+$  in aqueous solution ( $\lambda_{\text{em}} = 680 \text{ nm}$ ). The observed blue shift of  $\text{MB}^+$  in  $\text{Na}^+ - \text{Nf}$  film is due to the interaction of  $\text{MB}^+$  in the hydrophobic region of the Nafion film. The emission intensity decreased and  $\lambda_{\text{em}}$  was blue-shifted while drying the wet  $\text{Na}^+ - \text{Nf} / \text{MB}^+$  film. When water was removed from the Nafion film, the microenvironment provided by the  $\text{Na}^+ - \text{Nf}$  film became less polar and the  $\text{MB}^+$  in the dry  $\text{Na}^+ - \text{Nf}$  film showed a blue-shifted emission. A similar blue shift was reported<sup>7</sup> for  $\text{DA}^+$  and pyrene molecules in  $\text{Na}^+ - \text{Nf}$  film. The decrease in the emission intensity was due to the formation of a nonfluorescing dimer  $\text{MB}^+$  in the  $\text{Na}^+ - \text{Nf}$  film during drying. Similarly, wet  $\text{Na}^+ - \text{Nf} / \text{PS}^+$  showed an emission



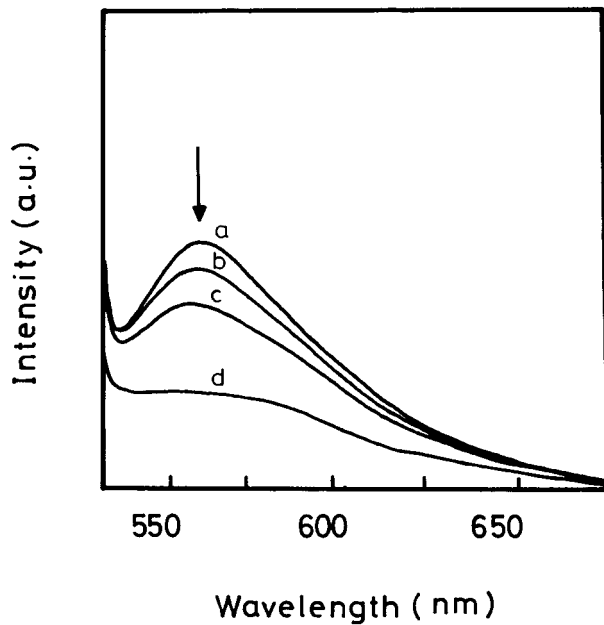
**Figure 5** Absorption spectra recorded at different drying times for wet  $\text{Na}^+ - \text{Nf}/\text{MB}^+$  film: (a) 0 min; (b) 5 min; (c) 10 min. Inset: Plot of concentrations of  $(\text{MB}^+)$  versus square of concentrations of  $(\text{MB}^+)$  (○) wet and (●) dry  $\text{Na}^+ - \text{Nf}$  films.

maximum at 562 nm and this was blue-shifted while drying the wet  $\text{Na}^+ - \text{Nf}/\text{PS}^+$  film.

#### Effect of Hydrophobicity on the Dye Molecules Adsorbed into the Nafion Film

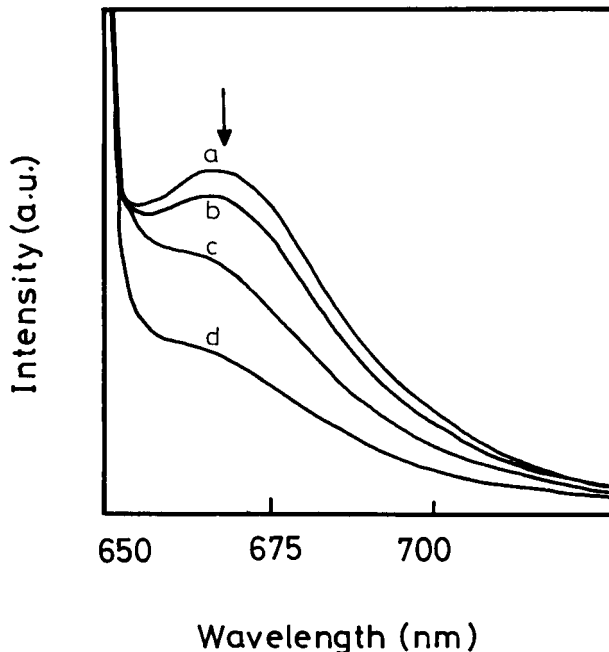
The absorption spectrum recorded for  $\text{Nf}/\text{Bu}_4\text{N}^+/\text{TH}^+$  is shown in Figure 8(a). It shows an absorption band at 610 nm with a less intense band at 565 nm which corresponds to the monomeric and dimeric forms of thionine, respectively. When the  $\text{Nf}/\text{Bu}_4\text{N}^+$  was dipped into a high concentration of thionine solution, only a small amount of thionine molecules was incorporated into the film. Since the  $\text{Bu}_4\text{N}^+$  is more hydrophobic, it strongly binds to the interfacial region of the Nafion film and interacts with  $-\text{SO}_3^-$  groups and the water content in the ionic cluster region is also reduced.<sup>7</sup> Thus, only a small amount of dye molecules was

exchanged into the Nafion film as evidenced from the absorption spectrum [Fig. 8(a)]. The  $\text{Nf}/\text{Et}_4\text{N}^+/\text{TH}^+$  film shows an absorption band at 560 nm with a shoulder band at 600 nm and the amount of thionine exchanged into the film is comparatively higher than that of the  $\text{Nf}/\text{Bu}_4\text{N}^+$  film [Fig. 8(b)]. In the case of the  $\text{Nf}/\text{Bu}_4\text{N}^+$  film, the  $\text{Bu}_4\text{N}^+$  ion is more hydrophobic with a higher free volume which will lead to the formation of a narrow ionic cluster region in the Nafion film. The exchange of the hydrophobic cation ( $\text{Bu}_4\text{N}^+$ ) into the Nafion film will reduce the polarity of the Nafion film and also the electrostatic interaction between the  $-\text{SO}_3^-$  and dye cation. Hence, a lower number of dye molecules are adsorbed and the adsorbed dye molecules exist as a monomer. However, in the  $\text{Nf}/\text{Et}_4\text{N}^+$  film, the  $\text{Et}_4\text{N}^+$  is less hydrophobic with a lower free volume than that of the  $\text{Bu}_4\text{N}^+$  ion and, hence, the higher amount of

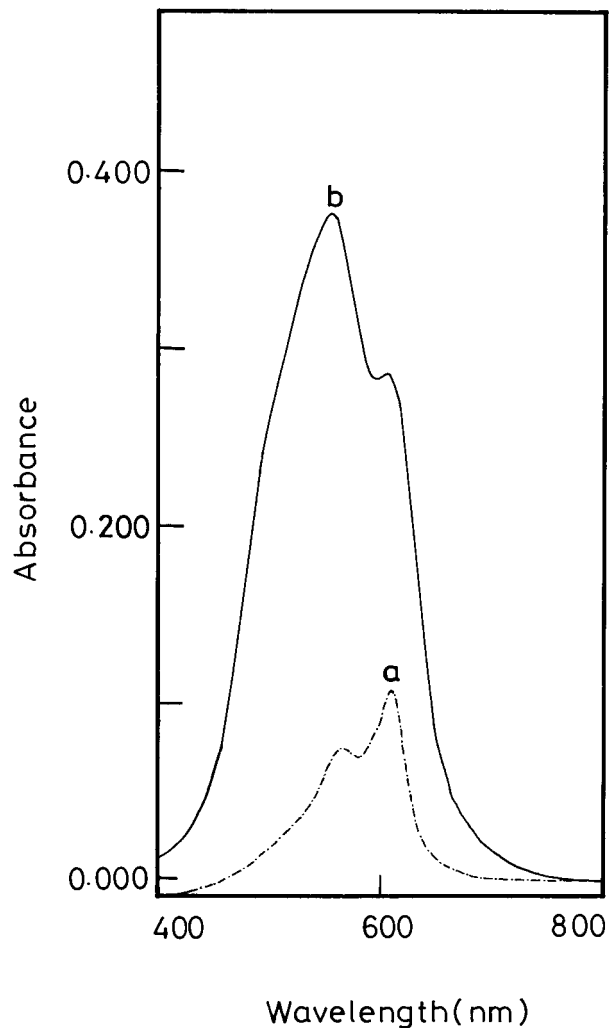


**Figure 6** Fluorescence emission spectra recorded at different drying times for wet  $H^+$ -Nf/PS $^+$  film: (a) 0 min; (b) 2 min; (c) 5 min; (d) 10 min.

adsorbed dye molecules led to dimerization. Very similar spectral changes are also observed for PS $^+$  in Nf/Bu $_4$ N $^+$  and Nf/Et $_4$ N $^+$  films.



**Figure 7** Fluorescence emission spectra recorded at different drying times for wet Na $^+$ -Nf/MB $^+$  film: (a) 0 min; (b) 2 min; (c) 5 min; (d) 10 min.

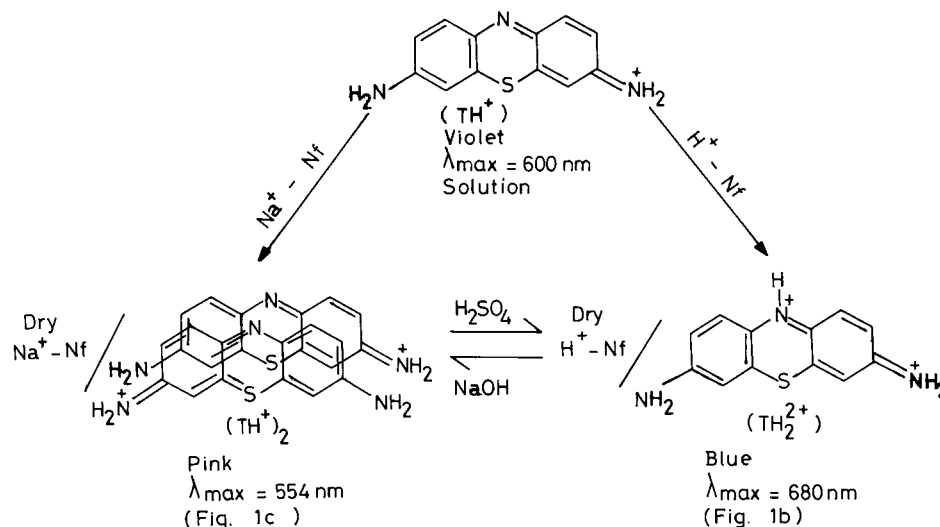


**Figure 8** Absorption spectra of (a) Nf/Bu $_4$ N $^+$ /TH $^+$  and (b) Nf/Et $_4$ N $^+$ /TH $^+$  films.

#### Acid-Base Sensor Property of the Dye-Adsorbed Nafion Film

Absorption spectrum recorded for the dry  $H^+$ -Nf/TH $^+$  film is shown in Figure 1(b). When the same film is dipped in 0.1 M NaOH, the blue color observed for the dry  $H^+$ -Nf/TH $^+$  film [Fig. 1(b);  $\lambda_{\max} = 680$  nm] was changed to pink [Fig. 1(c);  $\lambda_{\max} = 554$  nm] in the dry condition. The blue color of the film resulted from the protonated thionine (TH $_2^{2+}$ ) and the pink color resulted from the dimer thionine [(TH $^+$ ) $_2$ ]. The incorporation of NaOH into the  $H^+$ -Nf film neutralizes the film and the adsorbed dye molecules dimerizes in the dry film which shows a pink color [Fig. 1(c)]. When the same film was again dipped in 0.1 M H $_2$ SO $_4$ , the color of the Nafion film changed from pink to blue in the dry form and showed an





**Scheme 2** Schematic representation of the reversible color changes observed in the dry  $\text{Na}^+ - \text{Nf}/\text{TH}^+$  and  $\text{H}^+ - \text{Nf}/\text{TH}^+$  films.

absorption band at 680 nm, indicating the presence of protonated thionine ( $\text{TH}_2^{2+}$ ) in the film. The change of color from blue to pink and pink to blue is highly reversible even when dipped in 0.001M of NaOH or  $\text{H}_2\text{SO}_4$ . The reversible color change that occurred in the dry  $\text{Nf}/\text{TH}^+$  film

when dipped in NaOH or  $\text{H}_2\text{SO}_4$  is shown in Scheme 2. A similar reversible color change was also observed for dry  $\text{Nf}/\text{PS}^+$  film. The dry  $\text{Na}^+ - \text{Nf}/\text{PS}^+$  film showed a red color, whereas the dry  $\text{H}^+ - \text{Nf}/\text{PS}^+$  film showed a violet color. It is found that the reversible color change is highly

**Table I** Spectral Data Obtained for  $\text{Nf}/\text{Dye}$  at Different Conditions

$\text{Na}^+ - \text{Nf}$		$\text{H}^+ - \text{Nf}$	
Dry	Wet	Dry	Wet
TH <sup>+</sup> monomer 600 nm (shoulder)	TH <sup>+</sup> monomer 600 nm (main)	TH <sup>2+</sup> 680 nm (main)	TH <sup>2+</sup> 670 nm (shoulder)
TH <sup>+</sup> dimer 554 nm (main)	TH <sup>+</sup> dimer 554 nm	TH <sup>+</sup> monomer 610 nm	TH <sup>+</sup> monomer 600 nm (main)
		TH <sup>+</sup> dimer 554 nm (shoulder)	TH <sup>+</sup> dimer 570 nm (shoulder)
MB <sup>+</sup> monomer 650 nm (shoulder)	MB <sup>+</sup> monomer 647 nm (main)	MBH <sup>2+</sup> 750 nm (main)	MBH <sup>2+</sup> 745 nm (shoulder)
MB <sup>+</sup> dimer 600 nm (main)		MB <sup>+</sup> monomer 665 nm	MB <sup>+</sup> monomer 650 nm (main)
		MB <sup>+</sup> dimer 620 nm (shoulder)	MB <sup>+</sup> dimer 609 nm (shoulder)
PS <sup>+</sup> dimer 500 nm (main)	PS <sup>+</sup> dimer 500 nm (main)	PSH <sup>2+</sup> 600 nm (main)	PS <sup>+</sup> monomer 520 nm (main)
PS <sup>+</sup> monomer 520 nm (shoulder)	PS <sup>+</sup> monomer 520 nm (shoulder)		PSH <sup>2+</sup> 600 nm (shoulder)

**Table II Summary of the Control of Dye Assembly Within Nafion Films**

Film	Condition	Predominant Form of Dyes
H <sup>+</sup> -Nf	Dry	Protonated
H <sup>+</sup> -Nf	Wet	Monomer
Na <sup>+</sup> -Nf	Dry	Dimer
Na <sup>+</sup> -Nf	Wet	Monomer

stable for several cycles and is sensitive to only  $> 0.001N$  H<sup>+</sup> or OH<sup>-</sup> solutions.

## CONCLUSIONS

We have shown that the aggregation of dyes can be successfully controlled and monitored using different forms of Nafion films by changing the acidity and water content in the films. The adsorbed dye molecules (TH<sup>+</sup>, MB<sup>+</sup>, and PS<sup>+</sup>) in the dry H<sup>+</sup>-Nf film existed in the protonated form, whereas in the dry Na<sup>+</sup>-Nf film, the dyes existed in the dimeric form. When the dry H<sup>+</sup>- and Na<sup>+</sup>-Nf films converted into the wet form, the volume of the ionic cluster and interfacial regions was expanded with wider interconnecting channels and the adsorbed dye molecules predominantly existed in the monomeric form with enhanced electrostatic interaction between the -SO<sub>3</sub><sup>-</sup> group and the dye cation in the well-solvated ionic cluster region. In the Bu<sub>4</sub>N<sup>+</sup>/Nf film, the adsorbed dye molecules existed in the monomeric form, whereas in the Et<sub>4</sub>N<sup>+</sup>/Nf film, they existed in the dimeric form. The concentration of the dye molecules in the Nafion film was in the range of ca. 10<sup>-3</sup> to 10<sup>-4</sup>M and higher concentrations predominantly resulted in the formation of dimer dye molecules in the Nafion films. The control of protonation or dimerization or deaggregation was explained on the basis of the acidity and the structure of the Nafion film (Tables I and II). The Nf/dye films may find applications in acid-base sensors.

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