Detection of volatile organic compounds in the vapor phase using solvatochromic dye-doped polymers

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Abstract

The solvatochromic dye, Reichardt's Betaine [2,6-diphenyl-4-(2,4,6-triphenylpyridinio)phenolate] (RDye), was investigated for use in chemical sensing applications. The polarity-sensitive dye was incorporated into several polymer films of differing polarity and sorbent characteristics, and exposed to the headspace above a variety of solvents. Reversible and reproducible changes in the absorption maximum ($\lambda_{\text{max}}$) of RDye were observed for the series of vapors comprising a range of polarities. The polymers absorbed and concentrated the analyte vapors, thereby influencing the environment surrounding the dye embedded in the polymer. Comparison of the vapor/film results with those of RDye dissolved in the neat solvents were favorable. Methanol and ethanol vapors produced large blue shifts in $\lambda_{\text{max}}$ (avg $\approx$ 103 and 63 nm, respectively) for most of the polymer films tested, while isopropanol, acetone, and some chlorinated hydrocarbons produced varying responses in the different films. Water, the most polar vapor tested, did not have much influence on $\lambda_{\text{max}}$ in the films. This is attributed to RDye's low solubility in water and the hydrogen-bonded clustering of water in the films. Exposure of the films to vapors of binary methanol-water mixtures demonstrated that the dye molecules were preferentially solvated by methanol, indicating the detectability of polar vapors in humid environments.

Keywords: Sensors; Polarity-sensitive dye; Solvatochromic dye; Polymer matrix

1. Introduction

The development of real-time chemical sensors for remote detection of Volatile Organic Compounds (VOCs) is an important part of the Navy's Environmentally-Sound Ship program. As environmental regulations for the protection of waterways have become more stringent in recent years, the development of in-situ, remote sensors to monitor the remediation of gray (non-sewage waste water) and bilge water for toxic and hazardous materials has become more urgent. Sensor systems, by definition, should be capable of continuously and reversibly reporting the concentration of an analyte [1]. Additional, desirable sensor characteristics for this application are selectivity, sensitivity, and ease of use. Fiber optic chemical sensors (FOCSs) offer many advantages for chemical analysis, including remote, in-situ sensing, miniaturization, lack of electrical interferences, and the coupling of several sensors into an array for immediate, multi-analyte analysis [2,3]. Extrinsic FOCSs use the fiber as a means to transport light to and from a matrix
containing an immobilized indicator [1,4] as opposed to intrinsic FOCSs, which use the fiber directly as the detector [5,6]. We are investigating solvatochromic or environment-sensitive dyes incorporated into polymer films as coatings for fiber optic sensors. These coatings would ultimately be used on the fiber core or located at the tip of the fiber, for the development of low cost, simple optical sensors.

The term solvatochromism is used to describe the shift in an electronic absorption band of a molecule in response to changes in the polarity of its solvational cage [7,8]. This shift is a result of physical intermolecular solute–solvent interactions (dipole–dipole, dipole–induced dipole, hydrogen-bonding, etc.) which alter the energy difference between the electronic ground and excited states of the absorbing species [9]. Reichardt’s Betaine [2,6-diphenyl-4-(2,4,6-triphenylpyridinio)phenolate], shown in Fig. 1, and henceforth referred to as RDye, exhibits one of the largest solvatochromic effects ever observed [10]. This is a result of the highly dipolar, zwitterionic ground state of RDye (15 Debye) and the less polar excited state (6 Debye), brought about by the intramolecular charge transfer from the phenoxide group into the pyridinium moiety, occurring upon the absorption of light [7]. In the ground state, the positive charge on the pyridinium group is delocalized and sterically shielded, while the phenoxide moiety (–O–) has a highly basic, electron-pair donating capacity. As a result, the longest wavelength absorption maximum (λmax) blue shifts as the polarity of the solvent phase increases, stabilizing the ground state [11].

The molar transition energy (Et(30)) of RDye has been used as an empirical parameter to scale solvent polarity in over 200 solvents [12,13]

\[ E_T(30) = \frac{h c \nu_{\text{max}} N_A}{\lambda_{\text{max}}} \]  

where \( E_T(30) \) is kcal mol\(^{-1}\), \( h \) is Plank’s constant (6.62 \times 10^{-34} J), \( c \) is the speed of light (2.998 \times 10^{10} \text{ cm s}^{-1}), \( \nu_{\text{max}} \) is the frequency of absorption expressed in cm\(^{-1}\) and \( N_A \) is Avagadro’s number (6.023 \times 10^{23} \text{ mol}^{-1}). This can be reduced to

\[ E_T(30) = \frac{28591}{\lambda_{\text{max}}} \]  

where \( \lambda_{\text{max}} \) is the wavelength of maximum absorbance expressed in nm. Interest in characterizing liquid solvent properties has led to many approaches, including the Z scale (polarity) of Kosower [14], and the π* scale (dipolarity/polarizability) of Kamlet, Abboud, and Taft (KAT) [15], further refined to include hydrogen-bond acidity (\( \alpha \)) and hydrogen-bond basicity (\( \beta \)) characteristics [16,17]. Recently \( E_T(30) \) values of RDye in binary mixtures have been used to explore preferential solvation by one of the components [18–20]. The non-linear relationship between \( E_T(30) \) values and solvent composition is complicated not only preferential solute–solvent interactions, but also but solvent-solvent interactions (hydrogen-bonding, etc.) as well [21].

Our selection of polymer substrates was based on earlier work at the Naval Research Laboratory investigating the use of polymers as coatings on surface acoustic wave (SAW) devices for sensor applications [22]. The polymers functioned as a sorbent phase, attracting and concentrating analyte vapors when present, but also allowing the vapors to diffuse out of the matrices, providing a reversible response. The
sensitivity and selectivity of each individual SAW sensor was controlled by tailoring the chemical and physical properties of the coating material to maximize particular solubility interactions. The KAT solvation parameters mentioned above were used to characterize numerous polymers for their solubility properties (polarizability/dipolarity, hydrogen-bond basicity, hydrogen-bond acidity, etc.) [23–25]. McGill and co-workers have investigated the use of solvatochromic dyes, including RDye, to characterize various polymers by observing differences in the absorption maxima of the dyes dissolved in polymer films [26,27]. They observed that polymers with an affinity for water produced a greater absorption shift than those that did not readily absorb water, thus suggesting sensor applications [27].

Recently, there have been reports describing the use of dyes immobilized in polymeric matrices for potential application as fiber-optic alcohol sensors [4,28,29]. Two reports examine the fluorescent emission behavior of covalently bound chromophores in either a styrene-divinylbenzene [4] or a polydimethylsiloxane network [28], exposed to alcohol/hydrocarbon solutions. Another describes the inclusion of RDye in a poly(methylmethacrylate) matrix for the detection of polar additives in hydrocarbon naphtha blends in the liquid phase [29]. This paper describes our investigation of RDye incorporated into a variety of polymer films and exposed to the headspace above various solvents and water-methanol mixtures. The solvent vapor effects on the absorption characteristics of RDye in the different polymer matrices are reported and compared to results for RDye dissolved in the liquid solvents. The varied responses for the RDye films to vapors of different polarities is examined with the purpose of using different solvatochromic dyes in polymer films for a sensor array.

2. Experimental

Reichardt’s Betaine was purchased from Aldrich and used without further purification. All solvents: methanol and isopropanol (Mallinckrodt); acetone and carbon tetrachloride (Aldrich); dichloromethane and chloroform (Fisher Scientific); and ethanol (Warner-Graham) were used as received. All water was 18.2 MΩ (Millipore). Poly(vinyl pyrrolidone) (PVP), poly(isobutylene) (PIB), and poly(epichlorohydrin) (PECH) were purchased from Aldrich; poly(styrene) (PS) was acquired from Scientific Polymer Products and OV-1 from Chromotography Research Supplies. The fluoropolyl (FPOL) was synthesized inhouse at NRL [30].

RDye stock solutions (2 × 10⁻⁴ M) were prepared in chloroform (dark green solution) or methanol (wine red solution). Polymer stock solutions were prepared by dissolving 0.03 g of the selected polymer in 10 ml of either methanol or chloroform. RDye/polymer films were prepared by spraying a mixture of the RDye and polymer stock solutions onto three clean glass slides (12 × 25 mm), using a Badger air brush (Model 200-3) connected to an N₂ tank. The RDye/polymer spraying solutions were prepared just prior to spraying by mixing 0.5 ml of the RDye stock solution with 1.0 ml of the polymer stock solution. The OV-1, PIB, PS, and PECH films were sprayed using chloroform solutions, while the PVP and FPOL films used methanol as the solvent phase. Prior to spraying, the glass slides were soaked in a series of solvents (chloroform, methanol and then acetone) and then dried [31]. After spraying, the films (~100–300 μm in thickness) were placed in a vacuum oven overnight, for removal of any residual solvent. The vacuum oven was operated at room temperature (23°C) and provided a vacuum of 20 mTorr.

The slides were examined spectroscopically, by positioning them diagonally into quartz cuvettes in a Hitachi UV–Vis spectrophotometer, using films sprayed without RDye as the reference. In other words, all films (including reference) were examined at a 45° angle to the excitation beam. All initial measurements were made in room air at room temperature (23°C), where the relative humidity was approximately 35%. Upon removal from the vacuum oven, we expect the films to equilibrate with the humidity in the room air, resulting in the incorporation of water vapor into the films. The λ_max values obtained for PVP agree with the results of McGill et al. for PVP at ~25–35% relative humidity [27]. For the experiments involving exposure to solvent vapors, a small cup was placed in the bottom of both the reference and sample cuvettes and 200 μl of the analyte solvent was added. The polymer-coated slides were inserted into the appropriate cuvettes onto the top ridge of the cup and the cuvettes were capped. After equilibrating for
3–5 min, a spectrum was initiated. A similar procedure was followed for film exposures to water-methanol mixtures. Precise amounts of water and methanol were mixed to yield solutions with the mole fraction of water \((x_{\text{Water}}) = 0.3, 0.6, \text{ and } 0.9\). Saturated head space concentrations (ppm) of the neat solvents and the water-methanol mixtures were calculated from vapor pressure data [32] and are reported in the text. The reference slides were handled in an identical fashion as the sample slides in all the studies. The Hitachi spectrophotometer was calibrated monthly on the 656.1 nm band of the D\(_2\) lamp.

3. Results and Discussion

We investigated RDye dissolved in neat methanol or chloroform to explore the effect of adding small amounts of either a more polar or less polar solvent on \(\lambda_{\text{max}}\). After 0.5 ml of chloroform (5–100 µl additions) had been added to a 3 ml RDye/methanol solution (16.7% (v/v)), there was a slight change in the value of \(\lambda_{\text{max}}\) from 516 to 530 nm. However, when 100 µl of methanol was added to a 3 ml RDye/chloroform solution (3.3% (v/v)), there was an immediate, large blue shift in \(\lambda_{\text{max}}\) from 708 to 620 nm. We also examined the addition of 5–10 µl aliquots of chloroform to an RDye/benzene solution (1.7% (v/v)), and saw \(\lambda_{\text{max}}\) shift from 814 to 790 nm. These results confirm that RDye, in a non-polar or slightly polar environment, is very sensitive to the presence of a more polar molecule. The results further suggest that RDye, dissolved in a non-polar polymer film, should have a large response to a polar analyte vapor absorbed into the matrix, while the opposite scenario would produce little or no response.

To test this, we investigated RDye embedded in six different polymer films (Fig. 1), chosen for their different solvational characteristics. PIB and PS are non-polar films with only dispersion interactions, with PS displaying weak polarizability through its aromatic groups. OV-1 is also non-polar, with weak hydrogen-bond basicity through its bridging –O– groups. PVP and PECH are moderately dipolar with moderate and weak hydrogen-bond basicity, respectively. FPOL is polar and is distinguished by its high hydrogen-bond acidity characteristics. All of these polymers satisfy the essential requirements of a sensor coating, in that they are non-volatile and allow the diffusion of vapors into and out of the films.

The OV-1, PIB, PS, and PECH films remained green after spraying the dark green, chloroform-based solutions. Both PVP and FPOL films, using wine-red methanol solutions, turned pink while spraying onto the glass slides. After spraying, the FPOL film remained pink, while the PVP film visibly changed from pink, to purple, to blue, to finally a blue-green color in \(\sim 1–2\) s. The changing colors reflect the diffusion of methanol vapors out of the film, influencing the polarity of RDye’s solvational shell in the PVP matrix. The unchanging color of the FPOL film reflects the polymer’s ability to stabilize the polar ground state of RDye, similar to methanol. This would involve the interaction of FPOL’s hydrogen-bond acidic moieties with RDye’s basic phenoxide group (Fig. 1) [7,27].

Table 1 reports \(\lambda_{\text{max}}\) values for RDye in the different polymer films and their corresponding \(E_T(30)\) values, with Fig. 2 showing the absorbance spectra obtained for each polymer when exposed to chloroform. The \(\lambda_{\text{max}}\) values, averages of 6–12 films prepared over a period of several months, distinguish FPOL as the most polar film, and PECH as the least polar. The prediction of PECH as the least polar polymer is rather surprising, as its dipolarity/polarizability characteristics are similar to PVP [18]. The normalized spectra reveals narrow absorbance bands for the polar polymers, while the non-polar polymers yielded weak and broad absorbance bands. The band-broadening in the non-polar polymers indicate a greater distribution of ground states in these environments. The differences in the spectral profiles may also be related to the partitioning of RDye throughout the films, resulting in the large variation in \(\lambda_{\text{max}}\) reported for the OV-1 films (and less so for PIB and PS). We investigated the physical appearance of the

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Absorption maximum and (E_T(30)) values of RDye-polymer films</th>
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</thead>
<tbody>
<tr>
<td>Polymer (color)</td>
<td>(\lambda_{\text{max}}) (nm)</td>
</tr>
<tr>
<td>FPOL (pink)</td>
<td>524±0.5</td>
</tr>
<tr>
<td>PVP (blue-green)</td>
<td>634±0.5</td>
</tr>
<tr>
<td>OV-1 (green)</td>
<td>641±3.0</td>
</tr>
<tr>
<td>PIB (green)</td>
<td>646±1.5</td>
</tr>
<tr>
<td>PS (green)</td>
<td>648±1.0</td>
</tr>
<tr>
<td>PECH (green)</td>
<td>655±0.5</td>
</tr>
</tbody>
</table>
films under a low power (50×) optical microscope and found that the OV-1, PIB, PS, and PECH films seemed to have an "island/network" appearance, while PVP and FPOL films appeared smooth, with RDye homogeneously distributed throughout the films. For OV-1, RDye appeared to be situated in large, patchy, granular "islands", interspersed between a clear network. PIB also had a similar appearance, but the "islands" were smaller, less granular, and more homogeneous. Both PS and PECH formed deep green "networks" between small "islands", an appearance similar to pigskin leather. Therefore, the differences in the $\lambda_{\text{max}}$ values reported in Table 1 may be related to how homogeneously RDye is distributed in the individual films and may not accurately describe the polarity differences of the films, as expected.

The films were exposed to a series of solvent vapors of differing polarity: water, methanol, ethanol, isopropanol, acetone, dichloromethane, chloroform, and carbon tetrachloride. Table 2 reports the $\lambda_{\text{max}}$ values observed, after the films and vapors equilibrated for 3–5 min. An example of the changes in the absorption spectra of an RDye/OV-1 film exposed to the vapors is presented in Fig. 3(B). These results parallel the response of RDye in the neat solvents, presented in Fig. 3(A). The films (except FPOL, see below)

<table>
<thead>
<tr>
<th>Vapor</th>
<th>FPOL</th>
<th>PVP</th>
<th>OV-1</th>
<th>PIB</th>
<th>PS</th>
<th>PECH</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O (453)$^b$</td>
<td>520</td>
<td>608</td>
<td>620</td>
<td>624</td>
<td>625</td>
<td>636</td>
</tr>
<tr>
<td>CH$_3$OH (516)</td>
<td>524</td>
<td>532</td>
<td>538</td>
<td>540</td>
<td>546</td>
<td>552</td>
</tr>
<tr>
<td>CH$_3$CH$_2$OH (551)</td>
<td>538</td>
<td>571</td>
<td>584</td>
<td>578</td>
<td>583</td>
<td>592</td>
</tr>
<tr>
<td>CH$_3$(CH$_2$)$_2$OH (608)</td>
<td>543</td>
<td>607</td>
<td>637</td>
<td>644</td>
<td>660</td>
<td>632</td>
</tr>
<tr>
<td>CH$_3$COCH$_3$ (668)</td>
<td>521</td>
<td>645</td>
<td>660</td>
<td>661</td>
<td>660</td>
<td>654</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$ (701)</td>
<td>533</td>
<td>648</td>
<td>675</td>
<td>660</td>
<td>665</td>
<td>660</td>
</tr>
<tr>
<td>CHCl$_3$ (708)</td>
<td>536</td>
<td>654</td>
<td>670</td>
<td>664</td>
<td>667</td>
<td>661</td>
</tr>
<tr>
<td>CCl$_4$ (882)$^b$</td>
<td>530</td>
<td>636</td>
<td>645</td>
<td>651</td>
<td>644</td>
<td>665</td>
</tr>
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</table>

$^a$ $\lambda_{\text{max}}$ for RDye in the respective neat solvents are given in parentheses.
$^b$ See ref. [7].
responded well to the polar alcohols, especially ethanol and methanol, changing the colors of the films to purple and pink, respectively. These changes were reversible and reproducible for all of the films, changing back to their original green color upon removal with in seconds to minutes, depending on the polymer. The similarity of the different films' responses would indicate that both methanol and ethanol can easily diffuse into these films and interact with the RDye molecules in a similar way, through protic hydrogen bonding. Our film results for methanol vapors compare favorably to those reported by Hubert et al., for RDye in a poly(methylmethacrylate) film exposed to methanol in hydrocarbon solutions [29].

Except for FPOL, the different RDye/polymer films had similar trends when exposed to solvent vapors. Fig. 4 shows the correlation of the $E_T(30)$ values of the films exposed to both vapors and air, with the $E_T(30)$ values of RDye dissolved directly in the neat solvents. In the ideal case, the interaction of the vapors and RDye molecules in air would result in an identical shift of $\lambda_{max}$, and thus a $1:1$ correlation of $E_T(30)$ values. This is not the case in Fig. 4, due to the influence of the polymeric matrices surrounding the RDye molecules. The "in Air" $E_T(30)$ values of all the films were higher than when the films were exposed to chlorinated vapors, indicating some ability for these vapors to weakly influence the microenvironment of the polymer. As the polarity of the vapors was increased from non-polar $\text{CCl}_4$, to $\text{CHCl}_3$, $\text{CH}_2\text{Cl}_2$ and acetone, variations in the individual film responses were seen. As reported above, and seen in Fig. 4, as the polarity and protic hydrogen-bonding ability of the vapors increased from isopropanol to methanol, there was a dramatic shift in all of the RDye films' $E_T(30)$ response. The polar alcohols had a strong effect, producing reversible and reproducible color changes. In all of the films tested, we are assuming the presence of water vapor in the films, which will also compete and interact with the vapors. Surprisingly, when exposed to water, there was a sharp drop in the $E_T(30)$ values of the films (other than FPOL), indicating that RDye within these polymers was not sensing the high polarity of the water molecules, but was being influenced more by the polymer itself (see below).

As noted, the response of FPOL films was different from all of the other polymers examined. The electron withdrawing ability of the $-\text{CF}_3$ groups results in the high hydrogen-bond acidity of the polymer's $-\text{OH}$ groups (Fig. 1), which strongly interact with the $-\text{O}-\text{phenoxide}$ group of RDye. As a result, the initial $E_T(30)$ value was very high, indicating the polar environment that RDye was experiencing. When less polar vapors diffused into the polymer, causing a swelling and separation between the polymer chains, there was some redshifting in $\lambda_{max}$, indicating that the RDye molecules were influenced by the presence of the less polar vapors, including non-polar $\text{CCl}_4$.

The direction and magnitude of the $\lambda_{max}$ shift, and the initial $E_T(30)$ value in the films, were dependent on both the vapors and the different solvational properties of the polymers. The more polar the vapor, relative to the polymer, the stronger the $E_T(30)$ change. This would account for the small changes noted for exposure to vapors that are less polar than the polymer environment, e.g. FPOL. The different polymeric structures of the films also influence the rate of diffusion into the films. This could be observed by the rate at which films visibly changed color, as the polarity surrounding the RDye molecules was changing upon exposure to, or removal from, the methanol or ethanol vapors. From visible observation, the order of the films' responses were: OV-1(immediate))PVP(within

Fig. 4. Correlation of RDye $E_T(30)$ values in polymer films, exposed to saturated headspace vapors, with RDye $E_T(30)$ values in neat solvents. For most films, there was little response from the initial values (Air, on Y axis), until exposure to the alcohol vapors. Note the sudden drop in $E_T(30)$ when the films were exposed to the most polar vapor, water. (■) FPOL; (○) PVP; (▲) OV-1; (▼) PIB; (◇) PS; (□) PECH.
FIG. 5. The change in the absorption maximum of RDye/polymer films upon exposure to (A) low polarity solvent vapors (black, acetone; light gray, dichloromethane; dark gray, chloroform; white, carbon tetrachloride) and (B) polar solvent vapors (black, water; light gray, methanol; dark gray, ethanol; white, isopropanol).

2-3 s) >> PIB~PS~PECH (within 10 s). FPOL had no observable changes in color.

Fig. 5(A) shows the response of the films to acetone (~291,000 ppm) and the chlorinated hydrocarbon vapors (CH2Cl2: ~543,000 ppm; CHCl3: 244,000 ppm; CCl4: ~144,000 ppm) by reporting the change in the films' $\lambda_{max}$ value when going from room air to the saturated vapor environment. The films exhibited a red-shift in $\lambda_{max}$ for most of these vapors indicating that the vapors were distributed into the solvational cage of the RDye, and that RDye was sensitive to the less-polar molecules, even while integrated in a more-polar matrix. These results mimic the solution results above, when chloroform was added to RDye/methanol. It is interesting to note that even in FPOL, the chlorinated hydrocarbon vapors (including the non-polar CCl4) caused a red shift in $\lambda_{max}$. The red-shifts are indicative of the ability of the vapors to influence the environment surrounding RDye, even in the strongly interacting environment of FPOL. Carbon tetrachloride had the largest effect on $\lambda_{max}$ for PECH, while dichloromethane or chloroform in PECH produced the smallest responses. This was surprising, as previous work had indicated that PECH was a good sorbent for chlorinated hydrocarbon vapors [25]. There may be an affinity between the chloride groups of PECH and RDye which prevents a more obvious interaction with the absorption of the chlorinated vapors [33]. The response of the OV-1 film to both dichloromethane and chloroform vapors was much greater than all the other films. Surprisingly, the OV-1 $\lambda_{max}$ value for dichloromethane was red-shifted from the chloroform $\lambda_{max}$ value (675 vs 670 nm), while the response of the other films were similar to RDye in the neat solvents, where the RDye/dichloromethane $\lambda_{max}$ was blue-shifted slightly from the RDye/chloroform $\lambda_{max}$ value.

Fig. 5(B) shows the response of the films to the polar vapors: water, methanol, ethanol, and isopropanol (~29,500, 156,000, 74,200, and 64,100 ppm, respectively). The responses to methanol and ethanol vapors were similar blue-shifts for all the films (other than FPOL), ~103 and ~63 nm, respectively. The ability of isopropanol to penetrate and interact with RDye in the films is shown to be different for all the films. The blue-shifts for isopropanol in both the PVP and PECH films were reflected in their color change to blue. For all of the films, there was a pronounced lack of response to the most polar vapor, water, exhibiting an average blue shift of ~22 nm. PVP, the most water absorbent film of those tested [27], shifted an average of 26 nm while PECH was lowest at 19 nm. The similarity of the films' response to water vapor may be due to the hydrophobic character of most of the films, and the known tendency of water to cluster in hydrophobic polymers [34,35]. The moisture present in the films could be distributed in a combination of hydrogen-bound clusters, which do not interact much with the RDye present, and weakly interacting solvating vapors, due to RDye's low solubility in water. As a result, $\lambda_{max}$ was recorded at both 5 and 10 min intervals for all the films, to be sure that equilibration had been achieved.

The possibility of using pattern recognition techniques to selectively determine an analyte vapor is demonstrated in Fig. 6, where a comparison of three of the films giving different responses to the vapors
tested is presented. FPOL, had small, but very unique responses to the polar alcohol vapors when compared to the other films, here represented by OV-1 and PECH. All three films displayed red-shifts for the less polar and non-polar chlorinated species, but in different proportions. The aprotic, polar acetone vapors yielded little or no response in FPOL or PECH, but a strong red-shift in OV-1. The use of other dyes that respond differently to each vapor in this series of polymers would enhance the capabilities of a sensor array for selective detection.

Water and methanol, both highly polar, protic solvents, each produced very different responses in the films. Since the ultimate goal of this effort is to produce a F-OCS for use in headspace analysis of water-saturated environments, RDye's response to vapors of water-methanol solutions of differing mole fraction was investigated. Because water vapor can be expected to act as an interferent in this system, we wanted to see how it affected the Rdye response to methanol, which had produced the biggest response in the films and is completely miscible in water. The preferential solvation of RDye in solution phase binary water-methanol mixtures has previously been explored by several groups [18,19,36]. Preferential solvation of RDye by methanol was demonstrated by the non-linearity of the solvatochromic shift as the fraction of methanol in the mixtures was increased [37]. The preferential solvation of RDye by methanol would also be expected in the vapor phase due to the high volatility of methanol compared to water, and from our initial results from the neat solvents. However, the response of RDye in the films is complicated by several factors, including: (1) the similarity-dissimilarity of the vapor composition to the solution composition, (2) the ease with which the vapor mixture partitions into the particular films, and (3) once in the films, the partitioning of the individual components of the vapor mixture within the films and their interaction with RDye. All of these factors can play a role in RDye's response, beyond preferential solvation.

Fig. 7(A) shows the results of the different RDye/polymer films to the headspace of several water-methanol solutions by relating the observed $E_{r}(30)$ value to the mole fraction of water. FPOL was not tested due to the limited response of RDye to both water and methanol. As the amount of water in the solution increased, there was a non-linear decrease in
the $E_T(30)$ values. Clearly, the presence of water vapor affected the RDye films' response, but the non-linearity of the decrease suggests something other than a random, non-specific interaction between RDye and the solvating vapors. The decrease in the polarity that RDye experienced, as evidenced by the dropping $E_T(30)$ values, is counter to Dawber's results for the preferential solvation of RDye in water-methanol solutions [18], and is probably related to how water may be clustering within the network environment [33,34]. Hydrogen-bonding interactions between methanol and water within the polymer matrix will also play a role in the resulting RDye response, increasing the influence of the polymer on $E_T(30)$. The influence of the individual polymer films on accommodating the vapors is evident by the separation of the symbols in the plot for each polymer. In going from methanol to water, PVP consistently was a more polar environment for RDye and PECH was the least polar, supporting the initial polymer results in air.

The response of the RDye/polymer films submerged in the water-methanol solutions and exposed to headspace vapors were examined. Polystyrene films exhibited stability in all the solutions, while the other polymer films began to leach RDye into the solutions when $\chi_{\text{Water}} \leq 0.6$. Fig. 7(B) is a plot of the change in $E_T(30)$ of RDye in polystyrene exposed to both headspace vapors and dipped into the water-methanol solutions. There is a similar trend for both situations: near linearity from $\chi_{\text{Water}}=0.0-0.6$, and then a steeper decline in $E_T(30)$ as $\chi_{\text{Water}}$ increases. The results of the binary mixture study indicates that in a water-saturated environment, it may be possible to detect small amounts of polar compounds, as they will preferentially solvate RDye in the film networks and produce a detectable response.

4. Conclusions

The inclusion of the solvatochromic dye, Reichardt's Betaine, into polymer films of different polarities and solvational characteristics was investigated. Reversible and reproducible changes in the absorption maximum of the dye, when the films were exposed to a series of vapors of different polarities, were observed. The effect of the different polymers on that response was observed and is expected to be a greater influence at low vapor concentrations. However, the variety of responses that were achieved in these initial experiments, indicate that the ability to distinguish between certain vapors via pattern recognition techniques may be possible. Due to the preferential solvation of RDye in the polymer networks by methanol, the detection of small amounts of polar vapors in a water-saturated environment was indicated. The incorporation of environment-sensitive dyes into various polymeric films could produce a low cost sensor array with in-situ detection capabilities for several analyte vapors.

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References

[33] It was previously reported by McGill et al. [27] that poly(vinyl chloride) films containing R dye, were initially green in color but faded to a light yellow over a period of days. Our experience with R/Dye/PECH films also showed this behavior, but the fading occurred over a period of weeks rather than days.